Favorskii rearrangement of **2** in dimethylamine (Scheme I) can be expected to give mainly *cis* **3**. *cis* products **3**, **6a**, and **6b** were shown by gas chromatography to be present in the products derived from Scheme I but not among those from Scheme II. Scheme II was shown to give the expected *trans* products **4**, **7a**, and **12** by comparing **12** with an authentic sample,[6] obtaining the nmr spectrum of the mixture of **4** and **5**, and comparing this with a reported nmr spectrum which showed a single $-N(CH_3)_2$ group δ 2.85 (6 H). However, the nmr spectrum of the mixture of **3**, **4**, and **5** from Scheme I showed two different $-N(CH_3)_2$ groups at δ 3.18 and 2.85 in the ratio **3**:**4** = 3:2. This ratio is maintained in the reduction products **6a** and **7a**. It is of interest that the ratio of **12**:**13**, **4**:**5**, and **7a**:**8** remained 5:1 throughout the reactions in Scheme II. These data support the stereochemical assignments shown in Schemes I and II and allow assignment of absolute configuration to (−)-*cis* **6a** and *cis* **6b** as 1*R*, 5*R*, and (+)-*trans* **7a** and *trans* **7b** as 1*S*,5*R*.[7]

The presence of the parent ions *m/e* 181 in the mass spectra of **6a** and **7a** and **8** and *m/e* 183 for **6b** and **7b** confirms the molecular weights.

Experimental Section[8]

Pulegone Dibromide (2).[9]—To a well stirred solution of 76 g (0.5 mol) of (+)-pulegone at ice-bath temperature in 200 ml of glacial acetic acid was added dropwise 80 g (0.5 mol) of bromine during 30 min. The reaction mixture was stirred for another 30 min and then poured onto 100 g of crushed ice, and extracted with eight 100-ml portions of low-boiling petroleum ether. The combined petroleum ether fractions were washed with a dilute sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and filtered. The resulting solution containing crude **2** was used without further treatment.

***cis*- and *trans*-2-Isopropylidene-(5*R*)-N,N-trimethylcyclopentanecarboxamides (3 and 4).**—All of the solution containing crude **2** (estimated 156 g, 0.5 mol) was added in one portion to 100 g (2.1 mol) of dimethylamine, which was previously cooled in a Dry Ice–acetone bath. Precipitation of dimethylamine hydrobromide occurred immediately after the addition. The flask was stoppered and allowed to come to room temperature, and the contents were stirred for an additional 5 hr. The stopper was removed and the excess dimethylamine was evaporated. The resulting mixture was stirred with 200 ml of ether and filtered, and the ether was washed with three 50-ml portions of 5% solution of hydrochloric acid and then with distilled water until the washings were neutral to litmus paper. The ether solution was dried over anhydrous magnesium sulfate, filtered, and distilled to yield 80 g (82%) of a mixture (**3**:**4**:**5** = 64:33:3): bp 75° (0.2 mm); nmr (CCl_4) δ 3.10 and 2.85 (6 H, 2 s, two $-N(CH_3)_2$ in ratio 3:2), 1.59 (3 H, s), 1.49 (3 H, s), an envelope centered at 2.2 (6 H), and 1.02 and 0.90 ppm (3 H, 2 d, *J* = 6 Hz); ν_{max}^{film} 2950, 2900, 1655, 1490, 1460, 1400, 1310, 1290, 1270, 1165, 1125, and 1060 cm^{-1}.

(−)-*cis*- and (+)-*trans*-2-Isopropylidene(5*R*)-N,N-trimethylcyclopentanemethylamine (6a and 7a).—To a well-stirred solution of 4 g (0.11 mol) of lithium aluminum hydride in 100 ml of anhydrous ether was added dropwise 11 g (0.06 mol) of a mixture of amides **3**, **4**, and **5** prepared above. The solution was heated at reflux temperature for 4 hr. The solution was cooled; the excess lithium aluminum hydride was destroyed with water; and the salts were filtered out and washed with ether. The ether fractions were combined, washed with three 50-ml portions of distilled water, dried over anhydrous magnesium sulfate, filtered, and concentrated to yield 7.8 g (76%) of a 3:2 mixture of (−)-**6a** and (+)-**7a**, bp 45° (0.3 mm), which showed 20- and 15.5-min retention times, respectively, on a 15 ft × 0.25 in. column of base-washed Chromosorb W coated with 15% Carbowax 20M operating at 120°.

