tained at 172–230° (9 mm.) and solidified to a yellow solid on cooling.

Analysis of Fraction 1.—Vapor phase chromatographic separation and examination of infrared spectra indicated the presence of acetic acid, toluene, methyl acetate, and ethyl acetate (trace). Toluene and methyl acetate were determined quantitatively on a 10-ft. Ucon column, and acetic acid by titration with standard base. The fraction contained 31% toluene, 19% methyl acetate, and 38% acetic acid by weight. Water was not determined in this fraction but would theoretically amount to 13.6%.

Analysis of Fraction 2.—A small portion of fraction 2 was extracted with water, the water evaporated, and the infrared spectrum of the residue in chloroform shown to be identical in every respect with that of the authentic material prepared from methylethylphenylbenzylphosphonium iodide by treatment with sodium hydroxide.[4a] The methylethylphenylphosphine oxide was analyzed spectrophotometrically in chloroform solution with a Baird Atomic double beam infrared spectrophotometer using the absorption peak at 8.95 mμ and was shown to represent 67% by weight of fraction 2. Another portion of fraction 2 when treated with 2,4-dinitrophenylhydrazine reagent[13] yielded the 2,4-dinitrophenylhydrazone of phenylacetone, m.p. 152–154°; reported[14] m.p. 152.5–153.5°, m.m.p. 152–154°. Vapor phase chromatographic analysis of fraction 2 on a 10-ft. Ucon column gave the following results: 4% phenylacetone, 19% *trans*-2-methyl-1,3-diphenyl-1-propene, and 14% *cis*-2-methyl-1,3-diphenyl-1-propene by weight. The latter two compounds displayed retention times and ultraviolet spectra identical with the authentic materials prepared by dehydration of methyldibenzylcarbinol.[8] The isomers were separated on a 10-ft. Ucon column from the fraction boiling at 162–164° (9 mm.).[15] The *cis* and *trans* isomers absorbed at 218, 245 and 218, and 249 mμ, respectively.

Fraction 3.—Fraction 3 was recrystallized twice from ethyl acetate–ligroin to yield a compound of m.p. 112–113°; reported[16] m.p. for ethylphenylbenzylphosphine oxide, 110–111°. This compound melted undepressed with purified ethylphenylbenzylphosphine oxide prepared by air oxidation of ethylphenylbenzylphosphine.[16]

Acknowledgment.—This research was supported by a type B grant from the Petroleum Research Fund. Appreciation also is expressed to Mary E. Pate, Richard McAtee, and Larry Becker for their help in the initial phase of this work.

(13) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 111.

(14) R. T. Gilsdorf and F. F. Nord, *J. Am. Chem. Soc.*, **74**, 1837 (1952).

(15) Although the mixture of isomers has been reported (ref. 8) this is apparently the first account of their separation. This fraction was shown to consist of 61% *trans* and 39% *cis* isomer.

(16) J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt, and W. Samuel, *Ann.*, **449**, 213 (1926).

Mechanism Study of a Benzilic Acid-Type Rearrangement[1]

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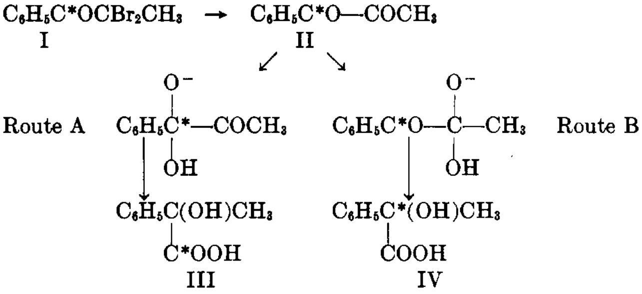
α,α-Dibromopropiophenone (I) rearranges to atrolactic acid (III or IV) during treatment with concentrated sodium hydroxide solution. It has been suggested[4] that the reaction proceeds by way of the intermediate, methyl phenyl diketone (II), which then undergoes a benzilic acid rearrangement.



When these authors subjected dibromo compound I to dilute alkali, no atrolactic acid was recovered; the sole product was 2,5-diphenyl-1,4-benzoquinone, formed in 13% yield by an aldol condensation of two molecules of the diketone. The action of concentrated sodium hydroxide on II produced atrolactic acid in low yield, whereas dilute alkali produced only tar.[4]

The use of carbon-14 as a tracer has been applied here in following the mechanism in the rearrangements starting with both the dibromo compound and the diketone. These two compounds (I and II) were prepared, labeled in the α-position. The atrolactic acid produced by rearrangement of these compounds was degraded by oxidation to acetophenone and carbon dioxide. In both cases essentially all of the original carbon-14 was found in the carbon dioxide. Since this labeled carbon atom was originally adjacent to the phenyl group, 100% phenyl migration must have occurred in both alkaline-catalyzed rearrangements, thereby eliminating route B as a possible mechanism. It is possible that the carbonyl group of II, α to the phenyl group, may be the preferred one for hydroxyl ion attack. However, if hydroxyl ion attack were rapid and reversible, the observed preference of route A also could be explained as due to a tendency of the phenyl group to migrate in preference to the methyl group.

