

dryness at room temperature on a rotating evaporator. The residue was taken up in the minimum volume of diethyl ether and cooled to 0°. The crystals which formed were filtered, washed with 50:50 diethyl ether-petroleum ether, and dried. The yield was 23 g. (63%), m.p. 121–122°.

Anal. Calcd. for $C_{22}H_{18}Br_2$: C, 60.82; H, 3.99; Br, 35.19. Found: C, 60.64; H, 3.96; Br, 34.98.

α -(*p*-Isopropenylphenyl)- β -diphenylevinyl Bromide (VIII).—A mixture of 150 g. (0.31 mole) of α -[*p*-(2-bromoisopropyl)phenyl]- β -diphenylevinyl bromide and 100 g. (1 mole) of potassium acetate in 1500 ml. of glacial acetic acid was heated on a steam bath for 3 hr. The reaction mixture was cooled to room temperature and poured onto 1 kg. of cracked ice. The solid product was filtered and washed thoroughly with water and acetone. The residue was recrystallized from glacial acetic acid to give 80.5 g. (68.6%) of pale yellow flakes, m.p. 165–166°.

Anal. Calcd. for $C_{23}H_{17}Br$: C, 74.00; H, 4.59; Br, 21.41. Found: C, 74.23; H, 4.49; Br, 21.14.

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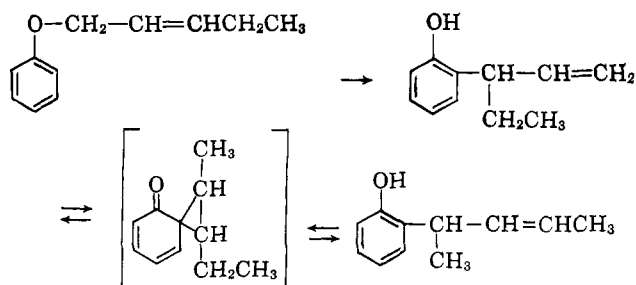
The Rearrangement of Crotyl- δ - C^{14} *p*-Carbomethoxyphenyl Ether

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Earlier studies² have shown that the thermal rearrangement of γ -alkyl allyl phenyl ethers gives rise to products which would not be expected on the basis of the normal Claisen rearrangement. Unlike the normal rearrangement products, which involve γ -attachment of the substituted allyl group to the aromatic nucleus, these products require an over-all shift of a hydrogen atom from the δ - to the α -position and a β -attachment of the substituted allyl group. Accordingly γ -ethyl allylphenyl ether yielded two products, *o*-(α -ethyl allyl)phenol and *o*-(α - γ -dimethyl allyl)phenol. Recently, Marvell, Anderson, and Ong³ demonstrated that the *o*-(α , γ -dimethyl allyl)phenol arises from a thermal rearrangement of *o*-(α -ethyl allyl)phenol and that these two products which are obtained by the pyrolysis of γ -ethyl allyl phenyl ether are the result of consecutive rather than concurrent processes. They formulate the transformations as follows.



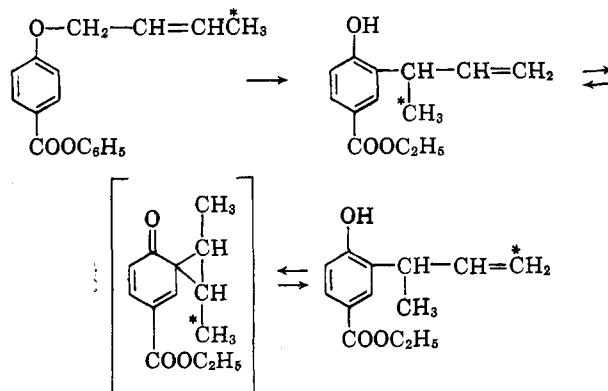
(1) Ph.D., University of Minnesota, 1962.

(2) W. M. Lauer and W. F. Filbert, *J. Am. Chem. Soc.*, **58**, 1388 (1936); C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939); W. M. Lauer and R. M. Leekley, *J. Am. Chem. Soc.*, **61**, 3043 (1939).

(3) E. N. Marvell, D. R. Anderson, and J. Ong, *J. Org. Chem.*, **27**, 1110 (1962).

This formulation is consistent with the structural changes observed earlier.

A recent study from this laboratory⁴ dealt with the rearrangement of C^{14} -labeled crotyl *p*-carbomethoxyphenyl ether, and the present work describes its extension in view of these findings. If this pyrolysis is formulated in a similar manner, the intermediate becomes symmetrical.



