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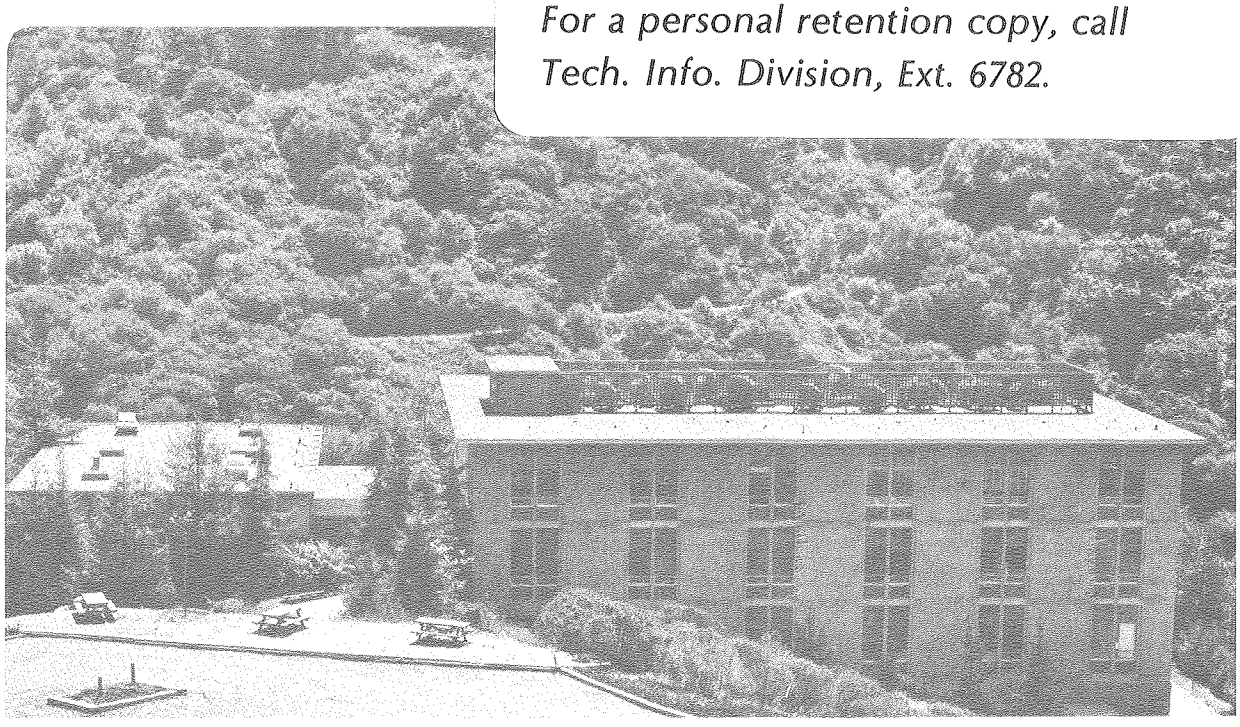

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DISCLAIMER

TERTIARY-BUTYL SUBSTITUTED CYCLOOCTATETRAENES

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Abstract

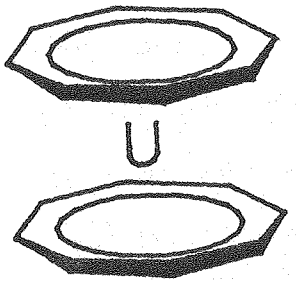
Reaction of cyclooctatetraene (COT) with t-butyllithium provides a convenient synthesis of t-butylcyclooctatetraene, 4. As a by-product of the reaction mixture, 1,4-di-t-butylcyclooctatriene has been isolated and converted to 1,4-di-t-butylcyclooctatetraene, 5, by deprotonation with potassium amide and oxidation with iodine. An independent synthesis of 5 was developed from 9-oxabicyclo[6.1.0]-octa-2,4,6-triene (cyclooctatetraene oxide), 9. The highly substituted compound 1,3,5,7-tetra-tert-butylcyclooctatetraene (6) has been prepared in 24% overall yield in 4 steps. The acetylenic ketone 27, prepared from (tert-butylethynyl)copper and pivaloyl chloride, undergoes condensation with dimethyl malonate to give the pyrone ester 28. This ester undergoes facile hydrolysis and decarboxylation in hot concentrated sulfuric acid to yield 4,6-di-tert-butyl-(2H)-pyran-2-one (22) which is converted to 6 in one step by photolysis in dilute solution.

Although uranocene (bis-π-cyclooctatetraeneuranium(IV), 1) exhibits remarkable hydrolytic and thermal stability, it is oxygen sensitive, and enflames when exposed to air.[1] Virtually all uranocenes exhibit this oxygen sensitivity. The only known exception is bis-(1,3,5,7-tetraphenylcyclooctatetraene)uranium(IV), 2,[2] a rather air stable compound that requires elevated temperatures for air oxidation. This air stability is attributed to steric hindrance provided by the bulky phenyl groups towards attack by oxygen at the central uranium. Unfortunately, 2 has such low solubility that solution studies are limited. Consequently, we have examined another bulky substituent, tert-butyl, with the objective of the corresponding octa-tert-butyluranocene, 3. In this paper we discuss the preparation of the cyclooctatetraene (COT) ligands, tert-butylcyclooctatetraene, 4, 1,4-di-tert-butylcyclooctatetraene, 5, and 1,3,5,7-tetra-tert-butylcyclooctatetraene, 6.

tert-Butylcyclooctatetraene, 4, and 1,4-di-tert-butylcyclooctatetraene, 5.

Paquette, et al., have prepared 4 by the reaction of lithium dicyclooctatetraenylcuprate with tert-butyl bromide in low yield (13%).[3] The compound has also been prepared in our laboratory from bromocyclooctatetraene and lithium tert-butyl(thiophenoxy)-cuprate in 40% yield.[4] However, this preparation requires a rather careful fractional distillation to remove 4 from unreacted bromocyclooctatetraene.

The reaction of tert-butyllithium with COT appeared to be a



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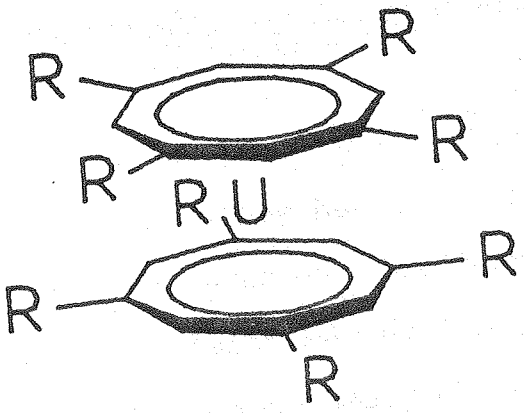


2, R = ph

3, R = t-Bu

potential route to tert-butyl substituted cyclooctatetraenes. Several years ago, Cope and coworkers reported that aryl- and alkyllithium reagents add to COT to give, after hydrolysis, a mixture of monosubstituted COT and cyclooctatrienes.[5] In later work, the Cope group reported the reaction of phenyllithium with phenylcyclooctatetraene to give a mixture of all four possible isomeric diphenylcyclooctatetraenes.[6] Low yields and the general separation problems in workup have limited the usefulness of the reaction of lithium reagents with COT. Recently, however, Miller, Dekock and Branit[7] have reported a detailed study of the reaction. Addition of lithium reagents to COT with exclusion of oxygen and water leads to substituted COT dianions from which the cyclooctatetraenes are obtained in moderate to good yield by oxidation with oxygen. In this manner, 4 was obtained in 45% yield (by GC) along with some unidentified higher molecular weight material.

We have found independently that 4 can be obtained preparatively in >95% purity in 39% distilled yield by reaction of tert-butyllithium with COT. In addition, we have investigated the higher molecular weight material formed in the reaction. In our study, slow addition of one equivalent of tert-butyllithium to an ether solution of COT at -78° resulted in an intensely purple solution. After warming to 0°C, the still purple solution was quenched by addition of an ethereal iodine solution to oxidize the COT dianions presumed to be present. Distillation of the product mixture

yielded three distinct fractions. Gas chromatographic analysis of the first fraction showed it to be a mixture of COT and another material, probably cyclooctatriene. The second fraction contained 4 and tert-butylcyclooctatriene as determined by mass spectral data. The third fraction was an almost colorless, viscous oil which was identified as a mixture of di-tert-butylcyclooctatrienes by ^{1}H-NMR and mass spectral data.

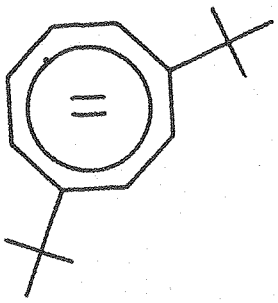
Analysis of the deuterated cyclooctatrienes obtained by D_2O quench of the cold reaction mixture revealed that both COT dianion and tert-butylcyclooctatetraene dianion were present in the reaction mixture. Thus, it appears that the lithium reagent adds to COT giving a monoanion which is further deprotonated by a second mole of lithium reagent to form the dianion of 4. In the presence of COT, this dianion transfers electrons to COT since the substituted dianion has a higher reduction potential than COT. The lithium reagent then adds to 4 to give a di-tert-butylcycloocta-trienyl anion which is not deprotonated but persists until the water quench where the triene is formed.

