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Carbenes from Alkyl Halides and Organolithium Compounds. III.¹ Syntheses of Alkyltropones from Phenols²

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Chlorocarbene, generated from methylene chloride and methyl lithium, was found to add to lithium phenolate with ring expansion to yield tropone and 2-methyl-3,5-cycloheptadienone (VII). The latter product predominated and presumably was formed by a fast nucleophilic addition of the lithium reagent to the tropone initially produced. Similarly, *o*-cresol in methylene chloride gave 2,7-dimethyl-3,5-cycloheptadienone (XIV) on treatment with methyl lithium. Evidence was found for the addition of methyl lithium to the 1-position of both tropone and 2-methyltropone as a minor pathway which yielded methyltropylium and 1,2-dimethyltropylium ion, respectively, on acidification. On the other hand, the reaction of 2,6-di-*t*-butylphenol with methylene chloride and methyl lithium provided 2,7-di-*t*-butyltropone in good yield. It is suggested that the bulky *t*-butyl groups prevent further attack on the tropone derivative by methyl lithium.

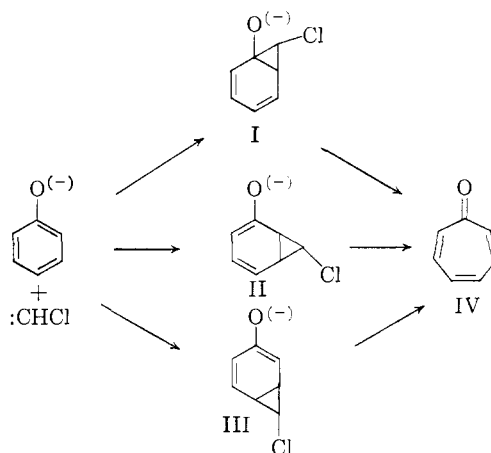
Ring expansion of benzenoid compounds is used frequently as a key step in the preparation of tropones and tropolones.³ These syntheses involve the addition of a divalent carbon species to benzene or its derivatives providing a cycloheptatriene which consecutively is oxidized to the seven-membered aromatic molecule. Whereas the reaction proceeds in the desired mode when photochemically generated methylene or carbalkoxymethylene are employed as addends, no reports of the ring expansion of simple benzenoid compounds with dihalocarbenes are available in the literature.⁴ These derivatives of methylene, easily generated by base-catalyzed elimination of hydrogen halide from haloforms,⁵ appear to be too weakly electrophilic to attack non-activated aromatic hydrocarbons.⁶ The reaction with more nucleophilic phenols generally leads to substitution rather than ring expansion as demonstrated by the well known Reimer-Tiemann reaction.⁷

Chlorocarbene, conveniently prepared from methylene chloride and alkyl lithium compounds,⁸ was shown to be a better electrophile than dihalocarbenes.¹ This observation suggested that chlorocarbene would react with aromatic compounds with ring expansion. Confirming these expectations it has been demonstrated that chlorocarbene combines with benzene to form tropylium chloride.⁹ This product, however, is obtained only in poor yield because of the further addition of methyl-

lithium, the reagent used to generate the carbene. It is the purpose of this paper to describe reactions of chlorocarbene with phenols leading to ring expansion products.

Results and Discussion

Assuming in analogy to the reaction with isolated double bonds,⁸ a simultaneous attack on two adjacent carbon atoms of the aromatic ring, three possible intermediates (I, II and III) can be foreseen in the reaction with phenolate ion.



However, each adduct can rearrange by valence bond tautomerism followed by loss of chloride ion to yield tropone (IV). Whether the tropone will be the final product of the reaction or will be attacked further by the lithium reagent depends on the relative rates of the carbene formation and the possible reaction of tropone with the alkyl lithium compound.

