3–8) and 2,6-dimethyloctene-2 (fractions 10–15) with a trace of another substance of lower boiling point in fractions 1 and 2 (b.p. 76.8–79.3° (50 mm.)). The pot residue (7% of the charge) was not examined. Fractionation of another sample of this mixture at 20 mm. pressure was less satisfactory, three intermediate fractions being obtained, probably because of a lower column efficiency due to the reduction in pressure.

2,6-Dimethyloctene-1.—This olefin is a pleasant smelling mobile liquid of b.p. 79.3 ± 0.3° (50 mm.), $n^{25}D$ 1.4226, d^{25}_4 0.7443 (corrected for buoyancy) and $[\alpha]^{27}D$ +1.80° (not optically pure and corresponding to $[\alpha]^{27}D$ +2.34° for 2,6-dimethyloctene-2).

Anal. Calcd. for $C_{10}H_{20}$: C, 85.7; H, 14.35. Found: C, 85.8; H, 14.35.

Ozonolysis of 2,6-Dimethyloctene-1.—The olefin (15 ml., $[\alpha]^{27}D$ +1.80°) in 50 ml. of acetic acid was cooled in ice-water and 17 l. per hour of ozonized oxygen (7.7% by weight of O_3) was passed for 2.5 hours when the production of fog ceased. The solution was poured into 250 ml. of water and the aqueous layer was separated and refluxed under an oil-trap. The water-insoluble ozonide was washed with a little water into a flask containing an excess of zinc dust and a trace of silver nitrate and hydroquinone. The suspension was brought to the boil while being vigorously stirred and was then also refluxed under the oil-trap. The total oil (12.5 ml.) obtained yielded 8.35 g. (74% yield) of crude ketone b.p. 68–75° (10 mm.). Redistillation yielded **6-methyloctanone-2**, b.p. 70–71° (10 mm.), $n^{25}D$ 1.420, d^{25}_4 0.822 and $[\alpha]D$ +1.4° (not optically pure).

Anal. Calcd. for $C_9H_{18}O$: C, 76.2; H, 12.75. Found: C, 76.5; H, 12.4.

The **2,4-dinitrophenylhydrazone**, m.p. 61–62°, crystallized from ethanol.

Anal. Calcd. for $C_{15}H_{22}O_4N_4$: C, 55.9; H, 6.87. Found: C, 56.0; H, 6.95.

The **semicarbazone**, m.p. 130.5–131.5°, crystallized from ethanol.

Anal. Calcd. for $C_{10}H_{21}N_3O$: C, 60.25; H, 10.62. Found: C, 60.3; H, 10.6.

Thioglycolic Acid Adduct of 2,6-Dimethyloctene-1.—By the method described, 3.78 g. (67% yield) of crude **S-benzylthiuronium 5,9-dimethyl-3-thiahendecanoate**, m.p. 138–139°, was obtained from 2.0 g. of olefin. Crystallization from acetone raised the melting point to 145–145.5° (immersed at 140°), but examination of the mother liquors did not reveal a second component of different melting point.

Anal. Calcd. for $C_{20}H_{34}N_2O_2S_2$: C, 60.3; H, 8.60. Found: C, 59.9; H, 8.30.

BRISBANE, AUSTRALIA

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

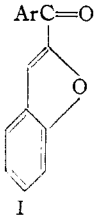
Grignard Reactions Involving Opening of the Furan Ring

BY REYNOLD C. FUSON AND HARLAN P. WALLINGFORD[1]

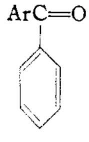
RECEIVED JULY 21, 1953

2-Mesitoylfuran reacts with mesitylmagnesium bromide, with opening of the furan ring, to form 1,5-dimesityl-2,4-pentadien-2-ol-1-one. 2-Duroylfuran gives a similar product.

