A Convenient Procedure for the Preparation of 2-Arylazirines

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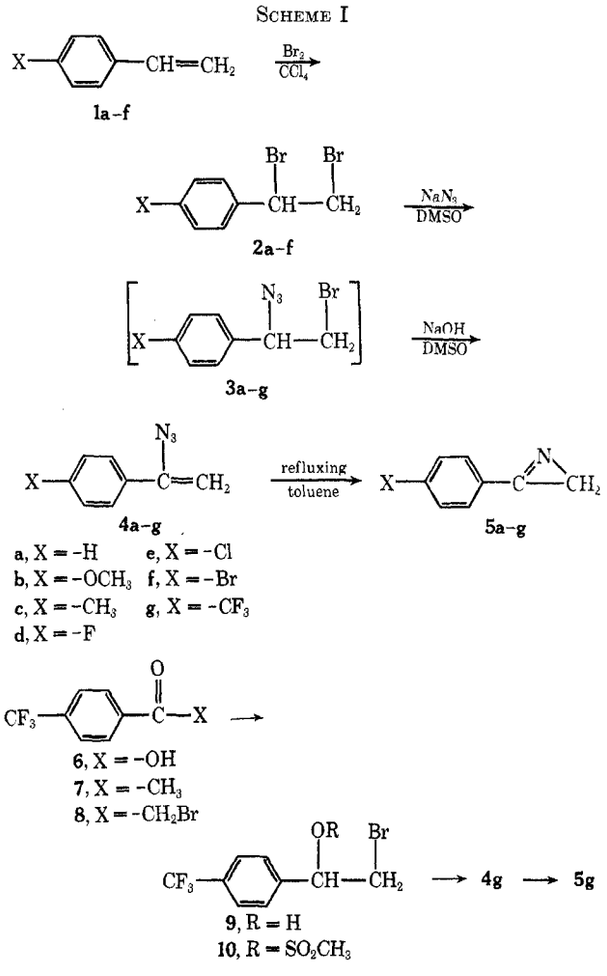
In connection with studies on the synthesis and reactions of 3-aryl-1-azabicyclobutanes,[1] a series of 2-(para-substituted)phenylazirines was required. We have found that several simple modifications of Smolinsky's original route[2] to 2-phenylazirine result in a convenient procedure for the preparation of large quantities of these substances in consistently high overall yield. Continuing interest in the reactions[1,3] and photochemistry[4] of azirines prompts us to record this procedure which has been in use in our laboratory for several years.

The original route[2] from **1a** to **5a** involves conversion of **2a** into **3a** using NaN_3 in dimethylformamide, isolation and treatment of crude **3a** with potassium *tert*-butylate in benzene to yield **4a** (after work-up and chromatography), and finally a pyrolysis of **4a** which was accomplished by passing a stream of its vapor in nitrogen through a hot tube at 350° and 20 mm to produce crude **5a** in about 60% overall yield.

Our attempts to prepare **5a** in comparable yield on a large scale failed, primarily as a result of losses incurred during the lengthy pyrolysis step due to polymerization of the vinyl azide **4a** in the reservoir. The difficulty was overcome by heating a solution of **4a** in refluxing toluene for about 1.5 hr.[5] However, the azirine **5a** obtained in this manner (~70% yield) was contaminated with about 5% of 1-bromostryrene from which it could be separated only by careful fractional distillation.

Further studies indicated that the bromostyrene impurity arose from dehydrohalogenation of **2a** which was always present in the crude bromo azide **3a** (along with small amounts of vinyl azide **4a**) when the specified *equimolar* amounts[2] of **2a** and NaN_3 were used to convert **2a** to **3a**. It could be demonstrated[6] that azide ion is a sufficiently strong base to effect dehydrohalogenation of some of the azido bromide **3a** as it is formed; consequently, some of the limited quantity of azide ion used in this step is converted to hydrazoic acid which is ineffective in converting the remaining **2a** to **3a**. It was found that, if instead a large excess of NaN_3 (>2.1 equiv) is used, then complete conversion of **2a** to **3a** and further conversion of **3a** to **4a** could be effected almost completely at room temperature without requiring the use of any other base. However, the method, as a direct route from **2a–f** to **4a–f** necessitated long reaction times for complete conversion, and thus an alternate procedure (Scheme I) was developed whereby