To test this hypothetical scheme methyl lithium in ether was added to a solution of lithium phenolate in methylene chloride. The major product resulting from this reaction was a ketone, C₈H₁₀O, isolated in 30% yield.¹⁰ It was assigned the structure of 2-methyl-3,5-cycloheptadienone (VII) on the basis of spectroscopical and chemical evidence. The presence of an unconjugated carbonyl group was indicated by infrared absorption at 1703 cm⁻¹. Moreover, the ultraviolet spectrum was found to be in agreement with a conjugated diene system (λ_{max} 225 mμ, ε 6000). On hydrogenation

(10) Yields are based on methyl lithium and are significantly higher if calculated on consumed phenol (see Experimental).

(1) Part II, G. L. Closs and G. M. Schwartz, *THIS JOURNAL*, **82**, 5720 (1960).

(2) Presented in part at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

(3) For recent reviews of tropone and tropolone syntheses see: (a) T. Nozoe, "Non-Benzenoid Aromatic Compounds," edited by D. Ginsberg, Interscience Publishers, Inc., New York, N. Y., 1959, p. 339; (b) J. Schreiber, M. Pesaro, W. Leimgruber and A. Eschenmoser, *Helv. Chim. Acta*, **41**, 2103 (1958); (c) P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955).

(4) The only exception appears to be a private communication of W. E. Parham to H. Wynberg reporting the conversion of 1-methoxynaphthalene to 2,3-benzo-7-chlorotropone, *Chem. Revs.*, **60**, 181 (1960).

(5) J. Hine, *THIS JOURNAL*, **72**, 2438 (1950); W. v. E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).

(6) W. v. E. Doering and Wm. A. Henderson, *ibid.*, **80**, 5274 (1958).

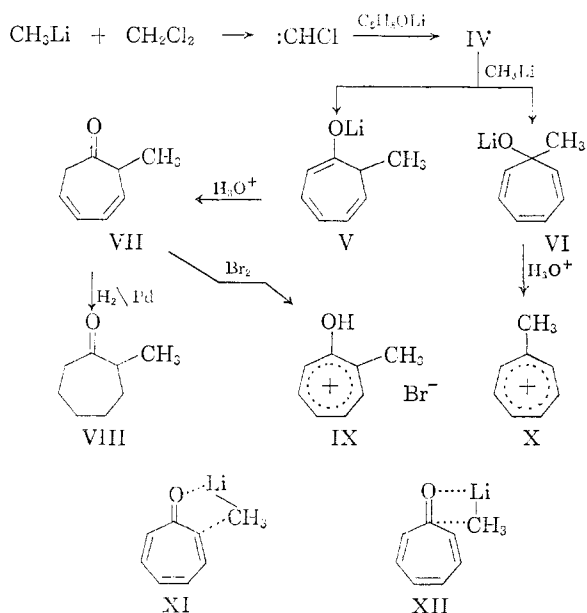
(7) H. Wynberg, *Chem. Revs.*, **60**, 169 (1960); see also J. Hine and J. M. Van Der Veen, *THIS JOURNAL*, **81**, 6446 (1959).

(8) G. L. Closs and L. E. Closs, *ibid.*, **81**, 4996 (1959); **82**, 5723 (1960).

(9) G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **10**, 38 (1960); compare also: M. E. Volpin, D. N. Kursanov and V. G. Dulova, *Tetrahedron*, **8**, 13 (1960).

the compound consumed two moles of hydrogen to yield a saturated ketone (infrared 1698 cm.^{-1}) which proved to be identical with 2-methylcycloheptanone (VIII). Finally, the nuclear magnetic resonance (n.m.r.) spectrum of the reaction product provided unequivocal proof for structure VII. The presence of a methyl group on a carbon atom bearing one hydrogen was indicated by a doublet at high field (225 and 232 c.p.s. relative to external benzene at 40 m.c.) while the olefinic protons gave rise to a multiplet between 18 and 72 c.p.s. In analogy with previously described procedures,¹¹ VII was smoothly dehydrogenated with bromine to give 2-methyltroponone hydrobromide (IX) which was characterized by its infrared and ultraviolet spectra and conversion to 2-methyltroponone picrate.

