carbon tetrachloride and filtered. The solvent was removed under reduced pressure to give an oil which was distilled to give **2a** (63%), bp 185–190° (0.05 mm) [lit.[6] bp 182° (0.04 mm)], and **2b** (57%), bp 195° (0.1 mm).

Aromatization of Dimers 2a and 2b.—N-Bromosuccinimide (2.6 g, 14.5 mmol) was added in portions to a refluxing solution of 5.0 g (13 mmol) of **2a** and 0.1 g of azoisobutyronitrile in 40 ml of carbon tetrachloride. When dissolution of N-bromosuccinimide was complete, the reaction mixture was refluxed for an additional 0.5 hr, cooled to room temperature, and kept at 5° overnight. Succinimide (1.2 g, 84%) separated, was removed by filtration, and was washed with carbon tetrachloride. The combined carbon tetrachloride solutions were concentrated under reduced pressure to yield an oil which was dissolved in 40 ml of benzene. A solution of 10.0 g (100 mmol) of triethylamine in 20 ml of benzene was added slowly with stirring to this solution. After the addition was completed, the reaction mixture was refluxed with stirring for 1 hr, cooled, and held at 5° overnight. Triethylammonium bromide (2.3 g, 96%) was removed by filtration and the filtrate was concentrated under reduced pressure to give an oil which was distilled to yield 2.5 g of an oil, bp 198–210° (0.08 mm). This product was further purified by chromatography on neutral alumina using successive elutions with hexane, benzene, and chloroform. The combined chloroform eluents were dried over sodium sulfate, concentrated, and distilled to give 2.0 g (40%) of **diethyl *o*-(2-diethoxyphosphonoethyl)-phenylphosphonate** (**5**), bp 181° (0.03 mm).

Anal. Calcd for $C_{16}H_{28}O_6P_2$: C, 50.80; H, 7.47; P, 16.37. Found: C, 50.99; H, 7.51; P, 16.51.

The reaction of **2a** with 2 equiv of N-bromosuccinimide was carried out in the same manner. The crude product was not distilled, but was purified by chromatography on neutral alumina. Two purifications gave analytically pure **diethyl *o*-(2-diethoxyphosphonovinyl)phenylphosphonate** (**6**, 13%).

Anal. Calcd for $C_{16}H_{26}O_6P_2$: C, 51.18; H, 6.88; P, 16.44. Found: C, 51.31; H, 7.08; P, 16.59.

The same procedure was employed for the aromatization of **2b**. A 30% yield of **dimethyl *o*-(2-dimethoxyphosphonovinyl)-phenylphosphonate** was obtained: pmr (CCl_4) τ 6.25 (d, J_{PH} = 11 Hz, CH_3), 3.78 [2 × 2, $J_{HH} \cong J_{PH} \cong 17$ Hz, H(P)C=], 2.0–3.0 (m, C_6H_4), and 1.88 ppm (2 × 2, $J_{HH} \cong J_{PH} \cong 17$ Hz).

Anal. Calcd for $C_{12}H_{18}O_6P_2$: C, 45.10; H, 5.64; P, 19.32. Found: C, 45.20; H, 5.74; P, 19.21.

Diels–Alder Reactions of Dienes 1a and 1b. A. With Diethyl Vinylphosphonate.—A mixture of 7.0 g (37 mmol) of **1a**, 30.0 g (183 mmol) of diethyl vinylphosphonate, and 0.1 g of hydroquinone was placed in an autoclave which was then evacuated and heated at 150° for 12 hr. Distillation of the reaction mixture gave 26.1 g of diethyl vinylphosphonate, bp 48–55° (0.1 mm), 1.0 g (11%) of **3,4-bis(diethoxyphosphono)cyclohexene** (**3b**), bp 200–205° (0.1 mm), and polymeric residue (7.1 g).

B. With Acrylonitrile.—A mixture of 16.0 g (100 mmol) of **1b**, 15.9 g (300 mmol) of acrylonitrile, and 0.1 g of hydroquinone was heated in an autoclave under an atmosphere of nitrogen at 125° for 12 hr. The reaction mixture was concentrated under reduced pressure in a rotary evaporator and the residue was distilled to give 4.5 g of **1b**, 4.5 g of crude **3e**, bp 130–137° (0.2 mm), 1.0 g of a mixture of **3e** and **2b**, bp 137–175° (0.2 mm), and 8 g of a rubbery residue. The two higher boiling fractions were combined and redistilled to give 3.5 g (23%) of **3-dimethoxyphosphono-4-cyanocyclohexene** (**3e**), bp 134–135° (0.2 mm). The same conditions were employed for the reactions of **1a** with ethyl acrylate and acrolein and of **1b** with dimethyl maleate. In each of these cases, the mixture of adduct and dimer could not be separated by distillation.

C. With Dimethyl Acetylenedicarboxylate.—A mixture of 5.0 g (31 mmol) of **1b**, 4.4 g (31 mmol) of dimethyl acetylenedicarboxylate, and 0.1 g of hydroquinone was heated under a nitrogen atmosphere for 12 hr at 100°. The reaction mixture was concentrated under reduced pressure in a rotary evaporator (bath temperature 130°) to give a 6.0-g residue, which was chromatographed on silicic acid (100 g). Elution with *n*-hexane gave small amounts of the acetylene dicarboxylate. **1,2-Dicarbomethoxy-3-dimethoxyphosphonocyclohexa-1,4-diene** (**8**, 3.0 g, 32%) was eluted with 1:1 benzene–*n*-hexane.