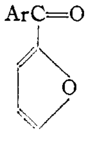
In earlier studies[2] it was found that, by imposing steric hindrance on the carbonyl group, certain furyl ketones could be made to react in the 1,4-manner with Grignard reagents. The 2-benzofuryl ketones I are examples. Subsequent work with hindered ketones in the benzene series II has shown that certain reagents attack the *p*-position even when the *o*-positions are unoccupied, *i.e.*, reactions corresponding to 1,6-addition take precedence over 1,4-addition when both are possible.[3] This same choice is offered by the 2-furyl ketones III, in which the 5-position corresponds to the *p*-position of the phenyl ketones II. Thus 2-mesitoylfuran (III, Ar = Mes) is analogous to the *p*-methoxyphenyl ketones IV. However, it has the possible advantage that the ether oxygen atom, together with that of the carbonyl group, may form a chelate ring involving magnesium.



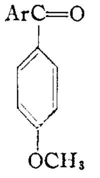
I



II



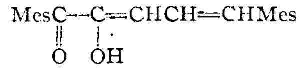
III



IV

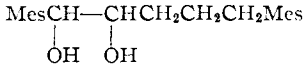
When treated with mesitylmagnesium bromide 2-mesitoylfuran was found to be attacked at the 5-position, the reaction involving opening of the ring to produce 1,5-dimesityl-2,4-pentadien-2-ol-1-one (V). The opening of the ring corresponds to methoxyl displacement in the *p*-methoxyphenyl series.[4] An analogous pentadienolone (VI) was produced when 2-duroylfuran was allowed to react with the mesityl reagent.

Catalytic hydrogenation converted the dimesitylpentadienolone (V) to the corresponding 1,2-glycol VII. The carbon skeleton was established by reduction of the glycol to the parent hydrocarbon VIII, which was prepared by an independent method. The keto enol V was identified by comparison with an authentic specimen made by the oxidation of 1,5-dimesityl-2,4-pentadien-1-one.[5] The two samples have identical infrared spectra and a mixed melting point determination showed no depression.



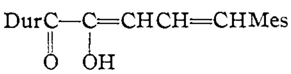
$$\text{Mes}\underset{\underset{\displaystyle \text{O}}{\|}}{\text{C}}-\underset{\underset{\displaystyle \text{OH}}{|}}{\text{C}}=\text{CHCH}=\text{CHMes}$$

V



$$\text{Mes}\underset{\underset{\displaystyle \text{OH}}{|}}{\text{CH}}-\underset{\underset{\displaystyle \text{OH}}{|}}{\text{CH}}\text{CH}_2\text{CH}_2\text{CH}_2\text{Mes}$$

VII



$$\text{Dur}\underset{\underset{\displaystyle \text{O}}{\|}}{\text{C}}-\underset{\underset{\displaystyle \text{OH}}{|}}{\text{C}}=\text{CHCH}=\text{CHMes}$$

VI

$Mes(CH_2)_5Mes$

VIII

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(1) du Pont Fellow, 1951–1952.

(2) (a) R. C. Fuson, E. W. Kaiser and S. B. Speck, *J. Org. Chem.*, **6**, 845 (1941); (b) R. E. Lutz and W. G. Reveley, THIS JOURNAL, **63**, 3178 (1941).

(3) For a leading reference, see R. C. Fuson and R. Tull, *ibid.*, **71**, 2543 (1949).

(4) R. C. Fuson and R. Gaertner, *J. Org. Chem.*, **13**, 496 (1948).

(5) R. C. Fuson, H. O. House and L. R. Melby, THIS JOURNAL, **75**, 5952 (1953).

It should be pointed out that certain furan derivatives had been shown previously to react with Grignard reagents, under somewhat drastic conditions, to suffer cleavage of the furan ring.[6] The cleavage reported by Lutz and Reveley[2a] of a 3-furyl ketone appears to follow a course which differs from that of the ring opening described here.