In addition to COT dianion and tert-butylcyclooctatetraene dianion, when one equivalent of tert-butyllithium is used substantial amounts of tert-butylcyclooctatrienyl anion were present in the solution as shown by deuteration data. This was presumed to give rise to the tert-butylcyclooctatriene contaminant in the tert-butyl-cyclooctatetraene fraction. Indeed, treatment of 4 with more than one equivalent of lithium reagent resulted in a reduction of the amount of tert-butylcyclooctatriene in the product mixture.

Whereas a full two equivalents of lithium reagent gave large amounts of higher molecular weight material, 1.4 equivalents was found to be optimal resulting in a product containing virtually no tert-butylcyclooctatriene.

To facilitate determination of the substitution pattern of the components of the di-tert-butylcyclooctatriene mixture obtained in the reaction of tert-butyllithium with cyclooctatetraene, the mixture was deprotonated to the dianion by treatment with potassium amide in liquid ammonia.[8] Formation of the planar, conjugated dianion eliminated the possibility of stereo- and double bond isomerism, thus simplifying the mixture greatly.

^{1}H NMR spectral evidence revealed that the dianion was a single isomer since only one tert-butyl resonance was observed in the spectrum. The ^{13}C NMR spectrum of the dianion also showed only one tert-butyl group, but in addition, in the ring carbon region, three resonances of virtually identical intensity and one small resonance (presumably the quaternary carbon) were observed. The presence of four and only four resonances in the ring carbon region of the ^{13}C NMR spectrum is strong evidence that the dianion is 1,4-di-tert-butylcyclooctatrienediide, 7. The 1,3- and 1,5-di-tert-butylcyclooctatrienediides can be eliminated since they should exhibit five and three ring carbon resonances, respectively. The 1,2 isomer would be expected to exhibit four ring carbon resonances, but this isomer is highly unlikely on steric grounds. Therefore, the reaction of tert-butyllithium with tert-butylcyclooctatetraene appears to give a mixture of isomeric trienes having



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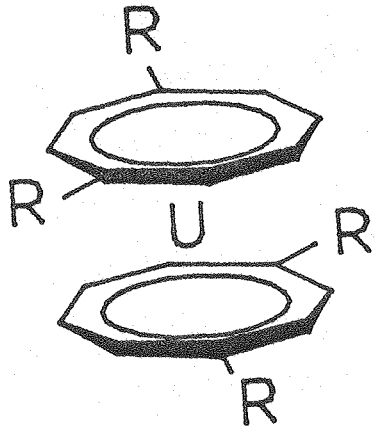


8, R = t-Bu

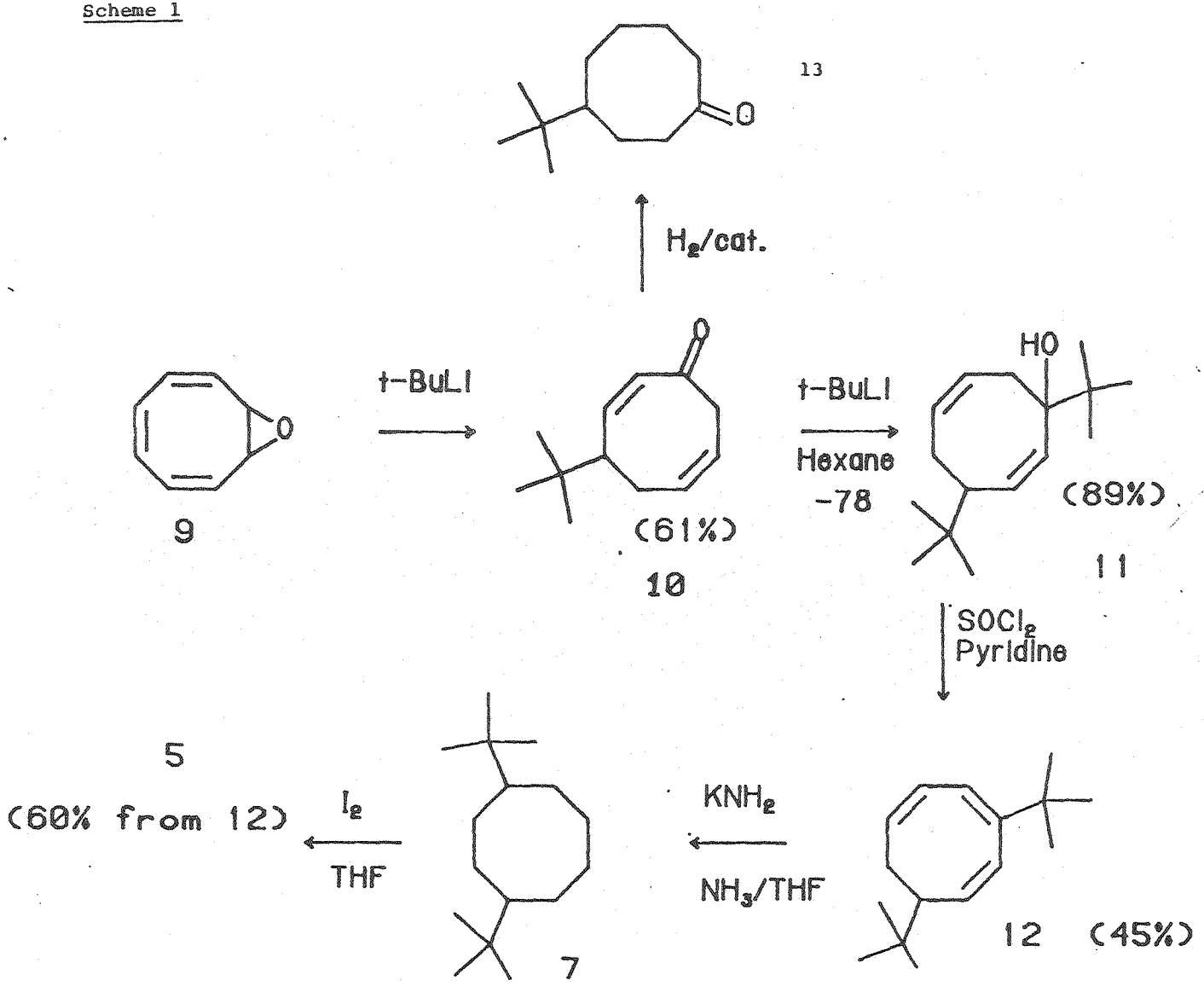
a 1,4 arrangement of tert-butyl groups and differing only with respect to double bond isomerization.

Additional evidence for the structure of the dianion comes from its conversion to 1,1',4,4'-tetra-tert-butyluranocene, 8, and its nmr properties, particularly at low temperature; the barrier to rotation about the ring-metal axis has been measured and is reported separately.[9] The dianion was also prepared by an independent route from 9-oxabicyclo[6.1.0]octa-2,4,6-triene (COT oxide), 9 (Scheme 1).

