Well-defined infrared absorption bands at 3425 and 3521 cm.$^{-1}$ suggest the presence of two non-symmetrical hydroxyl groups.

A 3-g. sample of the diol in ethanol was stirred with periodic acid at room temperature according to the procedure of Fuson and Tan.[10] From the product, which was a mixture of liquids, it was possible to isolate only mesitaldehyde, b.p. 135–137° (30 mm.), $n^{20}\text{D}$ 1.5343. The identity of the aldehyde was confirmed by conversion to its dinitro derivative,[11] m.p. 166.5–167.5°.

The mother liquors from the crystallization of the glycol were further concentrated, diluted with water and chilled. A yellow oil separated and crystallized after 2 days in the ice-box. Recrystallization from an ethanol solution, to which enough water was added at the boiling point to produce cloudiness, led to the isolation of a second hydrogenation product of the dimesityl enol V, believed to be one of the two possible 1,5-dimesityl-1,2-pentanolones, m.p. 70°, yield 5%.

Anal. Calcd. for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.56; H, 9.05.

Infrared absorption occurs at frequencies usually associated with the hydroxyl (3418, 3483 or 3522 cm.$^{-1}$), carbonyl (1696 cm.$^{-1}$) and mesityl (850 and 1610 cm.$^{-1}$) groups. That the position of the carbonyl absorption band does not justify a choice between the two possible structures is indicated by inspection of the spectra of structural analogs.

To a solution of this keto alcohol (0.15 g.) in a mixture of 5 ml. each of acetic anhydride and glacial acetic acid was added dropwise 5 ml. of hydriodic acid (48%). Evolution of heat caused the mixture to boil. After being heated under reflux for 20 minutes, the mixture was poured into water. The product, believed to be 1,5-dimesityl-2-pentanone, crystallized from ethanol in long, silky, colorless needles, m.p. 114–114.5°.

Anal. Calcd. for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.55; H, 9.42.

The pentanone was made also by treating the 1,2-glycol VII (0.6 g.) with 48% hydrobromic acid (20 ml.). A few milliliters of xylene were added to dissolve the glycol and the resulting mixture (two liquid layers) was heated under reflux for 12 hours. The product (0.35 g., 61%), melting at 114.5–115°, was shown by a mixed melting point and by comparison of infrared spectra to be identical to the pentanone prepared from the keto alcohol.

Evidence for the presence of carbonyl (1705 cm.$^{-1}$) and mesityl (1617 cm.$^{-1}$) groups and for the absence of a hydroxyl function is found in the infrared spectrum. Unfortunately the frequency of the carbonyl absorption band lies mid-way between the frequencies usually associated with a hindered ketone (1695–1700 cm.$^{-1}$) and an isolated ketone (1710–1715 cm.$^{-1}$) preventing a choice between the 1-pentanone and 2-pentanone structures on the basis of spectral evidence. But by comparison with the known behavior of aromatic 1,2-glycols in boiling mineral acids the 2-pentanone structure seems more likely.

1,5-Dimesitylpentane (VIII).—To a mixture of 1 g. of the glycol VII and 5 ml. each of acetic anhydride and glacial acetic acid was added dropwise 10 ml. of 48% hydriodic acid. The evolution of heat caused violent boiling, which was allowed to subside before additional reducing agent was added. A colorless oil rose to the surface as the reduction was brought to completion by heating the solution under reflux for 30 minutes. The mixture was cooled, poured into water and refrigerated overnight. The flocculent precipitate was recrystallized four times from ethanol, the solution being treated with Darco at each step. The hydrocarbon separated in long, silky, colorless needles, m.p. 114.5–115°, yield 0.45 g. (50%). The melting point of a sample prepared for analysis by sublimation *in vacuo* (0.3 mm., 125–130°) remained unchanged.

Anal. Calcd. for $C_{23}H_{32}$: C, 89.54; H, 10.46. Found: C, 89.32; H, 10.42.

