cient stirrer, thermometer and two dropping funnels, were added simultaneously 200 g. of cyclohexanone (Matheson) and 630 ml. of 30% hydrogen peroxide. The temperature of the reaction mixture was maintained at 50 ± 5° with the aid of a cold water-bath during the 70 min. required for the addition. The solution was extracted with two 150-ml. portions of ether to remove any unreacted cyclohexanone. The aqueous solution was acidified to congo red with concd. hydrochloric acid[10] and extracted with one 250-ml. and three 150-ml. portions of ether. The combined ether extracts were dried over sodium sulfate containing some sodium sulfite to remove diethyl peroxide from the ether.[11] Distillation of the ether on the steam-bath left 192 g. of crude ε-hydroxycaproic acid and its lactone which solidified on cooling.

To 218 g. of the crude acid and lactone, prepared as above, was added a cooled solution of 240 ml. of concentrated sulfuric acid in 1 l. of 48% hydrobromic acid. Much heat was evolved when the first portions of the acid solution were added to the mixture. The solution was left standing at room temperature two hours and then warmed on the steam-bath four hours. The solution was diluted with three liters of water, approximately 200 g. of ammonium sulfate was added and the ε-bromocaproic acid was extracted with 400 ml. and 200 ml. of ether. The combined ether extracts were dried over a mixture of sodium sulfate and sodium sulfite and distilled. Attempts to fractionate the residue through a 13-plate column at 10 mm. resulted in decomposition through the loss of hydrogen bromide; however, the product was readily distillable through a short Vigreux column at a lower pressure. The yield of product, b.p. 128–130° at 0.2 mm., was 113 g. (28% of the cyclohexanone).

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[10] When the acid and lactone were distilled, the peroxides were destroyed at this point by adding sodium sulfite to the hot acid solution until a negative starch–iodide test was obtained.

[11] The presence of diethyl peroxide in the ether is conveniently detected by a starch–iodide test. In one run in which no attempt was made to remove the peroxides a violent explosion occurred when the last traces of solvent were being distilled.

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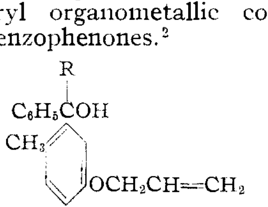
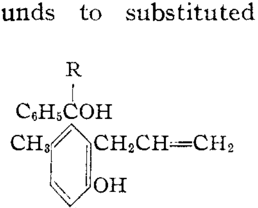
A Claisen Rearrangement of an Allyloxybenzophenone

BY REYNOLD C. FUSON AND FRANKLIN E. MUMFORD

The Claisen rearrangement of suitably constituted aromatic ethers appears to offer an attractive route to certain types of closely packed molecules, since the allyl group migrates by an intramolecular reaction.[1] In the triarylcarbinol series, for example, the rearrangement of the allyl group in 2,4-dimethyl-5-allyloxyphenylmesitylphenylcarbinol (I, R = mesityl) would yield a product (II, R = mesityl) in which two of the rings have the ortho positions occupied. Such a degree of crowding has not been achieved by addition of aryl organometallic compounds to substituted benzophenones.[2]

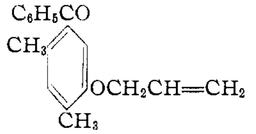


I

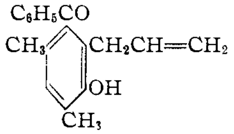


II

An approach to the synthesis of carbinols of type I has been made by way of the allyl ether (III) of 2,4-dimethyl-5-hydroxybenzophenone. The corresponding methyl ether had been prepared by benzoylation of 2,4-dimethylanisole in the presence of aluminum chloride.[3] By treatment with hydriodic acid the methyl ether was converted to the corresponding hydroxy ketone, which was allylated with allyl bromide in the presence of potassium carbonate. It is of interest that the keto ether (III) rearranged readily and in good yield to the allyl phenol (IV), for this confirms the surprising finding of Meisenheimer, Hanssen and Wächterowitz,[3] that the benzoyl group introduced into 2,4-dimethylanisole by the method of Friedel and Crafts is situated in a position meta to the methoxyl group. The rearrangement is unusual in that the aromatic nucleus involved bears a meta-directing group in a position meta to the allyloxyl group.[4]



III



IV

Condensation of the allyloxy ketone (III) with *o*-tolyl- and mesityllithium converted it to carbinols of type I in which R is, respectively, *o*-tolyl and mesityl. It was found, however, that the mesityl carbinol did not rearrange when heated at 200° for one hour. More drastic treatment converted it to resinous materials. It may be that the rearrangement fails because of steric factors, although models of the allylphenol (II, R = mesityl) indicate that it is capable of existence. Moreover, failure was met also with the carbinol in which R is *o*-tolyl, a molecule in which the space exigency is not great.