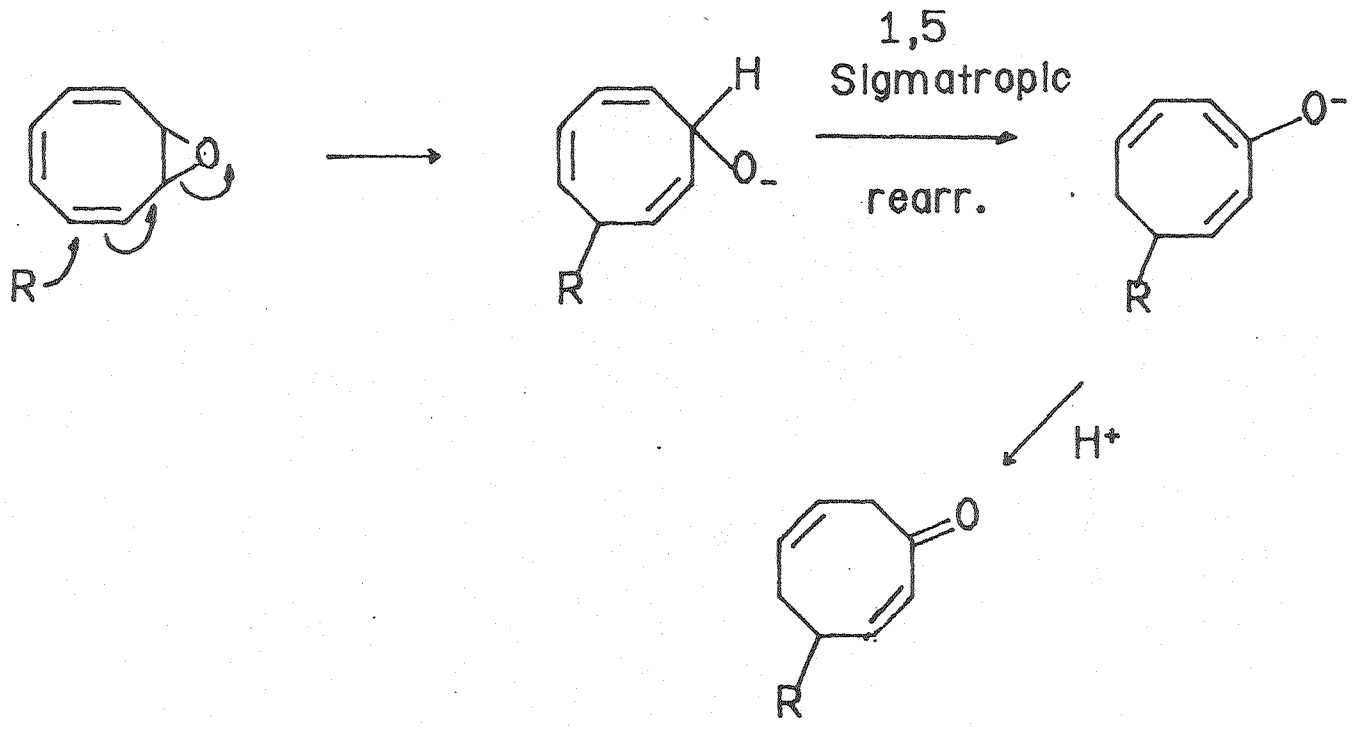
The reaction of 9 with phenyllithium has been reported[10] to give an unsaturated ketone with unelucidated structure. More recently, the reaction of 9 with ethyllithium was reported to give the dienone 14.[11] This result appeared to us to be unlikely on reaction mechanism grounds. Indeed, reaction of 9 with tert-butyllithium gave an unsaturated ketone, $C_{12}H_{18}O$, which on catalytic hydrogenation gave a tert-butylcyclooctanone showing 10 resonances in the ^{13}C-nmr spectrum. Accordingly, it could not be 5-tert-butylcyclooctanone which should from symmetry show only 7 resonances. The structure 10 is assigned to the unsaturated ketone on the basis of ^{13}C and ^{1}H nmr spectra. We note also the comparison of the UV λ_{max} 231 nm (ε=7774) with that of cycloocta-2,6-dien-1-one, λ_{max} 227 nm (ε=7200).[12] The formation of 10 is rationalized by the reaction mechanism given in Scheme 2. We note that sigmatropic rearrangements are facilitated by the presence of an alkoxide group.[13] Moreover, 2,4-cyclooctadien-1-ol has been shown to rearrange thermally to cyclooct-3-en-1-one.[14]

The tert-alcohol 11 produced by reaction of 10 with tert-

Scheme 1


13
O
H_2/cat.
9
t-BuLi
(61%)
10
t-BuLi
Hexane
-78
HO
(89%)
11
$SOCl_2$
Pyridine
5
(60% from 12)
I_2
THF
7
KNH_2
NH_3/THF
12 (45%)

Scheme 2



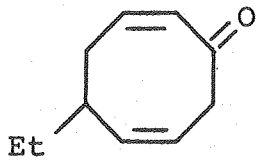
butyllithium in hexane at low temperature could be obtained in crystalline form but the broad melting range, 70-75°, suggests the formation of cis, trans-isomers. Dehydration with $SOCl_2$ gave a triene formulated as 12. The UV λ_{max} 257 (ε=1436) compares with that of cycloocta-1,3,5-triene, λ_{max} 260.[15] The nmr spectrum suggests that 12 is relatively pure and has the structure shown; the nmr spectrum differs significantly from the product obtained above by treating COT with tert-butyllithium which appears to be a mixture containing little if any 12. Deprotonation of 12 with KNH_2 in NH_3-THF at -33° gave 7, identical to that obtained above.

Oxidation of 7 with iodine gave 1,4-di-tert-butylcycloocta-tetraene in 60% yield as a slightly yellow viscous liquid having a complex ^1H nmr spectrum corresponding to the presence of the two double bond isomers of 5 in a 2:1 ratio. The separation of these isomers and their rates and equilibria for interconversion is being communicated separately.[16]

1,3,5,7-Tetra-tert-butylcyclooctatetraene, 6.

Although a few 1,3,5,7-substituted cyclooctatetraenes have been prepared, their syntheses have not been generalized. The preparation of 1,3,5,7-tetraphenylcyclooctatetraene[17] relies on the solid state photodimerization of trans-cinnamic acid in the initial step and is therefore not capable of extension to other systems. The catalytic oligomerization of alkylacetylenes generally yields trimers rather than cyclooctatetraenes and also is not applicable to the synthesis of 5.

A potentially new route was explored by the dimeric coupling of the keto-ylide 15. Wittig type reactions to form cycloocta-



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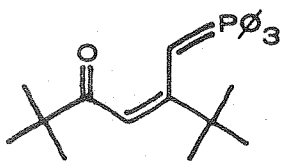

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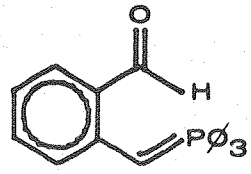

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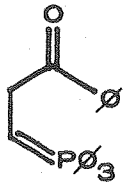
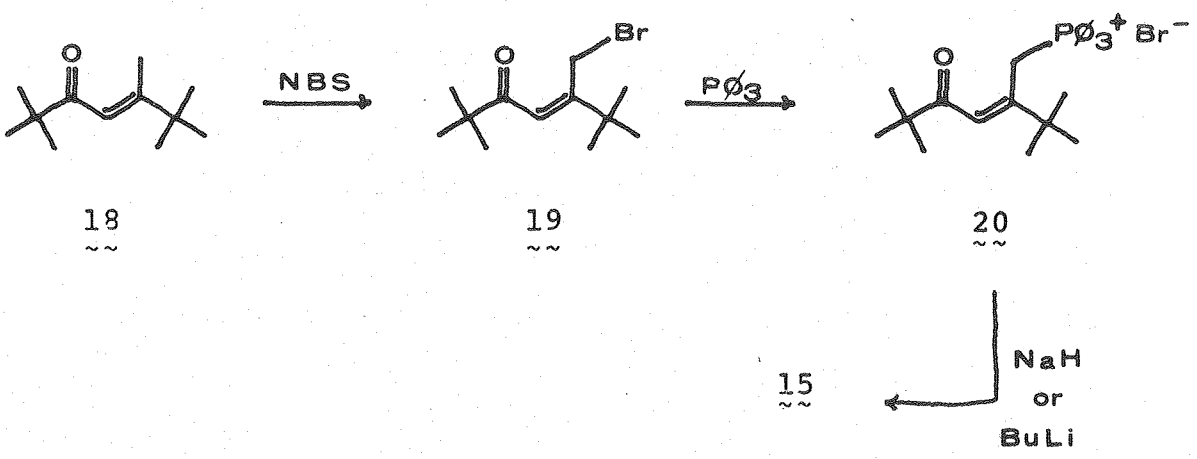


17

tetraenes are well known, but ordinarily a dicarbonyl compound is treated with a diylide to form the cyclooctatetraene.[18] However, there is precedent for the type of reaction envisioned here in the dimerization of ylide 16 to form dibenzocyclooctatetraene[19] and of ylide 17 to form 1,4-diphenylcyclohexa-1,4-diene.[20]

The synthesis of 15 was relatively straightforward and is summarized in Scheme 3. Enone 18, the self-condensation product of pinacolone, was treated with N-bromosuccinimide to give the moderately stable bromide 19 in good yield. The very hygroscopic phosphonium salt 20 was obtained by treatment of 19 with triphenylphosphine in benzene. Treatment of 20 with sodium hydride in THF or n-butyllithium in benzene afforded the ylide 15 as a yellow, crystalline, air stable solid. The ylide proved to be unreactive with respect to dimerization and remained virtually unchanged on refluxing in THF for several days or heating above the melting point (120°) for several hours. Under no circumstances could any trace of cyclooctatetraene 6 be detected.

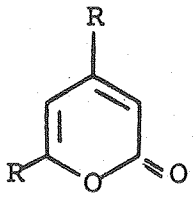
Of the symmetrical 1,3,5,7-tetrasubstituted cyclooctatetraenes that have been prepared, 1,3,5,7-tetramethylcyclooctatetraene is the only cyclooctatetraene substituted strictly with alkyl groups. The synthesis of 1,3,5,7-tetramethylcyclooctatetraene appeared to be the most capable of extension to the synthesis of 6. The tetramethyl compound has been prepared by photolysis of 4,6-dimethyl-2H-pyran-2-one, 21, in concentrated benzene solution.[21] Heating of the resulting dimers above 200°C affords tetramethylcyclooctatetraene. We anticipated that 4,6-di-tert-butyl-2H-pyran-2-one (22) would undergo a similar transformation to afford 6.



