[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY AND NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Cleavage and Rearrangement of Ethers with Bases. III. Ethers of Benzoin and Ethyl Mandelate[1a]

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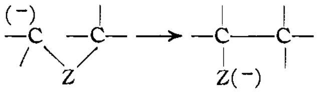
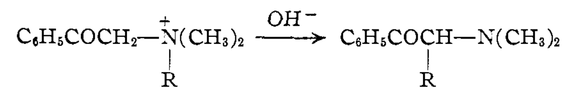
Benzyl desyl ether has been synthesized and found to undergo oxygen-to-carbon benzyl migration under the influence of 1 *N* ethanolic potassium hydroxide. Desyl *p*-nitrophenyl ether (but not desyl phenyl ether) with methanolic potassium hydroxide undergoes a similar rearrangement which, however, is followed by oxidation–reduction to give *p*-azobenzophenone and *p*-aminobenzophenone. The oxygen-to-carbon rearrangement has also been extended to an ester, ethyl mandelate benzhydryl ether, which rearranges to ethyl α,β,β-triphenyllactate under the influence of ethanolic sodium ethoxide. Desyl phenyl ether reacts with triphenylmethylsodium in an unusual reduction to give desoxybenzoin, phenol and triphenylmethyl peroxide. Desyl *p*-nitrophenyl ether has been found to undergo unexpected oxidation–reduction with potassium hydroxide in aqueous dioxane to give desoxybenzoin, benzilic acid and *p*-nitrophenol.

Many internal displacement reactions of the general type



have been reported of which the two most important classes are the rearrangement of α-quaternary ammonium ketones with aqueous hydroxyl ion[2]

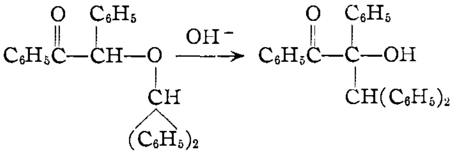


$$C_6H_5COCH_2{-}\overset{+}{\underset{\substack{|\\R}}{N}}(CH_3)_2 \xrightarrow{OH^-} C_6H_5CO\underset{\substack{|\\R}}{C}H{-}N(CH_3)_2$$

and the rearrangement of benzyl and related ethers with strong bases such as phenyllithium[3] or potassium amide.[4]

The usefulness of these reactions has been limited, however, by their rather specialized structural requirements and, in examples of the second type, because of the necessity for the use of highly active (and therefore non-selective) reagents and, often, rather severe conditions.

In a previous publication[5] it was reported that benzhydryl desyl ether readily rearranged with benzhydryl migration on treatment with 1 *N* potassium hydroxide under reflux to give α-benzhydrylbenzoin although the situation was complicated by further reaction of the initial product.



Since benzyl is apparently a less effective migrating group than benzhydryl in related rearrangements such as the Stevens,[6] benzyl desyl ether (I) was chosen as the first compound for study.

The synthesis of I presented somewhat more of a synthetic problem than had been anticipated. It previously had been reported[7] that the potassium salt of benzoin reacts with benzyl chloride to give the C-methylated product, α-benzylbenzoin rather than I. The reaction of benzoin with benzyl alcohol in the presence of *p*-toluenesulfonic acid in benzene solvent gave recovered benzyl alcohol, a small amount of benzil and a substance, m.p. 171–173°, probably tetraphenylfuran. When ether interchange of benzoin with dibenzyl ether was attempted with toluenesulfonic acid in benzene the principal products were diphenylmethane, benzhydryl phenyl ketone and benzil together with a small amount of what was probably tetraphenylfuran.

The reaction of phenylbenzoyldiazomethane with benzyl alcohol in the presence of *p*-toluenesulfonic acid gave principally benzyl diphenylacetate (formed by rearrangement of the phenylbenzoylmethane to diphenyl ketene followed by reaction of the latter with benzyl alcohol). However, when phenylbenzoyldiazomethane was allowed to react with carefully purified benzyl alcohol in ether containing boron trifluoride etherate by the procedure of Newman and Beal[8] a 40% yield of I was obtained.

A second method which served as a confirmation of the structure of I consisted of treating benzyl iodide with benzoin in the presence of dry silver oxide. This procedure was less satisfactory than that above because of the unpleasant qualities of benzyl iodide. Use of benzyl chloride under the same conditions led to no reaction.

The structure of I was further supported by cleavage to benzoin (57% yield) with aqueous ethanolic hydrochloric acid.

When I was heated for one hour under reflux with 1 *N* ethanolic potassium hydroxide a 33% yield of α-benzylbenzoin (II) was obtained, together with 17% of benzylphenylcarbinol and 34% of benzoic acid.

II has previously been reported to be cleaved to benzoic acid and benzylphenylcarbinol[9] and was probably an intermediate in their formation. Indeed, when I was refluxed with 25% methanolic

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(1) (a) Taken from a Dissertation submitted by William R. Proops to Columbia University in partial fulfillment of the requirements for the Ph.D. in Chemistry. (b) Department of Chemistry, University of Illinois, Urbana, Illinois.

(2) (a) J. L. Dunn and T. S. Stevens, *J. Chem. Soc.*, 279 (1934) and references cited there; (b) see also A. Campbell, A. H. J. Houston and J. Kenyon, *ibid.*, 93 (1947); (c) J. H. Brewster and M. W. Kline, THIS JOURNAL, **74**, 5179 (1952), for stereochemistry of reaction.

(3) (a) G. Wittig and L. Lohman, *Ann.*, **550**, 260 (1942); (b) G. Wittig and W. Happe, *ibid.*, **557**, 205 (1947); (c) G. Wittig, H. Döser and I. Lorenz, *ibid.*, **562**, 192 (1949).

(4) C. R. Hauser and S. W. Kantor, THIS JOURNAL, **73**, 1437 (1951).