If methyl phenyl diketone is the intermediate in the rearrangement of α,α-dibromopropiophenone, it is obvious that the rearrangement of the diketone must be much faster than the rate of formation. Any appreciable concentration of the diketone would lead to the aldol condensation mentioned previously.

Experimental

(α,α-Dibromopropio-1-C^{14})-phenone (I).—To 9.7 g. (0.4 mole) of magnesium turnings contained in a 250-ml., round-bottomed, three-necked flask was added slowly a solution of 53.6 g. (0.5 mole) of ethyl bromide in 95 ml. of ether. While the flask was cooled in ice, 12.1 g. (0.1 mole) of carbonyl-labeled benzamide was slowly added under dry nitrogen. After a reflux period of 24 hr. the reaction mixture was hydrolyzed with ice and sulfuric acid and extracted with ether. From the extract was obtained 7.5 g. (56% yield) of propiophenone.

One gram of the unpurified propiophenone was treated with a solution of 2.50 g. of bromine in 7.5 ml. of chloroform and allowed to stand at 25.5° for 0.5 hr. before it was refluxed for 4 hr. The solvent was carefully removed to give 2.13 g. (97% theoretical yield) of crude α,α-dibromopropiophenone (I).

Hydrolysis and Rearrangement of α,α-Dibromopropiophenone.—The crude dibromide (I) was stirred vigorously with 42.6 g. of 20% aqueous sodium hydroxide for 3.5 hr. The aqueous phase was extracted with ether and acidified with concentrated hydro-

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(1) This paper is based upon work performed at Oak Ridge National Laboratory, which is operated for the Atomic Energy Commission by Union Carbide Corp.

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(4) R. Levine and J. R. Stephens, *J. Am. Chem. Soc.*, **72**, 1642 (1950).

chloric acid. The precipitated crystalline atrolactic acid was removed by filtration and sublimed at 70 to 75°; m.p. 91 to 92°.

Methyl Phenyl Diketone-3-C^{14} (II).—This compound was prepared by the treatment of carbonyl-labeled propiophenone with butyl nitrite, followed by acid hydrolysis of the resultant monoxime.

Rearrangement of Methyl Phenyl Diketone.—The diketone (II), dissolved in a large volume of ether, was stirred vigorously for 1 hr. with an equal volume of 20% sodium hydroxide solution maintained at 0°. Under these conditions, a yield of about 25% of the desired atrolactic acid (III) could be isolated after neutralization of the aqueous layer.

Oxidation of Atrolactic Acid (III).—In a typical degradation, 83 mg. of III was decarboxylated at room temperature by treating with a mixture of 44 mg. of chromium trioxide and 2 ml. of glacial acetic acid in a small flask connected to a barium hydroxide absorption train. The apparatus was swept with nitrogen gas and the evolved carbon dioxide was converted to barium carbonate. The precipitated barium carbonate was washed with water and centrifuged several times before air drying. The residue in the reaction flask was extracted with ether and the ether extract was washed with sodium bicarbonate and then evaporated. The residual acetophenone was converted to the semicarbazone which after two crystallizations from 25% alcohol melted at 198°.

Radioactivity Assay of Oxidation Products.—The determination of carbon-14 was conducted by the wet combustion of small samples of the barium carbonate and acetophenone semicarbazide according to the technique of Raaen and Ropp.[5] The results are given in Table I.

TABLE I

RADIOACTIVITY OF CARBON^{14} IN μc./MMOLE

	—Rearrangement experiment with—	
	Dibromo compound I	Diketone II
Original material	1.028	0.935
Acetophenone semicarbazide	0.00579	0.005
Barium carbonate	.909[a]	.857[a]

[a] The approximately 90% material balances of the radiocarbon are attributed to exchange with dissolved carbon dioxide in the wash water (Melvin Calvin and co-authors, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 124) as well as exchange with atmospheric carbon dioxide (M. D. Kamen, "Isotopic Traces In Biology," 3rd Ed., Academic Press, New York, N. Y., 1957, p. 308) during drying of the wet, centrifuged barium carbonate.

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[5] V. F. Raaen and G. A. Ropp, *Anal. Chem.*, **25**, 174 (1953).

