

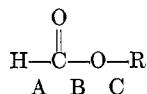
However, when benzyl formate was refluxed with palladium on charcoal, the major products were toluene and carbon dioxide (Table II).

TABLE II
DECARBOXYLATION PRODUCTS OF BENZYL FORMATE

Liquid	% by glc	Gas	Mol %
C ₆ H ₅ CH ₃	96.7	CO ₂	91.07
C ₆ H ₆	1.3	CO	6.97
C ₆ H ₅ CHO	0.2	H ₂	1.96
C ₆ H ₅ CH ₂ OH	0.2		
(C ₆ H ₅) ₂ CH ₂	0.4		
(C ₆ H ₅ CH ₂) ₂	0.9		
(C ₆ H ₅) ₂ CHCH ₃	0.2		

In both these cases, the products, and especially the by-products, can be explained on the basis of free-radical mechanisms, although these may occur only on the surface of the catalyst. (1,1-Diphenylethane appears to be a rearrangement product.)

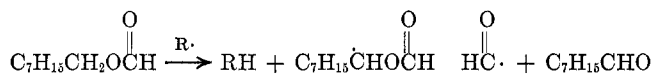
In the molecule shown, calculations of the homolytic bond dissociation energies (BDE) of bonds A, B,



and C by the method of Benson⁵ indicate that benzyl formate and *n*-octyl formate should cleave at C to yield carbon dioxide, but only benzyl formate does this.

It appears that in octyl formate, the catalyst weakens bond B sufficiently to overcome the 11-kcal difference between bonds B and C (*ca.* 14 kcal), to induce cleavage at bond B. However, in benzyl formate, bond C is still weaker by *ca.* 10 kcal, and hence the pyrolysis of benzyl formate proceeds *via* rupture of this bond to yield carbon dioxide.

Examination of the by-products in Tables I and II tend to bear out that the reactions occurring, even if on the surface of the catalyst, are proceeding *via* radical intermediates. The occurrence of octanal (Table I) can arise from alkoxy radical *via* hydrogen abstraction or disproportionation. Another possibility is as follows.



This reaction would be followed by decarbonylation of the aldehyde to produce hydrocarbons or higher molecular weight products. This accounts in part for the formation of hydrogen. Octyl formate was unchanged on heating at 200° alone or with activated charcoal (Darco G60). Tests for aldehyde were negative on heating octyl alcohol with palladium on charcoal; so octanal cannot arise in this way.

More interesting by-products were obtained with benzyl formate, since the intermediate benzyl radical is more stable. This can explain the formation of bibenzyl and diphenylmethane. Overall, very little of the reaction (1.7%) proceeds *via* the alkoxy radical, which leads to benzyl alcohol, benzaldehyde, and benzene. Benzyl formate itself was recovered unchanged on prolonged heating at reflux without the catalyst or with added activated charcoal.

(5) S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968.

Experimental Section

The octyl formate and benzyl formate used were at least 99% pure according to glpc. The 10% palladium-on-charcoal catalyst was purchased from E. H. Sargent & Co. Products were separated on an F & M 720 chromatograph using a 9 ft × 0.125 in. column of 30% Embaphase silicone on Chromosorb. Individual unknown peaks were identified by combined mass-glpc and ir-glpc analysis. Material balances were usually 90–95%.

Decarbonylation of *n*-Octyl Formate.—In a typical experiment, a 25-ml, two-neck flask was equipped with a serum cap on one neck. On the other neck a ground joint tube 8 in. long and bent at a right angle was attached to a plastic bag. Into the tared flask was weighed 9.0500 g of octyl formate and 0.1236 g of palladium on charcoal. The outlet tube was connected to the evacuated plastic bag and the flask was lowered into a heated bath at 200°. The flask contents were magnetically stirred. At intervals, 0.2-μl samples were removed through the serum cap for analysis until the reaction indicated *ca.* 97% completion. The reaction was cooled and filtered, and the gas and liquid products were identified as indicated above.

Glpc showed that there was a 98.3% conversion into the products listed in Table I. There was a total material balance of 92%.

Registry No.—Palladium, 16065-88-6; *n*-octyl formate, 112-32-3; benzyl formate, 104-57-5.

Reaction of Terephthalic Acid with Formaldehyde in Sulfur Trioxide Media

LEROY S. FORNEY

Research and Development Laboratories,
Mobil Chemical Company,
Edison, New Jersey 08817

Received August 29, 1969

The aromatic ring of terephthalic acid is highly deactivated toward electrophilic substitution. However, scattered references are found in the literature for its reaction with inorganic species.¹ Nitration provides a route to nitroterephthalic acid, and, while terephthalic acid is remarkably stable to sulfonation in the absence of a catalyst, it reacts with sulfuric acid in the presence of mercuric salts to give sulfoterephthalic acid. Chlorination leads to the commercially important dimethyl tetrachloroterephthalate, "Dacthal." In spite of these references, no substitution of terephthalic acid with an electron-deficient carbon species has been observed.