(5) D. Y. Curtin and S. Leskowitz, *ibid.*, **73**, 2633 (1951).

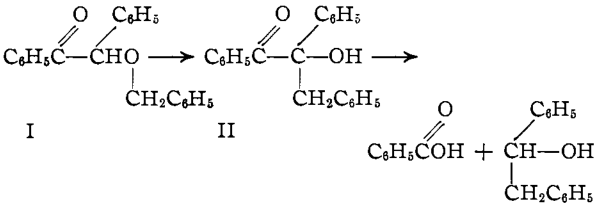
(6) T. S. Stevens, *J. Chem. Soc.*, 2107 (1930).

(7) G. Scheunig and A. Hensle, *Ann.*, **440**, 82 (1924).

(8) M. S. Newman and P. F. Beal, THIS JOURNAL, **72**, 5161 (1950).

(9) J. Pascual Vila and J. Cerezo, *Anal. soc. espan. fis. quim.*, **24**, 395 (1926).

potassium hydroxide for 25 minutes, a 91% yield of benzoic acid and an 84% yield of benzylphenylcarbinol were obtained.


$$C_6H_5COCH(C_6H_5)OCH_2C_6H_5 \longrightarrow C_6H_5COC(C_6H_5)(OH)CH_2C_6H_5 \longrightarrow C_6H_5COOH + C_6H_5CH(OH)CH_2C_6H_5$$

I II

In view of the ready rearrangement of I, desyl phenyl ether (III) was next examined since it should have still less tendency to rearrange.[2a,3c,4] III was prepared by the reaction of phenolate ion with desyl chloride.[10] Treatment of III for 1 hour with 1.0 *N* ethanolic potassium hydroxide solution gave no detectable acid product and 78% of the starting material was recovered. Methanolic potassium hydroxide (25%) after 1 day under reflux effected 76% conversion to benzyl phenyl ether. The other cleavage product, benzoic acid, was isolated in 84% yield.

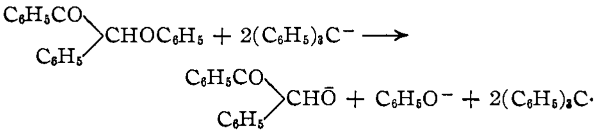
Since triphenylmethylsodium is a strong base which shows little tendency to undergo addition to the carbonyl it seemed likely to favor oxygen-to-carbon rearrangement over cleavage in its reaction with I. The reaction took an entirely different course, however. The products obtained after two days at room temperature are listed in Table I.

TABLE I

PRODUCTS FROM THE REACTION OF DESYL PHENYL ETHER (III) (0.069 MOLE) WITH TRIPHENYLMETHYLSODIUM (1.20 MOLES/MOLE OF III)

Product	No. moles product per mole of III employed
Desoxybenzoin	0.25
Phenol	.38
Triphenylmethyl peroxide	.39
Triphenylmethane	.20
Benzaldehyde	.03
Benzoic acid	.02
Recovered III	.38

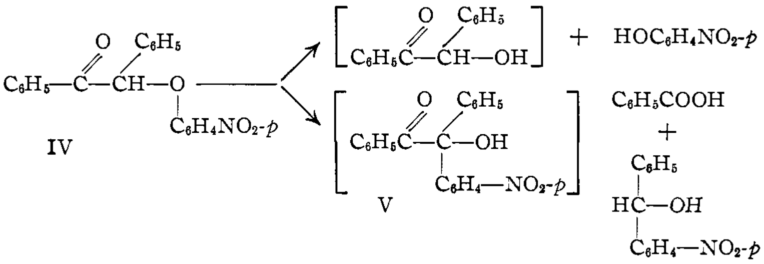
The formation of desoxybenzoin, phenol and triphenylmethyl peroxide in roughly equal amounts indicates that the principal reaction was that given by


$$(C_6H_5CO)(C_6H_5)CHOC_6H_5 + 2(C_6H_5)_3C^- \longrightarrow (C_6H_5CO)(C_6H_5)C\bar{H} + C_6H_5O^- + 2(C_6H_5)_3C\cdot$$

The reaction seems to be related to the ready conversion of α-alkoxyketones to the alcohol and ketone by mild treatment with sodium amalgam,[11] the reduction of α-hydroxyketones to ketones with hydrogen and palladium or zinc and acetic acid,[12] and the reduction of α-acetoxyketones with sodium amalgam in glacial acetic acid[13] or with zinc in acetic anhydride.[14]

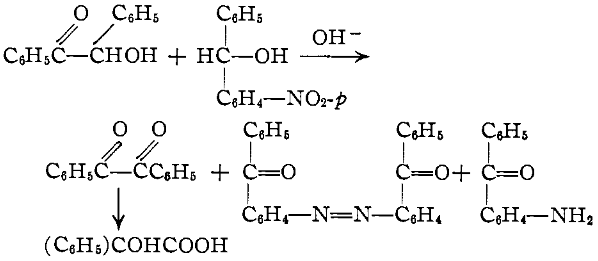
In view of the similarity of the oxygen-to-carbon migration to the intermolecular displacement reaction, it seemed that a *p*-nitro substituent should aid phenyl migration.[15] For this reason *p*-nitrophenyl desyl ether (IV) was prepared by a method analogous to that which had been used for III. When IV was treated with 25% potassium hydroxide in boiling methanol for 1 hour, *p*-azobenzophenone (15%), *p*-aminobenzophenone (6%), *p*-nitrophenol (47%), benzilic acid (56%) and benzoic acid (38%) were obtained. The formation of *p*-azobenzophenone and *p*-aminobenzophenone is of particular interest since they have a carbon skeleton which is not present in the original molecule and must therefore have resulted from a rearrangement.