The fraction due to **6a** was separated by preparative gas chromatography on the previously mentioned gas chromatography column and collected; it showed nmr (CCl_4) δ 2.15 (6 H, s), 1.65 (3 H, s), 1.59 (3 H, s), and 0.91 ppm (3 H, d, *J* = 6 Hz); $\nu_{max}^{CHCl_3}$ 2950, 2850, 2800, 2775, 1460, 1380, 1330, 1290, 1265, 1235, 1200, 1165, 1125, 1100, 1040, 1005, 995, 865, 835, 805, and 775 cm^{-1}; *m/e* 181 (parent ion) and 58 (100%); $[\alpha]^{23}_D$ −48° (*c* 0.49, $CHCl_3$).

Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.73. Found: C, 79.63; H, 12.50; N, 7.54.

The fraction due to **7a** was also collected and it showed nmr (CCl_4) δ 2.15 (14 H, envelope), 1.60 (6 H, broad s), and 0.90 ppm (3 H, d, *J* = 6 Hz); ν_{max}^{neat} 2950, 2850, 2775, 1450, 1370, 1265, 1180, 1170, 1155, 1100, 1060, 1045, 1030, 895, 862, 840, and 785 cm^{-1}; *m/e* 181 (parent ion) and 58 (100%); $[\alpha]^{23}_D$ +68° (*c* 0.17, $CHCl_3$).

(1*R*)-*cis*- and (1*S*)-*trans*-2-Isopropylidene-(5*R*)-N,N-trimethylcyclopentanedideuteriomethylamine (6b and 7b).—The procedure for the preparation of **6a** and **7a** was repeated using 2 g (0.01 mol) of a mixture of the amides **3** and **4** and 0.4 g (0.01 mol) of lithium aluminum deuteride in 20 ml of tetrahydrofuran to give 1.5 g (82%) of deuterated amines **6b** and **7b**. These were separated by preparative gas chromatography as described for **6a** and **7a**. The fraction (20-min retention time) due to **6b** showed nmr (CCl_4) δ 2.15 (12 H, envelope), 1.65 (3 H, s), 1.55 (3 H, s), and 1.05 ppm (3 H, d, *J* = 7 Hz); ν_{max}^{neat} 2950, 2850, 2800, 2775, 2200, 2150, 2000, 1460, 1380, 1265, 1120, 1110, 1100, 1080, 1045, 995, 910, 895, 830, 820, and 775 cm^{-1}; *m/e* 183 (parent ion) and 60 (100%).

The fraction due to **7b** (15.5-min retention time) was also collected and showed nmr (CCl_4) δ 2.15 (12 H, envelope), 1.61 (3 H, s), 1.57 (3 H, s), and 0.90 ppm (3 H, d, *J* = 7 Hz); ν_{max}^{neat} 2950, 2850, 2800, 2775, 2200, 2070, 1465, 1380, 1285, 1270, 1240, 1175, 1160, 1120, 1100, 1050, 1000, 895, 825, and 815 cm^{-1}; *m/e* 183 (parent ion) and 60 (100%).

Registry No.—**3**, 17943-81-6; **4**, 17943-82-7; **6a**, 17943-83-8; **6b**, 17943-84-9; **7a**, 17943-85-0; **7b**, 17943-86-1.

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[6] We thank Dr. C. Brandenburg for a sample and nmr spectrum of pure methyl pulegenate.

[7] (a) E. J. Eisenbraun and S. M. McElvain, *J. Amer. Chem. Soc.*, **77**, 3383 (1955); (b) R. S. Cahn, V. Prelog, and C. K. Ingold, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966).

[8] The analyses of the amines were made on the combination mass spectrometer–gas chromatography apparatus (prototype of the LKB-9000) using a 16 ft × 0.25 in. glass column packed with 120-mesh, base-washed firebrick coated with 20% Carbowax 20M. The operating conditions were column at 120°, injection port at 200°, and helium flow of 45 ml/min. The nmr spectra were obtained on a Varian A-60 spectrometer.

[9] J. Wolinsky and D. Chan, *J. Org. Chem.*, **30**, 41 (1965).

Reactions of Nitro Alcohols. III. The Reaction of 2,2,2-Trinitroethanol and Phosgene in the Presence of Some Tertiary Amines

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The esterification of 2,2,2-trinitroethanol (**1**) by acyl chlorides has been reported to proceed both with[1] and without[2] a catalyst. Since none of these methods is particularly suitable for the preparation of bis(2,2,2-trinitroethyl) carbonate (**2**) from **1** and phosgene, it was decided to use the pyridine-catalysis method developed by Kissinger, *et al.*,[3] for the esterification of 2,2-dinitropropanol by phosgene.

The desired biscarbonate was indeed obtained by

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[1] (a) M. H. Gold and K. Klager, *Tetrahedron, Suppl. 1*, **19**, 77 (1963); (b) M. B. Frankel, *J. Org. Chem.*, **27**, 331 (1962).

