TABLE II

REACTION OF 1,5-DIIODOPENTANE, 5-IODO-1-PENTENE, AND CYCLOPENTYL IODIDE WITH *t*-BUTYL AND BENZOYL PEROXIDES

	Per cent yield[a]					
	Benzoyl peroxide, 70 min, 115°			*t*-Butyl peroxide, 1 hr, 168°		
Product	$I(CH_2)_5I$	Cyclopentyl iodide	$CH_2{=}CH(CH_2)_3I$	$I(CH_2)_5I$	Cyclopentyl iodide	$CH_2{=}CH(CH_2)_3I$
Cyclopentane	4.5	22		8.2	49	Trace
Cyclopentene		13			21	Trace
$Ph(CH_2)_3CH{=}CH_2$			4.4			1.4
Cyclopentyl benzoate		6.0	Trace			
Cyclopentylcyclopentane		0.3			Trace	
Cyclopentylbenzene		9.5			0.5	
Cyclopentyl iodide	Trace		Trace	Trace		Trace
$PhCO_2(CH_2)_3CH{=}CH_2$	Trace		Trace			

[a] By "trace" we mean an amount which corresponds to less than 10% of the lowest yield reported in this table.

reaction. In addition, there is a precedented route: 5-iodo-1-pentene, which is a very minor product, could yield the 5-penten-1-yl radical which could then cyclize to the cyclopentyl radical and go on to cyclopentane. In order to help us decide whether this possibility, or any other which involves the cyclopentyl radical, need be considered seriously, we have performed experiments designed to indicate the fates of 5-iodo-1-pentene and the cyclopentyl radical (generated from cyclopentyl iodide) under the reaction conditions.[5] Presented in Table II are the yields of those products derived from reaction of cyclopentyl iodide, 5-iodo-1-pentene, and 1,5-diiodopentane with benzoyl and di-*t*-butyl peroxides which we feel are pertinent to this question. We believe that the results obtained with 1,5-diiodopentane are sufficiently different from those obtained with cyclopentyl iodide and 5-iodo-1-pentene so as to enable us to conclude that it is unlikely that the products formed from 1,5-diiodopentane, particularly cyclopentane, result to a significant extent from reaction of either 5-iodo-1-pentene or the cyclopentyl radical.

Experimental Section

Reactions were run in sealed nmr tubes in benzene as solvent. Products for which numerical yields are reported have been identified by direct comparison with independently obtained samples. Yields were estimated by use of nmr spectroscopy and gas chromatographic analysis.

1,5-Diiodopentane, di-*t*-butyl peroxide, benzoyl peroxide, cyclopentane, cyclopentyl iodide, pentenes, 1-iodopentane, 1-phenylpentane, iodobenzene, methyl iodide, toluene, acetone, *t*-butyl alcohol, isobutylene, benzene, cyclopentene, cyclopentylcyclopentane, and cyclopentylbenzene were commercial materials.

5-Iodo-1-pentene[6] and (4-pentenyl)benzene[7] were prepared by literature procedures.

(4-Pentenyl) benzoate and cyclopentyl benzoate were prepared by reaction of the corresponding alcohols with benzoyl chloride in pyridine.

(5-Iodopentyl) benzoate and (5-iodopentyl)benzene were prepared by reaction of (5-bromopentyl) benzoate[8] and (5-bromopentyl)benzene,[9] respectively, with sodium iodide in acetone.

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(5) In these circumstances one unfortunately cannot rigorously determine the expected fate of a given substance, were it formed during the reaction, by introducing that substance into the reaction mixture or by subjecting it to the "reaction conditions" since the mere presence of the material in an artificially created concentration or in the absence of other materials results in a perturbed system, particularly with regard to the probability of occurrence of various bimolecular steps. The difficulty is compounded by our poor material balances.

(6) T. D. Perrine, *J. Org. Chem.*, **18**, 1356 (1953).

(7) J. von Braun, *Ber.*, **45**, 1246 (1912).

(8) J. von Braun, *ibid.*, **46**, 1782 (1913).