It seems probable that IV underwent decomposition by two major paths: the first, cleavage by hydroxyl at the position para to the nitro group leading to benzoin and *p*-nitrophenol; the second, an oxygen-to-carbon rearrangement to α-(*p*-nitrophenyl)-benzoin (V) followed by cleavage (behavior analogous to that of the benzyl ether, I) to give *p*-nitrobenzhydrol and benzoic acid.


$$C_6H_5COCH(C_6H_5)OC_6H_4NO_2\text{-}p \longrightarrow [C_6H_5COCH(C_6H_5)OH] + HOC_6H_4NO_2\text{-}p$$
$$C_6H_5COCH(C_6H_5)OC_6H_4NO_2\text{-}p \longrightarrow [C_6H_5COC(C_6H_5)(OH)C_6H_4\text{—}NO_2\text{-}p] \longrightarrow C_6H_5COOH + C_6H_5CH(OH)C_6H_4\text{—}NO_2\text{-}p$$

IV V

The further reactions of *p*-nitrobenzhydrol required to arrive at *p*-azobenzophenone and *p*-aminobenzophenone are oxidation of the secondary alcohol function and reduction of the nitro group. Reductions of nitro groups to azo compounds in the presence of base are well known.[16] Since, however, there are insufficient alcohol groupings in *p*-nitrobenzhydrol to account for the amount of reduction observed they must have been assisted by the benzoin formed in the first reaction and possibly


$$C_6H_5COCHOHC_6H_5 + C_6H_5CH(OH)C_6H_4\text{—}NO_2\text{-}p \xrightarrow{OH^-} C_6H_5COCOC_6H_5 + C_6H_5C(=O)C_6H_4\text{—}N{=}N\text{—}C_6H_4C(=O)C_6H_5 + C_6H_5C(=O)C_6H_4\text{—}NH_2$$
$$C_6H_5COCOC_6H_5 \downarrow (C_6H_5)COHCOOH$$

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[10] C. K. Bradsher and R. Rosher, THIS JOURNAL, **61**, 1524 (1939).

[11] R. Fittig and A. Erlenbach, *Ber.*, **21**, 2647 (1888).

[12] H. Staudinger and L. Ruzicka, *Helv. Chim. Acta*, **7**, 377 (1924).

[13] C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.*, 402 (1928).

[14] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, THIS JOURNAL, **74**, 4225 (1952).

[15] Wittig, Döser and Lorenz[3c] reported the rearrangement of *p*-nitrophenyl fluorenyl ether to 9-[*p*-nitrophenyl]-9-fluorenol with lithium methoxide at 100°. The reaction of phenyl fluorenyl ether under the same conditions was apparently not studied but treatment of the latter ether with phenyllithium at 100° failed to give rearrangement.

[16] D. Vorlaender, *Ber.*, **40**, 1422 (1907); P. Carre, *Ann. chim.*, [8] **6**, 408 (1905); H. Nisbet, *J. Chem. Soc.*, 3121 (1928).

by methanol used as solvent. The benzoin was, in turn, oxidized to benzil, which rearranged to give the benzilic acid found.

Of the many possible alternative paths which can be written, one of the most likely has as one of its first steps cleavage of IV to benzyl *p*-nitrophenyl ether (VI) and benzoic acid. The rearrangement, which is of primary interest, would then have been a rearrangement of VI to *p*-nitrobenzhydrol.

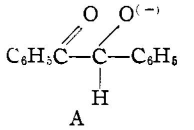
$$\text{IV} \xrightarrow[\text{OH}^-]{\cdots\cdots} \underset{\text{VI}}{C_6H_5CH_2OC_2H_4—NO_2} \xrightarrow{\cdots\cdots}$$

$$C_6H_5CHOHC_6H_4NO_2 \xrightarrow{\cdots\cdots} + C_6H_5COOH$$

This path appears very unlikely since when VI was treated with benzoin in methanolic potassium hydroxide for one hour the products were *p*-nitroanisole (16%), *p*-aminophenyl benzyl ether (26%) and *p,p'*-dibenzyloxyazoxybenzene (30%). No product with a rearranged carbon skeleton was obtained. When the same reaction was carried out in the absence of benzoin the products were *p*-nitroanisole (61%) and benzyl alcohol (56%). No reduction of the nitro group was observed.[17]

It seems highly probable, then, that substitution of a *p*-nitro group in desyl phenyl ether (III) promoted rearrangement to an extent such that at least 21% of the reaction of IV went by rearrangement to V.

In an effort to prevent that part of the reduction of the nitro group for which methanol was responsible, IV was refluxed for 1 hour with 1.0 *N* potassium hydroxide in aqueous dioxane. Under these conditions the products obtained were significantly different from those obtained in methanol. No *p*-azobenzophenone was found. *p*-Aminobenzophenone (2%), benzoic acid (9%), *p*-nitrophenol (73%) and benzilic acid (40%) were isolated as before but in addition desoxybenzoin (24%), was obtained. Apparently part of the IV reacted by a course similar to that in methanol. The formation of desoxybenzoin which, however, had not been observed previously was of unusual interest. It seems likely that a displacement is involved in which a *p*-nitrophenoxide ion of IV is displaced by a hydrogen and electron pair which are transferred from some ion such as A or B below. Such a process is rather similar to the hydrogen transfer step in the Cannizzaro reaction.[18]



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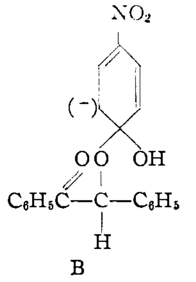
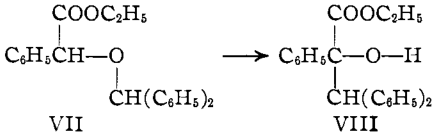


B

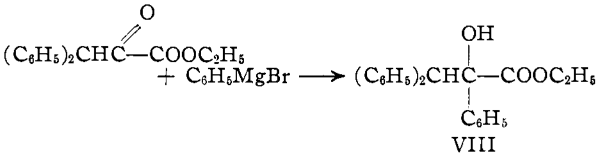
Attempts to replace the ketonic carbonyl function with an ester carbonyl in the Stevens rearrangement, although limited, had been unsuccessful.[19] It was, nevertheless, desired to attempt the rearrangement of an ether of an α-hydroxy ester. The benzhydryl ether (VII) of ethyl mandelate was selected for this study.

