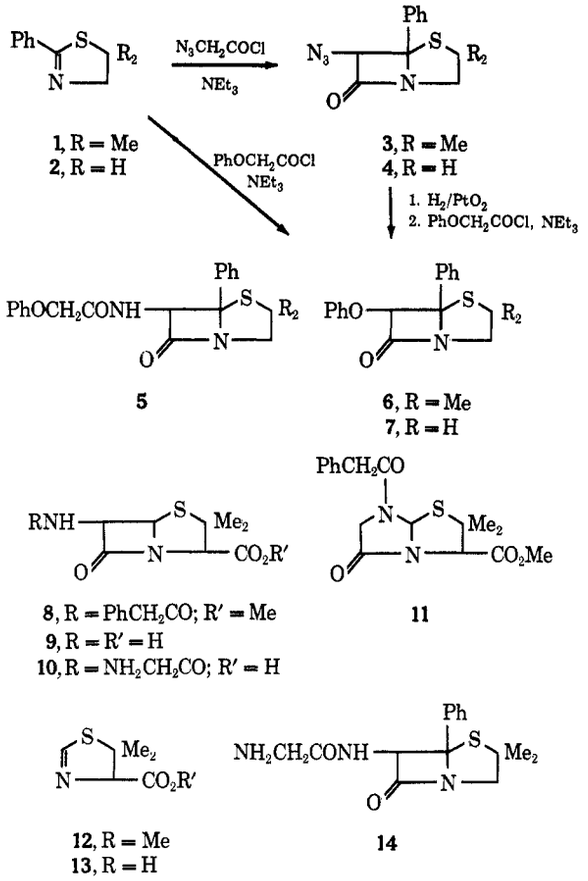

that the amino compounds formed by the reduction of **3** and **4** undergo β-lactam ring scission to the thiazolines **1** and **2**, respectively. To test this possibility, **1** in ethyl acetate solution was shaken with hydrogen for about 70 hr at room temperature in presence of Adams catalyst. From this reaction mixture a small amount of a solid and a yellow liquid were isolated. The solid, which was insoluble in common organic solvents, showed the highest peak in its mass spectrum at *m/e* 305 and a strong peak at *m/e* 191. We believe this product to be **14** (mol wt 305) by analogy with **10**. The main constituent of the liquid was deduced to be the thiazoline **1** on the basis of the mass spectrum (M^+, *m/e* 191), nmr peaks, and tlc comparison with authentic **1**. Further studies on this unusual β-lactam cleavage are necessary for establishing the exact pathway from the α-azido-β-lactams to the thiazolines under our reaction conditions.

Experimental Section

The melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer, the nmr spectra were taken on a Varian A-60A instrument, and the mass spectra were obtained on a Hitachi Perkin-Elmer RMU-7 mass spectrometer. The microanalysis were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany.

6-Azido-7-oxo-5-phenyl-4-thia-1-azabicyclo[3.2.0]heptane (4).—A solution of triethylamine (7.2 g) in 250 ml of CH_2Cl_2 was added dropwise with constant stirring and under anhydrous conditions to a refluxing solution containing 12.65 g of 2-phenyl-2-thiazoline in 800 ml of CH_2Cl_2 and 9.2 g of azidoacetyl chloride in 750 ml of CH_2Cl_2. The addition of triethylamine was completed in 1 hr and the reaction mixture was stirred for an additional period of 17 hr. The solvent was then evaporated and the residue was extracted with ether. The ethereal extract was washed with water, dried ($MgSO_4$), and evaporated *in vacuo* to a viscous residue. Chromatography of this residue over a Florisil column using benzene as the eluent afforded 12.73 g (70%) of the pure title compound: mp 65–67°; ir (Nujol) 4.75 (azide), 5.64 μ (β-lactam carbonyl); nmr ($CDCl_3$) τ 2.55 (s, 5), 5.07 (s, 1), 5.67 (m, 1), 6.75 (m, 3 H); mass spectrum M^+ at *m/e* 246.