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The Structure of Phthalaldehydic Acid[1]

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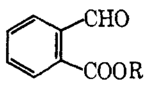
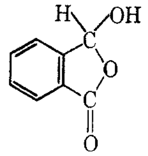
Because phthalaldehydic acid was known to give derivatives of either 2-carboxybenzaldehyde (I) or 3-hydroxyphthalide (II), its actual structure has been in doubt ever since it was first described.[2]



I, R = H
III, R = D



II

The failure of chemical techniques to ascertain the structure of phthalaldehydic acid led Buu-Hoi and Lin-Chen-Kin[3] to examine its ultraviolet spectrum. They concluded that the two forms I and II were in a solvent-dependent equilibrium and that, whereas II was the only form present in dioxane, water solutions contained a mixture of I and II. Later, three groups examined the infrared spectrum of phthalaldehydic acid in the solid state and in aqueous solution.[4-6] All agreed that in both cases the compound existed in the cyclized form II. Furthermore, it was shown that upon alkali treatment the lactol ring was opened, forming the anion of I.[6]

In view of the historical interest of this problem and because a recent article[7] has implicitly challenged the above results, we wish to present the results of a reinvestigation of the structure of phthalaldehydic acid by nuclear magnetic resonance.

The resonance of aldehyde protons occurs near

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are also grateful to the National Science Foundation for assistance during the course of this work.

(2) S. Racine, *Chem. Ber.*, **19**, 778 (1886); *Ann.*, **239**, 78 (1887).

(3) Buu-Hoi and Lin-Chen-Kin, *Compt. Rend.*, **209**, 221 (1939).

(4) J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 877 (1951).

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(6) E. Bernatek, *Acta Chem. Scand.*, **14**, 785 (1960).

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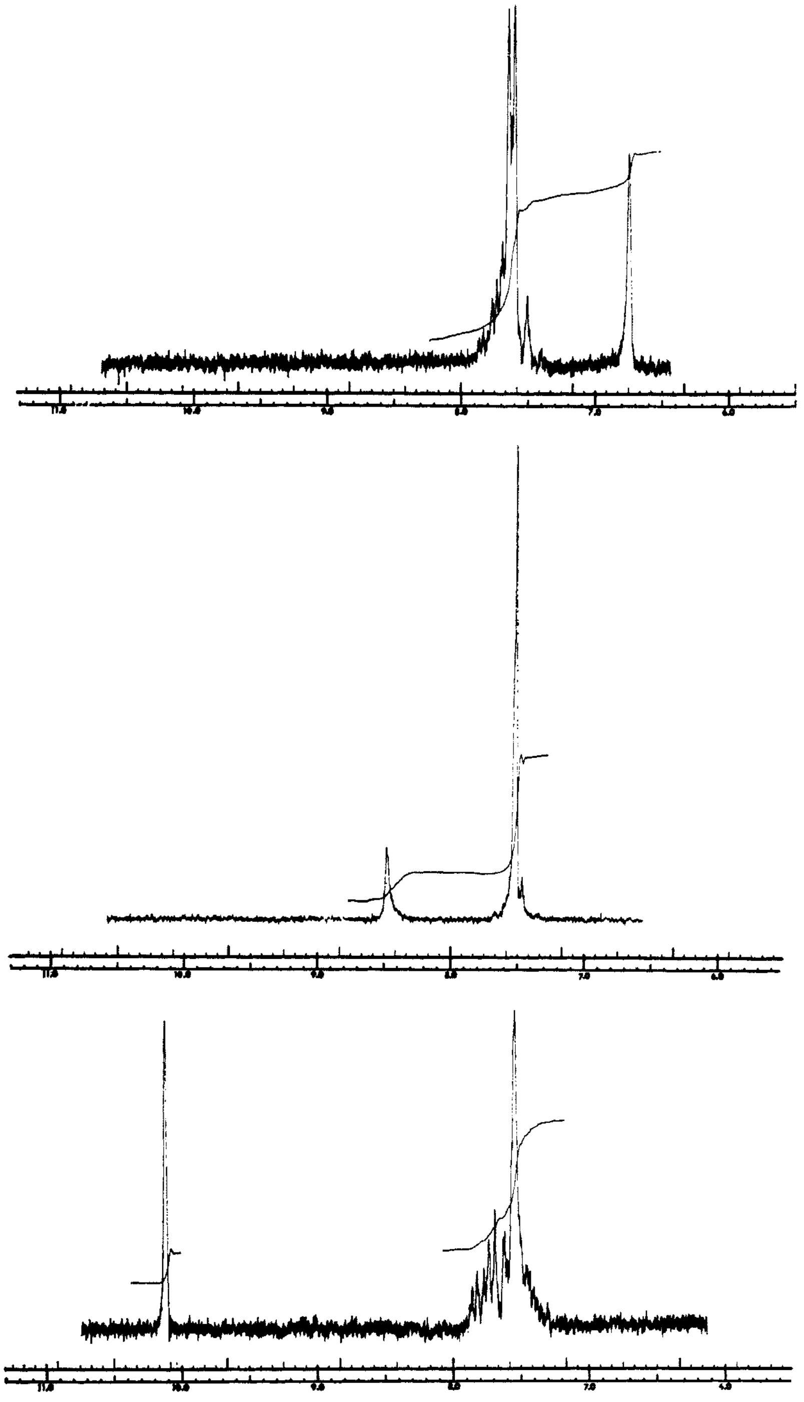