The formation of 2-methyl-3,5-cycloheptadienone from lithium phenolate and chlorocarbene indicated that the reaction scheme outlined above had been realized. However, in a consecutive reaction the troponone apparently added methyl lithium and was converted to the enolate V which on hydrolysis was protonated to give the least stable, unconjugated dienone VII.¹² This nucleophilic addition of methyl lithium to troponone must be a much faster reaction than proton abstraction from methylene chloride which, serving as solvent, is present in large excess. Only traces (0.1%) of troponone, detected by its characteristic ultraviolet spectrum, could be found in the reaction mixture.



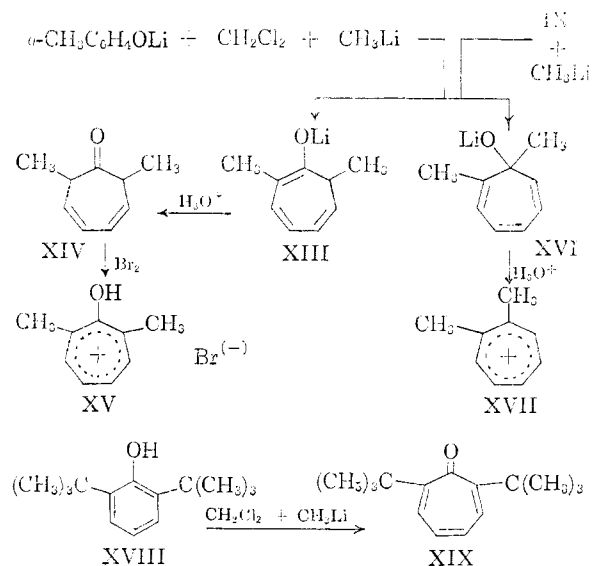
Although the addition of the methyl lithium to the 2-position of troponone predominated, attack at carbon atom 1 also occurred to a minor extent. The resulting lithium alkoxide VI was converted on acidification to methyltroponylium ion (X) detected in the acidified aqueous washings of the reaction mixtures by its ultraviolet spectrum and isolated as its chloroplatinate.

(11) E. E. van Tamelen and G. T. Hildahl, *THIS JOURNAL*, **78**, 4405 (1956).

(12) On standing, the compound slowly rearranged to a conjugated dienone, 2-methyl-2,4-cycloheptadienone or the isomeric 2-methyl-4,6-cycloheptadienone.

No evidence could be found for the formation of products resulting from the addition of methyl lithium on either carbon atom 3 or 4 of the troponone, although both positions are formally suited for nucleophilic attack. The observed specificity can be explained on the basis of chelation of the lithium atom with the carbonyl oxygen. Transfer of the methyl group to position 2 leads to a less strained transition state (XI) than four-center addition to the carbonyl group (XII).

The reaction of chlorocarbene with *o*-cresol gave strictly analogous results. Ring expansion of the cresol by the addition of the carbene led to 2-methyltroponone which added methyl lithium at position 7 with the formation of enolate XIII.



Upon acidification, 2,7-dimethyl-3,5-cycloheptadienone (XIV) was isolated as the major product. The structure of XIV was confirmed by spectroscopic evidence similar to that described for VII. The n.m.r. spectrum provided some evidence for the presence of both *cis* and *trans* stereoisomers by exhibiting additional splitting of the doublet caused by resonance of the methyl protons. The structural isomer, 2,2-dimethyl-3,5-cycloheptadienone, could not be detected in the reaction mixture. This product could have been present only in minor quantities since the conversion of the crude dienone XIV to 2,7-dimethyltroponone hydrobromide (XV) was accomplished in good yield. Attack of methyl lithium at position 1 of 2-methyltroponone occurred to a much smaller extent yielding 3% 1,2-dimethyltroponylium ion (XVII) upon acidification. This troponylium salt was identified and its yield estimated by ultraviolet spectroscopy.