Anal. Calcd for $C_{11}H_{10}N_4OS$: C, 53.66; H, 4.09; N, 22.76; S, 13.39. Found: C, 53.72; H, 4.06; N, 22.83; S, 13.13.

6-Azido-3,3-dimethyl-7-oxo-5-phenyl-4-thia-1-azabicyclo[3.2.0]heptane (3).—This penam was prepared in 87% yield from 5,5-dimethyl-2-phenyl-2-thiazoline and azidoacetyl chloride using the procedure outlined above: mp 102–104°; ir (Nujol) 4.7 (azide), 5–6 μ (β-lactam carbonyl); nmr (CDCl) τ 2.58 (s, 5), 4.98 (s, 1), 5.92 (d, 1, *J* = 12.5 Hz), 7.05 (d, 1, *J* = 12.5 Hz), 8.43 (s, 3), 8.56 (s, 3); mass spectrum M^+ at *m/e* 274.

Anal. Calcd for $C_{13}H_{14}N_4OS$: C, 56.97; H, 5.14; N, 20.43; S, 11.63. Found: C, 56.97; H, 5.27; N, 20.47; S, 11.67.

Reduction of 3 and Its Reaction with Phenoxyacetyl Chloride.—6-Azido-3,3-dimethyl-7-oxo-5-phenyl-4-thia-1-azabicyclo-[3.2.0]heptane (3.5 g) was dissolved in 50 ml of ethyl acetate and 2.1 g of Adams catalyst was added to it. The mixture was stirred in an atmosphere of hydrogen (41 psi pressure) for 54 hr. Solvent and the catalyst were removed and the product was used for the next operation without further purification.

The reduced material was dissolved in 200 ml of CH_2Cl_2, and 2 g of triethylamine was added to it. Phenoxyacetyl chloride (2.15 g) in 50 ml of CH_2Cl_2 was then added dropwise over a period of 0.5 hr. The reaction mixture was stirred overnight, then washed with water and dried ($MgSO_4$). Removal of solvent and chromatography over Florisil using methylene chloride–hexane (2:1) provided 3 g (70%) of 3,3-dimethyl-7-oxo-5-phenyl-6-phenoxy-4-thia-1-azabicyclo[3.2.0]heptane (6): mp 93–95°; ir (Nujol) 5.6 μ (β-lactam carbonyl); nmr ($CDCl_3$) τ 2.92 (broad, 10), 4.38 (s, 1), 5.9 (d, 1, *J* = 12 Hz), 7.08 (d, 1, *J* = 12 Hz), 8.4 (s, 3), 8.52 (s, 3); mass spectrum M^+ at *m/e* 325.

Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 68.68; H, 5.09; N, 4.71; S, 10.76. Found: C, 68.70; H, 5.12; N, 4.60; S, 10.80.

Reduction of **4** using Adams catalyst followed by treatment with phenoxyacetyl chloride under conditions outlined above afforded **7**, mp 132–134°, in 80% yield: ir (Nujol) 5.65 μ; nmr ($CDCl_3$) τ 2.9 (broad, 10), 4.5 (s, 1), 5.65 (m, 1), 6.7 (m, 3); mass spectrum M^+ at *m/e* 297.

Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 70.14; H, 5.89; N, 4.31; S, 9.83. Found: C, 70.31; H, 5.86; N, 4.24; S, 9.74.

Registry No.—**1**, 37950-61-1; **2**, 2722-34-1; **3**, 37950-63-3; **4**, 37950-64-4; **6**, 37950-65-5; **7**, 37950-66-6; azidoacetyl chloride, 30426-58-5; phenoxyacetyl chlorides, 701-99-5.

