[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

# The Dienone–Phenol Rearrangement. II. A Second Path[1]

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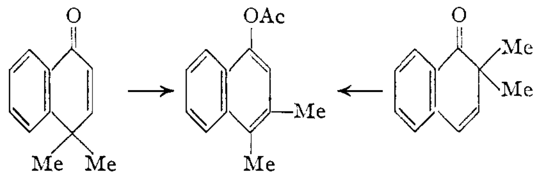
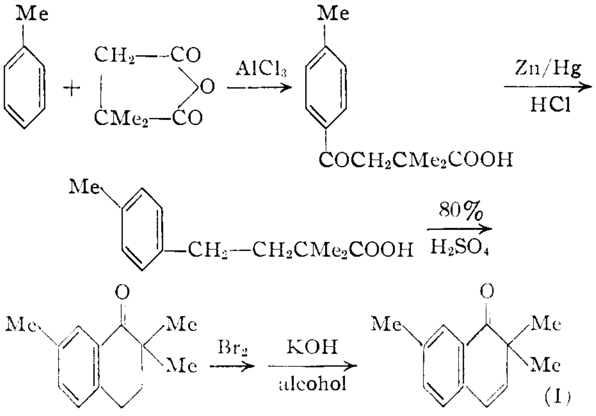
The dienone, 2,2,7-trimethyl-1-oxo-1,2-dihydronaphthalene, has been prepared and rearranged. Isolation of 3,4,6-trimethyl-1-naphthyl acetate shows that during the course of the rearrangement the oxygen function migrates from carbon one to carbon four. A mechanism is suggested to account for these observations.

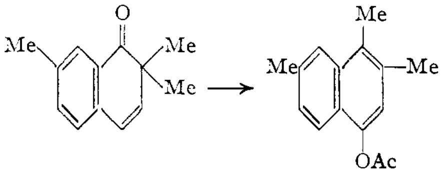
The path which, by virtue of its frequent occurrence,[2] may be considered to be normal for the dienone–phenol rearrangement is exemplified by the rearrangement of 4,4-dimethyl-1-oxo-1,4-dihydronaphthalene to 3,4-dimethyl-1-naphthyl acetate.[2c] Recently attention has been drawn to an alternate course which the reaction may pursue under appropriate conditions.[3] In this case 3,4-dimethyl-1-naphthyl acetate results from rearrangement of 2,2-dimethyl-1-oxo-1,2-dihydronaphthalene. Although a mechanism to account for the normal path has been proposed,[2c] none has yet been published for the alternate path. The work reported here was undertaken to provide information about the course of that latter rearrangement.

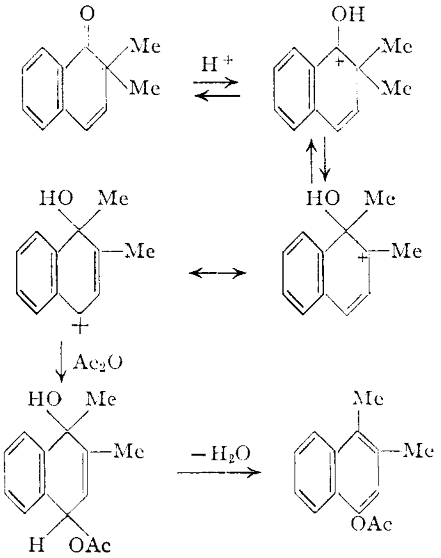


The simplest explanation of the alternate course of the dienone–phenol rearrangement involves a shift of the oxygen function from carbon one to carbon four. Tagging the aromatic ring provides an easy way to reveal whether this is indeed the case. Accordingly we have prepared 2,2,7-trimethyl-1-oxo-1,2-dihydronaphthalene (I) by the series of reactions shown below. Since toluene succinoylates in the *para* position[4] and the preparation of 2,2-dimethyl-1-oxo-1,2-dihydronaphthalene was carried out previously[3] by the same method, the structure I was assigned to the product. All steps in the synthesis as far as 2,2,7-trimethyl-1-oxo-1,2,3,4-tetrahydronaphthalene have been carried out previously[5] and identical structural assignments were made at that time.