The Structure of Hexachlorinated 2,4-Dicarbethoxy-3,5-dimethylpyrrole

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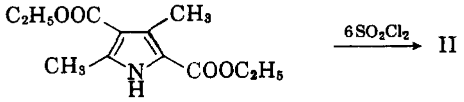
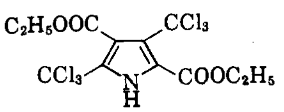
Chlorination with sulfuryl chloride followed by hydrolysis has been a commonly used technique for the oxidation of α-methyl substituents on pyrroles.[1-3] In general, one, two, and three moles of sulfuryl chloride yield, respectively, the mono-, di-, and trichloromethylpyrroles which can be hydrolyzed to the hydroxymethyl-, formyl-, and carboxypyrroles. In this reaction, β methyl groups are not attacked and unsubstituted positions are chlorinated.

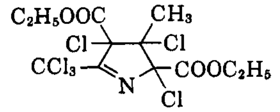
The product from the action of three moles of sulfuryl chloride and subsequent hydrolysis on Knorr's pyrrole, 2,4-dicarbethoxy-3,5-dimethylpyrrole (I), is a mixture of the 5-formyl- and 5-carboxypyrroles.[3] Fischer, *et al.*,[1] reported the isolation in high yield of a hexachloro derivative (II) from the action of six moles of sulfuryl chloride on I. Structure III was assigned to II apparently on the basis of the analyses for C, N, Cl, and OC_2H_5. However, hydrolysis with potassium hydroxide did not yield the tetracarboxypyrrole diester, but rather fragmented the compound. The hexachloro derivative could be reduced to 2,4-dicarbethoxy-3-methyl-5-hydroxymethylpyrrole and oxidized to a compound containing one additional oxygen and one less chlorine.[1]



I



III



IV

The n.m.r. spectrum of II shows three bands: a triplet at δ 1.37 (p.p.m., tetramethylsilane, 0), a singlet at 2.24, and two almost coincident quartets centered at 2.62 and 2.64. The ratios of triplet/singlet/quartet areas are 6:3:4. This shows that II retains a methyl group (the singlet) which was corroborated by a C-methyl determination. The infrared spectrum of II shows no absorption in the pyrrole NH stretching region (3400–3500 cm.$^{-1}$) or the pyrrole ring vibration region (1470–1600 cm.$^{-1}$).[4] Two bands are observed in the carbonyl region at 1740 and 1760 cm.$^{-1}$, above the normal pyrrole ester positions.[4] There is a band at 1612 cm.$^{-1}$, the position reported for the imine stretching band of Δ^1-pyrrolines.[5] The ultraviolet spectrum of II shows only end absorption with a slight shoulder at 215 mμ (ε 4850). This supports a structure for II in which the imine is not in conjugation with the α ester carbonyl. For example, glyoxylic acid semicarbazone absorbs at 252–253 mμ (ε 12,400), whereas acetone semicarbazone absorbs at 224 mμ (ε 11,000).[6] The iodide test for N-Cl was negative.[7]

The evidence points clearly to structure IV for the hexachloro derivative II.

Experimental

2,4-Dicarbethoxy-3-methyl-5-trichloromethyl-2,3,4-trichloro-$\Delta^{1(5)}$-pyrroline (II and IV).—Knorr's pyrrole (I) in ether was chlorinated with freshly distilled sulfuryl chloride as described by Fischer, Sturm, and Friedrich[1]; m. p. 72° (lit.[1] m.p. 72°).

Anal. Calcd. for $C_{12}H_{13}Cl_6NO_4$: C, 32.12; H, 2.9; Cl, 47.5; C–CH_3, 3/446; mol. wt., 446. Found: C, 32.2; H, 3.0; Cl, 47.0; C–CH_3, 3.1/446; mol. wt., 426 (osmometer).

A sample of II in ether acidified with acetic acid was shaken with aqueous potassium iodide. An iodine color developed only after 4 days.

The n.m.r. spectrum was taken in carbon tetrachloride with tetramethylsilane as internal standard with a Varian Model A-60

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[1] H. Fischer, E. Sturm, and H. Friedrich, *Ann.*, **461**, 244 (1928).

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[3] A. H. Corwin, W. A. Bailey, and P. Viohl, *J. Am. Chem. Soc.*, **64**, 1267 (1942); A. H. Corwin and J. L. Straughn, *ibid.*, **70**, 1418 (1948).

[4] U. Eisner and R. L. Erskine, *J. Chem. Soc.*, 971 (1958).

[5] J. H. Burckhalter and J. H. Short, *J. Org. Chem.*, **23**, 1278 (1958).

[6] J. A. Olson, *Arch. Biochem. Biophys.*, **85**, 225 (1959).

[7] M. Z. Barakat and M. F. Abd El-Wahab, *Anal. Chem.*, **26**, 1973 (1954).