Synthesis and Some Properties of *O*-Acyl- and *O*-Nitrophenylhydroxylamines

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O-Acyl- and *O*-nitrophenylhydroxylamines, useful aminating agents,[1,2] have usually been prepared by the following two methods:[3] (i) Carpino's method[2]

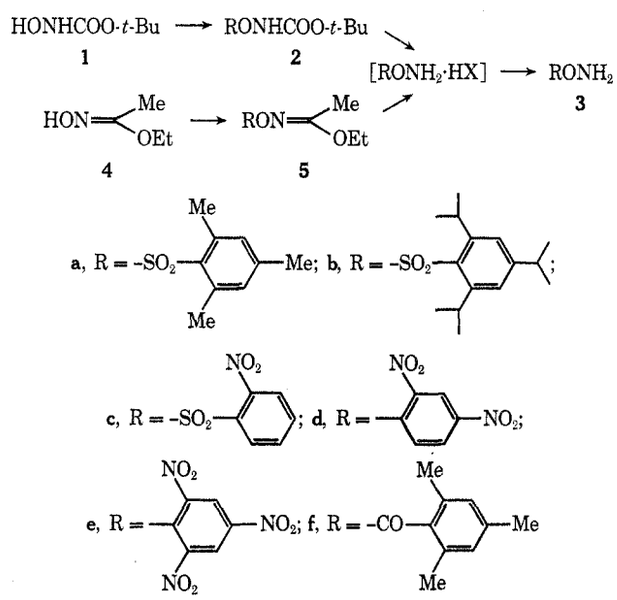
(1) (a) Y. Tamura, J. Minamikawa, Y. Miki, S. Matsugashita, and M. Ikeda, *Tetrahedron Lett.*, 4133 (1972); (b) Y. Tamura, K. Sumoto, J. Minamikawa, and M. Ikeda, *ibid.*, 4137 (1972).

(2) (a) L. A. Carpino, C. A. Giza, and B. A. Carpino, *J. Amer. Chem. Soc.*, **81**, 955 (1959); (b) L. A. Carpino, *ibid.*, **82**, 3133 (1960); (c) J. G. Kraus, *Synthesis*, 140 (1972); (d) T. Sheradsky, *J. Heterocycl. Chem.*, **4**, 413 (1967); *Tetrahedron Lett.*, 1909 (1968); T. Sheradsky and Z. Nir, *ibid.*, 77 (1969).

(3) Other methods include (a) S. E. Meyer and T. Bellman, *J. Prakt. Chem.*, [II] **33**, 18 (1886); A. W. Scott and B. L. Wood, Jr., *J. Org. Chem.*, **7**, 508 (1942); (b) W. P. Jencks, *J. Amer. Chem. Soc.*, **80**, 4581, 4585 (1958); (c) L. Francesconi and A. Paracozzani, *Gazz. Chim. Ital.*, **31II**, 334 (1901); O. Exner, *Collect. Czech. Chem. Commun.*, **23**, 272 (1958); G. Zinner, *Arch. Pharm. (Weinheim)*, **291**, 1 (1959); (d) G. Zinner, *ibid.*, **293**, 657 (1960); (e) G. Zinner, *ibid.*, **296**, 57 (1963).

using *tert*-butyl *N*-hydroxycarbamate (**1**) and (ii) Zinner's method[4] using ethyl acetohydroxamate (**4**). Carpino's method has been successfully applied to the preparation of *O*-aryloyl-,[2a] *O*-arylsulfonyl-,[2b,c] and *O*-2,4-dinitrophenylhydroxylamines,[2d] but it has the disadvantage of rather high cost of the starting material, *tert*-butyl azidoformate. Zinner's method appears to be more economical, but has been restricted only to the preparation of *O*-aryloyl- and *O*-carbalkoxyhydroxylamines.

In this paper an improved preparation of *O*-arylsulfonyl- and *O*-nitrophenylhydroxylamines (**3**) by a modification of Zinner's method is described. Some of their properties are also described.



Ethyl *O*-arylsulfonylhydroxamates (**5a–c**), prepared from the readily accessible ethyl hydroxamate (**4**)[5] and arylsulfonyl chloride, were treated with 70% perchloric acid at 0° for 10 min. The reaction mixture was poured into ice water to give crystalline *O*-arylsulfonylhydroxylamines (**3a–c**) in high yields. The products were characterized by ir and nmr spectra, details of which are given in the Experimental Section. Compound **3c** decomposes quickly on exposure to air, so that no further investigation was carried out. In contrast, compounds **3a** and **3b** are noticeably more stable and can be kept in a freezer for several weeks. The products **3a** and **3b** obtained by this method usually contain 20–30% of water (estimated by iodometry) but can be used without further purification. If necessary, they can be recrystallized from ether and petroleum ether, as suggested by Carpino.[2b] They were found to be soluble in common organic solvents.