The structure of this hydrocarbon was proved by an independent synthesis described below.

1,5-Dimesitylpentane-1,5-diol.—An ethanolic solution of 1,3-dimesitylpropane was treated for 4 hours with hydrogen (135 atmospheres) at 175° in the presence of a copper-chromium oxide catalyst. The solution, containing a colorless solid in suspension, was boiled and filtered. The filtrate was found to contain starting material. The solid (m.p. 226–228°), which was insoluble in all common organic solvents, was prepared for analysis by dissolving in boiling dimethylformamide and precipitating with water; m.p. 229–230°, yield 1.70 g. (50%).

Anal. Calcd. for $C_{23}H_{32}O_2$: C, 81.13; H, 9.47. Found: C, 80.69; H, 9.22.

A solution of 1 g. of the 1,5-diol in a mixture of 10 ml. each of acetic anhyride and glacial acetic acid was treated with hydriodic acid as described previously for the 1,2-diol VII. The hydrocarbon crystallized from ethanol in long, silky, colorless needles, yield 0.82 g. (81%), m.p. 114.5–115°. A mixed melting point determination with the 1,5-dimesitylpentane obtained from the 1,2-diol showed no lowering. The infrared spectra of the two samples are superimposable.

URBANA, ILLINOIS

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[10] R. C. Fuson and T. L. Tan, THIS JOURNAL, **70**, 602 (1948).

[11] L. E. Hinkel, E. E. Ayling and W. H. Morgan, *J. Chem. Soc.*, 1170 (1931).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

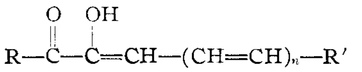
Open Chain Analogs of Tropolone

BY REYNOLD C. FUSON, HERBERT O. HOUSE[1] AND L. RUSSELL MELBY

RECEIVED JULY 21, 1953

A series of six keto enols of type I (in text) have been prepared and their infrared absorption spectra determined.

This investigation was undertaken in the hope of preparing enolic ketones of type I, of especial interest because of their structural similarity to tropolone. The method adopted was the oxidation of



$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{C}=CH-(CH=CH)_n-R' \qquad \text{I}$$

the corresponding α,β-unsaturated ketones with alkaline hydrogen peroxide. The intermediate epoxy ketones were not isolated, the reaction mixtures being made strongly alkaline and heated to effect rearrangement to the desired keto enols. The procedure, a modification of that employed by Barnes and co-workers to prepare 1-mesityl-3-phenyl-2-propen-2-ol-1-one,[2] 3-mesityl-1-phenyl-1,2-propanedione[3] and 1,3-dimesityl-2-propen-2-ol-1-one,[4] proved to be satisfactory for our purpose provided the keto group is joined to a radical such as mesityl. The steric hindrance afforded by such radicals reduces the susceptibility of the α-diketones to further reaction, either with the sodium peroxide or the alkali remaining in the reaction mixture. Thus, when mesitalacetophenone was

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[1] Atomic Energy Commission Predoctoral Fellow, 1951–1953.

[2] R. P. Barnes, THIS JOURNAL, **57**, 937 (1935).

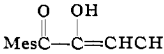
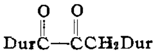
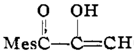
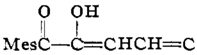
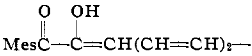
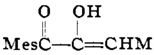
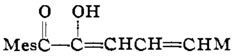
[3] R. P. Barnes and R. J. Brown, *ibid.*, **65**, 412 (1943).

[4] R. P. Barnes and A. E. Brandon, *ibid.*, **65**, 2175 (1943).

subjected to the above reaction conditions, the product was mesitylacetic acid. When the procedure was applied to mesityl propenyl ketone the product, a yellow liquid, appeared to be a mixture of 1-mesityl-2-propen-2-ol-1-one (II) and the corresponding diketone. 1,3-Diduryl-1,2-propanedione (III) was made by the selenium dioxide oxidation of *sym*-didurylacetone, and its isomer, 1,3-diduryl-1,3-propanedione, was synthesized from acetodurene and duroyl chloride.