As a further test of the reaction scheme, 2-methyltroponone was treated with methyl lithium directly. The reaction also provided the dienone XIV and 1,2-dimethyltroponylium ion XVII. Moreover, the ratio of troponylium ion to dienone produced was found to be nearly the same as that obtained in the reaction of *o*-cresol in methylene chloride with methyl lithium. This may be regarded as further support for the hypothesis that 2-methyltroponone is the intermediate in the latter reaction.

The absence of detectable amounts of products resulting from addition of methyllithium to carbon atom 3 or 4 of the tropones suggested that the reaction could be halted at the troponone stage with a suitable substituted phenol. This notion was tested by a study of the products obtained with 2,6-di-*t*-butylphenol (XVIII). When XVIII in methylene chloride was allowed to react with methyllithium, 2,7-di-*t*-butyltroponone (XIX) was indeed isolated in good yield. The reaction mixture was essentially free of any addition products of methyllithium to the troponone. This reaction represents the first example of a one-step transformation of a monocyclic benzenoid compound to the corresponding tropenoid homolog in preparative yields. The structure proof of XIX is based on catalytic hydrogenation with the consumption of three moles of hydrogen to give a saturated cyclic ketone, and upon its n.m.r. spectrum. The latter showed the equivalence of all nine methyl groups giving rise to a single sharp line at 220 c.p.s. (relative to external benzene at 40 m.c.). The olefinic protons showed a multi-component resonance pattern consisting of 12 resolved lines spaced symmetrically on either side of the center of the multiplet at -6 c.p.s. The complete symmetry of this pattern with regard to spacing and intensities is indicative for an A_2B_2 system.¹³ This together with the elementary analysis and the results from the hydrogenation are only compatible with structure XIX.

The ultraviolet and infrared spectra of XIX are sufficiently unusual to merit some discussion. Similarly to troponone³ and its 2-methyl and 2,7-dimethyl derivatives, XIX exhibits an ultraviolet spectrum consisting of two bands. However, the long wave length band of XIX is displaced by 26 to 37 $m\mu$ to shorter wave length (λ_{\max} 286 $m\mu$, ϵ 6500) compared to troponone or its 2,7-dimethyl derivative, respectively. The low wave length band is reduced in intensity but shifted only insignificantly from the position of the corresponding band in 2,7-dimethyltroponone (λ_{\max} 237 $m\mu$, ϵ 15000, for XIX versus λ_{\max} 234 $m\mu$, ϵ 30500, for 2,7-dimethyltroponone). When the ultraviolet spectrum of XIX was measured in concentrated hydrochloric acid, partial protonation caused the appearance of a new band at 329 $m\mu$, a region where normal tropones show their second maximum.

Similarly, the infrared spectrum of XIX differs remarkably from spectra of other tropones. Troponone and all alkyl tropones reported so far³ show a band of medium intensity at 1635 to 1620 cm^{-1} attributed to the carbonyl absorption, and a very strong band at 1575 to 1585 cm^{-1} usually associated with double bond stretching vibrations. The spectrum of XIX shows these bands with reversed intensities. An extremely strong band is noted at 1635 cm^{-1} and only weak absorption is found at 1610 and 1590 cm^{-1} .

These spectral anomalies may reflect a larger contribution by the cycloheptatrienone structure to the resonance hybrid than in the normal tropones where the tropylium oxide structure predominates. The strongly reduced basicity of XIX compared

to other tropones can be explained by the same argument, although steric hindrance of solvation of the resulting ion will also reduce the tendency of its formation. A conceivable explanation for the reduced aromaticity of XIX may be found in non-bonded interactions of the *t*-butyl groups with the carbonyl group which tend to stretch the bonds between carbon atom 1 and carbons 2 and 7, respectively. This will result in increased single bond character of these bonds and may seriously disturb the aromaticity of the ring system.

Experimental

General.—All reactions involving methyllithium were carried out under an atmosphere of dry nitrogen. Melting and boiling points are not corrected. Infrared spectra were recorded with a Perkin-Elmer model 21 spectrophotometer; n.m.r. spectra were measured with a Varian high-resolution spectrometer, V-4300 B at 40 m.c. Chemical shifts are reported relative to external benzene and were measured in 10% carbon tetrachloride solution.