SCHEME I



the dibromides **2a–f** were dissolved in DMSO and treated with about 1.5 mol equiv of NaN_3 followed after 12–24 hr by addition of NaOH directly to the DMSO solutions in the form of either pellets or (preferably) 50% aqueous solution to hasten the dehydrohalogenation. Pyrolysis of the crude azidostryrenes **4a–f** in refluxing toluene afforded the azirines **5a–f** in 55–65% overall yield from **1a–f** after simple distillation.

The commercial nonavailability of *p*-trifluoromethylstyrene prompted the development of an alternate route to **5g** (**6** → **7** → **8** → **9** → **10** → [**3g**] → **4g** → **5g**). Interestingly, only **10** and **4g** were in evidence as the reaction between **10** and NaN_3 proceeded;[6] none of the intermediate azido bromide **3g** could be detected.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra (ir) were recorded on a Perkin-Elmer Model 457 spectrophotometer; nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60A instrument using TMS (δ = 0.00) as an internal standard. Basic alumina (Alcoa F-20; 100–200 mesh) was used

(1) (a) A. G. Hortmann and D. A. Robertson, *J. Amer. Chem. Soc.*, **89**, 5974 (1967); (b) J. L. Kurz, B. K. Gillard, D. A. Robertson, and A. G. Hortmann, *ibid.*, **92**, 5008 (1970).

(2) G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).

(3) G. Smolinsky and B. I. Feuer, *ibid.*, **31**, 1423 (1966); S. Sato, H. Kato, and M. Ohta, *Bull. Chem. Soc. Jap.*, **40**, 1014 (1967); N. J. Leonard and B. Zwanenburg, *J. Amer. Chem. Soc.*, **89**, 4456 (1967); A. Hassner and F. W. Fowler, *ibid.*, **90**, 2869 (1968); J. Ciabattoni and M. Cabell, Jr., *ibid.*, **93**, 1482 (1971).

(4) A. Padwa and J. Smolanoff, *ibid.*, **93**, 548 (1971); B. Singh and E. F. Ullman, *ibid.*, **88**, 1844 (1966); F. P. Woerner, H. Reimlinger, and D. R. Arnold, *Angew. Chem., Int. Ed. Engl.*, **7**, 130 (1968).

(5) Formation of azirines upon pyrolysis of vinyl azides in refluxing aprotic solvents has also been observed by others; see F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967); K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Lett.*, 3499 (1968); F. P. Woerner and H. Reimlinger, *Chem. Ber.*, **103**, 1908 (1970).

(6) The reactions were studied by withdrawal of aliquots from the reaction mixtures and assay of the organic products by nmr spectroscopy after isolation *via* a normal work-up procedure.