Using the same procedure as described above, *O*-(2,4-dinitrophenyl)-[2d] and *O*-picrylhydroxylamines (**3d** and **3e**) were also prepared in high yields. Compound **3e** is stable enough to be recrystallized from hot chloroform, and sparingly soluble in most organic solvents at room temperature. For comparison *O*-mesitoylhydroxylamine (**3f**) was also prepared according to the Zinner method.

The reactivity of these O-substituted hydroxylamines (**3**) was compared by their ability to aminate various substrates such as tri-*n*-butylamine, pyridine, diphenyl sulfide, diphenyl sulfoxide, and triphenylphosphine. The reactions were generally carried out in the methylene chloride solution at room temperature, but in some cases this procedure was modified as shown in the footnotes of Table I. The structures of the new compounds were proved by elemental analysis (Table II) and spectral data. The yields of the products listed in Table I revealed the marked dependency upon the nature of the leaving group.

In summary, on the basis of this result, together with its relative stability and solubility in organic solvents, *O*-mesitylenesulfonylhydroxylamine (**3a**) is recom-

TABLE I

COMPARISON OF YIELDS (PER CENT) IN REACTIONS OF **3** WITH VARIOUS NUCLEOPHILES

Starting material	Product	3a	3b	3d	3e[a]	3f
(*n*-Bu)$_3$N	(*n*-Bu)$_3$N$^+$NH$_2$·$^-$OR (**7**)	87[f]	72	85	0	15
C$_5$H$_5$N	C$_5$H$_5$N$^+$NH$_2$·$^-$OR (**8**)	80[i]	68	55	80[g]	Trace
Ph$_2$S	Ph$_2$S$^+$NH$_2$·$^-$OR (**9**)	90[j]	79	61[b]	87	
Ph$_2$S(O)	Ph$_2$S$^+$(O)NH$_2$·$^-$OR (**10**)	65[j]	40[c]	<20[d]	<30[e]	
Ph$_3$P	Ph$_3$P$^+$NH$_2$·$^-$OR (**11**)	86	76	92	91[h]	

[a] Amination effected in methylene chloride–ethanol (5:1) solution. [b] The reaction mixture was heated at 40–50° for 5 min, followed by allowing the mixture to stand at room temperature until the product separated. [c] The product was characterized by conversion[1b] to diphenylsulfoximine, mp 101–102° [lit. mp 103–104°: M. Barash, *Chem. Ind. (London)*, 1261 (1964)]. [d] S-Amination was accompanied by the formation of high-melting by-product. [e] The reaction mixture was heated at 50–60° for 2–3 min, and then allowed to stand at room temperature for 2 days. A mixture of **10e** and **3e**, mp 129–130°, was obtained. Attempts to separate **10e** from **3e** were unsuccessful. [f] Y. Tamura, J. Minamikawa, Y. Kita, J. H. Kim, and M. Ikeda, *Tetrahedron*, in press. [g] Y. Tamura, N. Tsujimoto, and M. Mano, *Chem. Pharm Bull.*, **19**, 130 (1971). [h] R. Appel, W. Buchner, and E. Guth, *Justus Liebigs Ann. Chem.*, **618**, 53 (1958). [i] Reference 1a. [j] Reference 1b.