The keto enols and diketones prepared, along with their significant infrared absorption bands,[5] are listed in Table I. The infrared results are in accord with previous findings.[6,7]

TABLE I

Formula	Absorption in 3μ region, cm.$^{-1}$	Absorption in 6μ region, cm.$^{-1}$
 $\mathrm{Mes}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{OH}}{\vert}}{\mathrm{C}}=\mathrm{CHCH_3}$ (II)[a]	3400 (m)[d]	1706 (vs) 1688 (vs) 1636 (s) 1613 (s) 1579 (m)
 $\mathrm{Dur}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2Dur}$ (III)[b]		1711 (s) 1693 (s)
 $\mathrm{Mes}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{OH}}{\vert}}{\mathrm{C}}=\mathrm{CHC_6H_5}$ (IV)[c]	3380 (m)	1661 (s) 1619 (vs) 1577
 $\mathrm{Mes}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{OH}}{\vert}}{\mathrm{C}}=\mathrm{CHCH{=}CHC_6H_5}$ (V)[c]	3400 (m)	1648 (s) 1608 (vs) 1595 (s)
 $\mathrm{Mes}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{OH}}{\vert}}{\mathrm{C}}=\mathrm{CH(CH{=}CH)_2{-}C_6H_5}$ (VI)[c]	3400 (m)	1647 (s) 1621 (s) 1596 (vs) 1585 (vs)
 $\mathrm{Mes}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{OH}}{\vert}}{\mathrm{C}}=\mathrm{CHMes}$ (VII)[b]	3380 (m)	1657 (m) 1632 (s) 1616 (m)
 $\mathrm{Mes}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{OH}}{\vert}}{\mathrm{C}}=\mathrm{CHCH{=}CHMes}$ (VIII)[b]	3360 (s)	1647 (s) 1603 (vs)

[a] Spectrum of pure liquid. [b] Spectrum of Nujol mull. [c] Spectrum of 5% solution in chloroform. [d] (vs) = very strong, (s) = strong, (m) = medium.

Experimental[8]

Cinnamalacetomesitylene.—To a mixture of 4.9 g. of acetomesitylene and 4.0 g. of cinnamaldehyde was added a solution of 3 g. of potassium hydroxide in 40 ml. of 95% ethanol. After the mixture had been allowed to stand in an ice-box overnight, the solid product was collected and washed well with water. Crystallization from 95% ethanol afforded the ketone as light-yellow needles, m.p. 94–96°, yield 4.8 g. (58%).

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.92; H, 7.30. Found: C, 86.79; H, 7.29.

1-Mesityl-5-phenyl-2,4-pentadien-2-ol-1-one (V).—To a solution of 2.0 g. of cinnamalacetomesitylene and 3.0 ml. of 6 *N* aqueous sodium hydroxide in 100 ml. of ethanol was added dropwise, with stirring, 5.0 ml. of 30% hydrogen peroxide. The solution was stirred, at room temperature for 2 hours and, after treatment with a solution of 3.0 g. of sodium hydroxide in 50 ml. of water, was boiled for 20 minutes. The clear, amber-colored solution was cooled, acidified with hydrochloric acid and cooled in an ice-box for several hours. The solid crystallized from 95% ethanol as light-amber needles, m.p. 162–164°, yield 1.41 g. (66%). Two additional recrystallizations from ethanol gave the pure pentadienolone melting at 164–165°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.90. Found: C, 82.04; H, 6.90.

This enol gives an almost black color with ferric chloride.

The acetate was prepared by heating overnight on the steam-bath a mixture of 0.2 g. of the enol, 0.2 g. of powdered, fused sodium acetate and 5.0 ml. of acetic anhydride. It crystallized from ethanol as tiny, glistening, slightly yellow platelets, m.p. 130–136°. After three additional recrystallizations of the compound the melting range was 132–137°.