for column chromatography. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

2-Phenyl-1-azirine (5a).—Bromine (80 g, 0.50 mol) in 100 ml of CCl_4 was added slowly to a stirred and cooled (15–20°) solution of styrene (52.1 g, 0.50 mol) in 400 ml of CCl_4. After the addition was complete, the CCl_4 was removed *in vacuo* and the remaining residue of crystalline 1,2-dibromostyrene (**2a**) was dissolved in 750 ml of dimethyl sulfoxide (Fisher, certified). The resulting solution was placed in a three-necked flask fitted with a heavy-duty mechanical stirrer and a gas inlet tube. A slow stream of N_2 was passed through the apparatus. With the aid of an ice bath, the solution was maintained at 15–20° during the addition of 49 g (0.75 mol) of sodium azide and for 45 min afterward. The mixture became thick with precipitated azido bromide **3a** and was stirred for a further 13 hr at 24–26°.[7] After cooling to 12° the reaction mixture was treated with a solution of 20.0 g (0.50 mol) of NaOH in 20 ml of H_2O. The temperature rose to 19°. Stirring was continued at ambient temperature (24–26°) for 24 hr. The mixture was poured into 2 l. of 2% aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 (technical). The combined extracts were washed with H_2O, filtered through cotton (premoistened with CH_2Cl_2), and evaporated to yield crude 1-azidostyrene **4a** as a red oil: nmr (CCl_4) δ 4.82 (d, 1, J = 2.1 Hz), 5.27 (d, 1, J = 2.1 Hz), and 7.1–7.6 (m, 5).[8] The oil was diluted with 200 ml of petroleum ether (bp 63–69°) and passed through a column of alumina (200 g) using an additional 800 ml of the same solvent as an eluent. The eluate was evaporated and the residual pale yellow oil was dissolved in toluene (1.2 l., reagent grade). The solution was refluxed until the evolution of nitrogen ceased (1.5 hr). Removal of the solvent and distillation of the crude product, using a 6-in. Vigreux column, afforded 36.7 g (63%) of 2-phenyl-1-azirine (**5a**), bp 58.0–58.5° (2.8 mm). The azirine was ~97–98% pure, as determined by comparison of the integrated area of the peaks in the phenyl region (215 units) *vs.* the area of the 2 H singlet at δ 1.61 (84 units).

2-(4′-Methoxyphenyl)-1-azirine (5b).—Azirine **5b** was prepared essentially as described for **5a**, starting with dibromide **2b** prepared from 16.78 g (0.125 mol) of 4-methoxystyrene (**1b**) (Borden Chemical Co.) and reducing the quantities of other reagents accordingly. A solution of **2b** in 180 ml of DMSO was stirred for 20 hr after the addition of NaN_3 (12.35 g, 0.188 mol) and for 7.5 hr after the addition of NaOH [6.75 ml, 0.125 mol, 1:1 (w/w) solution in H_2O]; the usual work-up procedure (including filtration of crude **4b** through 50 g of alumina) was followed by refluxing a solution of **4b** in toluene (600 ml) for 1.5 hr. Distillation afforded 9.93 g (54%) of **5b** as a pale yellow liquid, bp 101–102.5° (2.8 mm), which readily solidified. An nmr assay indicated that the distilled product was of ≥97% purity.

A sample of **5b** obtained earlier using the procedure described by Smolinsky for the preparation of **5a** exhibited mp 29–31°; ir (CCl_4) 1730, 1610, 1500, 1450, 1440, 1320, 1300, 1280, 1240, 1160, 1030, 980, and 830 cm^{-1}; nmr (CCl_4) δ 1.64 (s, 2), 3.87 (s, 3), and 6.9–8.0 (m, 4).

Anal. Calcd for C_9H_9NO: C, 73.45; H, 6.16; N, 9.62. Found: C, 73.40; H, 6.08; N, 9.70.

2-(4′-Methylphenyl)-1-azirine (5c).—Azirine **5c** was prepared essentially as described for **5a**, starting with dibromide **2c** obtained from 29.5 g (0.25 mol) of 4-methylstyrene (**2a**) (Borden Chemical Co.). A solution of **2c** in 350 ml of DMSO was stirred for 21 hr after the addition of 24.7 g (0.38 mol) of NaN_3 and for 60 hr after addition of 10 g (0.25 mol) of NaOH (pellets). The usual work-up procedure followed by filtration through alumina, pyrolysis, and distillation, as described for **5a**, afforded 18.7 g (57%) of **5c**: bp 74.8–76.3° (5 mm); nmr (CCl_4) δ 1.60 (s, 2), 2.37 (s, 3), and an A_2B_2 pattern centered at δ 7.25 and 7.70. An nmr assay indicated that the distilled product was of ~96% purity.