TABLE II

ANALYTICAL DATA OF THE AMINATED PRODUCTS[a]

Compd	Mp, °C (recrystd from)	Empirical formula
7b	259–260 (CH_2Cl_2–Et_2O)	$C_{27}H_{52}N_2O_3S$
7d	81–82 (CH_2Cl_2–pet. ether)	$C_{18}H_{32}N_4O_5$
7f	213–215 (CH_2Cl_2–pet. ether)	$C_{22}H_{40}N_2O_2$
8b	183–184 (CH_2Cl_2–Et_2O)	$C_{20}H_{30}N_2O_3S$
8d	160–161 (EtOH–Et_2O)	$C_{11}H_{10}N_4O_5$
9b	239–240 (CH_2Cl_2–pet. ether)	$C_{27}H_{35}NO_3S_2$
9d	123–124 (CH_2Cl_2–pet. ether)	$C_{18}H_{15}N_3O_5S$
9e	137–138 (CH_2Cl_2–pet. ether)	$C_{18}H_{14}N_4O_7S$
11a	154–155 (CH_2Cl_2–Et_2O)	$C_{27}H_{28}NO_3PS\cdot H_2O$
11b	214–216 (CH_2Cl_2–pet. ether)	$C_{33}H_{40}NO_3PS$
11d	141–142 (CH_2Cl_2–pet. ether)	$C_{24}H_{20}N_3O_5P$

[a] Satisfactory analytical data (±0.3% for C, H, and N) were reported for all compounds in this table.

(4) G. Zinner, *Arch. Pharm. (Weinheim)*, **293**, 42 (1960); **303**, 317 (1970).
(5) J. Houben and E. Schmidt, *Chem. Ber.*, **46**, 3616 (1913).

mended as the most convenient general reagent for amination.

Experimental Section[6]

Ethyl *O*-(Mesitylenesulfonyl)acetohydroxamate (5a).—Mesitylenesulfonyl chloride (72 g) was added to a solution of ethyl acetohydroxamate[5] (4) (34 g) and triethylamine (33 g) in dimethylformamide (90 ml) in portions with stirring under ice cooling. After addition was complete, the reaction mixture was stirred for 20 min at 0° and then poured into ice water. A white precipitate was filtered and recrystallized from petroleum ether (bp 30–60°) to give colorless needles (83 g, 86%) of **5a**: mp 57–58°; ir (KCl) 1635, 1600, 1200, 1180, and 670 cm^{-1}; nmr ($CDCl_3$) τ 8.85 (3 H, t, J = 8 Hz), 8.02 (3 H, s), 7.75 (3 H, s), 7.42 (6 H, s), 6.15 (2 H, q, J = 8 Hz), and 3.08 (2 H, b s).

Anal. Calcd for $C_{13}H_{19}NO_4S$: C, 54.73; H, 6.71; N, 4.91. Found: C, 54.66; H, 6.44; N, 4.95.

Ethyl *O*-(2,4,6-Triisopropylbenzenesulfonyl)acetohydroxamate (5b).—Using the procedure described above for **5a**, **5b** was prepared from **4** (10.3 g) and 2,4,6-triisopropylbenzenesulfonyl chloride (30.3 g). Recrystallization from ethanol–water (20:1) gave colorless prisms (32 g, 87%) of **5b**: mp 75–76°; ir (KCl) 1630, 1600, 1350, 1195, and 670 cm^{-1}; nmr ($CDCl_3$) τ 8.88 (3 H, t, J = 6.8 Hz) 8.79 (18 H, d, J = 6.8 Hz), 8.00 (3 H, s), 7.13 (1 H, m), 6.09 (2 H, m), 5.83 (2 H, m), and 2.86 (2 H, s).

Anal. Calcd for $C_{19}H_{31}NO_4S$: C, 61.76; H, 8.46; N, 3.79. Found: C, 61.77; H, 8.34; N, 3.85.

Ethyl *O*-(*o*-Nitrobenzenesulfonyl)acetohydroxamate (5c).—Using the procedure described for **5a**, **5c** was prepared from **4** (1.0 g) and *o*-nitrobenzenesulfonyl chloride (2.1 g). Recrystallization from ligroin afforded white prisms (2.0 g, 73%) of **5c**: mp 79–80°; ir (KCl) 1615, 1530, 1380, 1325, and 1195 cm^{-1}; nmr ($CDCl_3$) τ 8.83 (3 H, t, J = 6.9 Hz), 7.96 (3 H, s), 6.09 (2 H, q, J = 6.9 Hz), and 2.28 (4 H, m).