VII was readily prepared from the reaction of diphenyldiazomethane with ethyl mandelate. Its structure was confirmed by the infrared absorption spectrum (no hydroxyl; ester carbonyl at 1745 cm.$^{-1}$), by hydrolysis with acid to mandelic acid, and by hydrolysis with ethanolic potassium hydroxide to mandelic acid benzhydryl ether.

When VII was allowed to react for 1 hour with sodium ethoxide in ethanol under reflux, ethyl α,β,β-triphenyllactate (VIII) was obtained in 39% yield together with 22% of recovered starting material. The structure of VIII was established by its infrared spectrum and by comparison with an authentic specimen prepared by the reaction of phenylmagnesium bromide with ethyl diphenylpyruvate.[20]



VII VIII



VIII

The work reported here together with that of Curtin and Leskowitz[5] suggests the same general order of ease of migration as in the Stevens rearrangement.

$$C_6H_5— \ll p\text{-}NO_2C_6H_4— < (C_6H_5)_2CH—$$
$$C_6H_5CH_2—$$

The ease with which the rearrangement of these α-alkoxyketones proceeds and the extension of the reaction to an α-alkoxy ester lead to the hope that the reaction may be of use in synthesis.

Experimental[21]

Synthesis of Benzyl Desyl Ether (I). (a) From Benzyl Iodide and Benzoin.—To a solution of benzoin (14.6 g., 0.0688 mole) and benzyl iodide[22] in 200 ml. of dry acetone was added with stirring a slurry of dry silver oxide[23] (42 g., 0.18 mole) in 50 ml. of acetone. The mixture refluxed spontaneously for 10 minutes and was then heated under reflux for 1 hour and allowed to stand for an additional hour. The silver iodide formed was removed by filtration. Acetone was then distilled and excess benzyl iodide removed at 0.1

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[17] G. Kumpf, *Ann.*, **224**, 96 (1884), reported that benzyl *p*-nitrophenyl ether (VI) when refluxed with ethanolic potassium hydroxide for five hours gave only a yellow resin.

[18] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 350.

[19] T. S. Stevens, W. W. Snedden, E. T. Stiller and T. Thompson, *J. Chem. Soc.*, 2119 (1930).

[20] E. P. Kohler, N. K. Richtmeyer and W. F. Hester, This Journal, **53**, 205 (1931).

[21] All melting points are corrected. Microanalyses were carried out by the Schwarzkopf Microanalytical Laboratory, Elmhurst, Long Island; and by Miss E. Davis, Mrs. E. Fett and Mr. J. Nemeth at the University of Illinois. Infrared spectra were measured by Miss H. Miklas and Mrs. R. F. Hill with a Perkin-Elmer Double Beam Spectrophotometer, Model 21, with sodium chloride cells. Ultraviolet spectra were determined by Mr. H. Birch, Mr. Ramania and Miss E. Richards using a Cary Recording Spectrophotometer, Model 11, with a 1-cm. quartz cell.

[22] G. H. Coleman and C. R. Hauser, This Journal, **50**, 1193 (1928).

[23] H. T. Clarke and L. D. Behr, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 20, Note 5.

mm. (with a bath at 35–85°). From the residue to which ether had been added, benzoin (3.08 g., m.p. 127–130°, no depression with authentic sample) was recovered. The residue was washed with 5% aqueous sodium bicarbonate, water and then dissolved in 200 ml. of ethanol and a solution of 30 g. (0.13 mole) of periodic acid dihydrate in 200 ml. of water was added to destroy any benzoin remaining. The suspension was stirred for 13 hours, 500 cc. more water added, and the product extracted with ether. The ether solution was washed with 5% sodium bicarbonate and saturated sodium bisulfite to remove benzoic acid and benzaldehyde and finally, after drying, the ether was removed under vacuum.

The brown oil which remained was dissolved in 200 ml. of ethanol containing 20 ml. of acetic acid and 14 g. (0.083 mole) of Girard T reagent. The solution was refluxed for 2 hours, poured into 500 ml. of an ice–water mixture and extracted with ether. The aqueous fraction was then acidified with 15 ml. of concentrated sulfuric acid and allowed to stand for 2 days. The yellow oil that formed was extracted with ether, washed with 10% sodium carbonate solution, dried and evaporated under vacuum. The residue was crystallized from ethanol to give 6.7 g. (0.022 mole) of benzyl desyl ether, m.p. 58–60° (32 or 41% based on recovered starting material). Further recrystallization from ethanol gave m.p. 60–60.5°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.5; H, 6.0. Found: C, 83.7; 83.5; H, 6.0, 5.9.

(b) **From Phenylbenzoyldiazomethane, Benzyl Alcohol.**—In an adaptation of the method of Newman and Beal,[8] benzyl alcohol (b.p. 96–98° (15 mm.)) (52 g., 0.48 mole) (purified by extraction with sodium bisulfite and treatment with refluxing sodium hydroxide solution) and boron trifluoride etherate (0.7 g.) were added to a solution of 13.3 g. (0.0598 mole) of phenylbenzoyldiazomethane,[24] m.p. 64–68° in 175 ml. of anhydrous ether. The gas evolved was collected and when the reaction mixture was kept at 29–31°, the theoretical quantity of nitrogen was evolved in 45 minutes. The ether layer was extracted with 10% sodium bicarbonate, dried and the ether and benzyl alcohol removed by distillation, first on a steam-bath and then in a bath held at 135° and 0.3 mm.