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.03; H, 6.63. Found: C, 78.85; H, 6.42.

The infrared absorption spectrum of the acetate shows a well resolved doubling of band structure assignable to vinyl ester carbonyl (1772 and 1758 cm.$^{-1}$) and conjugated ketone (1665 and 1657 cm.$^{-1}$) groups. The rather large melting range of the acetate and this split in ester and ketone carbonyl absorption bands strongly suggest that the acetate comprises a mixture of two geometrical isomers.

A sample of the acetate, prepared in another experiment, melted at 134–139° after three recrystallizations. Its infrared spectrum exhibits the same doubling of ester and ketone carbonyl band structure. The relative intensities of these pairs of bands suggest that this sample contained the isomers in a proportion different from that of the lower-melting acetate sample.

1,5-Dimesityl-2,4-pentadien-1-one.—A mixture of 3.8 g. of mesityl propenyl ketone[9] and 3.0 g. of mesitaldehyde was treated with a solution of 1.0 g. of potassium hydroxide in 12 ml. of ethanol in the manner described for the preparation of cinnamalacetomesitylene. The mesityl ketone crystallized from ethanol as pale yellow needles, m.p. 114–117°, yield 3.34 g. (52%). After four recrystallizations of the ketone from ethanol the melting point was 119–120°.

Anal. Calcd. for $C_{23}H_{26}O$: C, 86.76; H, 8.23. Found: C, 86.72; H, 8.11.

1,5-Dimesityl-2,4-pentadien-2-ol-1-one (VIII).—The crude solid pentadienolone, prepared in the usual way, was crystallized twice from an ethanol–benzene mixture and separated as thick, amber-colored needles, m.p. 198–199.5°,[7] yield 1.26 g. (60%).

Anal. Calcd. for $C_{23}H_{26}O_2$: C, 82.60; H, 7.83. Found: C, 82.44; H, 7.70.

The acetate, prepared as described above, crystallized from ethanol as white, hair-like needles, m.p. 97–98°.

Anal. Calcd. for $C_{25}H_{28}O_2$: C, 79.75; H, 7.50. Found: C, 79.99; H, 7.64.

The infrared spectrum of the acetate exhibits a band at 1757 cm.$^{-1}$ assignable to the vinyl ester carbonyl and at 1670 cm.$^{-1}$ imputed to the conjugated ketone carbonyl group.

1-Mesityl-7-phenyl-2,4,6-heptatrien-1-one.—This ketone was produced by the treatment of 3.8 g. of mesityl propenyl ketone and 2.6 g. of cinnamaldehyde with a solution of 1.0 g. of potassium hydroxide in 10 ml. of ethanol. Crystallization from ethanol afforded 3.42 g. (57%) of bright yellow needles, m.p. 124–125.5°. For analysis it was recrystallized once from ethanol; m.p. 125–126.5°.

Anal. Calcd. for $C_{22}H_{22}O$: C, 87.38; H, 7.34. Found: C, 87.40; H, 7.29.

1-Mesityl-7-phenyl-2,4,6-heptatrien-2-ol-1-one (VI).—The heptatrienolone, produced by applying the oxidation procedure to the heptatrienone, crystallized from ethanol as glistening, light-brown needles, m.p. 135–137°, yield 0.58 g. (36%). The pure enol melts at 136–137°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.99; H, 6.97. Found: C, 83.06; H, 7.20.

The heptatrienolone gives a transient, almost black color with ferric chloride. The keto enol was found to be very sensitive to air oxidation. After having stood in an ordinary cork-stoppered container for 50 days, the originally well-formed crystals had assumed a somewhat sticky consistency. This material melted over the range 65–120°.