Experimental

2-Duroylfuran.—A solution of 175 g. of furoyl chloride in 100 ml. of carbon disulfide was added dropwise, with stirring, to a mixture of 227 g. of durene, 226 g. of anhydrous aluminum chloride and 200 ml. of carbon disulfide. The reaction was initiated by application of external heat, and the mixture was kept below 25° during the course of the addition, which required about 2 hours. Heat was then applied cautiously; a heavy tan precipitate appeared, and an additional 100 ml. of carbon disulfide was added to facilitate stirring. After being heated on the steam-bath for 1 hour, at the end of which time the evolution of hydrogen chloride had ceased, the mixture was decomposed with dilute hydrochloric acid. The crude product melted at 165–167°, yield 269 g. (88%). It was recrystallized from methanol and then from ethanol; m.p. 167.5–168.0°.

Anal.[7] Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 78.80; H, 7.01.

2-Mesitoylfuran.—By a procedure similar to that employed for the duryl analog 203 g. of mesitylene was condensed with 2-furoyl chloride. The crude product, a brown solid, was recrystallized from high-boiling petroleum ether and washed on the filter with additional cold solvent; m.p. 104–104.5°, yield 83%.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.47; H, 6.59. Found: C, 78.39; H, 6.77.

1-Duryl-5-mesityl-2,4-pentadien-2-ol-1-one (VI).—Magnesium powder, washed twice with dry ether and dried by igniting the residual solvent, was found to react with bromomesitylene very readily. The magnesium powder was placed in a flask carrying a reflux condenser. A few crystals of iodine were added and sufficient heat was applied to cause the iodine to sublime into the condenser. Immediately a solution of 5 g. of freshly distilled bromomesitylene in 20 ml. of dry ether was introduced into the hot flask. The reaction, which commenced at once, was allowed to proceed 10 minutes. Dry ether (100 ml.) was then introduced and the reaction mixture heated for 2 hours under reflux. The 2-duroylfuran (5 g.) was then added in 1-g. portions over a 15-minute period and the mixture was heated 14 hours under reflux. At the end of the first hour a fine yellow precipitate had appeared. Decomposition of the mixture with dilute hydrochloric acid yielded the dienolone as a yellow solid. It separated from methanol in tiny yellow prisms; m.p. 175–177°, yield 3.0 g. (40%). The pure compound was obtained by two additional recrystallizations from methanol; m.p. 180.5–181°.

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.80; H, 8.18.

The enol was soluble in Claisen alkali (10%) and gave a dark red coloration with ferric chloride. It reacted sluggishly with bromine in carbon tetrachloride and with dilute permanganate, and was recovered unchanged after being heated under reflux for 2 days with constant-boiling hydrobromic acid. It was unaffected by an attempted hydrogenation with Adams catalyst and hydrogen at 2–3 atmospheres.

The infrared spectrum[8] of the product exhibits an absorption band at 1647 cm.$^{-1}$, attributable to a conjugated carbonyl group, a second unusually intense band at 1604 cm.$^{-1}$ believed to arise from the diene system conjugated with carbonyl group, and a third well-defined absorption band at 3370 cm.$^{-1}$, attributable to an unchelated hydroxyl group. The ultraviolet spectrum[9] has, in addition to minor peaks at 2100 and 2580 Å., a maximum at 3525 Å. (E_{max} 26,100). This maximum, at a wave length unusually long for an isolated 2,4-pentadien-1-one system, suggests that at least one of the mesityl radicals is conjugated with the pentadienolone system.

The acetate was made by heating overnight on the steam-bath a mixture of 1 g. of the enol, 2 g. of freshly fused and powdered anhydrous sodium acetate and 5 ml. of acetic anhydride. The colorless product remaining after hydrolysis of the acetic anhydride crystallized from ethanol in ivory prisms, m.p. 140–141°, yield 0.96 g. (85%).

Anal. Calcd. for $C_{25}H_{30}O_3$: C, 79.97; H, 7.74. Found: C, 79.79; H, 7.83.

While no oxygen–hydrogen stretching band is present in the infrared spectrum of the acetate, absorption bands are found at 1608, 1669 and 1767 cm.$^{-1}$. The latter, not present in the parent enol, is attributed to the carbonyl group of the vinyl ester.

The acetate gave a negative test with ferric chloride solution. A small amount of the acetate was dissolved in cold Claisen solution and the solution, after being heated for 0.5 hour on the steam-bath, was acidified with dilute hydrochloric acid. The regenerated enol VI was identified by a mixture melting point determination and by its infrared spectrum.