Heating for a period sufficiently long to reach equilibrium conditions, should give rise to a 50:50 distribution of the radioactivity. This distribution of radioactivity has been observed in samples which have been heated for 280 hours at $220 \pm 10^\circ$. Degradation studies have also established the fact that all of the radioactivity resides in the two positions indicated. The oxidation of *o*-(α -methylallyl)-*p*-carboxyanisole- x - C^{14} yielded nonradioactive 4-methoxyisophthalic acid. The transformation of the semicarbazone of α -(2-methoxy-5-carboxyphenyl)propionaldehyde to (2-methoxy-5-carboxyphenyl)acetone, followed by the conversion of this methyl ketone to iodoform, led to a sample of radioactive iodoform, which, together with that found in dimedone derivative of the formaldehyde produced on ozonolysis, accounted for all of the radioactivity of the starting material.

Similar results have been obtained by Habich, Barner, Roberts, and Schmid.⁵ These investigators studied the behavior of crotyl- δ - C^{14} *p*-methylphenyl ether upon heating. They demonstrated that the radioactivity which initially resided in the position predicted on the basis of a normal Claisen rearrangement was distributed between the methyl and methylene groups upon heating in accordance with the formulation of Marvell, Anderson, and Ong.³ It is, therefore, clear that the abnormal products which were described earlier result from consecutive and not concurrent processes.

Experimental

Crotyl- δ - C^{14} *p*-carbomethoxyphenyl ether (988×10^3 c.p.m./mmoles) was prepared according to the procedure described by Lauer, *et al.*⁴ A number of rearrangements were carried out under the following conditions: (1) heating in a metal bath at $220 \pm 10^\circ$ after evacuating the container using a heat lamp to prevent the refluxing liquid from crystallizing on the walls of the container; (2) heating in an oven at $220 \pm 10^\circ$ after evacuating a Pyrex tube to approximately 1 mm. and sealing with a torch; (3) heating in an oven at $220^\circ \pm 10^\circ$ after repeatedly evacuating and admitting carbon dioxide, the tube being sealed at a pressure

(4) W. M. Lauer, G. A. Doldouras, R. E. Hileman, and R. Liepins, *ibid.*, **26**, 4785 (1961).

(5) A. Habich, R. Barner, R. M. Roberts, and H. Schmid, *Helv. Chim. Acta*, **45**, 1943 (1962).

of 0.025 mm; (4) heating one sample in a evacuated tube containing a small amount of hydroquinone.

The rearrangement product in each case was crystallized from petroleum ether. Infrared and ultraviolet spectroscopic studies showed no differences in the rearrangement product, and they were identical with the rearrangement product described earlier.

o-(α -Methylallyl)-*p*-carboxyanisole-*x*-C¹⁴ was prepared and degraded as described in the previously cited article by ozonolysis. The dimedone derivative of formaldehyde and the semicarbazone of α -(2-methoxy-5-carboxyphenyl)propionaldehyde were purified to constant activity. The analysis of the semicarbazone for carbon previously reported is in error; the found value should be 54.55 instead of 55.55.

The dimedone derivative of formaldehyde, purified to constant radioactivity, was radioassayed for a number of rearrangement products produced under different conditions. The most significant results were obtained in those rearrangements in which a long heating period (280 hr.) was used. The results in c.p.m./mmoles $\times 10^3$ are 494 (a), 483 (b), 496 (b), 493 (a,c), 497 (a,c), and 498 (b,c) where a signifies rate-of-charge method, b signifies planchet method, and c stands for 2 mole % of hydroquinone added.

Oxidation of *o*-(α -methylallyl)-*p*-carboxyanisole-*x*-C¹⁴ to 4-methoxisophthalic acid was accomplished by means of potassium permanganate in the presence of potassium hydroxide. The crystalline product, m.p. 275–276° (lit.⁷ m.p. 275–276°), was found to be nonradioactive.

Anal. Calcd. for C₉H₈O₅: C, 55.10; H, 4.11. Found: C, 54.91; H, 4.28.

Transformation of the Semicarbazone of α -(2-Methoxy-5-carboxyphenyl)propionaldehyde to (2-Methoxy-5-carboxyphenyl)acetone, and Its Conversion to Iodoform.—The semicarbazone (0.32 g.) and sulfuric acid (100 ml., 25%) were refluxed with stirring for 2 hr. The reaction mixture was filtered and after the addition of water, the solid material was heated under reflux. The water insoluble residue was removed (0.13 g.) and the filtrate was extracted with three 75-ml. portions of ether. The ethereal solution was evaporated to dryness and the residue was dissolved in hot water. Upon cooling, a crystalline product (89.2 mg., m.p. 143–144°) was obtained. A second crop (23.8 mg., m.p. 138–140° after sublimation) was collected. The impure semicarbazone of this ketone, 2-methoxy-5-carboxyphenylacetone, melted at 246–247°, about 20° higher than that of the starting material. The ketone (70 mg.) was dissolved in potassium hydroxide (5 ml., 5%) and a solution of iodine in aqueous potassium iodide was added dropwise until a brown color persisted. The solution was decolorized by adding a few drops of aqueous potassium hydroxide. The iodoform was collected after 30 min., dried in a desiccator under nitrogen, and then sublimed. The yield was 40 mg. The rate of charge method for radioassay was 791 $\times 10^3$ c.p.m./mmole. The semicarbazone of α -(2-methoxy-5-carboxyphenyl)propionaldehyde which was used as starting material for the preparation of the iodoform was obtained by the degradation of a rearrangement product of crotyl- δ -C¹⁴ *p*-carboxyphenyl ether (988 $\times 10^3$ c.p.m./mmole). The dimedone derivative of the formaldehyde which results from the ozonolysis of the methyl ether of the rearrangement product showed an activity of 210 $\times 10^3$ c.p.m./mmole. Thus the remainder of the radioactivity resided in the methyl group which was assayed as iodoform.