1,3-Dimesityl-2-propen-2-ol-1-one (VII).—When 2.00 g. of mesitalacetomesitylene was subjected to the oxidation and rearrangement procedure, the product was a white solid, m.p. 138–141°, yield 2.07 g. (99%). Recrystallization from an ethanol–water mixture followed by recrystallization from petroleum ether (b.p. 90–120°) gave the propenolone as white needles, m.p. 141.5–142.5°.[4]

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[5] The infrared absorption spectra were measured and interpreted by Miss Helen Miklas.

[6] R. P. Barnes and G. E. Pinkney, THIS JOURNAL, **75**, 479 (1953).

[7] R. C. Fuson and H. P. Wallingford, *ibid.*, **75**, 5950 (1953).

[8] All melting points are corrected. The microanalyses are by Mrs. Katherine Pih, Mrs. Esther Fett and Mr. Joseph Nemeth.

[9] R. C. Fuson, R. E. Christ and G. M. Whitman, THIS JOURNAL, **58**, 2450 (1936).

1-Mesityl-3-phenyl-2-propen-2-ol-1-one (IV).—By the same procedure, 2.00 g. of benzalacetomesitylene was converted to the crude propenolone in quantitative yield. Two recrystallizations from methanol–water mixtures gave light-yellow needles, m.p. 98.5–99.5°.[2]

Epoxidation of Mesityl Propenyl Ketone.—In the manner previously described, 5.00 g. of mesityl propenyl ketone[8] was converted to the oxidation product, which was distilled *in vacuo;* b.p. 91–95° (0.2 mm.), yield 2.65 g. (49%). A fraction of the product, a yellow liquid, boiling at 95° (0.2 mm.), was collected for analysis. The infrared spectrum of the material (Table I) indicates that it is a mixture of the keto and enol (II) forms.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.41; H, 7.89. Found: C, 76.13; H, 7.73.

Oxidation of Mesitalacetophenone.—The oxidation and subsequent ring cleavage of 2.00 g. of mesitalacetophenone gave a product, which was recrystallized from a methanol–water mixture and then from petroleum ether (b.p. 90–120°). It formed white needles melting at 165–166.5°. The material was identified as mesitylacetic acid by a mixed melting point with an authentic sample.

Chloromethylation of Durene. A.—Chloromethylation of durene by the method of Nauta and Dienske[10] gave α^3-chloropentamethylbenzene in a yield of 47.6%, m.p. 67–68°, b.p. 138–148° (12–15 mm.). The high-boiling residue contained the dichloromethylation product, α^1,α^4-dichlorohexamethylbenzene, which crystallized from petroleum ether (b.p. 90–120°) as white needles melting at 195–196°.

Anal. Calcd. for $C_{12}H_{16}Cl_2$: C, 62.33; H, 6.98; Cl, 30.67. Found: C, 62.40; H, 6.99; Cl, 30.42.

B.—Chloromethylation by the following method was found to be more satisfactory. To a solution of 26.84 g. of durene and 28 g. of chloromethyl ether in 120 ml. of dry carbon disulfide, cooled to −5°, was added dropwise, with stirring, 7.4 ml. (0.064 mole) of anhydrous stannic chloride. The cold mixture, after being stirred for 1 hour, was poured on ice. The carbon disulfide layer was removed and the aqueous phase extracted with 100 ml. of carbon disulfide. The combined carbon disulfide solutions were dried over calcium chloride and the solvent was removed on a steam-bath. The residue, upon distillation *in vacuo*, yielded 21.6 g. (59.4%) of α^3-chloropentamethylbenzene, b.p. 140–148° (15 mm.), m.p. 66–68°. Recrystallization of the high-boiling residue from petroleum ether (b.p. 90–120°) gave 2.6 g. of the crude dichloromethylation product, m.p. 180–192°.