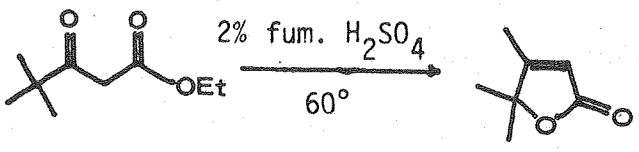
18 19 20

15

Scheme 3



21, R=Me
22, R=t-Bu

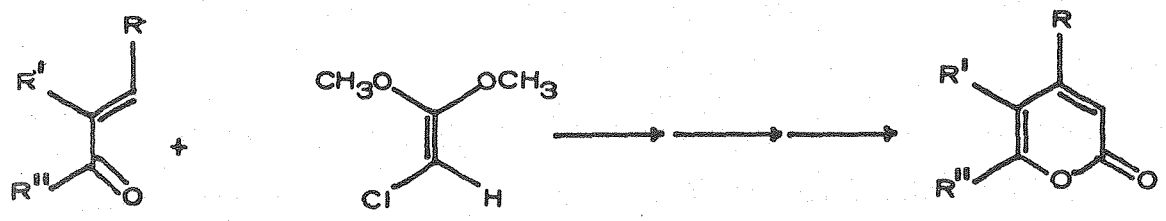


23 24

By analogy to the synthesis of 21,[22] ethyl pivaloylacetate, 23, was subjected to treatment with strong acid. Earlier work in this group[23] had shown that treatment of 23 with conc. sulfuric acid under the same conditions as those used in the condensation of ethyl acetoacetate did not effect reaction. In our further study a variety of acids was tested but sulfuric acid appeared to be the best catalyst for the condensation. However, for substituted acetoacetates such as ethyl n-butyrylacetate, higher temperatures are required to obtain a reasonable reaction rate. Use of a stronger acid was explored by treating 23 with 2% fuming sulfuric acid at 60°; reaction was effected but destruction of the starting material resulted without formation of the desired coumalic acid. Only a low yield of the butenolide 24 was isolated.

Treatment of α,β-unsaturated ketones with chloroketene dimethyl acetal (25) leads to substituted α-pyrones in good yield (Scheme 4).[24] To apply this approach to the synthesis of 23 the known enone 26[25] was investigated. Treatment of 26 with 25 under the normal conditions (150°) gave no reaction even after 60 hours. Above 170°, however, slow polymerization of the ketene acetal occured while addition of Lewis acids caused immediate polymerization of the ketene acetal. Treatment of the mixture at high pressure (7000 atm)[26] also did not effect reaction. Thus, the enone 26 is apparently too hindered to undergo cycloaddition to the ketene acetal 25.

Reaction of acetylenic ketones with the anion of dimethyl malonate is known to give 4,6-disubstituted pyrone esters in a



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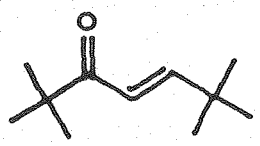


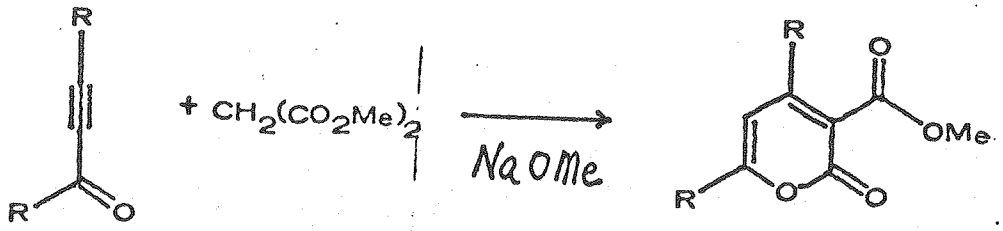
+ 25 ⟶ No Rx.

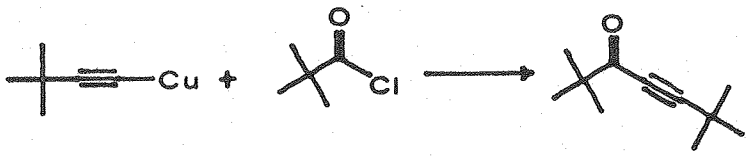
26

few cases.[27] The ester can then be converted to the α-pyrone by hydrolysis with methoxide and subsequent pyrolytic decarboxylation. It was envisaged that treatment of the acetylenic ketone 27 would lead to the substituted pyrone ester in an analogous fashion (Scheme 5).

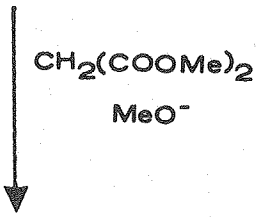
The acetylenic ketone 27 was prepared in 69% yield by the addition of pivaloyl chloride to a solution of (tert-butylethynyl)-copper. Use of the copper reagent was necessary since the lithium acetylide gave a large amount of higher molecular weight by-product formed by addition of the acetylide to the product ketone. Preparation of the pyrone ester 28 proved to be relatively straightforward, although somewhat more forceful conditions were required than those normally used for the condensation. Reaction of 27 with dimethyl malonate and sodium methoxide in refluxing methanol for 3 hours afforded the crystalline ester 28 in moderate yield (56%). Although the ester was quite resistant to hydrolysis by treatment with sodium methoxide in methanol, dissolution of the ester in concentrated sulfuric acid and heating at 110° for 1.5 hours yielded a crystalline solid upon cooling and dilution with water. The solid proved to be not the expected pyrone acid but rather the α-pyrone, 22. Quite fortuitously, the ester had hydrolyzed and decarboxylated in one step to yield the pyrone in 86% yield (Scheme 5).

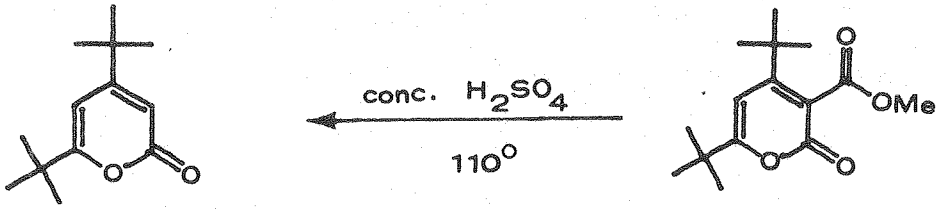
By analogy to the preparation of 1,3,5,7-tetramethylcyclooctatetraene, the next step was photodimerization of the α-pyrone in concentrated solution. Photolysis of a saturated solution of





27



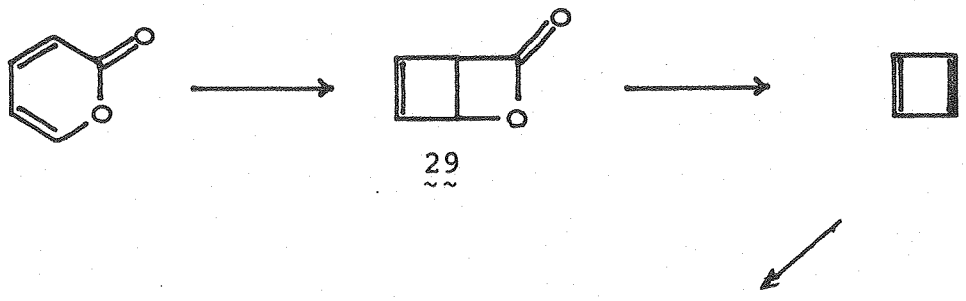


22 28

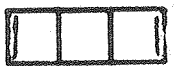
Scheme 5

22 in benzene afforded a very viscous solution and solid. Removal of the solvent at high vacuum gave a white solid which was not the starting pyrone. However, characterization was difficult due to the very low solubility of the product. A rather crude ^{1}H-nmr showed three broad resonances consistent with a mixture of dimer structures. The mass spectrum, however, showed no parent ion peak, but instead was the same spectrum as the parent pyrone. In actual fact, the dimers were found to be thermally unstable with respect to the pyrone 22. Upon pyrolysis, the dimers reverted cleanly to the starting pyrone and did not extrude carbon dioxide. All attempts to induce extrusion of carbon dioxide either thermally or with acid catalysis failed.

In contrast to the photolysis of pyrones in concentrated solution, photolysis of α-pyrone in dilute solution in Corex has been shown to yield the bicyclic photo-α-pyrone 29.[28] Photolysis of the photo-α-pyrone at low temperature in quartz then leads to the formation of cyclobutadiene[29] which dimerizes on warming to give the tricyclooctadiene 30, the immediate precursor to cyclooctatetraene. Thus, photolysis of 22 in dilute solution seemed a viable route to the syn-dimer of 1,3-di-tert-butylcyclobutadiene[30] and subsequently the cyclooctatetraene 6. Indeed, a related transformation has been reported.[31] Photolysis of 4,5-diphenyl-2-pyrone yields 1,2,4,7-tetraphenylcyclooctatetraene although the reaction was not proposed to involve the intermediacy of a cyclobutadiene.