Unreacted benzoin was destroyed with periodic acid and the I extracted with Girard T reagent as in procedure (a) to give a residue which, after crystallization from methanol, gave 7.8 g. (0.026 mole or 43%) of I, m.p. 57.5–59°, which showed no m.p. depression when mixed with that prepared by procedure (a).

Reaction of I with Hydrochloric Acid.—A solution of 0.50 g. (0.0017 mole) of I in 15 ml. of ethanol and 12 ml. of concentrated hydrochloric acid was refluxed for 44 hours. Crystals appeared on cooling. These were filtered and recrystallized twice from ethanol to give 0.20 g. (0.00095 mole, 57%) of benzoin, m.p. and mixed m.p. with authentic benzoin, 128–130°.

Thermal Cleavage of I.—I (1.0 g., 0.0033 mole) was heated under 10 mm. pressure at 185° for 45 minutes and then at 205° for 2 hours, after which it was distilled (b.p.o. 178–182° (15 mm.)). From the distillate and residue after recrystallization from ethanol was obtained 0.45 (0.0015 mole, 45%) of unreacted I, m.p. 58–60°, as shown by mixed m.p. A very small drop of liquid had accumulated in the Dry Ice trap. This was heated with 0.15 g. of 2,4-dinitrophenylhydrazine, and 0.2 ml. of concentrated hydrochloric acid for 5 minutes to give 0.01 g. of benzaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. with an authentic sample 239–240°. This corresponds to a 1% yield of benzaldehyde.

Reaction of I with Potassium Hydroxide. (a) With 1.0 *N* Ethanolic Potassium Hydroxide.—I (7.0 g., 0.023 mole) was treated for 1 hour with 70 ml. of boiling 1 *N* ethanolic potassium hydroxide and the solution poured into 200 ml. of water and extracted with ether. From the ethereal extract after drying, evaporation of the ether and crystallization from 35 ml. of ethanol was obtained 1.95 g. of α-benzylbenzoin (II), m.p. and mixed m.p. with authentic material prepared by the method of Banus and Vila,[25] 116–118°. Evaporation of the ethanolic filtrate gave a yellow oil which when treated with Girard T reagent yielded no ketonic fraction. The ethereal extract remaining from the Girard T extraction were dried and the oil remaining after removal of the ether was distilled to give 0.98 g. of benzylphenylcarbinol, b.p. 131–137° (1 mm.), which after recrystallization from benzene–hexane amounted to 0.79 g. (0.0039 mole, 17%), m.p. and mixed m.p. with authentic material, 62–64°. Recrystallization of the residue from 3 ml. of ethanol gave 0.41 g. of crude II, m.p. 105–112°, which on further recrystallization amounted to 0.32 g., m.p. 116–118°. The total amount of II was thus 2.27 g. or 33%.

Acidification of the original aqueous layer above gave 0.95 g. (0.0078 mole or 34%) of benzoic acid, m.p. 115–118° (no m.p. depression with authentic sample).

(b) **With 25% Methanolic Potassium Hydroxide.**—I (2.5 g., 0.00827 mole) was treated with 20 ml. of refluxing 25% methanolic potassium hydroxide for 25 minutes. The yellow suspension was poured into 75 ml. of water and extracted with ether. Evaporation of the ether and recrystallization of the residue from petroleum ether (b.p. 30–60°) gave 1.37 g. (0.00693 mole or 84%) of benzylphenylcarbinol, m.p. 63–65°. The benzoate melted at 68–69° (lit.[26] 70°). Mixed melting points of the benzylphenylcarbinol and its benzoate with the corresponding authentic samples showed no depression.

Acidification of the aqueous solution above and extraction with ether gave 0.92 g. (0.075 mole or 91%) of benzoic acid, m.p. 116–118°, which showed no mixed m.p. depression with an authentic sample.

Reaction of Desyl Phenyl Ether (III) with Potassium Hydroxide. (a) With 1.0 *N* Ethanolic Potassium Hydroxide.—III (10.0 g., 0.0348 mole) was allowed to react for 1 hour under reflux with 100 ml. of 1.0 *N* ethanolic potassium hydroxide. The mixture was extracted with ether. After evaporation of the ether and recrystallization of the residue from ethanol, 7.8 g. (0.028 mole or 78%) of III, m.p. and mixed m.p. with authentic III, 83–85°. The aqueous layer above gave no acid upon acidification.

(b) **With 25% Methanolic Potassium Hydroxide.**—III (7.50 g., 0.0261 mole) was treated with 65 ml. of 25% methanolic potassium hydroxide under reflux for 1 day. The suspension was poured into 200 ml. of water and extracted with ether.

Evaporation of the ether and recrystallization of the residue from ethanol gave 3.6 g. (0.019 mole, 76%) of benzyl phenyl ether m.p. and mixed m.p. with authentic sample,[27] 37–38.5°.

Acidification of the aqueous layer with carbon dioxide and ether extraction gave no phenolic fraction. Further acidification with concentrated hydrochloric acid, extraction with ether and evaporation of the ether gave 2.68 g. (0.0219 mole, 84%) of benzoic acid, m.p. and mixed m.p. with an authentic sample, 121–123°.

Reaction of III with Triphenylmethylsodium.—To a solution of 20.0 g. (0.0694 mole) of III in ether was added under nitrogen 700 ml. of ether shown by titration to contain 0.0834 mole of triphenylmethylsodium.[28] The mixture was allowed to stand for 2 days at room temperature (under nitrogen). The ether layer was washed with water (300 ml.), 5% sodium hydroxide (300 ml.), 5% hydrochloric acid (200 ml.) and water (100 ml.). The considerable amount of solid material which remained suspended in the ether layer was collected by filtration and shown to be 13.8 g. (0.0267 mole, accounting for 64% of the triphenylmethylsodium) of triphenylmethyl peroxide, m.p. 177–180° (dec.); mixed m.p. with an authentic sample[29] undepressed.