Reaction of Methyllithium with Lithium Phenolate in Methylene Chloride.—Lithium phenolate was prepared by adding lithium hydride (10 g.) to a solution of phenol (66 g., 0.7 mole) in methylene chloride (350 ml.) and heating the suspension to reflux for 5 hours. To the resulting solution was added methyllithium (0.35 mole) in ether (250 ml.) over a period of 2 hours at room temperature. The mixture was then cooled to 0° and poured into a vigorously stirred solution of 5 *N* hydrochloric acid (500 ml). During the addition ice was added to keep the temperature below 10°. The organic layer was separated and washed twice with 5% sodium hydroxide solution (800 ml.) to remove the excess phenol. The solution was then washed with water, dried and the solvent was removed *in vacuo*. The residue was distilled at 0.1 mm. and the fraction distilling up to 25° was collected in a receiver cooled with a Dry Ice-bath. An ill-defined residue remained in the distillation flask and resisted purification. The distillate was redistilled at 3.5 mm. and 2-methyl-3,5-cycloheptadienone (6.5 g., 0.053 mole, 30% based on methyllithium, 44% based on recovered phenol) was collected at 58–61°; ultraviolet spectrum (ethanol): λ_{\max} 225 $m\mu$ (6000); infrared spectrum (neat liquid): $>CO$ 1703 cm^{-1} .

Anal. Calcd. for $C_8H_{10}O$ (122.09): C, 78.65; H, 8.20. Found: C, 78.31; H, 8.25.

The aqueous phase of the hydrolysis mixture was extracted exhaustively with ether to remove all traces of phenol. The ultraviolet spectrum of the resulting solution exhibited maxima at 288 and 225 $m\mu$ with relative intensities of 1:6.6. The solution was neutralized with sodium carbonate and extracted with ether. The ether extract was reextracted with 2 *N* hydrochloric acid (10 ml.) and the aqueous solution was added to a solution of chloroplatinic acid in hydrochloric acid. The resulting precipitate proved to be identical with methyltropylium chloroplatinate prepared by a previously described procedure¹⁴ (identical ultraviolet and infrared spectra and decomposition points); total yield of methyltropylium ion as determined by ultraviolet spectrum of the original hydrolysis solution: 7 mmoles or 4%. Extinction coefficient of maximum at 288 $m\mu$ was obtained from chloroplatinate and was found to be 4900.

Troponone was detected in the original hydrolysis solution by its ultraviolet absorption at 312 $m\mu$. To obtain the spectrum free from interference by methyltropylium ion, an aliquot of the solution was adjusted to pH 5 and extracted several times with ether. The solution was then essentially free from methylcycloheptatrienol and exhibited the pure troponone spectrum including the fine structure between 225 and 240 $m\mu$.¹⁵ The spectroscopically determined yield based on the absorption at 312 $m\mu$ was 0.14%.

Hydrogenation of 2-Methyl-3,5-cycloheptadienone.—2-Methyl-3,5-cycloheptadienone (2.0 g.) was dissolved in ethanol (30 ml.) and hydrogenated over 5% palladium-on-charcoal (100 mg). After hydrogen uptake had ceased

(14) D. N. Kursanov and M. E. Volpin, *Doklady Akad. Nauk S.S.S.R.*, **113**, 339 (1957).

(15) H. J. Dauben and H. J. Ringold, *THIS JOURNAL*, **73**, 876 (1951).

(13) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 142.

(810 ml., 24° (755 mm.)) the solution was filtered, the ethanol distilled off and the residue distilled. **2-Methylcycloheptanone** was collected at 184–186° (1.65 g., 79%), n_D^{20} 1.4587 (reported¹⁶ b.p. 185–186°, n_D^{20} 1.461); 2,4-dinitrophenylhydrazone, m.p. 119–121° (reported¹⁶ 121–122°).