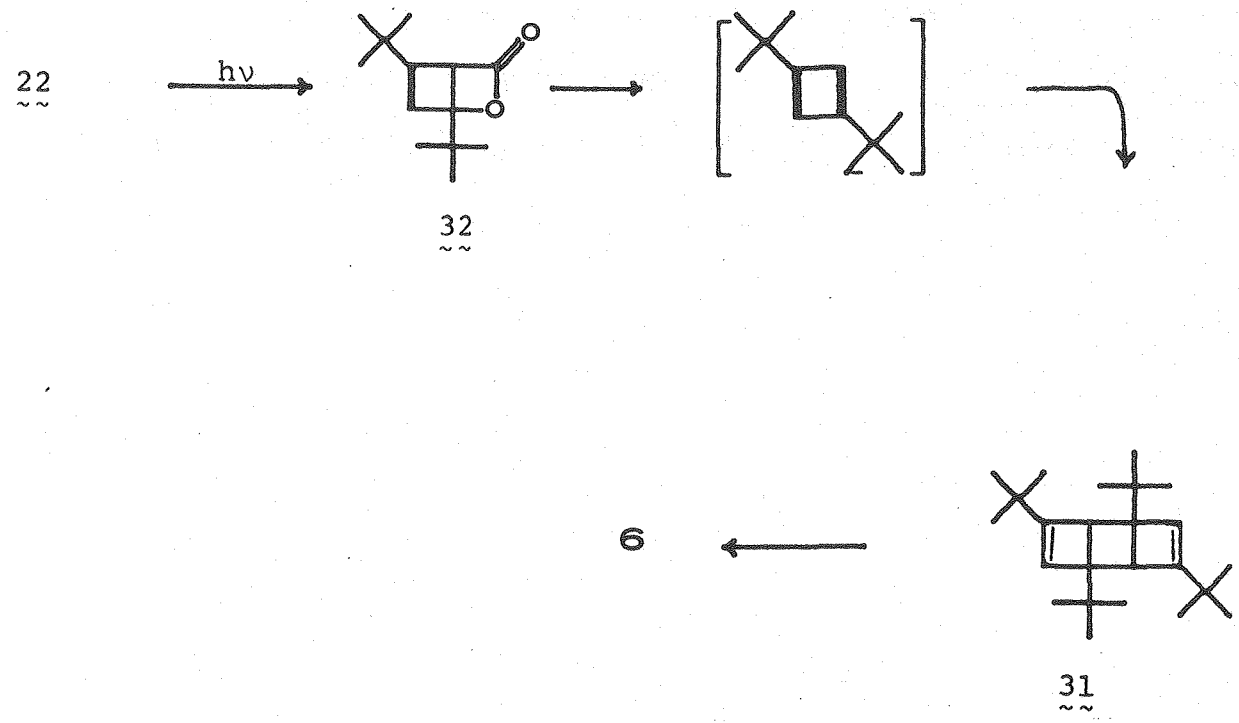
29



30

Photolysis of a dilute ether solution of pyrone 22 in quartz for 11 hours afforded a viscous, colorless oil which proved to be the desired cyclooctatetraene 6. The cyclooctatetraene was obtained in 72% yield from the α-pyrone (24% overall from tert-butylacetylene and pivaloyl chloride). Further purification by preparative GC provided 6 as a low melting (32-34°) white solid exhibiting two resonances in its ^{1}H NMR spectrum at 1.1 and 5.75δ.

Although the mechanism of the conversion of pyrone 22 to 6 was not completely elucidated, some pertinent information was obtained. Upon irradiation of a solution of 22, the UV absorbance at 293 nm attributed to the pyrone was completely absent after only 30 min. An aliquot of the reaction mixture after 40 minutes of irradiation showed a 40:60 ratio of 6 and the tricyclooctadiene 31. Only a small amount of other unidentified material was present in the mixture. After 3.5 hours of irradiation, 6 and 31 exist in a 70:30 ratio in the reaction mixture. These data are consistent with the mechanism proposed in Scheme 6 in which loss of carbon dioxide from the intermediate photo-α-pyrone 32 gives rise to 1,3-di-tert-butylcyclobutadiene and subsequently the syn dimer 31. Formation of the dimer is fast whereas its conversion to 6 is quite slow. Although the observation of the dimer 31 in the reaction mixture suggests that the mechanism involves formation and dimerization of a cyclobutadiene, other mechanism cannot be eliminated. In particular, the mechanism proposed by Padwa[31] for the conversion of 4,5-diphenyl-α-pyrone to 1,2,4,7-tetraphenyl-



Scheme 6

cyclooctatetraene, cycloaddition of the intermediate photopyrone to the starting pyrone and subsequent loss of carbon dioxide, cannot be discounted. However, the presence of the phenyl groups in that system may cause the mechanism of the photochemical reaction to be different from that in the present case.

The behavior of the dianion from 6 with UCl_4 will be published separately. Thorium derivatives of 4 and 5 have also been described.[4]

Experimental Section

Melting and boiling points are uncorrected. Visible and UV spectra were obtained on a Cary 118 spectrophotometer; ^{1}H NMR (NMR) spectra were obtained on a Varian T-60 (60 MHz) and the Berkeley 180 MHz and 250 MHz spectrometers; ^{13}C NMR (CMR) spectra were also recorded on a Nicolet Model TT23 (25.14 MHz) instrument. Mass spectra were obtained on a CEC-103 spectrometer at 70 ev. Analyses were performed by the Analytical Services Laboratory, University of California, Berkeley. GC analyses were performed on a Varian Aerograph 1520 equipped with a thermal conductivity detector and the following columns: Column 1: 4% SE-30 on Chromosorb G, 1/4 in x 6 ft; Column 2: 20% SE-30 on Chromosorb W, 3/8 in x 6 ft; Column 3: 4% Carobwax 20M on Chromosorb G, 1/4 in x 6 ft.

The following dry solvents were used: methanol was dried over magnesium; benzene, tetrahydrofuran (THF) and diethyl ether (ether) were dried either over lithium aluminum hydride or sodium benzophenone ketyl. Cyclooctatetraene was obtained from BASF and was used without further purification. tert-Butylacetylene was prepared by the method of Kocienski.[32] Pivaloyl chloride was prepared by the method of H. C. Brown.[33]

Treatment of Cyclooctatetraene with tert-Butyllithium in Ether at -78°C.

To a stirred solution of 4.9 g (0.047 mol) of cyclooctatetraene in 80 mL of dry ether at -78°C under argon was added 30 mL (0.048 mol) of 1.6 M tert-butyllithium in pentane over the course of 15 min. A beautiful, intensely purple solution resulted. After stirring for 1 h in the cold and then 1 h at 0°C, an ethereal solution of

iodine (6 g in 75 mL) was added dropwise at 0°C. During the addition, the mixture turned from purple to red to yellow and some white solid precipitated. Water was then added, the layers were separated and the organic layer was washed with H_2O, dried (Na_2SO_4) and reduced *in vacuo* to give 7.3 g of yellow liquid. Distillation of the liquid afforded 3 fractions: A, bp 59-69°C (40 mm), 0.69 g, yellow liquid; B, bp 54-58°C (0.75 mm), 1.40 g, yellow liquid; C, bp 60-63°C (0.15 mm), 0.78 g, colorless oil.

Gas chromatographic analysis (Column 1) revealed fraction A to be a mixture of cyclooctatetraene and presumably cyclooctatriene. Fraction B was identified as *tert*-butylcyclooctatetraene by comparison of its GC ret. time with that of authentic material but was contaminated with a small amount of another material. Mass spectral analysis showed parent ions at m/e 160 and 162 corresponding to *tert*-butylcyclooctatetraene (4) and *tert*-butylcyclooctatriene in a 77:23 ratio. Fraction C was identified as di-*tert*-butylcyclooctatriene on the basis of NMR evidence and the presence of a parent ion peak at m/e 218 in its mass spectrum.

Fraction B: NMR ($CDCl_3$)δ [0.95, 1.1](2s, 9H), 2.0-2.9 (1.2H), 5.3-6.3 (5.4H).

Fraction C: NMR ($CDCl_3$)δ [0.95, 1.0, 1.05](3s, 9H), 1.8-3.6 (3.5H), 5.2-6.4 (4.8H).

Treatment of Cyclooctatetraene with tert-Butyllithium-D_2O Quench.

The procedure above was followed exactly except that after the *tert*-butyllithium addition and stirring at -78°C for 1 h, 2.5 mL (0.125 mol) of D_2O was added; no visible change resulted. The mixture was allowed to warm to room temperature whereupon an

almost colorless solution and white solid resulted. Filtration and rotary evaporation of the solution afforded 7.0 g of slightly yellow liquid. Deuterated cyclooctatriene and tert-butylcyclooctatriene were isolated as colorless liquids by distillation.

Cyclooctatriene, bp 60-65°C (15 mm), 0.88 g.

tert-Butylcyclooctatriene, bp 49-58°C (0.8 mm), 2.09 g.

Mass spectral analysis of the two liquids afforded the deuteration data summarized below:

Table I

Deuterium content of reaction products

Compound	Average Deuteriums/Molecule	Percentages
Cyclooctatriene	1.93	d_0 = 1.16%
		d_1 = 5.01%
		d_2 = 93.83%
tert-Butylcyclooctatriene	1.54	d_0 = 6.83%
		d_1 = 35.30%
		d_2 = 54.96%
		d_3 = 2.91%

Treatment of Cyclooctatetraene with 1.4 Equivalents of tert-butyllithium. Preparation of tert-Butylcyclooctatetraene (4).

