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

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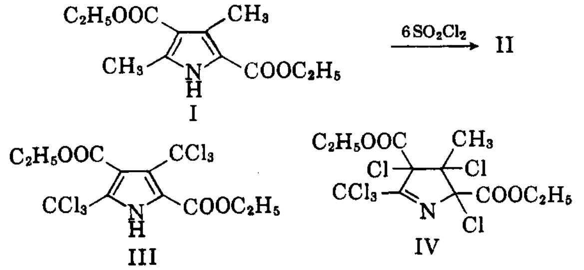
Chlorination with sulfuryl chloride followed by hydrolysis has been a commonly used technique for the oxidation of α-methyl substituents on pyrroles.[1-3] In general, one, two, and three moles of sulfuryl chloride yield, respectively, the mono-, di-, and trichloromethylpyrroles which can be hydrolyzed 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]



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 Freidrich[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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spectrometer. The infrared spectrum was taken in potassium bromide with a Perkin-Elmer Model 221 spectrophotometer. The ultraviolet spectrum was taken in ethanol with a Cary Model 14 spectrophotometer.

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Configuration Assignments in Symmetrical Alkyl-Aryl Pinacols[1]

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In a study of the mechanism of the pinacol-pinacolone rearrangement it became necessary to synthesize and characterize pure diastereoisomeric forms of Ph-RC(OH)C(OH)RPh where R = methyl, ethyl, and *n*-propyl. These diols previously have been reported as dimeric reduction products of their respective ketones—acetophenone,[3] propiophenone,[4] and *n*-butyrophenone[5]—or by appropriate Grignard additions to benzil.[3,6] In only one case has a configurational assignment of the *dl* and *meso* isomers been established and that by a synthesis of optically active and inactive 2,3-diphenyl-2,3-butanediol from (−)-methylbenzoin.[7]

Chiurdoglu and others have reported that hydrogen bonding studies could distinguish *threo* and *erythro* isomers in a series of aliphatic 1,2-diols and we have found such studies can provide information upon which to base reliable configurational assignments in aryl-alkyl diols.

By examination of the hydrogen bonding patterns of the three isomeric pairs (see Table I), it is possible to divide the diols into two sets. One member of each pair (II, IV, and VI) shows only a free hydroxyl peak in the 3605–3611-cm.$^{-1}$ region with an attendant shoulder while the other member shows a sharp, distinct pair of free and bonded peaks (in addition to the concentration dependent intermolecular bands).

Steric considerations dictate that in order to exhibit intramolecular hydrogen bonding between hydroxyls the *meso* isomers would have to exist in an unfavored conformation in which the bulky phenyl groups on adjacent carbons would be in close proximity.[9] The *dl*-diastereoisomers can intramolecularly bond their hydroxyls when the phenyls are in a favored *trans* orientation. Hence I, III, and V might be assigned the *dl*-configuration, and II, IV, and VI the *meso.*

TABLE I

HYDROGEN BONDING IN PhRC(OH)RPh

R	M.p., °C.	Free –OH (cm.$^{-1}$)	Bonded –OH (cm.$^{-1}$)	$\Delta\nu$	Position of C–O (cm.$^{-1}$)		Assignment
Methyl							
I	122–123^a	3615	3580 (s)	35	1143	1191	*dl*
II	117–118^a	3605	3570 (sh)^e	35	1126	1167	*meso*
Ethyl							
III	113^b	3616	3572 (s)	46	1143	1182	*dl*
IV	138–139^b	3609	3570 (w)^e	39	1125	1164	*meso*
n-Propyl							
V	95–96^c	3615	3569 (s)	46	1144	1180	*dl*
VI	128–129^d	3611	3561 (m)^e	50	1124	1159	*meso*

^{a} Prepared as in ref. 3. ^{b} Prepared as in ref. 4. ^{c} Prepared as in ref. 5. ^{d} Prepared as in ref. 6. ^{e} The characterization of the position of the bonded peak is approximate since it appears as a shoulder or broad weak band.

The same conclusion might be reached by considering that in *dl* isomers the intramolecularly bonding hydroxyls can attain a perfect *cis* orientation without the severe phenyl-phenyl eclipsing that would be necessary in the *meso* form.

This conclusion is strengthened by examination of the bands associated with C–OH stretching modes for the tertiary hydroxyl which appear at 1140 to 1190 cm.$^{-1}$. Each of the diols II, IV, and VI shows double absorption peaks in this region which shift to higher frequencies in those diols which show strong intramolecular hydrogen bonding, I, III, and V.[10] The shift is exactly in the direction predicted for increased rigidity imparted to the C–O bond by intramolecular associations.[11]

It is also possible that the C–O bond shifts in going from *meso* to *dl* isomers are due to differences in dipole-dipole interactions in the two configurational species. Support for this possibility arises from the fact that the peak displacements show a remarkable constancy, between 16 and 20 cm.$^{-1}$, in the various isomers (see Table I).

If the C–O bond shifts were solely due to increased rigidity imparted to the bond by increased intramolecular association in the *dl* forms then one might expect a proportional increase in the C–O shift differences (between *dl* and *meso* forms of the same compound) as the hydrogen bond becomes tighter. Such a correlation is not observed.

The constancy of the C–O peak displacements suggests that they might possibly serve as qualitative and quantitative tools for identifying such compounds in mixtures.[12]

It also has been observed that the small amount of intramolecular hydrogen bonding which occurs in the *meso* forms increases as one proceeds from methyl to ethyl to *n*-propyl. This is explained by the conformational consideration that the unfavored rotomer for intramolecular bonding in *meso* becomes less and less

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(1) Presented at the Fourth Delaware Valley Regional Meeting, American Chemical Society, January, 1962.

(2) A portion of this work is taken from the M.S. thesis of Ned D. Heindel, National Science Foundation Predoctoral fellow, 1959–63.

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