Anal. Calcd for $C_{10}H_{12}N_2O_6S$: C, 41.67; H, 4.20; N, 9.72. Found: C, 41.68; H, 4.16; N, 9.81.

Ethyl *O*-Picrylacetohydroxamate (5e).—Utilizing the previously reported procedure for the preparation of ethyl *O*-2,4-dinitrophenylacetohydroxamate,[7] **5e** was prepared from **4** (6.2 g) and picryl chloride (15.0 g). Recrystallization from ethanol afforded pale yellow needles (15.3 g, 81%) of **5e**: mp 93.5–94.5°; ir (KCl) 1600, 1525, 1460, and 1340 cm^{-1}; nmr ($CDCl_3$) τ 8.75 (3 H, t, J = 6.9 Hz), 7.88 (3 H, s), 6.10 (2 H, q, J = 7.2 Hz), and 1.28 (2 H, s).

Anal. Calcd for $C_{10}H_{10}N_4O_8$: C, 38.22; H, 3.21; N, 17.83. Found: C, 38.34; H, 3.27; N, 17.55.

***O*-Mesitylenesulfonylhydroxylamine (3a).**—To a solution of **5a** (75 g) in dioxane (50 ml) was added 70% perchloric acid (30 ml) with stirring at 0° over 10 min. The reaction mixture was poured into ice water to give a white solid, which was filtered and washed with water. Although the product (64 g) thus obtained contains 20% of water (by iodometry), it can be used simply by filtration of a methylene chloride solution to remove water separated. The solid was dissolved in ether and precipitated by the addition of petroleum ether to give white needles of **3a**: mp 93–94°; ir (KCl) 3340, 3250, 1600, 1350, 1190, 1180, and 780 cm^{-1}; acetone oxime mp 95–96° (lit.[2b] mp 95–96.5°).

***O*-(2,4,6-Triisopropylbenzenesulfonyl)hydroxylamine (3b).**—To a solution of **5b** (30 g) in dioxane (50 ml) was added 70% perchloric acid (30 ml) with stirring at 0° over 10 min. The reaction mixture was stirred for an additional 2 hr and poured into ice water. A white precipitate was treated as described for **3a** to give white crystals of **3b** (30 g, containing 31% of water): mp 137–138°; ir (KCl) 3340, 3260, 1600, 1350, 1200, 1190, and 665 cm^{-1}; acetone oxime mp 112–113° (from ethanol).

Anal. Calcd for $C_{15}H_{29}NO_3S$: C, 63.69; H, 8.61; N, 4.13. Found: C, 63.84; H, 8.84; N, 4.03.

***O*-(*o*-Nitrobenzenesulfonyl)hydroxylamine (3c).**—Using the same procedure described for **3a**, **3c** was prepared from **5c**[11] (3.0 g). Yellow crystals (0.35 g) of **3c** were obtained and characterized by its ir spectrum: ir (KCl) 3340, 3250, 1600, 1530, 1370, and 1200 cm^{-1}. Because this compound was found to decompose on exposure to air, no further investigation was carried out.

***O*-(2,4-Dinitrophenyl)hydroxylamine (3d).**—Using the same procedure described for **3a**, **3d** was prepared from **5d** (21.7 g). Recrystallization from ethanol gave pale yellow needles (12.5 g, 78%) of **3d**: mp 112–113° (lit.[2d] mp 112°); ir (KCl) 3325, 3250, 1600, 1510, and 1340 cm^{-1}; nmr ($CDCl_3$) τ 3.63 (2 H, b s, NH_2), 2.03 (1 H, d, J = 10 Hz), 1.62 (1 H, dd, J = 10 and 3 Hz), and 1.26 (1 H, d, J = 3 Hz).

***O*-Picrylhydroxylamine (1e).**—Using the same procedure described for **3a**, **3e** was prepared from **5e** (1.45 g). Recrystallization from chloroform gave yellow prisms of **3e** (0.7 g, 62%): mp 98–100° dec; ir (KCl) 3300, 3250, 1610, 1530, and 1350 cm^{-1}.