(7) F. D. Chattaway and F. Calvet, *J. Chem. Soc.*, 2916 (1928).

A Convenient Preparation of *n*-Alkyl Trityl Ethers and Bis(α -arylethyl)ethers

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In addition to the well known Williamson synthesis,¹ ethers derived from lower aliphatic alcohols are usually

(1) A. W. Williamson, *J. Chem. Soc.*, 4, 229 (1852).

prepared by heating the mixture of an alcohol and sulfuric acid at an appropriate temperature. Ethyl ether can also be obtained by passing the vapor of ethanol over heated aluminum oxide.² Alkyl trityl ethers result when the corresponding alcohols react with trityl halides in pyridine or with triphenyl carbinol in the presence of an acid. Symmetrical ethers derived from higher and unsaturated alcohols have been reported recently. For example, *p,p'*-dichlorobenzhydrol⁴ with 100% sulfuric acid and 3-hydroxycyclopentene⁵ with concentrated hydrochloric acid were transformed into their corresponding symmetrical ethers in good yields. We have found that diaryl carbinols and α -phenylethanol can be converted into their corresponding symmetrical ethers by simply passing the solution of the alcohol in a nonhydroxylic solvent such as benzene through an alumina column at room temperature. Although the reaction is not a general method for ether synthesis, it provides, nevertheless, an extremely convenient tool for the preparation of bis(diarylmethyl) and bis(α -phenylethyl) ethers. For example, benzhydrol was converted to benzhydryl ether in practically quantitative yield and α -phenylethanol to bis(α -phenylethyl) ether in 75% yield, while benzyl and *p*-methoxybenzyl alcohols failed to react.

Primary alkyl trityl ethers can also be prepared in good yield by passing a solution of trityl alcohol in a desired primary alcohol through alumina. Methanol and ethanol with triphenyl carbinol each furnished the corresponding ether in approximately 75% yield where isopropyl alcohol failed to furnish either the trityl isopropyl ether or the ditrityl ether. When diphenyl carbinol was treated with alumina in methanol, it yielded neither dibenzhydryl nor benzhydryl methyl ether. The different behavior of triphenyl carbinol and diphenyl carbinol with primary alcohols may be attributed at least partially to the difference of their basicity⁶ that, when the acidity of the column toward the carbinol is diminished in the presence of a hydroxylic solvent such as methanol instead of benzene, the concentration of benzhydryl carbonium ion from the less basic diphenyl carbinol becomes too low to effect the formation of any ether.

Experimental

Dibenzhydryl Ether.—A solution of 1 g. of benzhydrol (Eastman, m.p. 68–69°) in 50 ml. of benzene was passed through a column packed with 20 g. of alumina (M. Woelm-Eschwege, acid, activity grade 1) previously wet with petroleum ether (40–60°). The flow was approximately 2 drops per second. Upon concentration, the eluent furnished 0.88 g. of benzhydryl ether, m.p. 90–105°. Crystallization from ethanol raised the m.p. to 110° (lit.⁷ m.p. 109–111°). A mixture melting point with an authentic sample was not depressed. The infrared spectrum was obtained in chloroform: 3.4 (w), 3.55 (w), 5.1 (w), 5.2 (w), 5.5 (w), 6.2 (s), 6.7 (s), 6.88 (s), 7.5–7.8 (b), 8.5 (s), 9.2 (s), 9.5 (s), 9.81 (s), 10.9 (m), 11.7 (w).

Bis(α -phenylethyl) Ether.—A solution of 10 g. of *dl*- α -methylbenzyl alcohol (Eastman, b.p. 204–206°) in 100 ml. of benzene

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(3) B. Helferich, P. E. Spiedel, and W. Toeldte, *Ber.*, 56, 766 (1923).

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(5) K. Alder and F. H. Flock, *Ber.*, 89, 1732 (1956); M. S. Newman and N. C. Deno, *J. Am. Chem. Soc.*, 73, 3644 (1951).

(6) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, 77, 3044 (1955).

(7) H. Klinger and C. Lonnes, *Ber.*, 29, 2159 (1896).