[2] (a) H. Feuer, H. B. Haas, and R. D. Lowery, *ibid.*, **25**, 2070 (1960); (b) N. S. Marans and R. P. Zelinsky, *J. Amer. Chem. Soc.*, **72**, 5329 (1950).

[3] L. W. Kissinger, T. M. Benzinger, H. E. Ungnade, and R. K. Rowher, *J. Org. Chem.*, **28**, 2491 (1963).

this method in a yield of 51%, using a molar ratio of pyridine to **1** of one. Since the crude product was contaminated by pyridinium trinitromethide (**3**) the use of a base weaker than pyridine seemed desirable.[4] As expected the use of 4-nitropyridine or pyridine 1-oxide in place of pyridine eliminated **3** and increased the yield of **2** to 59 and 72%, respectively. Increasing the molar ratio of pyridine to **1** was found to cause nucleophilic attack of pyridine on **1** and resulted in the formation of a new compound, **4**, with the structure $[(C_6H_5N^+{-}CH_2O{-})_2C{=}O][(NO_2)_3C^-]_2$ (see Experimental Section).

Experimental Section

All chemicals were reagent grade except the phosgene gas (99%, The Matheson Co.) and the pyridine 1-oxide (technical grade, Reilly Tar and Chemical Co.). 4-Nitropyridine was made by deoxygenating 4-nitropyridine[5] 1-oxide with PCl_3.[6] The citation in ref 4 gives the methods for preparing 2,2,2-trinitroethanol and trinitromethane. The following instruments were used: a Varian HR-100 nmr spectrometer, a Bendix time-of-flight mass spectrometer, Beckman DU, Beckman IR-4, and Cary Model 14 spectrophotometers. The Cary was used for the CH_2O equivalent weight.

Bis(2,2,2-trinitroethyl) Carbonate (**2**).—Following the method of Kissinger,[3] 10.0 g of 2,2,2-trinitroethanol (0.0552 mol) was dissolved in 6 ml of methylene chloride and 13 ml of chloroform; 4.44 g of pyridine (0.0561 mol) was added; and phosgene was bubbled into the stirred solution at 18 cc/min until 40% excess had been introduced, keeping the temperature near 27°. The reaction mixture was allowed to stand for 1 hr at ambient temperature. The crude product was precipitated by the addition of *n*-hexane and was then stirred with water for 16 hr to remove **3**,[7] collected and air dried. The yield of **2**, mp 113–115°, was 5.44 g (51%). Two recrystallizations from chloroform raised the mp to 116–117°. A mull of **2** showed the expected absorption: a C=O doublet at *1783*[8] and *1795* cm^{-1}, C—O stretching at 1235 cm^{-1},[9] asymmetric and symmetric NO_2 stretching in nonsalt *gem*-dinitro compounds at 1595 and 1345 cm^{-1}, respectively, and C—H stretching at *2882* and *2967* cm^{-1}.

Using this procedure, with a reduction of the stirring period to 1 hr, 6.96 g of 4-nitropyridine (0.0561 mol) in place of the pyridine gave 6.29 g (59%) of **2**, and 5.34 g of pyridine 1-oxide in place of the pyridine gave 7.68 g (72%) of **2**.

Anal. Calcd for $C_5H_4N_6O_{15}$: C, 15.47; H, 1.04; N, 21.65. Found: C, 15.45, 15.50; H, 1.28, 1.41; N, 21.48, 21.54.

Pyridinium Trinitromethide (**3**).—Reaction of equimolar quantities of pyridine and trinitromethane in chloroform gave a yellow precipitate which had the absorption, as a mull, expected for **3**: 1900 and 2400 cm^{-1} for $C{=}N^+H$ of the pyridinium ion, 1613 and 1640 cm^{-1} for C=C, C=N stretching, 1050 and 1203 cm^{-1} for C—H deformation, and 3060 cm^{-1} for C—H stretching of the pyridine ring, 737, 787, 870, 1128, 1260, 1410, and 1544 cm^{-1} for a carbanion of the type $Z(NO_2)_2C^-$.[10]

Anal. Calcd for $C_6H_6N_4O_6$: C, 31.31; H, 2.63; N, 24.35. Found: C, 31.49, 31.32; H, 2.77, 2.83; N, 23.91, 24.17.

Compound 4, $[(C_5H_5N^+{-}CH_2O{-})_2C{=}O][(NO_2)_3C^-]_2$**, Data. A. Preparation.**—Phosgene (0.11 mol) was bubbled at 18 cc/min into a stirred solution of 4.00 g of **1** (0.020 mol) in a mixture of 20 ml of pyridine and 0.40 ml of water, keeping the temperature of the solution near 27°. Stirring the reaction mixture into 80 ml of ice–water caused the precipitation of a yellow solid which was collected, washed with 35 ml of ice–water, and air dried. The yield was 3.85 g of **4** (64%). The analytical sample, made by recrystallizing the crude product twice from acetonitrile, decomposed over a wide range (*ca.* 130–175°).