β-Durylpropionic Acid.—To a solution of sodiomalonic ester, prepared from 2.72 g. of sodium, 20.8 g. of ethyl malonate and 100 ml. of absolute ethanol, was added dropwise, with stirring, a solution of 21.6 g. of α^3-chloropentamethylbenzene in 200 ml. of absolute ethanol. The mixture was boiled under reflux, with stirring, until neutral to moist litmus. After one-half of the ethanol had been distilled from the reaction mixture, the remaining material was poured into 600 ml. of water. The resulting mixture was extracted with 200 ml. of ethyl ether and the solvent removed from the extract on a steam-bath. Saponification was accomplished by heating a mixture of the ester, 75 g. of potassium hydroxide and 100 ml. of water on a steam-bath, with stirring, for 4 hours. The cold mixture was diluted with 1.5 l. of water and filtered. Acidification with concentrated hydrochloric acid gave the dicarboxylic acid which was collected on a filter and then dried for 2 hours at 110°. The decarboxylation was completed by boiling for 8.5 hours, under reflux, a solution of the material in 300 ml. of xylene. After decolorization with Norit the xylene solution was allowed to cool; the propionic acid crystallized as white needles, m.p. 169–171°, yield 17.5 g. (72.1%).

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.67; H, 8.79. Found: C, 75.68; H, 8.73.

***sym*-Didurylacetone.**—A solution of 7.43 g. of α^3-chloropentamethylbenzene in 75 ml. of ethyl ether was added slowly, with stirring, to 5.45 g. of magnesium turnings, and the mixture was stirred for 30 minutes. To the solution of the Grignard reagent was added slowly, with stirring, a solution of 5.0 g. of durylacetonitrile in 50 ml. of ethyl ether. After being stirred for 16 hours, the reaction mixture was poured on an ice–hydrochloric acid mixture. The resulting solid was recrystallized from xylene. The yield of *sym*-didurylacetone, melting over the range 201–210°, was 5.70 g. (61.3%). An additional recrystallization from xylene followed by two recrystallizations from petroleum ether (b.p. 90–120°) gave white needles, m.p. 213–214°.

Anal. Calcd. for $C_{23}H_{30}O$: C, 85.64; H, 9.37. Found: C, 85.51; H, 9.56.

The infrared spectrum of the ketone contains an absorption band at 1717 cm.$^{-1}$ assignable to an unconjugated carbonyl group.

When the procedure was modified so that only slightly more than the stoichiometric amount of magnesium was used, the major product was 1,2-didurylethane, which, after two recrystallizations from benzene, melted at 234–235°.[11] In all runs the purification of the ketone was difficult, presumably because of contamination by the ethane.

The oxime of *sym*-didurylacetone was produced by heating under reflux for 6 hours a mixture of 1.0 g. of the ketone, 1.0 g. of hydroxylamine hydrochloride and 10 ml. of absolute ethanol. The residue, obtained by removing the solvents from the reaction mixture under an air blast, was triturated with water. Recrystallization of the water-insoluble material from xylene gave white needles, m.p. 251–252°.

Anal. Calcd. for $C_{23}H_{31}NO$: C, 81.84; H, 9.26; N, 4.15. Found: C, 81.95; H, 9.47; N, 4.08.

1,3-Diduryl-1,2-propanedione (III).—To a solution of 1.1 g. of selenium dioxide in 25 ml. of dioxane and 1 ml. of water was added 1.6 g. of *sym*-didurylacetone. The mixture was boiled under reflux for 69 hours. The hot mixture was filtered to remove the selenium which had separated and the solvent was evaporated under an air blast. A series of recrystallizations from glacial acetic acid served to remove the remainder of the selenium. The diketone, still impure, was dissolved in xylene and the solution allowed to stand; at the end of two weeks the diketone had separated as yellow needles, m.p. 191.5–193.5°. A second recrystallization of the product from xylene brought the melting point to 194–195°.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.08; H, 8.39. Found: C, 81.92; H, 8.65.