Figure 1.—Nmr spectra of phthalaldehydic acid. From top to bottom: in deuterium oxide, half-neutralized with bicarbonate, and completely neutralized.

10 ppm, at a field much lower than that of other protons attached to carbon atoms. On the other hand, the presence of a 3-hydroxyl is expected to lower the 5.3-ppm resonance of the 3-protons of phthalide by about 1.5 ppm. The structural problem can therefore be solved simply by checking for the presence of the "aldehyde" proton at either 7 or 10 ppm.

The nmr spectrum of phthalaldehydic acid was measured in the following solvents: acetic acid, acetone, acetonitrile, chloroform-*d*, dimethyl sulfoxide-d_6, dioxane, ethyl acetate, 2-propanol, methanol, and water. In all cases a signal near 7 ppm was observed[8,9] but no signal near 10 ppm could be found. Occasionally, the signal was broad because of coupling with the hydroxyl, but it became a sharp singlet after exchange of that proton with deuterium from a few drops of deuterium oxide added to the sample tube.

When the compound in water solution (Figure 1) was completely neutralized with base, the peak at 6.75 ppm was replaced by a sharp signal at 10.15 ppm, clearly showing that the anion was that derived from the uncyclized structure I. With less than 1 equiv of base, a sharp signal appeared at a position moving downfield toward 10.15 ppm proportionally to the amount of base added, indicating a rapid interconversion between the cyclized forms and the open forms.

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(8) Preliminary results of P. R. Jones and G. A. Berchtold pointing to a cyclic structure in acetone-d_6 have been recorded.[9]

(9) P. R. Jones, *Chem. Rev.*, **63**, 479 (1963).

These results fully confirm those obtained by infrared analysis. Any equilibrium I $\rightleftarrows$ II must lie very far to the right at the total concentrations used for infrared and nuclear magnetic resonance measurements. It is not impossible that at much lower concentrations, such as those used for ultraviolet spectroscopy, the relative concentration of I may become more significant.