To a stirred solution of 4.5 g (0.043 mol) of cyclooctatetraene in 100 mL of dry ether at -78°C under argon was added 50 mL (0.060 mol, 1.39 equiv.) of 1.2 M tert-butyllithium in pentane over the course of 15 min. The dark purple solution was stirred for 1 h whereupon a red tint appeared to the purple solution. Upon warming to 0°C, the color slowly faded to give a brown-yellow solution. An ethereal iodine solution (15.2 g in 125 mL) was added dropwise at 0°C. Upon addition of the first few drops, the mixture turned dark red and stayed this color until approximately half of the solution had been added, at which time it slowly turned to yellow. The iodine addition was stopped when a slight green tint appeared (approximately two-thirds of the solution had been added). The yellow solution was then poured into H_2O, the layers were separated and the organic layer was washed with H_2O, dried (Na_2SO_4) and rotary evaporated to give a yellow liquid and a small amount of brown solid.

Cyclooctatetraene and cyclooctatriene were removed by distillation at 56-59°C (15 mm). The residue was distilled to give 2.7 g (39%) of tert-butylcyclooctatetraene, bp 50-54°C (0.8 mm). Gas chromatographic analysis (Column 1) showed the material to be contaminated with very small amounts of cyclooctatetraene and di-tert-butylcyclooctatriene, but no tert-butylcyclooctatriene was detected. Fractional distillation through an 8 cm Vigreux column afforded 1.5 g of pure tert-butylcyclooctatetraene, bp 45.5°C (0.5 mm).

Deprotonation of Di-tert-butylcyclooctatriene with Potassium Amide in Liquid Ammonia. Formation of 7.

To a 300 mL flask equipped with a sidearm stopcock, stirrer and Dry Ice condenser with nitrogen inlet was added a few milligrams of $FeCl_3 \cdot 6H_2O$. The flask was heated sharply with a heat gun under nitrogen flow to dehydrate the $FeCl_3$. Upon dehydration, the $FeCl_3$ formed a dark red-brown solid. The flask and condenser were then cooled with dry ice-isopropanol and 100 mL of ammonia (dried over sodium) were condensed into the flask. To the stirred ammonia at -78°C was added 0.315 g (8.1 mg-atom) of freshly cut potassium metal. The mixture immediately turned dark blue and remained blue until the mixture was lifted out of the cold bath and allowed to warm somewhat. Upon warming, the mixture turned lighter blue and finally a grayish color. To this solution of KNH_2 was added 28 mL of dry THF. At -40°C, 0.88 g (4.0 mmol) of di-tert-butylcyclooctatriene was added in 5 mL of dry THF. The mixture immediately turned light brown and some solid was observed. After stirring for 3 h at -25 to -30°C, a dark brown solution remained. The ammonia was then allowed to evaporate through a bubbler giving a reddish-purple THF solution. This solution was degassed on the vacuum line, the THF was transferred off and the solid was dried at high vacuum for 9 h. The solid was washed twice with hexane in the glove box and dried to give 0.78 g (66%) of dipotassium 1,5-di-tert-butylcyclooctatriene-diide (7) as a purplish gray solid: NMR (THF-d_8) δ 1.6 (s, 18H), 5.7 (br s, 4H), 5.95 (br s, 2H); CMR (THF-d_8) 36.0 (t-Bu), 39.1 (t-Bu, quat.), [87.7, 87.9, 89.5, 108.3 (ring)].

9-Oxabicyclo[6.1.0]octa-2,4,6-triene 9.

The procedure of Cope and Tiffany[10] was followed to give 9 in 35% yield, bp (1 mm) 50° (Lit.[10] bp (12 mm) 75-6°); NMR ($CDCl_3$) δ 3.4 (s, 2H), 5.8 (s, 2H), 6.0 (s, 4H).

4-tert-Butylcycloocta-2,6-dien-1-one, 10.

To a solution of 8 g (67 mmol) of 9 in 600 mL of dry ether under nitrogen was added dropwise 40 mL of tert-butyllithium (2.1M in pentane, 84 mmol). The mixture turned red and was allowed to stir for 0.5 h after completion of the addition. The mixture was quenched with 100 mL of aqueous NH_4Cl and washed with water and brine. The organic layer was dried ($MgSO_4$) and evaporated. The residue was heated at 80° for 1 h and distilled, bp 75-85° (0.5 torr) to give 7.25 g (61% yield) of the desired ketone; IR 1678 cm^{-1} (C=O), NMR ($CDCl_3$) δ 1.0 (s, 9H), 1.4-2.0 (m, 1H), 2.4-2.6 (d, 1H), 2.8-3.2 (m, 2H), 3.6-3.9 (m, 1H), 5.5 (br s, 2H), 5.8-6.4 (m, 2H); MS m/e (rel. intensity): 178 (3.3), 163 (3.0), 109 (52.0), 91 (100), 57 (45.9); UV λ_{max} (EtOH) 231 nm (ε=7774). Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.15. Found: C, 80.73; H, 10.09.

4-tert-Butylcyclooctanone, 13.

Hydrogenation of 100 mg of 10 with 5% Pd/C in ethanol gave after filtration and evaporation 100 mg of a fragrant oil; IR 1700 cm^{-1} (C=O); MS m/e (rel. intensity) 182 (M^+, 4.3), 124 (19.6), 98 (61.1), 47 (100); CMR ($CDCl_3$, δ ppm from TMS) 22.4, 27.1, 27.6, 29.0, 30.4, 34.0, 39.7, 44.2, 47.9, 218.0. Anal. Calcd. for $C_{12}H_{22}O$: C, 79.12; H, 12.08. Found: C, 79.12; H, 11.97.

1,4-di-tert-Butylcycloocta-2,6-dien-1-ol, 11.

To a solution of 3.9 g (21.9 mmol) of 10 in 30 mL of dry hexane at -78° under nitrogen was added dropwise 17 mL (32.3 mmol) of 1.9M tert-butyllithium in pentane. After stirring for 1 h at -78° the solution was allowed to warm and was quenched with 50 mL of saturated aqueous NH_4Cl. The washed and dried ($MgSO_4$) organic layer was evaporated to give 4.6 g (89%) of yellow oil which was purified by chromatography on silica eluted with 8:1 hexane:ether. The product was white crystals, mp 70-75°; NMR ($CDCl_3$) δ 0.8-1.2 (dd, 18H), 1.4-3.4 (m, 5H), 5.4-5.8 (m, 4H); MS m/e (rel. intensity) 236 (M^+, 0.26), 218 (6.8), 179 (81.2), 57 (100); High Resolution MS: Calcd. for $C_{16}H_{28}O$, 236.2140; found: 236.2137.

3,8-di-tert-Butylcycloocta-1,3,5-triene, 12.

To a solution of 4.6 g (19.5 mmol) of 11 in 300 mL of dry ether at 0° under nitrogen was added 5 mL of pyridine followed by 2 mL of thionyl chloride. The cloudy suspension was stirred for 1 h and allowed to warm. After stirring for 3 h at RT the mixture was quenched with 50 mL of water and the washed and dried ($MgSO_4$) ether layer was evaporated to give a yellow oil. Chromatography on silica eluted with hexane gave 1.9 g (45%) of product with NMR ($CDCl_3$) δ 0.9 (s, 9H), 1.2 (s, 9H), 2.2-3.0 (m, 3H), 5.5-6.2 (m, 5H); MS m/e (rel. intensity) 218 (M^+, 3.0), 203 (1.7), 161 (7.0), 134 (28.0), 119 (100), 57 (38.4). Anal. Calcd. for $C_{16}H_{26}$: C, 88.07; H, 11.93. Found: C, 88.03; H, 11.92. This compound polymerizes on standing.

1,4-di-tert-Butylcyclooctatetraene, 5.

To a solution of KNH_2 (prepared from 1 g (25.6 mmol) of potassium and a small amount of $FeCl_3$) in 50 mL of ammonia and 20 mL of dry THF was added slowly 1.5 g (6.9 mmol) of 12 in 20 mL of THF. Ammonia was allowed to evaporate from the purple-brown mixture and a solution of iodine[34] in dry THF was added until the solution was a uniform milky yellow. This solution was poured into water and extracted with hexane. The washed (satd. $Na_2S_2O_3$, water, brine) and dried ($MgSO_4$) extract was evaporated to give an orange oil which was chromatographed on silica eluted with hexane. The product light yellow oil, 0.9 g (60%) had NMR ($CDCl_3$) δ 1.1 (d, 18H), 5.5-6.1 (m, 6H). Anal. Calcd for $C_{16}H_{24}$: C, 88.89; H, 11.11. Found: C, 89.05; H, 10.95.

1,1',4,4'-tetra-tert-Butyluranocene, 8.