Anal. Calcd for $C_6H_4N_4O_7$: C, 29.52; H, 1.65; N, 22.95. Found: C, 29.56; H, 1.79; N, 23.08.

The acetone oxime had mp 122–123° (from ethanol).

Anal. Calcd for $C_9H_8N_4O_7$: C, 38.03; H, 2.84; N, 19.72. Found: C, 38.03; H, 2.89; N, 19.93.

Reactions of 3a,b,d,e,f with Nucleophiles. General Procedure.—To a stirred solution of substrate (tri-*n*-butylamine, pyridine, diphenyl sulfide, diphenyl sulfoxide, and triphenylphosphine) (1 mmol) in methylene chloride (5 ml) was added a solution of **3** (1 mmol) in methylene chloride (5 ml) at 0°. After the reaction mixture was allowed to stand at room temperature for 10 min, ether or petroleum ether was added to precipitate the product. In some cases this procedure was modified (see the footnotes of Table I). The results are summarized in Tables I and II.

Registry No.—**3a**, 36016-40-7; **3b**, 38202-21-0; **3c**, 38202-22-1; **3d**, 17508-17-7; **3e**, 38100-34-4; **3f**, 37477-17-1; **4**, 10576-12-2; **5a**, 38202-27-6; **5b**, 38202-28-7; **5c**, 38202-29-8; **5e**, 38202-30-1; **7b**, 38202-31-2; **7d**, 38202-32-3; **7f**, 38202-33-4; **8b**, 38202-34-5; **8d**, 38202-35-6; **9b**, 38229-23-1; **9b**, 38202-36-7; **9e**, 38215-55-3; **11a**, 38215-56-4; **11b**, 38309-16-9; **11d**, 38229-24-2; $(n\text{-Bu})_3N$, 102-82-9; pyridine, 110-86-1; Ph_2S, 139-66-2; $Ph_2S(O)$, 945-51-7; Ph_3P, 603-35-0; triethylamine, 121-44-8; 2,4,6-triisopropylbenzenesulfonyl chloride, 6553-96-4; *o*-nitrobenzenesulfonyl chloride, 1694-92-4; picryl chloride, 88-88-0; *O*-picryl acetone oxime, 13194-03-1; *O*-(2,4,6-triisopropylbenzenesulfonyl) acetone oxime, 38215-59-7.

(6) Melting points are uncorrected. Nmr spectra were recorded on a Hitachi R-20 spectrometer using TMS as an internal standard. Infrared spectra were recorded on a Hitachi EPI-G2 instrument.

(7) A. O. Ilvespää and Q. Marxer, *Helv. Chim. Acta*, **46**, 2009 (1963).

Synthesis of Some 5-Carboxy-5-hydroxymethyl-1,3-dioxanes

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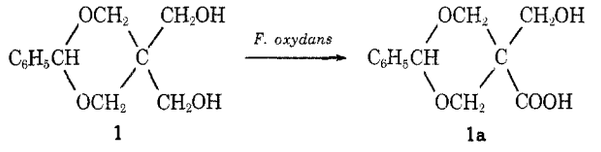
Oxidation of pentaerythritol with a mutant strain of *Flavobacterium oxydans* produces tris(hydroxymethyl)acetic acid, whereas the parent strain completely degrades pentaerythritol.[1]

Recent studies on the limits of oxidizing capability of the bacterium indicated that freeze-dried cells of the parent and mutant strains oxidized 2-phenyl-5,5-bis(hydroxymethyl)-1,3-dioxane (**1**) to 2-phenyl-5-carboxy-5-hydroxymethyl-1,3-dioxane (**1a**).[2]



1 **1a**

(1) C. T. Goodhue and J. R. Schaeffer, *Biotechnol. Bioeng.*, **11**, 1173 (1969).

(2) The conversion of **1** to **1a** was first observed during an unpublished investigation carried out in collaboration with Dr. C. T. Goodhue, of thees laboratories.