A green solid remained after evaporation of the ether filtrate and was steam distilled. Combined ether extractions of the distillate were dried over calcium chloride, filtered, and evaporated leaving a green liquid which solidified to colorless crystals, mp 63–65° (green melt) of nitrosobenzene, 3.8 g (0.0356 mol, 71% yield). In comparison with authentic material, identical ir spectra were obtained and a mixture melting point was undepressed.

Benzonitrile Oxide and the Oxime (I) of Benzanilide.—After 12 hr at room temperature a solution of 2.12 g (0.01 mol) of the oxime (I) in 30 ml of chloroform and 0.0042 mol of benzoni rile oxide[10] in ether added dropwise became pale yellow. Combined 2 *N* hydrochloric acid extracts were carefully neutralized by the addition of potassium hydroxide pellets whereupon a colorless precipitate separated and was extracted with ether. The ether extracts were dried over magnesium sulfate, filtered, and evaporated leaving a residue of 1.60 g (0.0075 mol) of recovered I, mp 135–136°.

The ether-chloroform substrate after acid extraction was dried over magnesium sulfate, filtered, and evaporated to leave a brown oil which was chromatographed over silica gel. Hexane–benzene (3:1) eluted a colorless solid, mp 112–114°, 110 mg (0.46 mmol, 21.9%) identified as diphenylfuroxan.[11]

Next benzene–chloroform (6:1) eluted 45 mg (0.22 mmol) of benzanilide, mp 160–161° (8.8% yield based on recovered I or 5.2% based on benzonitrile oxide).

Continued elution with benzene–chloroform (6:1) removed 0.60 g (1.89 mmol) of V, mp 114–116°, as colorless needles (75.8% yield based on recovered I or 45.0% based on benzonitrile oxide). A brown band remained on top of the column.

Registry No.—I, 3488-57-1; lead tetraacetate, 546-67-8; N-bromosuccinimide, 128-08-5; diethyl azodicarboxylate, 1972-28-7; N-phenylhydroxylamine, 100-65-2; benzonitrile oxide, 873-67-6.

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[10] From 0.65 g (0.0042 mol) of benzhydroxamoyl chloride and alkali according to P. Rajagopalan and B. G. Advani, *J. Org. Chem.*, **30**, 3369 (1965).

[11] A. Werner and H. Buss, *Ber.*, **27**, 2193 (1894).

Synthesis of (−)-(1*R*)-*cis*- and (+)-(1*S*)-*trans*-2-Isopropylidene-(5*R*)-N,N-trimethylcyclopentanemethylamines and Their Dideuterio Derivatives[1]

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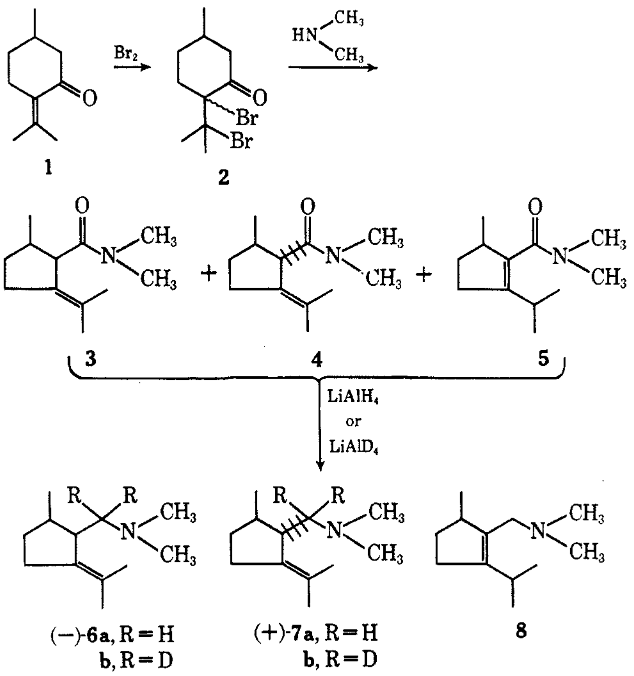
Received February 26, 1968