1,3-Diduryl-2-propene-1-one.—A solution of 10.0 g. of bromodurene in 100 ml. of absolute ether was stirred, under nitrogen, with 0.70 g. of lithium for 20 hours. Approximately one-half of the lithium remained. This solution of duryllithium was treated with a solution of 1.73 g. of 1-duryl-2-propene-3-ol-1-one[12] in 100 ml. of absolute ether. The resulting mixture, after being boiled under reflux, with stirring, for 21 hours, was decomposed with an ice–hydrochloric acid mixture. The ether layer was separated and washed, first with water, then with two 150-ml. portions of 5% aqueous sodium carbonate and finally with water. No acidic material was present in the sodium carbonate solution. The ether solution was evaporated to dryness and the residue heated for several hours on a steam-bath to remove the durene and bromodurene present. A solution of the residue in ethanol containing several ml. of concentrated hydrochloric acid was boiled for 10 minutes, decolorized with Norit and cooled to give yellow needles melting over the range 197–212°. A recrystallization from petroleum ether (b.p. 90–120°) followed by two recrystallizations from xylene gave 0.27 g. (10%) of white needles, m.p. 213–217°. An additional recrystallization from xylene raised the melting point to 216–218°.

Anal. Calcd. for $C_{23}H_{28}O$: C, 86.18; H, 8.80; mol. wt., 320.5. Found: C, 86.33; H, 8.74; mol. wt., 331 (Rast).

The infrared spectrum of the product closely resembles the spectrum of its mesityl analog, mesitalacetomesitylene.

1,3-Diduryl-1,3-propanedione.—A solution of 0.050 mole of the bromomagnesium enolate of acetodurene, prepared from 8.81 g. of acetodurene, 1.22 g. of magnesium and 5.45 g. of ethyl bromide in 100 ml. of ether, was treated with a solution of 4.92 g. of duroyl chloride in 40 ml. of ether. The mixture was boiled under reflux, with stirring, for 18 hours and then decomposed with an ice–hydrochloric acid mixture. The ether layer was separated, washed with water and then with 10% aqueous sodium carbonate. The ether solution was shaken with a saturated solution of cupric acetate in

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(10) W. T. Nauta and J. W. Dienske, *Rec. trav. chim.*, **55**, 1000 (1936).

(11) R. C. Fuson and S. C. Kelton, Jr., THIS JOURNAL, **63**, 1500 (1951).

(12) R. C. Fuson and L. R. Melby, *ibid.*, **75**, 5402 (1953).

water. The gray, cupric complex which separated was collected on a filter, suspended in ether and shaken with two portions of dilute hydrochloric acid. Removal of the ether from the organic layer left 3.27 g. (38.8%) of a white solid melting over the range 166–172°. Two recrystallizations from ethanol gave white needles, m.p. 172–173.5°.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.08; H, 8.39. Found: C, 82.09; H, 8.58.

The infrared spectrum of the material is very similar to that of the known 1,3-dimesityl-1,3-propanedione.[13]

The ether solution, from which the copper complex of the 1,3-diketone had been precipitated, was evaporated to dryness and the residue steam distilled. The unchanged acetodurene in the distillate, amounting to 6.04 g., was collected on a filter.

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[13] R. C. Fuson, W. O. Fugate and C. H. Fisher, *ibid.*, **61**, 2362 (1939).

URBANA, ILLINOIS

[CONTRIBUTIONS FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, AND THE HAVEMEYER LABORATORY, COLUMBIA UNIVERSITY]

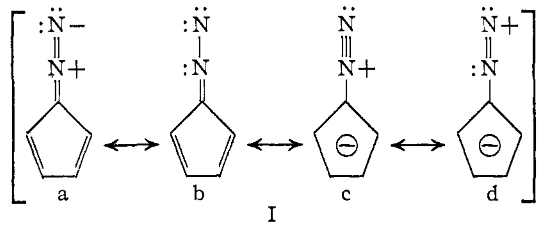
Diazocyclopentadiene[1]

BY W. VON E. DOERING AND C. H. DEPUY

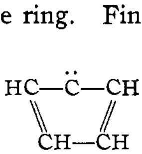
RECEIVED MAY 8, 1953

By the novel reaction of cyclopentadienyllithium and *p*-toluenesulfonylazide, diazocyclopentadiene has been prepared. The structure of this stable, red diazo compound has been established.