The ethereal solution above was distilled. The first fraction amounted to 4.84 g., b.p. 113–115° (0.1 mm.), and after recrystallization from ethanol amounted to 4.0 g., m.p. 46–50°. Further recrystallization from ethanol and hexane gave 3.4 g. (0.017 mole or 40% yield based on unrecovered starting material) of desoxybenzoin, m.p. and mixed m.p. 51–53°; 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 200–202°.

The next three fractions, b.p. 115–160° (0.07 mm.), were oils which yielded a total of 3.5 g. (0.015 mole, accounting for 17% of the triphenylmethylsodium) of triphenylmethane, m.p. 93–95°.

The triphenylmethane showed no m.p. depression when

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[24] C. D. Nenitzescu and E. Solomonica, ref. 23, p. 496.

[25] A. G. Banus and J. P. Vila, *Anal. soc. espan. fis. quim.*, **19**, 326 (1921).

[26] A. G. Banus, *ibid.*, **26**, 372 (1928).

[27] S. G. Powell and R. Adams, THIS JOURNAL, **42**, 646 (1920).

[28] W. B. Renfrow, Jr., and C. R. Hauser, ref. 23, p. 607.

[29] L. Gatterman, "Laboratory Methods of Organic Chemistry," The Macmillan Co., London, 1948, p. 352

mixed with an authentic sample and was further characterized by oxidation to triphenylcarbinol,[30] m.p. 161–163°.

From the mother liquors of fraction four (150–160°) above and from fraction five (b.p. 160–170° (0.7 mm.)) was obtained by crystallization from ethanol and hexane successively, 7.5 g. (0.026 mole, or 38% recovery) of III.

From the Dry Ice–acetone trap used in the distillation above was isolated 0.22 g. (3% yield) of benzaldehyde as the 2,4-dinitrophenylhydrazone.

The aqueous sodium bicarbonate solution obtained previously by saturating the combined aqueous extracts with carbon dioxide was washed with ether. Removal of the ether followed by distillation gave 2.5 g. (0.027 mole or 62% yield based on unrecovered starting material) of phenol, b.p. 83–84° (15 mm.); tribromo derivative, m.p. 92–94°.

Acidification of the aqueous layer after removal of the phenol gave 0.20 g. (0.00164 mole, 2% yield) of benzoic acid, m.p. and mixed m.p. 122–123°.

Desyl *p*-Nitrophenyl Ether (IV).—Desyl chloride (10.1 g., 0.435 mole) was allowed to react with 6.5 g. (0.047 mole) of *p*-nitrophenol together with 6.2 g. of potassium carbonate and 55 ml. of acetone under reflux for 5 hours. The reaction mixture was poured into 200 ml. of water, extracted with ether and the ether solution extracted with 10% sodium hydroxide, the ether removed and the residue recrystallized from 20 ml. of ethanol. The resulting solid was stirred for 8 hours with a solution of 5 g. of periodic acid dihydrate, 40 ml. of water and 40 ml. of ethanol. The resulting suspension was filtered, washed with 100 ml. of 50% aqueous ethanol and then water. Recrystallization from ethanol gave 4.0 g. (0.012 mole, 28%) of IV, m.p. 123–124°. The infrared spectrum in Nujol mull is given in Fig. 1, curve A.

Anal. Calcd. for $C_{20}H_{15}NO_4$: C, 72.1; H, 4.5; N, 4.1. Found: C, 72.0; H, 4.8; N, 4.1.

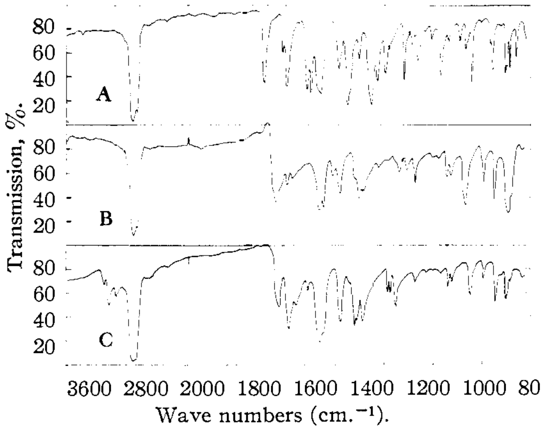

Fig. 1.—Curve A, desyl *p*-nitrophenyl ether in Nujol; curve B, *p*-azobenzophenone in Nujol; curve C, *p*-aminobenzophenone in Nujol.

Reaction of IV with Potassium Hydroxide. (a) 25% Methanolic Potassium Hydroxide.—IV (5.00 g., 0.0148 mole) was treated with 50 ml. of 25% potassium hydroxide in methanol under reflux for 1 hour. The shiny red crystals of *p*-azobenzophenone were filtered. The filtrate was poured into 200 ml. of water, and extracted with ether. The ether extract on evaporation gave a residue which when triturated with 5 ml. of acetone gave more *p*-azobenzophenone, the total being 0.85 g. (0.0022 or 15% of material, m.p. 220–221°). Recrystallization from benzene raised the m.p. to 221–222°. Mixed melting points with an authentic sample described below showed no depression. The infrared absorption spectrum is given in Fig. 1, curve B. The ultraviolet spectrum in ethanol showed the typical azo absorption at 450 mμ (λ 460) (azobenzene has λ_{max} 590 at 441 mμ).[31]

Anal. Calcd. for $C_{26}H_{18}N_2O_2$: C, 79.8; H, 4.6; N, 7.2. Found: C, 80.2; H, 4.8; N, 7.3.