The condensation of various methoxybenzoic acids with formaldehyde in concentrated hydrochloric acid has been reviewed by Charlesworth, *et al.*,² and phthalide formation was observed, frequently accompanied by chloromethylation. The action of formaldehyde on *m*-hydroxybenzoic acid in hydrochloric acid also yields phthalide derivatives exclusively.³ It has been shown that 2-chloromethylbenzoic acids frequently react to produce phthalides in high yields.⁴ Indeed, it may be expected that, whenever an aromatic methylol or potential methylol substituent is located *ortho* to a carboxyl

(1) "Encyclopedia of Chemical Technology," R. E. Kirk and D. F. Othmer, Ed., The Interscience Encyclopedia, Inc., New York, N. Y., 1953, Vol. X.

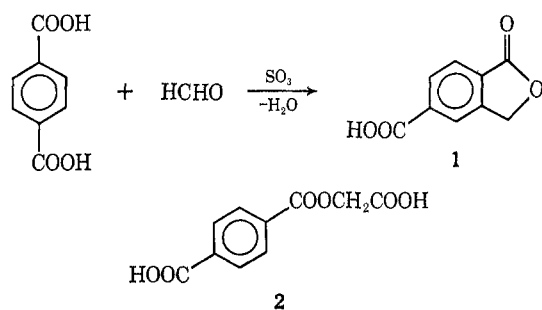
(2) E. H. Charlesworth, R. P. Rennie, J. E. Sinder, and M. M. Yan, *Can. J. Res.*, **23B**, 17 (1945).

(3) (a) C. A. Buechler, T. A. Powers, and J. G. Michels, *J. Amer. Chem. Soc.*, **66**, 417 (1944); (b) C. A. Buechler, J. G. Harris, C. Shacklett, and B. P. Block, *ibid.*, **68**, 574 (1946).

(4) J. C. Overeem and G. J. M. Van Der Kerk, *Rec. Trav. Chim. Pays-Bas*, **83**, 1023 (1964).

group under dehydrating conditions, a rapid loss of water would occur to produce a phthalide moiety. However, in the few reported instances of negatively substituted benzoic acids or benzoic acid itself undergoing reaction with formaldehyde, more vigorous conditions were required and only intermolecular condensation products were isolated. Thus benzoic acid reacted with formaldehyde in sulfuric acid to give 3,3'-dicarboxydiphenylmethane,⁵ and isophthalic acid provided 3,3',-5,5'-tetracarboxydiphenylmethane.⁶

We wish to report the condensation of terephthalic acid with formaldehyde in sulfur trioxide media, a process which produces 5-carboxyphthalide (1) cleanly and in excellent yield. The reaction is generally free of by-product formation over a fairly wide range of reaction conditions, although terephthaloyloxyacetic acid (2) has been identified (as its dimethyl ester) from reaction in the presence of excess formaldehyde and from reaction media containing <20% SO₃. Prior routes to 1 involved several-step processes or reduction of trimellitic anhydride, which provides a mixture of the 5- and 6-carboxyphthalides which are difficult to separate.⁷ This synthesis of 1 is believed to represent the first reported substitution of terephthalic acid with an electron-deficient carbon species.



Experimental Section

A Beckman IR-5A infrared spectrophotometer, Varian A-60 nmr spectrometer and 21-110B Consolidated Electronics mass spectrometer were used for spectral determinations. Gravimetric analysis utilized a Du Pont 950 Thermogravimetric Analyser. Carbon-hydrogen analyses were done by Galbraith Laboratories, Knoxville, Tenn. An F & M 5750 research chromatograph was used with a 12 ft × 0.25 in. 10% UCW 98 on an acid-washed Chromosorb W DMCS-treated column for analysis of esters.

5-Carboxyphthalide (1).—Sulfur trioxide (180 ml, 4.3 mol of "Sulfan B") was slowly added to terephthalic acid (200 g, 1.2 mol), with stirring, and formaldehyde (48 g, 1.6 mol of "Trioxane") added (exothermic). The resultant slurry was heated to 120–130° for 2 hr. The reaction was accompanied by a color change after the excess sulfur trioxide distilled off. After cooling, the mixture was poured into ice water (4 l.) and crude product received by filtration. The filter cake was slurried with water, partially neutralized with NaOH to remove residual sulfuric acid, filtered, and washed again, to give 192.3 g of pink solids, mp 285–290°. Chloroform extraction of the filtrates gave an additional 6.0 g of product (93% yield). The acid can be recrystallized from acetic acid or 50% aqueous dimethyl sulfoxide to provide purified 5-carboxyphthalide, mp 290–294° (literature value,⁸ 283–284°). Esterification with methanol-BF₃ gave 5-carbomethoxyphthalide, mp 166–167°, which exhibited ir bands at 5.70 (phthalide C=O) and 5.80 μ (carboxyl C=O); nmr