Experimental[5]

2,4-Dimethyl-5-allyloxybenzophenone (III).—This allyl ether was prepared by the method of Claisen and Eisleb.[6] A mixture of 6.79 g. of 2,4-dimethyl-5-hydroxybenzophenone, 4.36 g. of allyl bromide and 4.0 g. of potassium carbonate in 40 ml. of methyl ethyl ketone was heated under reflux for 12 hours. At the end of this period 100 ml. of water was added to dissolve the potassium bromide and excess potassium carbonate. The organic layer was removed, and the aqueous layer extracted exhaustively with ether. The extracts and organic layer were combined and washed successively with four 25-ml. portions of 10% potassium hydroxide solution and three 25-ml. portions of water. The ether boiled at 150–151° (0.07 mm.); n^{20}_D 1.5858. The yield of the light yellow liquid was 6.44 g. (80%).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.09; H, 6.80.

2,4-Dimethyl-5-hydroxy-6-allylbenzophenone (IV).—The allyl ether (III) (1.06 g.) was heated at 220° for 90 minutes in an atmosphere of carbon dioxide. The brown reaction mass, when recrystallized from high-boiling petroleum ether, gave 0.89 g. (84%) of crude product; m.p. 120–128°. After two recrystallizations from a mixture of benzene and high-boiling petroleum ether, colorless crystals of the hydroxy ketone (IV) were obtained; m.p. 126–127°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.03; H, 6.92.

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[1] C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

[2] (a) E. P. Kohler and L. W. Blanchard, Jr., THIS JOURNAL, **57**, 367 (1935); (b) R. C. Fuson, G. P. Speranza and R. Gaertner, *J. Org. Chem.*, **15**, 1155 (1950).

[3] J. Meisenheimer, R. Hanssen and A. Wächterowitz, *J. prakt. Chem.*, **119**, 315 (1928).

[4] See E. T. McBee and E. Rapkin, THIS JOURNAL, **73**, 2375 (1951).

[5] Infrared absorption data and interpretations by Miss Elizabeth Petersen.

[6] L. Claisen and O. Eisleb, *Ann.*, **401**, 21 (1913).

The infrared absorption spectrum showed bands at 1655 and 3370 cm.$^{-1}$, of the carbonyl and hydroxyl groups, respectively. Absorption bands for the terminal methylene group were found at 915 and 991 cm.$^{-1}$.

2,4-Dimethyl-5-allyloxyphenylmesitylphenylcarbinol (I, R = Mesityl).—Mesityllithium was prepared by the method described by Fuson, Speranza and Gaertner.[2b] Four grams of bromomesitylene and 0.28 g. of lithium in 100 ml. of dry ether were stirred under reflux in a nitrogen atmosphere for 3 hours. The milky solution was cooled to 10° and 1.33 g. of the ketone (III) in 20 ml. of dry ether was added. After being stirred one hour the complex was decomposed with crushed ice and the ether layer separated. Steam-distillation of the ether solution removed the ether and also the mesitylene formed by hydrolysis of the excess mesityllithium. The viscous, dark brown oil which remained was extracted from the water with ether and the extract dried. Evaporation of the ether gave a brown oil which crystallized when allowed to stand. Recrystallization from dilute methanol solution yielded 1.8 g. (93%) of crude product. Two more recrystallizations from the same solvent gave the carbinol in the form of colorless, cube-shaped crystals; m.p. 97–98°. If the methanol solution of the carbinol was subjected to prolonged heating it developed a violet color.

Anal. Calcd. for $C_{27}H_{30}O_2$: C, 83.90; H, 7.82. Found: C, 83.73; H, 7.66.

2,4-Dimethyl-5-allyloxyphenyl-*o*-tolylphenylcarbinol (I, R = *o*-Tolyl).—*o*-Tolyllithium was prepared from 3.42 g. of *o*-bromotoluene in the manner described for mesityllithium. The ketone (III) was added after the solution had been cooled and the carbinol was isolated in the manner described for the mesityl analog. The yield of crude product was 1.3 g. (73%); m.p. 78–81°. The pure carbinol melted at 81°.

Anal. Calcd. for $C_{25}H_{26}O_2$: C, 83.77; H, 7.32. Found: C, 83.94; H, 7.57.

Attempted Rearrangement of 2,4-Dimethyl-5-allyloxyphenylmesitylphenylcarbinol.—The carbinol (0.3 g.) was heated at 200–220° at a pressure of 0.05 mm. for one hour. Treatment of the resulting brown mass with alcohol gave 0.27 g. of the original carbinol. When the same procedure was employed with the exception that the heating was continued for two hours, an alcohol-insoluble, resinous mass was obtained from which no pure product was isolated.