In a glove box a solution of 0.40 g (1.36 mmol) of 7 in 40 mL of THF was stirred with 0.26 g (0.68 mmol) of UCl_4 in THF for 23 hours. Removal of solvent left a dark green solid which was extracted with hexane to give 0.14 g (31%) of air-sensitive 8 which was characterized by spectral data: NMR (THF-d_8, 40°) δ -9.8 (s, 36H), -24.4 (br s, 4H), -38.0 (br s, 4H), -40.4 (br s, 4H);[9] CMR (THF-d_8, ppm from TMS) -22.2, 44.5, 276.0, 281.3, 306.6, 331.4; MS m/e (rel. intensity) 670 (M^+, 100), 454 (35), 216 (5); Visible (rel. abs.), 631 (1.0), 658 (0.45), 677 (0.3), 725 (0.1) nm.

5-Bromomethyl-2,2,6,6-tetramethylhepten-3-one (19).

To a solution of 5.0 g (27 mmol) of 2,2,5,6,6-pentamethyl-hept-4-en-3-one (18)[35] in 50 mL of CCl_4 was added 4.9 g (27 mmol)

of finely ground N-bromosuccinimide. The mixture was stirred at reflux for 3 h at which time succinimide had encrusted around the top of the solution. After cooling, the yellow solution was separated by filtration and the solvent was removed in vacuo. Simple distillation afforded the bromide (6.5 g, 92%) as a liquid which discolored on standing at 0°C; bp 59-62°C (0.2 mm): NMR ($CDCl_3$) δ 1.20 (s, 9H), 1.25 (s, 9H), 4.5 (s, 2H), 6.55 (s, 1H); IR (film) 1686 cm^{-1} (C=O), 1603 cm^{-1} (C=C); m/e (rel. intensity) 260, 262 (M^+, 5), 203, 205 (56,54), 124 (61, 57 (100). Anal. Calcd. for $C_{12}H_{21}Br$: C, 55.18; H, 8.10; Br, 30.59. Found: C, 55.30; H, 8.18; Br, 30.50.

(5,5-Dimethyl-2-tert-butyl-4-oxohex-2-enyl)triphenylphosphonium bromide (20).

A solution of 1.5 g (5.7 mmol) of 12 and 1.5 g (5.7 mmol) of triphenylphosphine in 15 mL of dry benzene was stirred at reflux for 3 h forming a light colored suspension. The mixture was cooled to room temperature and the solvent was decanted (filtration proved impossible due to the highly hygroscopic nature of the salt). The solid was dried at high vacuum (10^{-3} Torr) for several hours to yield 2.56 g (85%) of a pinkish-white powder. The NMR spectrum exhibited the expected resonances, but, in addition, showed the presence of an unidentified impurity (~30%). Due to the hygroscopic nature of the material, it was not further characterized or purified but was taken on to the next step: NMR ($CDCl_3$) δ 0.9 (s, 9H), 1.15 (s, 9H), 4.95 (d, 2H, J=18Hz), 6.65 (d, 1H, J=6Hz), 7.7 (br s, 15H); Contaminant: 0.9 (s, 9H), 1.3 (s, 9H), 3.6 (br m, 1H), 4.5 (br s, 1H), 6.5 (d, 1H, J=18 Hz), 7.9 (br s, 15H).

Treatment of 20 with NaH.

Sodium hydride (57% oil dispersion, 0.037 g, 0.88 mmol) was washed twice with dry benzene and was then slurried in a mixture of 10 mL of dry benzene and 40 mL of dry THF. The phosphonium salt, 20 (0.40 g, 0.77 mmol) was added to the stirred mixture at room temperature under nitrogen. A yellow cloudy mixture resulted. After stirring for 1 h, the mixture was heated and maintained at reflux for 14 days. Upon cooling to room temperature and solvent removal- a viscous yellow oil was obtained which slowly formed yellow star-shaped crystals. This material was sublimed (100-120°C, 10^{-3} mm) to give 15 as a light yellow solid; mp 110-114°C: NMR ($CDCl_3$) δ 0.5 (s, 9H, 1.15 (s, 9H), 3.8 (br s, 1H), 5.3 (s, 1H), 7.2 (br s, 15H); m/e (rel. intensity) 442 (M^+, 1.1), 385 (17), 365 (16), 262 (100), 183 (47), 165 (36), 125 (28), 57 (30).

Pyrolysis of 15.

A small amount of the ylide 15 was placed in a thick-walled capillary tube (5 mm ID, 10 mm OD). The tube was evacuated to 10^{-3} mm and sealed. This small bomb was heated at 120-125°C for 22 h in an oil bath. On cooling to room temperature, the melt solidified to a brown mass. The tube was then cooled in ice, cracked open and the material was taken up in $CDCl_3$. Some insoluble brown material was removed by filtration. A NMR spectrum showed unchanged 15 and no evidence for the formation of 6.

Similar results were obtained using n-butyllithium as a base in benzene.

Treatment of Chloroketene Dimethyl Acetal (25) with 2,2,6,6-Tetramethyl-4-hepten-3-one 26.

A. An NMR tube containing a solution of 0.30 g (2.5 mmol) of 25[36] in 0.41 g (2.5 mmol) of 26[25] was degassed on the vacuum line (10^{-3} mm) and sealed off. A NMR spectrum showed the expected superposition of the spectra of the two compounds. The mixture was heated in an oil bath at 150°C for 60 h after which NMR spectrum was virtually the same as the initial spectrum. No cycloaddition product could be detected.

B. An NMR tube prepared as above was determined to contain 25 and 26 in a ratio of 1.0:0.91 by integration of the NMR spectrum. This tube was then placed in a fluidized sand bath at 135°C. The bath temperature was then allowed to rise to 210°C. After 11 h of heating, the tube was removed and an NMR spectrum of the orange material showed 25 and 26 to be present in a ratio of 1:1.3 and several new resonances had appeared in the region 2.8-3.4δ. Thus, the ketene acetal had undergone some polymerization, but no new peaks attributable to a cycloaddition adduct were observed.

C. Reaction at High Pressure: A solution of 0.30 g (2.5 mmol) of 25 and 0.41 g (2.4 mmol) of 26 in ether was added to a high pressure copper bellows reactor. Ether was added to fill the reactor along with a few crystals of hydroquinone. The capped reactor was placed in a press[26] and subjected to a pressure of 6.8 kilobars (approx. 7000 atm) for 3 h at room temperature.[37] The reactor was then cooled in a dry ice bath and opened. After solvent removal by rotary evaporation, a NMR spectrum of the neat

liquid showed that no reaction had occurred except for a small amount of destruction of the ketene acetal.

2,2,6,6-Tetramethylhept-4-yn-3-one (27).

A. From tert-Butylethynyllithium and Pivaloyl Chloride.

A solution of tert-butylethynyllithium was prepared by addition of 20.3 mL (0.049 mol) of 2.4M n-BuLi in hexane to a stirred solution of 4.0 g (0.049 mol) of tert-butylacetylene in 80 mL of dry ether at 0°C under argon. The resulting mixture was heated at reflux for 2 h and allowed to stand at room temperature for several hours. The acetylide solution was transferred to an addition funnel via cannula and was added dropwise to a stirred solution of 5.9 g (0.049 mol) of pivaloyl chloride under argon at -50 to -75°C. The mixture was allowed to warm slowly while still in the cooling bath. As the bath temperature reached -35°C, the mixture began to turn cloudy. At -10°C, the cooling bath was removed and the milky white suspension was allowed to warm to room temperature. The mixture was then poured into ice water and the layers were separated. The aqueous layer was washed with ether and the combined organics were washed with sat. NH_4Cl, sat. NaCl, and dried (Na_2SO_4). Solvent removal and simple distillation of the residue yielded two fractions. Fraction 1 was identified as the desired ketone 27, 3.5 g (43%) contaminated with a small amount of higher boiling material: bp 79-84°C (14 mm); NMR (CCl_4) δ 1.15 (s, 9H), 1.30 (s, 9H); IR (film) 4.58 (C≡C), 6.02 (C=O)μ; UV (EtOH) 220 (ε=6710), 309 (ε=40) nm.

A pure sample of the ketone was obtained for analysis by preparative GC (column 2, 212°C): m/e (rel. intensity) 151 (M^+-methyl, 3), 138 (7), 123 (37), 109 (99), 81 (90), 57 (100). A parent ion was not observed, even at low voltage.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91 Found: C, 79.39; H, 10.87.

Fraction 2 was obtained as a viscous oil; bp 117-124°C (14 mm). The NMR spectrum exhibited several resonances in the 1.0-1.3δ region. A strong ester carbonyl band at 5.74μ and a weak acetylene stretch at 4.5 μ were observed in the IR spectrum. A mass spectrum exhibited m/e 332 as the highest mass peak. The IR and mass spectral data are consistent with a structure obtained by addition of tert-butylacetylide to the product ketone and subsequent reaction with piraloyl chloride.