The formation of an oxime of phthalaldehydic acid in acidic solution[6] suggested the presence of some I in these conditions. When the compound was dissolved in 2 *N* hydrochloric or sulfuric acid, the nmr spectrum was practically identical with that recorded in water. However, when the concentration of acid was increased, the spectrum changed in a manner analogous to that observed in alkaline solution. The 6.75-ppm signal in water was at 7.18 in 50% sulfuric acid, 8.48 in 80% acid, 9.12 in 90% acid, and 9.45 ppm in pure sulfuric acid. In comparison, the 4-carboxybenzaldehyde showed a sharp singlet at 9.95 ppm and phthalide, a singlet at 5.05 ppm in the same conditions, indicating no drastic effect of the strong acid on the spectrum of these compounds. No good model compound was available for judging the possible effect on the nmr spectrum of protonation of II or formation of a carbonium ion derived from it.[10] We noted, however, that, whereas all the compounds mentioned above gave colorless sulfuric acid solutions, intense colors were observed when benzhydrol or benzylic acid were dissolved in this acid. Furthermore in these last two spectra the benzylic protons did not appear at a field lower than that of the aromatic ones. We believe, therefore, that our results indicate a rapid equilibrium between the open and cyclized forms of phthalaldehydic acid in strong acid, favoring the open form. In pure sulfuric acid, the equilibrium probably has close to 95% of the open form.

It is clear that in general the name 2-carboxybenzaldehyde should be avoided in designating phthalaldehydic acid, best described as 3-hydroxyphthalide, except in strong acids or in basic media. Furthermore, the claim that the deuterated acid III was easily isolated[7] is not supported by the results of either infrared or nmr spectroscopy. Although the structure of the described products may not be affected, the mechanistic discussions found in that article deserve a more critical evaluation.

Experimental Section

The starting material used in this work was purchased as 2-carboxybenzaldehyde from Aldrich Chemical Co., Milwaukee, Wis. After recrystallization from water, it melted at 97°. The sulfuric acid (95–98%) and all solvents for nmr determinations were reagent grade and were used without further purification.

The nmr spectra were determined on a Varian A60-A spectrometer, using a tetramethylsilane standard. In the case of the water and sulfuric acid solutions, the general position of the peaks being more important than their precise location, the standard was used externally.

3-Ethoxyphthalide was obtained by irradiating II in ethanol-containing chloroform.[11]

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(10) The study of 3-ethoxyphthalide in concentrated sulfuric acid shed no light. Immediate hydrolysis took place and the spectrum was identical with that of an equimolar mixture of II and ethanol.

(11) J. Kagan, unpublished results.

Synthesis of Organolead Compounds from Lead Tetraacetate

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The reactions of divalent lead salts with organometallic alkylating agents have been thoroughly studied.[1,2] The most frequently used laboratory preparation of tetraorganolead compounds is the reaction of lead dichloride with an organomagnesium or organolithium reagent (eq 1). The reactions of organometallic alkylating agents and tetravalent lead salts have been studied by several investigators.[3,4] The interest in tetravalent lead salts arises because one might expect them to be converted quantitatively to the desired tetraorganolead compound without formation of any by-product lead metal (eq 2). Previous investigations have found no advantage in using tetravalent lead salts with Grignard or lithium reagents since substantial reduction of the tetravalent lead by the organometallic occurred.[5]

$$4RM + 2PbCl_2 \rightarrow R_4Pb + Pb + 4MCl \qquad (1)$$

$$4RM + PbX_4 \rightarrow R_4Pb + 4MX \qquad (2)$$

This study was undertaken to investigate further the reaction of lead tetraacetate with Grignard reagents and attempt to find reaction conditions under which no by-product lead is obtained. Tetramethyllead and tetraethyllead were prepared in 89 and 94% yield, respectively, according to eq 2. Unexpectedly it was found that the most critical factors in obtaining these high yields is the order in which the reactants are mixed and the solvent used. The preferred method, resulting in no by-product lead formation, is the addition of lead tetraacetate to the Grignard reagent in tetrahydrofuran (THF). Higher yields are obtained by performing the reaction at lower temperature (5°) as compared to ambient temperature (25°). These three modifications of reaction conditions account for the success of these experiments and the failure of earlier workers in obtaining high yields without production of lead metal. Because of the availability of lead tetraacetate and ability to obtain high yields in short reaction times, this reaction is particularly useful for synthesis of many tetraalkyllead compounds.

An attempt to form tetraneopentyllead from the reaction of neopentylmagnesium chloride and lead tetraacetate at 5° resulted in a 50% yield of hexaneopentyldilead. Previous attempts in preparing tetraneopentyllead by several methods have also met with failure.[6,7] It was found that reaction of neopentyl-

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