Anal. Calcd for $C_{15}H_{14}N_8O_{15}$: C, 32.97; H, 2.58; N, 20.51. Found: C, 32.29, 32.83; H, 2.58, 2.45; N, 20.31, 20.60.

B. Spectral Measurements.—A mull of **4** showed the absorption expected: *3106*,[8] *3067*, and *3053* cm^{-1} for C—H stretching of the pyridine ring; *2924* and *2841* cm^{-1} for the methylene C—H stretching; *1773* cm^{-1} for C=O stretching of a carbonate; 1640, 1632, and 1540 cm^{-1} for C=C, C=N stretching of the pyridine ring (1-methylpyridinium iodide used for comparison); 1247 cm^{-1} for C—O stretching in a carbonate;[3,9] 778, 1054, and 1210 cm^{-1} for C—H deformation of the pyridine ring; 737, 785, 870, 1155, 1265, 1414, and 1540 cm^{-1} for a carbanion of the type $Z(NO_2)C^-$.

Strong evidence that **4** contains the quaternized pyridine ring was obtained from the pmr spectrum. τ values in parts per million and relative intensities for **4** in acetone were 0.88 (2), 1.72 (2), 1.19 (1), and −0.10 (2).[11] For comparison, 1-methylpyridinium iodide in acetone-d_6 gave 0.70 (2), 1.72 (2), and 1.27 (1) for the 2-, 3-, and 4-ring H, and 5.23 (3) for the methyl H.

C. Equivalent Weights.—Aqueous solutions of **4** were analyzed spectrophotometrically for $(NO_2)_3C^-$, using ϵ 14,418,[12] and for formaldehyde, using the method developed by Nash,[13] ϵ based on a sulfite-standardized[14] CH_2O solution and an optical density corrected for absorption by $(NO_2)_3C^-$. The amount of pyridine distilled from a basic solution of **4** was determined spectrophotometrically,[15] and the amount of gas generated by the acidification of a basic degassed solution of **4** was determined in a volume-calibrated system by the ideal gas law. Mass spectrographic analysis of the gas generated showed it to be at least 99.9% CO_2. The equivalent weights thus determined were $(NO_2)_3C^-$, 276; pyridine, 273; CH_2O, 283, CO_2, 543.

A single crystal of **4** was shown to have a density of 1.70 g/cc, a unit cell volume of 1097 Å,[3] and a unit cell molecular weight of 1123. These data required that the molecular weight of **4** be 281 or 562. A molecular weight of 562, the molecular weight required by the empirical formula $C_{15}H_{14}N_8O_{15}$ (546), in addition to the spectral data and equivalent weights justify the structure given for **4**.

Registry No.—**1**, 918-54-7; phosgene, 75-44-5; **2**, 17943-76-9; **3**, 17943-77-0; **4**, 17943-78-1.

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[4] Increasing the basicity of the solvent increases the extent to which **1** is dissociated into $(NO_2)_3C^-$ and CH_2O. See T. N. Hall, *J. Org. Chem.*, **29**, 3587 (1964).

[5] Made by nitrating pyridine 1-oxide according to E. Ochiai, *ibid.*, **18**, 534 (1953).

[6] M. Hamana and H. Yoshimira, *J. Pharm. Soc. Jap.*, **72**, 1051 (1952).

[7] Shown to be present by X-ray powder diffraction.

[8] A LiF prism assembly was used for the italicized frequencies and a NaCl prism assembly for the frequencies not italicized.

[9] J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 618 (1957).

[10] M. J. Kamlet, R. E. Oesterling, and H. A. Adolph, *ibid.*, 5838 (1965).

[11] A value of −0.10 for the methylene protons is unusual, but not unreasonable, for **4** if one considers that both oxygen and positively charged nitrogen are strongly deshielding.

[12] See footnote *c*, Table I, in citation of ref 4.

[13] T. Nash, *Biochem. J.*, **55**, 416 (1953).

[14] J. F. Walker, "Formaldehyde," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1964, p 486.

[15] H. D. LeRosen and J. T. Wiley, *Anal. Chem.*, **21**, 1175 (1949).

Conformations of *cis*- and *trans*-2,5-Diphenyl-1,4-dioxanes

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Bryan, Smedley, and Summerbell[1] obtained two compounds melting at 122 (I) and 173° (II) from the

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[1] L. A. Bryan, W. M. Smedley, and R. K. Summerbell, *J. Amer. Chem. Soc.*, **77**, 2206 (1950).