The acetone solution from the trituration gave a brown solid when the acetone evaporated which was washed with 5 ml. of ether to give 0.16 g. (0.00081 mole, 6%) of *p*-aminobenzophenone, m.p. 119–120° (lit.[32] 123°). The structure was confirmed by the solubility of the substance in 5% hydrochloric acid, infrared spectrum (Fig. 1, curve C), and mixed m.p. with an authentic sample.[32]

The aqueous layer remaining above was saturated with carbon dioxide, extracted with ether, the ether removed and the dark material remaining sublimed at 100° and 0.5 mm. for 2 hours to give 0.97 g. (0.0070 mole or 47%) of *p*-nitrophenol, m.p. 109–112°. Mixed melting points with an authentic sample showed no depression.

When the aqueous layer above was acidified and extracted with ether, the mixture of benzilic acid (1.88 g., 0.00825 mole, 56%, m.p. 149–150°) and benzoic acid (0.69 g., 0.0057 mole, 38%, m.p. 119–121°) was separated by selective sublimation of the latter at 100° and 1 mm.

(b) With 1.0 *N* Potassium Hydroxide in Aqueous Dioxane.—IV (3.75 g., 0.0113 mole) was treated with 50 cc. of 1.0 *N* potassium hydroxide in dioxane–water (2 volumes/3) under reflux for 1 hour. The products, isolated as above, were 1.15 g. (0.00827 mole, 73% of *p*-nitrophenol, m.p. 109–112°; 1.03 g. (0.00452 mole, 40%) of benzilic acid, m.p. 149–150°; 0.12 g. (0.00099 mole, 9%) of benzoic acid, m.p. 119–121°. This time, however, the non-acidic fraction contained no *p*-azobenzophenone. The *p*-aminobenzophenone (0.04 g., 0.0002 mole, 2%, m.p. 118–120°) was isolated by extraction with 10% hydrochloric acid, neutralization and filtration. The remaining neutral fraction was treated with Girard T reagent (6.0 g. in 75 ml. of ethanol and 7.5 ml. of acetic acid). Extraction of the non-ketonic neutral fraction followed by decomposition of the Girard derivative with 6 ml. of concentrated sulfuric acid in 225 ml. of water and recrystallization of the product from methanol gave 0.52 g. (0.0027 mole, 24%) of desoxybenzoin, m.p. 50–52°; 2,4-dinitrophenylhydrazone, m.p. 198–200°; mixed melting points, no depression.

Reduction of *p*-Nitrobenzophenone with Benzoin. *p*-Azobenzophenone.—Treatment under reflux for 1 hour of 1.00 g. (0.00441 mole) of *p*-nitrobenzophenone with 2.00 g. (0.00939 mole) of benzoin in 50 ml. of 25% methanolic potassium hydroxide gave 0.41 g. (0.0011 mole, 50%) of *p*-azobenzophenone, m.p. 217–219°; 0.03 g. (0.0002 mole, 3%) of *p*-aminobenzophenone, m.p. 117–120°; and 1.35 g. (0.0059 mole, 63%) of benzilic acid, m.p. 149–150°.

Reaction of Benzyl *p*-Nitrophenyl Ether (VI) with Potassium Hydroxide and Benzoin.—VI (5.40 g., 0.0236 mole) was allowed to react with 7.55 g. (0.345 mole) of benzoin in 20 ml. of 25% methanolic potassium hydroxide under reflux for 1 hour, during which time a solid precipitated. Addition of water, extraction of the resulting mixture with ether, evaporation of the ether, addition of 10 ml. of ethanol and recrystallization of the precipitate from benzene-hexane gave 1.63 g. (0.00398 mole, 30%) of ***p,p′*-dibenzyloxyazoxybenzene**. Additional recrystallization from benzene–hexane raised the m.p. to 152–153°.

Anal. Calcd. for $C_{26}H_{22}N_2O_3$: C, 76.1; H, 5.3; N, 6.8. Found: C, 76.2; H, 5.3; N, 7.1.

The ethanolic filtrate was evaporated, 100 ml. of benzene added, and the solution treated with 25 ml. of concentrated hydrochloric acid. The precipitate that formed was filtered and washed with benzene to give 1.42 g. (0.00605 mole, 26%) of *p*-benzyloxyaniline hydrochloride which was converted to the free amine, m.p. 52–54°, mixed m.p. with an authentic sample,[33] no depression.

The benzene filtrate was washed with water, evaporated to dryness and treated with 5 ml. of ethanol. Upon cooling, 0.57 g. (0.0037 mole, 16%) of *p*-nitroanisole, m.p. 48–51°, mixed m.p., no depression, was obtained.

Synthesis of Ethyl Mandelate Benzhydryl Ether (VII).—To a hot solution of ethyl mandelate (21.4 g., 0.119 mole) and diphenyldiazomethane (21 g., 0.011 mole) in 200 ml. of anhydrous benzene was added 5 drops of concentrated sulfuric acid. After the initial reaction had subsided the solution was refluxed for 2 hours, washed with 5% sodium carbonate and the benzene removed by distillation. The residue was treated with 300 ml. of ethanol and allowed to stand in the freezing compartment of a refrigerator. The material which first crystallized (6.2 g., m.p. 135–172°, probably benzophenoneazine and tetraphenylethylene) was removed, the solution evaporated to 200 ml. and cooled to

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[30] J. Schmidlin and A. Garcia-Banus, *Ber.*, **45**, 3188 (1912).

[31] P. E. Fanta and T. R. Hughes, This Journal, **72**, 5343 (1950).

[32] P. J. Montagne, *Rec. trav. chim.*, **42**, 499 (1923).