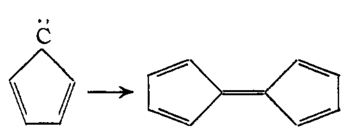
Among various points of interest associated with the unknown diazocyclopentadiene (I), three are noteworthy. The arrangement of π-orbitals is such that withdrawal of electrons from the diazo grouping to carbon leads to an aromatic resonance system of six electrons (Ic and Id).[2] This situation should be reflected in considerably different behavior from that shown by diazomethane. Related to diazocyclopentadiene by loss of nitrogen is a carbene, cyclopentadienylene (IIb), in which a linear arrangement (IIa) of divalent carbon and its bonded carbon atoms is denied by the small size of the ring. Finally, through its carbene or possibly through another intermediate, I might be a precursor of fulvalene (III), hypothetically a nonbenzenoid hydrocarbon of considerable resonance energy.[3]



I



IIa



IIb III

Synthesis of I was first attempted from the dimer of cyclopentadienone oxime (IV, 1,8-dioximino-4,7-methano-3a,4,7,7a-tetrahydroindene) by way of the bis-hydrazone and the bis-diazo compound, the dimer of I. Although this scheme was abandoned before completion in favor of another, a few observations are reported. The procedure of Thiele[4] for the preparation of IV involved a method of purification which could not be reproduced and has therefore been replaced. One of the two oximino groups in IV was found to hydrolyze rapidly to a ketoxime, presumably 1-oximino-8-keto-4,7-methano-3a,4,7,7a-tetrahydroindene. IV showed the interesting property of subliming to an unstable, low-melting, yellow isomer which rapidly reverted to IV and may be a nitroso tautomer.

By means of the mechanistic theory outlined below, a new reaction was designed for the synthesis of I. In order to utilize the readily accessible cyclopentadienyllithium, a reagent, N=N=A, is required in which A must perform three functions: the negative charge introduced by the addition of the carbanion to the terminal nitrogen must be stabilized; the proton remaining at C_1 of the cyclopentadiene ring in this intermediate must be transferred to some atom in A so that, in the final stage AH^- may break away (as a relatively stable anion) from its bond to the second nitrogen atom, thereby removing the negative charge from the five-membered ring and forming I. Among the many groups, A, considered, $RSO_2N=$ represented an available reagent which satisfied the conditions not only in theory, as illustrated below, but in practice as well.[5]

Diazocyclopentadiene (I) is prepared in 35% of the theoretical amount by adding a suspension of cyclopentadienyllithium to *p*-toluenesulfonyl azide. As a by-product *p*-toluenesulfonamide is isolated in 29% of the theoretical yield.

The structure of I is consistent with several observations. Analysis and molecular weight point to $C_5H_4N_2$ as the empirical formula. Catalytic reduction to a hexahydro derivative which was shown to be identical with cyclopentanone hydra-

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[1] Taken from a thesis submitted by C. H. DePuy to the faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree. This work was supported in part by Contract DA-; 9-059-ORD-950 between the Office of Ordnance Research, U. S. Army, and Yale University.

[2] E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, pp. 71–85.

[3] R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950).

[4] J. Thiele, *Ber.*, **33**, 669 (1900).

[5] Stimulus for this conception was the work of M. Beringer and coworkers at the Polytechnic Institute of Brooklyn on the reaction of nitrous oxide with organometallic compounds [F. M. Beringer, J. A. Farr and S. Sands, THIS JOURNAL, **75**, 3984 (1953)].