The dienone I rearranged smoothly to give a solid naphthyl acetate. This was hydrolyzed to the known 3,4,6-trimethyl-1-naphthol,[6] and the methyl ether and its trinitrobenzene complex, both of which have been made previously,[6,7] were also prepared. The isolation of the 3,4,6-trimethyl-1-naphthyl acetate proves that the oxygen function did indeed migrate during the reaction. The following mechanism for this path of the dienone–phenol rearrangement is in accord with these observations.[8]





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[1] Published with the approval of the Monographs Publications Committee, Oregon State College, as Research Paper No. 249, School of Science, Department of Chemistry.

[2] (a) G. Clemo, R. Haworth and E. Walton, *J. Chem. Soc.*, 1110 (1930); (b) A. L. Wilds and C. Djerassi, THIS JOURNAL, **68**, 1715 (1946); (c) R. T. Arnold, J. S Buckley and J. Richter, *ibid.*, **69**, 2322 (1947); (d) R. B. Woodward and T. Singh, *ibid.*, **72**, 494 (1950); (e) R. T. Arnold, J. S. Buckley and R. M. Dodson, *ibid.*, **72**, 3153 (1950); (f) C. Djerassi and T. T. Grossnickle, *ibid.*, **76**, 1741 (1954).

[3] E. N. Marvell and A. O. Geiszler, *ibid.*, **74**, 1259 (1952).

[4] (a) H. Limpricht, *Ann.*, **312**, 110 (1900); (b) E. de B. Barnett and F. G. Saunders, *J. Chem. Soc.*, 434 (1933).

[5] S. C. Sengupta, *J. prakt. Chem.*, **151**, 82 (1938).

[6] W. Cocker, A. K. Fateen and C. Lipman, *J. Chem. Soc.*, 926 (1951).

[7] L. Ruzicka, H. Hösli and K. K. Hofmann, *Helv. Chim. Acta*, **19**, 370 (1936).

[8] Prior to publication of the original paper[3] in this series Dr. R. T. Arnold suggested the mechanism given here to account for the results observed.

## Experimental

**2,2,7-Trimethyl-1-oxo-1,2,3,4-tetrahydronaphthalene.**—This compound was prepared by the method of Sengupta,[5] who reported only a boiling point of 121° (5 mm.). Our material, b.p. 141–142° (11 mm.), melted at 38–39°.

**2,2,7-Trimethyl-1-oxo-1,2-dihydronaphthalene.**—This unsaturated ketone was prepared by bromination and dehydrobromination of 2,2,7-trimethyl-1-oxo-1,2,3,4-tetrahydronaphthalene according to the directions used by Marvell and Geiszler[3] to prepare a similar ketone. The product was obtained in 45% yield, b.p. 122–124° (10 mm.), $n^{20}\text{D}$ 1.5682, $d^{20}{}_{20}$ 1.083.

*Anal.* Calcd. for $C_{13}H_{14}O$: C, 83.8; H, 7.58. Found: C, 83.3; H, 7.63.

**3,4,6-Trimethyl-1-naphthyl Acetate.**—A solution of 2.0 g. (0.11 mole) of the above ketone in 25 ml. of acetic anhydride containing 15 drops of sulfuric acid was allowed to stand for six hours. At the end of that time the solution was stirred with ice-water for one-half hour and the product isolated on a büchner funnel, 2.17 g. (95%), m.p. 59–66°. Recrystallization from an ethanol–water mixture raised the melting point to 87–88°.

*Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.8; H, 7.07. Found: C, 78.5; H, 7.16.

**3,4,6-Trimethyl-1-naphthol.**—One gram (0.0044 mole) of the acetate was treated for ten minutes with 20 ml. of boiling 5% methanolic potassium hydroxide. This solution was poured over a mixture of ice and sufficient dilute hydrochloric acid to neutralize the base. The solid product, 0.77 g. (96%), was isolated by suction filtration. After recrystallization from methanol–water mixture the naphthol melted at 99–101°. A melting point of 99–100° has been reported[6] for this naphthol.

**3,4,6-Trimethyl-1-methoxynaphthalene.**—A solution containing 0.4 g. (0.0021 mole) of the above naphthol in 2 ml. of dry methanol was mixed with 7.0 ml. of an ethereal solution of diazomethane. The mixture was allowed to stand 24 hours at room temperature, after which time the solvents were removed by evaporation. The yellow solid residue was dissolved in ether, washed with dilute sodium hydroxide and the ether removed by evaporation. The residue was recrystallized from ethanol giving a solid melting at 89.5–90° (lit.[6,7] m.p. 88, 89–90°).

