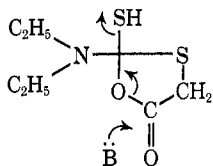


The acylating acids were prepared by condensation of carbon disulfide with aliphatic secondary amines in aqueous potassium hydroxide followed by treatment with chloroacetic acid.⁴

A mechanism for this reaction may be visualized as one proceeding through the cyclic 2-dialkylamino-2-mercapto-5-oxo-1,3-oxathiole intermediate as shown below, where B represents the attacking nucleophile.



Experimental Section⁵

Sodium 7-(N,N-Diethylcarbamoylmercaptoacetamido)cephalosporanate.—To a mixture of 1.4 g (0.005 mol) of 2 and 1.2 g (0.005 mol) of S-carboxymethyl-N,N-diethylthiocarbamate⁴ in 100 ml of pH 7 phosphate buffer was added 10% sodium hydroxide solution until the acids dissolved. A solution of 10 ml of 1 N sodium iodide-iodine solution was added with stirring at 5° over a 20-min period. The solution was maintained at pH 7 during this period by the addition of 10% sodium hydroxide. The reaction mixture was filtered to remove some insoluble impurities and acidified with dilute phosphoric acid to pH 2. The mixture was extracted with ethyl acetate, washed with water, dried over anhydrous magnesium sulfate, and treated with sodium 2-ethylhexanoate. The salt was collected and recrystallized from dimethylformamide and acetone to yield 580 mg (24%) of white crystals: mp 152–155° dec; ir (KBr) 3340 (amide NH), 1770 (β -lactam C=O), 1745 (ester C=O), 1685 (amide C=O), and 1650–1610 cm^{-1} [N(C=O)S and (C=O)O]; nmr (D_2O) 5.65 (d, 1, $J = 5$ Hz, NCHCO), 5.08 (d, 1, $J = 5$ Hz, NCHS), 4.88 (m, 2, CH_2OAc), 3.67 (s, 2, SCH_2CO), 3.40 (m, 4, $J = 7.5$ cps, CH_2NCH_2), 2.05 (s, 3, CH_3CO), and 1.12 ppm (t, 6, $J = 7.5$ Hz, CH_3 , CH_3). The C_2 protons are obscured in the 3.7–3.1-ppm region.

Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{NaN}_3\text{O}_7\text{S}_2 \cdot \text{H}_2\text{O}$: C, 41.64; H, 4.93; N, 8.57. Found: C, 41.91; H, 5.21; N, 8.60.

This same compound was also prepared from S-carboxymethyl N,N-diethylthiocarbamate.

S-Carboxymethyl N,N-Diethylthiocarbamate.—Carbonyl sulfide was bubbled into a solution of 14.6 g (0.2 mol) of diethylamine in 150 ml of ether at 5° until a total of 6 g (0.1 mol) had been added. The solution was stored for 15 hr at 30° and the solvent was removed under reduced pressure to a light yellow, crystalline solid which weighed 13.7 g. This was dissolved in 75 ml of water, and 7.7 g (0.06 mol) of sodium chloroacetate was added. The solution was stirred for 3 hr at 30° and for 50 min

at 50–55°. The solution was acidified to pH 2 with concentrated hydrochloric acid and extracted with ether. The ether was washed with water, dried over anhydrous sodium sulfate, and evaporated to yield a crystalline solid which weighed 6.5 g (34%), mp 36–38°.

Anal. Calcd for $\text{C}_7\text{H}_{13}\text{NO}_3\text{S}$: C, 43.96; H, 6.85. Found: C, 44.00; H, 7.01.