2-Methyltropone Hydrobromide.—2-Methyl-3,5-cycloheptadienone (5.35 g., 44 mmoles) was dissolved in carbon tetrachloride (110 ml.). To this solution was added a solution of bromine (7.0 g., 44 mmoles) in carbon tetrachloride (200 ml.). The temperature was kept at 0° and the addition was completed within 3 hours. The solution was then heated to reflux for 7 hours. To complete the precipitation of the hydrobromide the solution was then saturated with hydrogen bromide and the fluffy crystals were filtered off (5.6 g., 28 mmoles, 63%). For purification the compound was sublimed at 60° (0.1 mm.) and then recrystallized from methylene chloride; dec. p. 125–128°; ultraviolet spectrum (water): λ_{max} 229 (25,200), 233 (26,300), 236 (21,500), 240 (18,100), 317 m μ (8,100); infrared spectrum (free tropone as neat liquid) carbonyl and double bond region only: 1625, 1595, 1575, 1520 cm.⁻¹.

Anal. Calcd. for C₈H₉BrO (201.07): C, 47.78; H, 4.51; Br, 39.75. Found: C, 47.47; H, 4.52; Br, 39.85.

2-Methyltropone picrate was obtained by dissolving the hydrobromide in very little water and adding sodium carbonate. The free tropone was then extracted with ether and the picrate precipitated from the ether solution. Recrystallization from ethanol yielded yellow plates, dec. p. 125–128°.

Reaction of Methylithium with Lithium *o*-Cresolate in Methylene Chloride.—Lithium *o*-cresolate was prepared by adding lithium hydride (8 g.) to a solution of *o*-cresol (58 g., 0.53 mole) in methylene chloride (350 ml.) and heating the suspension to reflux for 8 hours. To the resulting solution¹⁷ was added methylithium (0.25 mole) in ether (200 ml.) over a period of 2 hours. After the addition was completed the reaction mixture was hydrolyzed by adding it to a solution of 5 *N* hydrochloric acid. The temperature of the hydrolysis mixture was not allowed to exceed 10°. The organic layer was separated and washed several times with a 10% solution of sodium hydroxide to remove the excess *o*-cresol. The solution was then washed with water, dried and the solvent removed *in vacuo*. The residue was distilled at 0.1 mm. and the crude **2,7-dimethyl-3,5-cycloheptadienone** was collected in a cooled receiver up to 30°. The remaining residue was a complex mixture of higher boiling compounds containing chlorine which were not further investigated. The distillate was redistilled at 3.5 mm. and the product collected at 61–63° (2.6 g., 0.019 mole 15% based on methylithium, 23% based on recovered *o*-cresol); ultraviolet spectrum (ethanol): λ_{max} 236 m μ (5,500); infrared spectrum (neat liquid) CO: 1705 cm.⁻¹.

Anal. Calcd. for C₉H₁₂O (136.18): C, 79.39; H, 8.88. Found: C, 79.16; H, 8.90.

The acidic hydrolysis solution was extracted several times with ether to remove all non-basic material. The resulting solution exhibited ultraviolet absorption maxima at 296 and 232 m μ with relative intensities of 1:7, attributed to 1,2-dimethyltropylium ion; yield 3.6 mmoles (3%), based on assumed extinction coefficient of 5000 for band at 296 m μ .

Reaction of 2-Methyltropone Hydrobromide with Methylithium.—2-Methyltropone hydrobromide (4.63 g., 23 mmoles) was suspended in ether (100 ml.) and a solution of methylithium (46 mmoles) in ether (45 ml.) was added over a period of 45 minutes. At the end of the addition a clear solution resulted. The reaction mixture was hydrolyzed

(16) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 181 (1939).

(17) In one experiment the lithium *o*-cresolate crystallized out of the supersaturated solution. The precipitate was redissolved by addition of 100 ml. of ether. The yield of the dienone was not affected by this dilution.

by adding it to 2 *N* hydrochloric acid to which sufficient ice had been added to keep the temperature below 10°. The organic layer was separated, washed with bicarbonate, dried, and the ether was distilled off. The residue was distilled at 3.5 mm. and the **2,7-dimethyl-3,5-cycloheptadienone** was collected between 62 and 64° (1.55 g., 11.4 mmoles, 50%). The infrared and ultraviolet spectra were identical with the spectra of the product obtained from *o*-cresol, methylene chloride and methylithium.