**The trinitrobenzene adduct** of the above ether crystallized from methanol as long orange needles, m.p. 191–193°. This adduct is reported[6] to melt at 193–194°.

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

# Displacement of Nuclear Halogen Atoms in Hindered Aryl Ketones by the Action of Grignard Reagents

BY REYNOLD C. FUSON, WILLIAM S. FRIEDLANDER[1] AND GEORGE W. PARSHALL[2]

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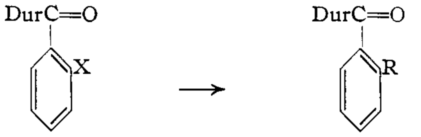
Duryl *p*-fluorophenyl ketone reacts with *t*-butylmagnesium chloride to give *p*-*t*-butylphenylduryl ketone in high yield. The analogous bromo ketone gives the same product accompanied by 2,4-di-*t*-butyl-2,3-dihydrophenyl duryl ketone. *o*-Bromophenyl duryl ketone undergoes replacement with phenylmagnesium bromide to give *o*-duroylbiphenyl. With the *t*-butyl reagent loss of bromine is also observed but the *t*-butyl radical enters the *para* position. Duryl *o*-fluorophenyl ketone also undergoes *p*-*t*-butylation with the *t*-butyl reagent, the fluorine atom being retained.

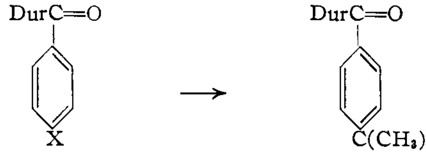
In the preceding papers of this series[3] it has been shown that Grignard reagents effect nucleophilic displacement of methoxyl, acyloxyl and cyano groups from the *ortho* and *para* positions of hindered aryl ketones. The present paper deals with the displacement of halogen atoms from such ketones. A displacement of this type was reported earlier for *o*-bromophenyl mesityl ketone, which reacted with phenylmagnesium bromide to give 2,6-diphenylphenyl mesityl ketone in a low yield.[4] Also, an attempted displacement of bromine from *p*-bromophenyl mesityl ketone by the phenyl and α-naphthyl reagents produced compounds which, while not identified, are known to contain bromine.[5]

In the present work, which deals with halogen derivatives of duryl phenyl ketone, it has been found that, although displacement at the *ortho* position occurs, the products are obtained only in low yields. *o*-Bromophenyl duryl ketone (I) reacts with phenylmagnesium bromide, for example, to give *o*-duroylbiphenyl (II) in a yield of only 6.7%. With *t*-butylmagnesium chloride and *o*-bromophenyl duryl ketone (I) the product, obtained in a yield of 15%, is *p*-*t*-butylphenyl duryl ketone (V) rather than the expected *ortho* isomer III. It is presumed that the dihydroaromatic compound, produced by addition, is aromatized by loss of the elements of hydrogen bromide. Under similar conditions, however, duryl *o*-fluorophenyl ketone (IV) gave duryl 2-fluoro-4-*t*-butylphenyl ketone, the halogen atom being retained; the yield was 35%.



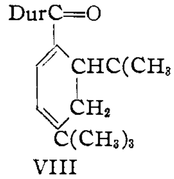
I, X = Br
IV, X = F

II, R = $C_6H_5$
III, R = $t$-$C_4H_9$

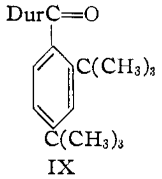


VI, X = F
VII, X = Br

V



VIII



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(1) Proctor and Gamble Company Fellow, 1953–1954.

(2) National Science Foundation Fellow, 1952–1953; Allied Chemical and Dye Corporation Fellow, 1953–1954.

(3) For the preceding communication see R. C. Fuson and W. S. Friedlander, THIS JOURNAL, **75**, 5410 (1953).

(4) R. C. Fuson and S. B. Speck, *ibid.*, **64**, 2446 (1942).

(5) R. C. Fuson, M. D. Armstrong and S. B. Speck, *J. Org. Chem.*, **7**, 297 (1942).