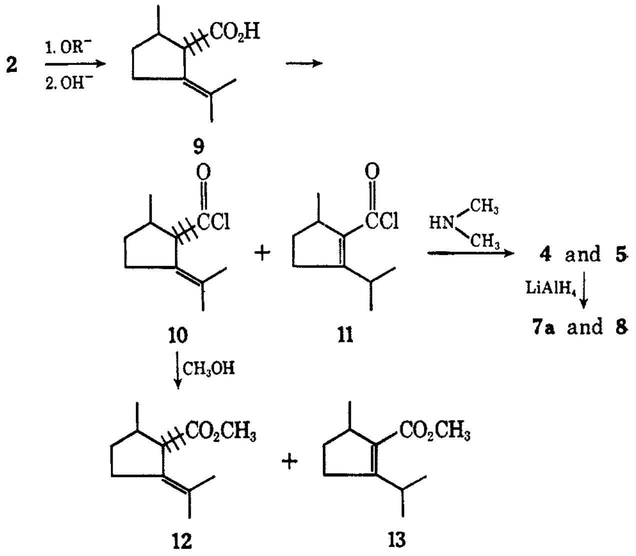
(−)-(1*R*)-*cis*-2-Isopropylidene-(5*R*)-N,N-trimethylcyclopentanemethylamine (**6a**) and (+)-(1*S*)-*trans*-2-isopropylidene-(5*R*)-N,N-trimethylcyclopentanemethylamine (**7a**) and their dideuterio derivatives (**6b** and **7b**) provided excellent model compounds for instrumental and chemical reaction comparisons with the elimination products obtained from Hofmann elimination reactions applied to α-, β-, γ-, and δ-skytanthines.[3] We now report the preparation of **6a**, **6b**, **7a**, **7b**, and **8** from (+)-pulegone (**1**) as shown in Scheme I.

Scheme I is a useful alternate route to the earlier synthesis of **7a** and **8** shown in Scheme II.[4] The major advantages in using Scheme I are a low yield of **8** and the formation of **6a** as the major product (**6a**:**7a**:**8** = 11:7:1) in three steps from **1**. In comparison, Scheme II requires five steps, and if carried out on pure **9**, does not provide **6a** in significant yield and does produce considerable unwanted **8**. In our hands, Scheme II provided **7a**:**8** = 5:1.

SCHEME I



SCHEME II



We used Scheme II to prepare authentic (+)-*trans* **7a** to serve as a reference compound in the assignment of stereochemistry and absolute configuration to (−)-**6a**, **6b**, (+)-**7a**, and **7b** from Schemes I and II. A stereochemical and absolute configuration assignment to (+)-*trans* **7a** had not been made. However, the data obtained from Schemes I and II are adequate to make this assignment. The major product of Favorskii rearrangement of **2** with aqueous alkali has been shown to be *cis*-pulegenic acid.[5] By analogy, the

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[1] Supported by the National Science Foundation Grant GB-5607.

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[3] H. Auda, H. R. Juneja, E. J. Eisenbraun, G. R. Waller, W. R. Kays, and H. H. Appel, *J. Amer. Chem. Soc.*, **89**, 2476 (1967).

[4] J. Wolinsky, B. Chollar, and M. D. Baird, *ibid.*, **84**, 2775 (1962).

[5] S. A. Achmad and G. W. K. Cavill, *Aust. J. Chem.*, **16**, 858 (1963).

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); $\nu_{\max}^{\text{film}}$ 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); $\nu_{\max}^{\text{CHCl}_3}$ 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%); $[\alpha]^{23}\mathrm{D}$ −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); $\nu_{\max}^{\text{neat}}$ 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%); $[\alpha]^{23}\mathrm{D}$ +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); $\nu_{\max}^{\text{neat}}$ 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); $\nu_{\max}^{\text{neat}}$ 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.

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[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.

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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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Received March 26, 1968

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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[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).

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