Attempted Rearrangement of 2,4-Dimethyl-5-allyloxyphenyl-*o*-tolylphenylcarbinol.—The carbinol (0.18 g.), blanketed with nitrogen, was heated at 200–210° for 90 minutes. At 150° the colorless, molten carbinol began to darken, finally becoming a red-brown, viscous mass. Attempts to obtain a pure fraction from this resinous material by crystallization from dilute acetone solution failed.

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Decomposition of Benzoyl Peroxide in Allyl Alcohol and Allyl Bromide[1,2]

BY NORMAN G. GAYLORD[3] AND FREDERICK R. EIRICH

The decomposition of benzoyl peroxide in solvents is a first order reaction accompanied by a free radical induced chain reaction.[4] This results in a variation of the rate of decomposition with the initial concentration of peroxide.[4a,5,6]

The initial decomposition of benzoyl peroxide in allyl alcohol is a very rapid, kinetically first order, reaction but some or all of the ultimate reaction products act as inhibitors, and their accumulation slows down the decomposition, as shown in Fig. 1.

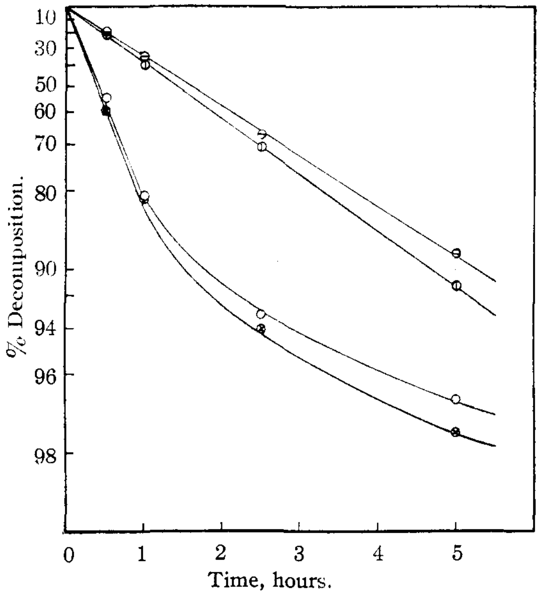

Fig. 1.—The decomposition of benzoyl peroxide in allyl compounds at 80°: allyl bromide: ⦶, P_0 = 0.172 m./kg.; ⊖, P_0 = 0.0848 m./kg.; allyl alcohol: ⊗, P_0 = 0.114 m./kg.; ○, P_0 = 0.0833 m./kg. The ordinate scale is proportional to log (100 − % decomposition).

Due to this retardation effect, a circumstance observed in the decomposition of benzoyl peroxide in other alcohols,[7] the rate constant shown in Table I was calculated from the initial first order decomposition. Percentage conversion to polymer in allyl alcohol is very small, polymerization ceasing after a short period, presumably after the catalyst is essentially used up. Originally Staudinger had believed that no polymer could be obtained from allyl alcohol.[8] It has since been shown that in order to obtain a reasonable yield of polymer from allyl alcohol it is necessary to add fresh catalyst to the reaction mixture to replace that which is destroyed or consumed.[9]

TABLE I

THE DECOMPOSITION OF BENZOYL PEROXIDE AT 80 ± 0.1°

Monomer	Initial wt. % peroxide	Peroxide, m./kg.	k_1, hr.$^{-1}$	% polymer 24 hr.
Allyl alcohol	2.02	0.0833	1.66[a]	3.0
	2.77	.114	1.69[a]	4.2
Allyl bromide	2.05	.0848	0.433	0
	4.16	.172	0.480	0

[a] Falling off of rate after one hour; k_1 calculated from initial decomposition.

The decomposition of benzoyl peroxide in allyl bromide is also a first order reaction as shown in Fig. 1. The rate constants, as indicated in Table I, are not as high as for the decomposition in allyl

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(1) Allyl Polymerization. I. This work was carried out with the support of the U. S. Navy, Bureau of Aeronautics.

(2) Abstracted from a portion of the dissertation submitted by N. G. G. to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) E. I. du Pont de Nemours and Co., Yerkes Research Laboratory, Buffalo, N. Y.

(4) (a) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946); (b) W. E. Cass, *ibid.*, **68**, 1976 (1946); (c) B. Barnett and W. E. Vaughan, *J. Phys. Colloid Chem.*, **51**, 926, 942 (1947); (d) C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5426 (1950).

(5) D. J. Brown, *ibid.*, **62**, 2657 (1940).

(6) P. D. Bartlett and R. Altschul, *ibid.*, **67**, 816 (1945).

(7) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

(8) H. Staudinger and T. Fleitmann, *Ann.*, **480**, 92 (1930).

(9) H. Dannenberg and D. E. Adelson, British Patent 566,344 (1944).