Sodium 7-(N,N-Diethylcarbamoylmercaptoacetamido)cephalosporanate by Direct Acylation.—To a solution of 3.2 g (0.017 mol) of S-carboxymethyl N,N-diethylthiocarbamate and 1.8 g (0.018 mol) of triethylamine dissolved in 100 ml of tetrahydrofuran at 0° was added dropwise 2.1 g (0.018 mol) of isovaleryl chloride. The mixture was stirred for 20 min and a solution of 4.8 g of 2 dissolved in 50 ml of water and 5 ml of triethylamine was added all at once. After stirring for 25 min the solution was diluted with cold water, acidified to pH 2 with 1:1 phosphoric acid, and extracted with ethyl acetate. The organic layer was washed twice with water, filtered, and evaporated to an oil. The oil was dissolved in acetone and treated with 20% sodium 2-ethyl hexanoate in acetone until the turbidity ceased. The white, crystalline solid was collected and recrystallized from water-acetone to yield 2.5 g. The ir and nmr spectra were identical with the spectra obtained from the product prepared by the iodine-sodium iodide reaction.

Registry No.—S-Carboxymethyl-N,N-diethylthiocarbamate, 20708-46-7; sodium salt of 3, 23740-36-5.

Palladium-Catalyzed Reactions of Formate Esters

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The decarbonylation of aldehydes by palladium was first reported by Newman and Zahm,¹ and its application to syntheses with all types of aldehydes has been reported by various workers.² Recently,³ evidence has been presented that this may be a free-radical process, although, if so, the radicals may exist only on the catalyst surface. That aldehydes can be decarbonylated *via* free radicals is already well known.⁴

Formates can be considered to have an aldehydic hydrogen and carbonyl, but the decarbonylation of formate esters by palladium has not been reported. In this case, if decarbonylation occurred, the expected intermediate would be an alkoxy radical, which could lead to the alcohol by abstraction of a hydrogen atom.

It was found that on refluxing *n*-octyl formate with palladium charcoal, carbon monoxide was eliminated and *n*-octyl alcohol was formed (Table I).

TABLE I
DECARBONYLATION PRODUCTS OF *n*-OCTYL FORMATE

	Liquid	% by glc	Gas	Mol %
Octan-1-ol		95.71	CO	85.50
Octyl formate		1.70	H ₂	12.27
Octanal		1.34	CO ₂	1.58
High molecular weight		1.25	Hydrocarbons	0.65

(4) G. Nachmias, *Ann. Chim. (Paris)*, **7**, 584 (1954); *Chem. Abstr.*, **48**, 597 (1954).

(5) Melting points were determined on a Fisher-Johns apparatus, and are uncorrected. The ir spectra were recorded on a Beckman IR-9 spectrometer. The nmr spectra were run on a Varian A-60 spectrometer at a sweep width of 500 cps using deuterium oxide as a solvent. The authors wish to thank Mr. R. M. Downing and Mr. D. F. Whitehead for the micro-analytical and spectral data, respectively.

(1) M. S. Newman and H. V. Zahm, *J. Amer. Chem. Soc.*, **65**, 1097 (1943).

(2) See, e.g., H. E. Eschinazi, *Bull. Soc. Chim. Fr.*, 967 (1962); M. S. Newman and N. Gill, *J. Org. Chem.*, **31**, 3860 (1966); J. O. Hawthorne and M. H. Wilt, *ibid.*, **25**, 2215 (1960); N. E. Hoffman, A. T. Kanakkanatt, and R. F. Schneider, *ibid.*, **27**, 2687 (1962).

(3) J. W. Wilt and V. P. Abegg, *ibid.*, **33**, 923 (1968).

(4) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

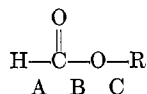
However, when benzyl formate was refluxed with palladium on charcoal, the major products were toluene and carbon dioxide (Table II).

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.)

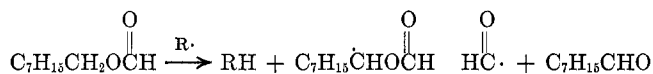
In the molecule shown, calculations of the homolytic bond dissociation energies (BDE) of bonds A, B,



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

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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).