The aqueous phase of the hydrolysis mixture was extracted with ether and exhibited ultraviolet absorption at 296 and 232 m μ , attributed to 1,2-dimethyltropylium ion; yield 2.0 mmoles (9%) based on assumed extinction coefficient of 5000 for band at 296 m μ .

2,7-Dimethyltropone Hydrobromide.—2,7-Dimethyl-3,5-cycloheptadienone (1.17 g., 8.6 mmoles) was dissolved in carbon tetrachloride (20 ml.). To this solution was added bromine (1.35 g., 8.5 mmoles) in carbon tetrachloride (40 ml.) over a period of 2.5 hours. The temperature was kept at 0°. After the addition was complete the solution was heated to reflux for 3 hours. The solvent was then evaporated *in vacuo* and ether (50 ml.) was added. Dry hydrogen bromide was passed into the solution, causing an instant precipitation. The crystals were filtered off and sublimed for purification (1.15 g., 5.4 mmoles, 62%).

Anal. Calcd. for C₉H₁₁BrO: Br, 37.1. Found: Br, 36.9.

2,7-Dimethyltropone was generated by neutralizing an aqueous solution of the hydrobromide with sodium bicarbonate and extracting the solution with ether. The ether was evaporated and the residue purified by bulb to bulb distillation at 2 mm.; ultraviolet spectrum (water): λ_{max} 234 (30,500), 241 (25,200), 323 (8,600), shoulder at 336 m μ (7,000); infrared spectrum (near liquid) carbonyl and double bond region only: 1620, 1600, 1570, 1520 cm.⁻¹.

Anal. Calcd. for C₉H₁₀O (134.10): C, 80.56; H, 7.51. Found: C, 80.25; H, 7.69.

2,7-Di-*t*-butyltropone.—2,6-Di-*t*-butylphenol (48 g. 0.23 mole) was dissolved in methylene chloride (250 ml.), and methylithium (0.41 mole) in ether (230 ml.) was added at room temperature over a period of 2.5 hours. The reaction mixture was poured into ice-water and the organic layer was separated and washed consecutively with diluted hydrochloric acid, sodium bicarbonate solution and water. The solvent was removed *in vacuo* and the residue distilled over a short Vigreux column at 0.15 mm. The excess 2,6-di-*t*-butylphenol (34.5 g., 0.17 mole) was collected at 57–58°. Following a small intermediary fraction (1.1 g.), the crude product distilled at 76–82°. A second distillation of this fraction at 0.10 mm. yielded **2,7-di-*t*-butyltropone** (9.1 g., 0.042 mole, 23% based on methylithium, 70% based on recovered 2,6-di-*t*-butylphenol) boiling at 67–70°. The compound crystallized on standing and was recrystallized twice from pentane to a constant m.p. of 70.5°; ultraviolet spectrum (60% ethanol): λ_{max} 286 (6,500), 237 m μ (15,000); (concd. aq. HCl): λ_{max} 329 (4,100), 290 (3,900), 245 m μ (15,000); infrared spectrum (CHCl₃) carbonyl and double bond region only: 1635, 1610, 1590 cm.⁻¹.

Anal. Calcd. for C₁₇H₂₀O (218.33): C, 82.51; H, 10.16. Found: C, 82.32; H, 10.25.

Catalytic hydrogenation of the 2,7-di-*t*-butyltropone (150 mg., 0.69 mmole) in ethanol (10 ml.) over 5% palladium-on-charcoal (30 mg.) proceeded under consumption of 100.3% (51.8 ml., 24° (750 mm.)) of the calculated uptake for 3 moles of hydrogen per mole of tropone. The resulting product showed infrared absorption at 1702 cm.⁻¹.

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