B. From (tert-Butylethynyl)copper and Pivaloyl Chloride.

A modification of the general procedure of Normant and Bourgain[38] was used. To a stirred solution of tert-butylacetylene (5.8 g, 0.071 mol) in 130 mL of dry ether at 0°C under Ar was added 34 mL (0.071 mol) of 2.1M n-butyllithium in hexane over 5-10 min. The cooling bath was removed and the mixture was stirred for 1.5 h. The resulting yellow solution was cooled to 0°C and 13.4 g (0.071 mol) of dry CuI was added over 5 min from a flask attached to the reaction flask by a length of tubing. After removing the cooling bath and stirring for 30 min, pivaloyl chloride (8.5 g, 0.071 mol) was added dropwise over 15 min to the black solution whereupon a purple-gray suspension resulted. The suspension was stirred for 39 h and then hydrolyzed with 120 mL of cold 5N HCl. The layers were separated

and the aqueous layer containing a grey gelatinous precipitate was washed several times with ether (300 mL overall). The combined organic solutions were washed with H_2O, sat. $NaHCO_3$, sat. NaCl, dried (Na_2SO_4) and reduced to give a slightly yellow liquid. More material (1-2 g) was obtained by allowing the original aqueous layer to stand for 1 h and washing with more ether. This ether solution was washed with sat. $Na_2S_2O_3$ to remove the yellow color which had developed and was worked up as above.

The combined residue was distilled to give 8.1 g (69%) of quite pure 27, bp 56.5-61.5° (5 mm), identical to the material obtained in A.

4,6-Di-tert-butyl-3-methoxycarbonyl-2H-pyran-2-one (28).

A solution of 1.05 g (6.3 mmol) of 27 and 0.82 g (6.3 mmol) of dimethyl malonate was prepared in 5 mL of dry MeOH. To this stirred solution at 60°C under Ar was added 1.5 mL (1.3 mmol) of a freshly prepared 0.87M solution of NaOMe in MeOH.[39] No apparent reaction had occurred (TLC:SiO_2 1:1 pet ether:Et_2O), so the mixture was heated at reflux. After 3.2 h, TLC showed no starting material remaining. The mixture was then cooled to room temperature and was acidified with 20% aqueous acetic acid whereupon a white crystalline solid precipitated. The solid was collected by filtration and dried to give 0.65 g of pyrone ester 28 which was quite pure by NMR. The filtrate was poured into H_2O and extracted with ether. The ether solution was washed with saturated Na_2CO_3, dried (Na_2SO_4) and reduced to give a slightly yellow, oily solid from which 0.28 g of 28 was obtained as white needles by recrystallization from hexane.

The combined yield of ester was 0.93 g (56%), mp 124.5-126°C: NMR (CCl_4) δ 1.31 (2s separated by 2Hz, 18H), 318 (s, 3H), 6.0 (s, 1H); IR (CCl_4) 5.74, 5.82 ; m/e (rel. intensity) 266 (M^+, 14), 238 (33), 235 (18), 223 (100), 209 (78), 57 (38), 41 (55). Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33. Found: C, 67.80; H, 8.30.

4,6-Di-tert-butyl-2H-pyran-2-one (22).

To 0.58 g (2.18 mmol) of 28 in a small tube was added 10 mL of conc. H_2SO_4. The tube was capped with a rubber septum containing a small hole and was placed in a 105-110°C oil bath. After 1.5 h, the orange-yellow mixture was allowed to cool somewhat and poured into ice water. The resulting tan crystals were collected by filtration. Recrystallization from MeOH-H_2O yielded 0.37 g (82%) of off-white crystalls, mp 110-111°C: NMR (CCl_4) δ 1.25 (s, 9H), 1.30 (s, 9H), 5.9 (m, 2H); NMR (C_6D_6) δ 0.9 (s, 9H), 1.1 (s, 9H), 5.85 (d, 1H, J=2Hz), 6.05 (d, 1H, J=2Hz); IR (CCl_4) 5.8 μ(broad) ; UV (EtOH) 293 nm; m/e (rel. intensity) 208 (M^+, 21), 165 (77), 151 (100), 95 (41), 57 (32), 41 (46). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.96; H, 9.68. Found: C, 74.76; H, 9.45.

Alternatively, the crude pyrone could be purified by sublimation (60-70°C, 0.1 mm) to give pure white pyrone, mp 111-112.5°C in 86% yield from ester 28.

Pyrex Photolysis of 7.

A concentrated solution was prepared by dissolving 0.098 g of pyrone 22 in 0.15 mL of warm C_6D_6 in an NMR tube. The tube was then degassed on the vacuum line, sealed, and attached to the side of

a water-cooled quartz immersion well. The entire apparatus was wrapped in aluminum foil and immersed in a large water bath. Irradiation of the tube was achieved with a 450 W medium pressure mercury lamp through a pyrex filter. After 4.8 h of irradiation, the NMR spectrum revealed that some starting material still remained, so the mixture was irradiated an additional 3 h. At this point, the tube contained a viscous solution and a colorless solid. NMR analysis showed no starting material, but instead, a large, broad peak at 1.2δ and two small, broad resonances at 3.6-4.3δ and 6.7δ, consistent with a mixture of dimer structures. The NMR tube was then cracked open and the white solid was removed as a slurry in ether (the solid was virtually insoluble in a variety of solvents). Solvent removal at high vacuum gave a white solid. A mass spectrum of the material was identical to that of the starting pyrone. No peak corresponding to an m/e greater than 208 was observed even at low voltage.

Pyrolysis of the Photolysis Product of 22.

A small amount of the white solid from above was placed in a small flask equipped with a reflux condenser. The flask was immersed in a 300°C sand bath for 2 min whereupon the material in the flask melted and turned brown. After cooling, the brown material was triturated with hexane and the resulting solution was chromatographed on silica gel (0.8 cm x 40 cm). Elution with hexane afforded no material, but 10% ether:hexane caused a white solid to elute. This solid proved to be the starting pyrone by NMR analysis.

Pyrolysis of the material by sublimation at >200°C from acidic alumina also resulted in isolation of the starting pyrone 22.

1,3,5,7-Tetra-tert-butylcyclooctatetraene (6).

To a dry 130 mL photolysis reactor was added 0.400 g (1.92 mmol) of pyrone 22. The reactor was fitted with a quartz immersion well, ether was added (approx. 130 mL), and the solution was purged with nitrogen for 1 h with stirring. The apparatus was then immersed in a dry ice-isopropanol bath contained in a large plastic bucket and the immersion well was cooled with an ethylene glycol circulating bath. The stirred solution was irradiated with a 450 W medium pressure mercury lamp while nitrogen was slowly bubbled through. During the photolysis, the glycol circulating bath was maintained at approximately 10°C and a large amount of dry ice was maintained in the outer cooling bath. After 11 h, the photolysis was discontinued and the reaction mixture was allowed to warm to room temperature. Rotary evaporation of the ether solution afforded a yellow oil which was chromatographed on silica gel (2 cm x 18 cm) with hexane to yield 0.23 g (72%) of 6 as a slightly yellow, very viscous oil. The oil was only slightly impure by NMR.

A small amount of the cyclooctatetraene was further purified by preparative GC (Column 1, 200°C) to yield 6 as a low melting, white crystalline solid, mp 32-34°C: NMR ($CDCl_3$) δ 1.1 (s, 9H), 5.75 (s, 1H); CMR ($CDCl_3$, in ppm from TMS) 29.8, 26.2, 121.5, 151.3; m/e (rel. intensity) 328 (M^+, 3), 271 (17), 215 (9), 159 (22), 57 (100). Anal. Calcd for $C_{24}H_{40}$: C, 87.73; H, 12.27. Found: C, 87.82; H, 12.00.

In subsequent preparations, chromatography on neutral alumina with hexane gave product of higher purity than with chromatography on silica gel. The photolysis must be run for at least 11 h. In another preparation in which the photolysis was carried out for only 9 h, the product was contaminated with 10-15% of another material identified as the tricyclooctadiene 31 by comparison of its NMR spectrum with the prviously reported spectrum:[30] NMR ($CDCl_3$) 0.9 (s), 1.1 (s), 2.8 (d, J=3Hz), 5.55 (d, J=3Hz).

Attempted Isolation of Intermediates in the Preparation of 6.

The photolysis was repeated as described above. A 30 mL aliquot of the solution was removed after 30 min of irradiation and was diluted with ether in a UV cell. A UV spectrum showed complete disappearance of the starting material peak at 293 nm (a similarly treated aliquot of the solution before reaction gave an absorbance of 0.83 at 293 nm). After 40 min, a 20 mL aliquot was removed. After solvent removal on a rotary evaporator, a NMR spectrum ($CDCl_3$) showed the presence of a 40:60 mixture of the COT 6 and the tricyclooctadiene 31 and very little other material. After 3.5 h, the photolysis was discontinued. Workup in the normal manner gave a crude oil that was a 70:30 mixture of the COT and tricycloctadiene respectively: NMR (CCl_4) δ [24, 0.90 (s), 1.00 (s), 2.75 (J=3Hz), 5.5 (d, J=3Hz)], [6, 1.05 (s), 5.65 (s)].

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