The benzoate was prepared by heating a mixture of 1 g. of the enol, 2 ml. of benzoyl chloride and 5 ml. of sodium hydroxide solution (20%) for 20 minutes on a steam-bath. The ester separated from ethanol in ivory crystals, m.p. 179.5°, yield 1.11 g. (85%).

Anal. Calcd. for $C_{31}H_{32}O_3$: C, 82.27; H, 7.13. Found: C, 81.93; H, 7.27.

The benzoate gave a negative ferric chloride test. Its infrared spectrum is closely similar to that of the acetate. The carbonyl group of the vinyl ester, being conjugated with a benzene ring, gives rise to an absorption band at a somewhat longer wave length (1741 cm.$^{-1}$). Hydrolysis of the benzoate regenerated the original enol, identified by a mixed melting point and by its infrared spectrum.

1,5-Dimesityl-2,4-pentadien-2-ol-1-one (V).—The dimesityl enol was made from 2-mesitoylfuran and mesitylmagnesium bromide by the method outlined for the duryl mesityl enol VI. It crystallized from ethanol in tiny yellow prisms, m.p. 198–199.5°, yield 42%.

Anal. Calcd. for $C_{23}H_{26}O_2$: C, 82.60; H, 7.83. Found: C, 82.52; H, 7.94.

Both the infrared and the ultraviolet spectra of the product are very similar to those of the 1-duryl-5-mesityl analog. The absorption bands in the infrared region are found at 1603, 1647 and 3360 cm.$^{-1}$; those in the ultraviolet region at 2050, 2575 and 3525 Å. (E_{max} 27,100).

A mixed melting point with an authentic specimen[5] showed no depression.

The methyl ether was prepared by adding, dropwise and with stirring, a solution of 5 g. of potassium hydroxide in 50 ml. of methanol to a boiling mixture of 1.7 g. of the enol, 30 ml. of methanol and 3.9 g. of methyl sulfate. The mixture was stirred under reflux for 0.5 hour and poured into water. The ether, recrystallized with difficulty from low-boiling petroleum ether, was a pale yellow powder, m.p. 113.5–114°, yield 1.2 g. (66%).

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.37; H, 7.94.

The infrared spectrum of the ether is in general closely similar to those of the previously described vinyl esters. It lacks the absorption band attributed to an ester carbonyl group and exhibits an additional band at 1167 cm.$^{-1}$, attributable to a carbon–oxygen bond.

1,5-Dimesitylpentane-1,2-diol (VII).—A sample (2.82 g.) of the dimesityl enol V was reduced in ethanol at 115° under hydrogen at 135 atmospheres, Raney nickel being used as catalyst. The pressure drop during 4 hours of shaking indicated that 3 moles of hydrogen were absorbed per mole of enol. By concentration of the alcohol solution and subsequent refrigeration, the diol was obtained in long, silky, colorless needles, m.p. 168–170°, yield 2.30 g. (80%). It was purified by recrystallization from ethanol; m.p. 172–173°.

Anal. Calcd. for $C_{23}H_{32}O_2$: C, 81.13; H, 9.47; mol wt., 340. Found: C, 81.41; H, 9.70; mol. wt. (camphor), 308, 323.

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[6] V. I. Kuznetsov, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 2263 (1939); **16**, 187 (1946).

[7] Microanalyses by Miss Emily Davis, Mr. Joseph Nemeth, Mrs. Katherine Pih and Mrs. Jeanne Fortney.

[8] The infrared spectra were determined and interpreted by Mrs. Elizabeth Leighly and Miss Helen Miklas.

[9] The ultraviolet spectra were recorded and interpreted by Mr. Homer Birch and Miss Emily Maverick, of this Laboratory and by Dr. V. H. Wallingford of the Mallinckrodt Chemical Works.

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]

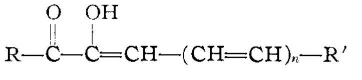
Open Chain Analogs of Tropolone

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



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

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).