(CDCl₃, 60 MHz) δ 8.08 (m, 3), 5.37 (s, 2, OCH₂), 3.98 (s, 3, OCH₃); mass spectrum (70 eV) *m/e* 192 (parent peak). Both the ester and phthalide linkages were cleaved under basic conditions, in accord with the literature.⁹

Anal. Calcd for C₁₀H₈O₄: C, 62.48; H, 4.20. Found: C, 63.57; H, 4.21; sapon equiv 96.05.

Esterification with ethanol-BF₃ gave 5-carbomethoxyphthalide, mp 147.5–148°.

Anal. Calcd for C₁₁H₁₀O₄: C, 64.05; H, 4.89. Found: C, 64.11; H, 4.86.

2-Hydroxymethylterephthalic Acid.—Acidification of the solution received from saponification of 5-carbomethoxyphthalide gave 2-hydroxymethylterephthalic acid, isolated by filtration and drying [85° (20 mm)]. It gave no phthalide C=O absorption at 5.70 μ in the ir.

Anal. Calcd for C₉H₈O₅: C, 55.10; H, 4.08. Found: C, 54.70, 54.88; H, 4.15, 4.18. Differential gravimetric analysis indicated loss of water at 200° (Calcd weight loss for -H₂O: 9.20%. Found: 10.21%) and melting at 296° (5-carboxyphthalide).

Terephthaloyloxyacetic Acid Dimethyl Ester (2).—Terephthalic acid (0.83 g, 5 mmol), formaldehyde (0.90 g, 30 mmol, "Trioxane"), and 5.0 ml of 98% sulfuric acid were sealed in a glass tube and heated to 150° for 2 hr. The tube was chilled and opened; the contents were poured into methanol (100 ml), concentrated, poured into water (700 ml), and extracted into dichloromethane. In this way, 0.71 g of esters was received, shown by gas chromatography to contain 83.2% dimethyl terephthalate, 1.1% 5-carbomethoxyphthalide, and 15.7% a third component, by peak areas. The unknown was trapped from the eluent gases and identified as dimethyl terephthaloyloxyacetic acid: nmr (CCl₄, 60 MHz) δ 3.80 (s, 3, OCH₃), 3.97 (s, 3, OCH₃), 4.82 (s, 2, CH₂), 8.13 (s, 4).

Anal. Calcd for C₁₂H₁₂O₆: C, 57.14; H, 4.80. Found: C, 56.78; H, 4.76.

Registry No.—Terephthalic acid, 100-21-0; formaldehyde, 50-00-0; 2-hydroxymethylterephthalic acid, 23405-34-7; 1 methyl ester, 23405-32-5; 1 ethyl ester, 23405-31-4; 2 dimethyl ester, 23405-33-6.

(9) W. H. Perkin, Jr., and J. F. S. Stone, *J. Chem. Soc.*, **127**, 2275 (1925).

Novel Fluorine-Containing β-Diketone Chelating Agents¹

W. G. SCRIBNER

Monsanto Research Corporation, Dayton Laboratory,
Dayton, Ohio 45407

B. H. SMITH, R. W. MOSHIER, AND R. E. SIEVERS

Aerospace Research Laboratories, ARC,
Wright-Patterson Air Force Base, Ohio 45413

Received July 24, 1969

Increasing interest in volatile chelating agents² (or volatile metal chelates derived therefrom) for separations of metals by distillation or gas chromatography, for ultratrace analysis of metals or metal mixtures, for vapor deposition, for use as solvent extraction reagents, and for use as reagents that react directly with metals or oxides to form chelates has prompted the synthesis and examination of two new β-diketones. These ligands are 1,1,1,2,2,6,6,6-octafluoro-3,5-

(5) R. W. Beattie and R. H. Manske, *Can. J. Chem.*, **42**, 223 (1964).

(6) J. R. LeBlanc, D. B. Sharp, and J. G. Murray, *J. Org. Chem.*, **26**, 4731 (1961).

(7) O. O. Juveland, U. S. Patent 3,261,780 (1966).

(8) J. Thiele and O. Giese, *Ber.*, **36**, 842 (1903).

(1) This work was supported in part by Aerospace Research Laboratory In-House Independent Laboratory Research Funds, and by Contract AF 33(615)-1093.

(2) R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, Oxford, 1965, and references therein.