[33] L. Spiegel and S. Sabbath, *Ber.*, **34**, 1935 (1901).

give 17 g. (0.50 mole, 45%) of VII, m.p. 48–50°. The infrared absorption spectrum is given in Fig. 2, curve A.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.7; H, 6.4. Found: C, 79.7; H, 6.4.

Hydrolysis of 1.0 g. of VII with 5 ml. of concentrated hydrochloric acid and 25 ml. of ethanol under reflux for 10 hours gave a 76% yield of mandelic acid, m.p. 117–118°, as shown by mixed m.p. with no depression.

Reaction of VII with Sodium Ethoxide.—VII (10.0 g., 0.0295 mole) was treated for 1 hour under reflux with a solution of sodium ethoxide prepared from 2.3 g. (0.10 g. atom) of sodium and 100 ml. of anhydrous ethanol. The reaction mixture was poured onto a mixture of 500 ml. of ice and water and 50 ml. of acetic acid. Extraction with ether, and extraction of the ether solution with 10% sodium hydroxide followed by acidification of the aqueous solution with concentrated hydrochloric acid and filtration gave 0.51 g. (0.0016 mole, 5%) of mandelic acid benzhydryl ether, m.p. and mixed m.p. with an authentic sample prepared below, 158–160°.

The ether extract remaining above was evaporated on a steam-bath under vacuum and 35 ml. of ethanol added. When the solution was allowed to stand in a refrigerator, tetraphenylethane (0.02 g., m.p. 208–210°) first crystallized, followed by 3.5 g. of material, m.p. 95–103°, which when recrystallized from ethanol amounted to 3.1 g., m.p. 108–112°. This was further purified by chromatography on activated alumina with benzene and chloroform, successively. The benzene solution, on evaporation, gave 0.17 g. of tetraphenylethane while the chloroform solution gave 2.9 g. of **ethyl α,β,β-triphenyllactate (VIII)**, m.p. 110–113° (lit.[20] 118–120°). In view of the discrepancy in melting points, the preparation of this substance by the method of Kohler, Richtmyer and Hester[20] was repeated and found to give a 32% yield, m.p. 112–113°, which gave no depression in m.p. when mixed with the sample prepared by the rearrangement of VII. The infrared spectrum is shown in Fig. 2, curve B.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.7; H, 6.4; C_2H_5O; 3.0. Found: C, 79.8; H, 6.3; C_2H_5O, 13.3.

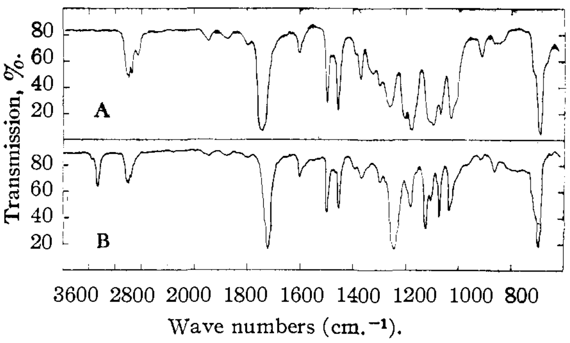

Fig. 2.—Curve A, ethyl mandelate benzhydryl ether in CCl_4; curve B, ethyl α,β,β-triphenyllactate in CCl_4.

The ethanolic filtrate from the rearrangement above was evaporated and the residue purified by chromatography on activated alumina with benzene and chloroform, successively. The benzene fractions gave unreacted VII which, after recrystallization from ethanol, amounted to 2.2 g. (0.00637 mole, 22%) and melted at 44–47°. The chloroform fractions gave 1.0 g. of additional VIII; total, 3.9 g. (0.011 mole, 39%).

Reaction of VII with Potassium Hydroxide. Mandelic Acid Benzhydryl Ether.—VII (5.0 g., 0.014 mole) was treated for 1 hour under reflux with 50 ml. of 1 *N* ethanolic potassium hydroxide. The reaction mixture was poured into 100 ml. of water, extracted with ether, the aqueous layer acidified and the mandelic acid benzhydryl ether (3.7 g., m.p. 153–155°) which precipitated collected. Recrystallization from ethanol gave 3.0 g. (0.0094 mole, 67%) of material, m.p. 161–163°.

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7. Found: C, 79.4; H, 5.8.

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

Carboxylate Ion Displacement in Dimesitylmethyl Esters

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Dimesitylmethyl esters of acetic, benzoic and mesitoic acids, when treated with certain Grignard reagents undergo carboxylate ion displacement by the the hydrocarbon radicals of the reagents. Grignard reagents with marked reducing power replace the carboxylate ions by hydrogen, *i.e.*, they bring about hydrogenolysis, to give dimesitylmethane. The hydrocarbons produced in this way are the same as those obtained by the action of the various Grignard reagents on dimesitylmethyl chloride.

Carboxylate ion displacement in esters has been observed with various nucleophilic agents such as amines,[3] phenoxides,[4] alkoxides[5] and dilute alkalies.[6] Grignard reagents have been found to be effective with certain hindered esters[7] with 2-methyl-10-acetoxy-9-anthrone,[8] and with the acetate and benzoate of 9-(hydroxymethyl)-carbazole,[9] of triphenylcarbinol[8,10] and dimethylvinylcarbinyl acetate.[11]

The resemblance of various dimesitylmethyl derivatives to the corresponding triarylmethyl compounds[12] led to a study of the action of Grignard reagents on esters of dimesitylcarbinol. Dimesitylmethyl mesitoate (I, R = Mes) was found to undergo displacement of the mesitoxyl group to yield hydrocarbons II when treated with Grignard reagents. With reagents possessing marked reducing power hydrogenolysis occurs also, the product being dimesitylmethane (III). Isopropylmagnesium bromide gave only the methane. The formation of dimesitylmethane is comparable

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(2) Socony–Vacuum Fellow, 1952–1953.

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