Aromatization of Diels–Alder Adducts.—The general procedure[3] is exemplified by the aromatization of **3b**. A mixture of 0.75 g (3 mmol) of **3b**, 1.0 g (8 mmol) of nitrobenzene, 1.5 g of 5% palladium on charcoal, and 80 ml of anhydrous ethanol was held at reflux temperature for 100 hr. The catalyst was removed by filtration and, after concentration under reduced pressure, the reaction mixture was distilled to give 0.4 g (80%) of **tetraethyl *o*-phenylenebisphosphonate** (**7b**), bp 180–185° (0.1 mm). The aromatizations of **3c** and **3d** to **7c** and **7d** were carried out in the same manner. Products **7b–7d** were identified by comparisons with authentic samples.[8,9,11]

Dimethyl 2,3-dicarbomethoxyphenylphosphonate (**9**) was prepared by refluxing a mixture of 3.0 g (10 mmol) of **8**, 6.0 g (49 mmol) of nitrobenzene, 3.0 g of 5% palladium on charcoal, and 60 ml of anhydrous methanol for 72 hr. The catalyst was removed by filtration and, after concentration under reduced pressure in a rotary evaporator (bath temperature 100°), the reaction mixture was chromatographed on silicic acid (100 g). Initial elution with *n*-hexane gave small amounts of nitrobenzene. Elution with benzene gave 1.5 g (50%) of **9**.

Anal. Calcd for $C_{12}H_{15}O_7P$: C, 47.71; H, 5.04; P, 10.25. Found: C, 47.33, 47.41; H, 4.87, 4.91; P, 10.03, 9.98.

Aromatization of the adduct of dimethyl maleate and **1b** and isolation of **9** was carried out in the same manner.

Adduct **3e** was aromatized by the bromination–elimination sequence used for the preparation of **6**. **Dimethyl *o*-cyanophenylphosphonate** (**7e**) was isolated by distillation, but was contaminated by **2b** and its aromatization products. Neither redistillation nor silicic acid chromatography achieved satisfactory purification, and the product was hydrolyzed with refluxing 2 *N* hydrochloric acid to yield **7a**. Identity was established by comparisons with an authentic sample.[9]

Registry No.—**1a**, 7158-35-2; **1b**, 4037-11-0; **5**, 23293-54-1; **6**, 23293-55-2; **9**, 23293-56-3; dimethyl *o*-(2-dimethoxyphosphonovinyl)phenylphosphonate, 23293-57-4.

Acknowledgment.—We are indebted to Dr. W. E. Byrne, Dr. M. Gordon, and Dr. M. P. Williamson for the determination of pmr spectra. This study was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-470-64.

A Novel Acylation of Amino Acids with S-Carboxymethyl Dialkyldithiocarbamates

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Received October 27, 1969

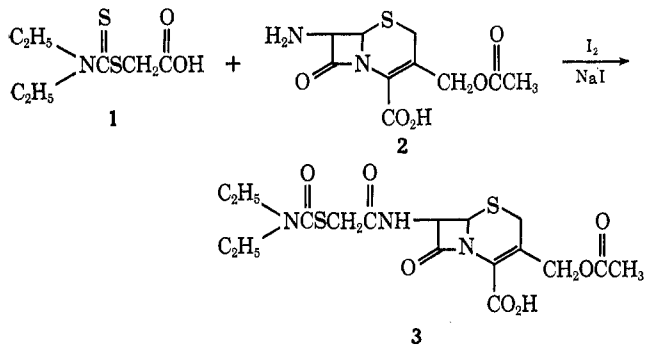
In an attempt to thioacylate[1,2] 7-aminocephalosporanic acid (**2**) with S-carboxymethyl N,N-diethyldithiocarbamate (**1**) in the presence of iodine–sodium iodide complex, we have unexpectedly isolated N,N-diethylcarbamoylmercaptomethylcephalosporin (**3**). This compound was identified by its ir and nmr spectra and by synthesis through the direct acylation of **2** with S-carboxymethyl N,N-diethylthiocarbamate mixed anhydride.

This acylation is not confined to **2**[3] but works equally well with other amino acids such as 6-aminopenicillanic acid and 2-phenylglycine. The reaction also proceeds readily with other S-carboxymethyl dialkyldithiocarbamates. However, in the absence of iodine, the reaction fails.

(1) J. F. W. McOmie, *Ann. Rep. Progr. Chem.*, **45**, 208 (1948).

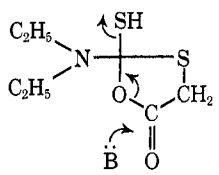
(2) R. H. Hall, H. D. Holingworth, D. P. Young, and R. Sherlock, British Patent 36,842,161 (1964); *Chem. Abstr.*, **60**, 15877*g* (1964).

(3) W. J. Gottstein and A. H. Eachus, U. S. Patent 3,391,141 (1968); *Chem. Abstr.*, **69**, 86992 (1968).



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 Section[5]

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-diethyldithiocarbamate[4] 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 $C_{17}H_{22}NaN_3O_7S_2 \cdot H_2O$: 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 $C_7H_{13}NO_3S$: 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.

(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 microanalytical and spectral data, respectively.

Palladium-Catalyzed Reactions of Formate Esters

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Received October 8, 1969

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

(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.