2-(4′-Fluorophenyl)-1-azirine (5d).—Azirine **5d** was prepared as described for **5a**, starting with 24.4 g (0.20 mol) of 4-fluorostyrene (Sigma Chemical Co.) and reducing the quantities of other reagents accordingly to yield 16.9 g (63%) of distilled azirine **5d** of >95% purity (nmr assay) after two distillations: bp 63–66° (5.5 mm); nmr (CCl_4) δ 1.63 (s, 2), 7.13 (~t, 2, J ~ 8.3 Hz), and 7.80 (~dd, 2, J ~ 5.5, 8.3 Hz).

2-(4′-Chlorophenyl)-1-azirine (5e).—Azirine **5e** was prepared as described for **5c**, starting with 34.5 g (0.25 mol) of 4-chlorostyrene (Borden Chemical Co.) and yielding 22.7 g (60%) of distilled product, bp 86–88° (5.5 mm), which was 87% pure by nmr assay. Sublimation at 40° (0.3 mm) afforded crystalline material (mp 42.5–44.5°) of ≥95% purity: nmr (CCl_4) δ 1.65 (s, 2) and 7.3–7.8 (sym A_2B_2 pattern, 4).

2-(4′-Bromophenyl)-1-azirine (5f).—Azirine **5f** was prepared on an 0.05-mol scale essentially as described for **5c**. The product (≥98% pure) was isolated in 54% yield by preparative sublimation: mp 72–73.7°; nmr (CCl_4) δ 1.66 (s, 2) and 7.61 (s, 4). A thrice-sublimed sample exhibited mp 73–74.5°.

4′-Trifluoromethylacetophenone (7).—A 300-ml three-necked flask containing a magnetic stirring bar was charged with 150 ml of anhydrous ether and 10.0 g (0.0525 mol) of 4-trifluoromethylbenzoic acid (**6**) (Pierce Chemical Co.). The solution was placed under N_2 and methyllithium [50 ml of a 2.1 M solution in ether (Alfa Inorganics)] was added dropwise at 0–5° over a period of 45 min. The reaction solution was poured onto ice and washed with H_2O until the washes were neutral, dried (Na_2SO_4), and evaporated to yield 9.6 g (99%) of crude ketone **7**. Chromatography on alumina using $CHCl_3$–petroleum ether (bp 63–69°) (1:4 by volume) as eluent afforded pure 4′-trifluoromethylacetophenone (**7**): mp 30–33° [lit. bp 79–80° (8 mm);[9] bp 81–84° (8–9 mm)[10]]; nmr (CCl_4) 2.56 (s, 3) and 7.55–8.14 ppm (m, 4); ir (CCl_4) 1695, 850, 720, and 610 cm^{-1}.

2-Bromo-1-(4′-trifluoromethylphenyl)ethanol (9).—Crude 2-bromo-4′-trifluoromethylacetophenone (**8**)[10] (7.5 g, 0.028 mol; contained about 2 mol % each of the corresponding dibrominated and unbrominated ketone by nmr analysis) was dissolved in 100 ml of CH_3OH. The solution was cooled in an ice bath and H_2O was added to the point of cloudiness (about 10–20 ml). A solution of 0.28 g (0.0074 mol) of sodium borohydride in ethanol (the minimum volume that would give complete solution) was added dropwise with stirring and continued cooling. Ten minutes after the addition was complete, the solution was concentrated to half volume *in vacuo*. The concentrated solution was diluted with 250 ml of H_2O and extracted with CH_2Cl_2. The extracts were dried (Na_2SO_4) and evaporated *in vacuo* leaving 7.4 g (98%) of crude 2-bromo-1-(4′-trifluoromethylphenyl)ethanol (**9**) as a mixture of diastereomers: nmr (CCl_4) 3.35–3.95 (m, 3), 4.70–5.05 (m, 1), and 7.2–7.7 ppm (m, 4); ir (neat) 3400, 1620, 1480, 1420, 1325, 1110–1180, 1070, 1025, 850, and 680 cm^{-1}.

2-(4′-Trifluoromethylphenyl)-1-azirine (5g).—Crude 2-bromo-1-(4′-trifluoromethylphenyl)ethanol (**9**) (20.6 g, 0.077 mol) was dissolved in 80 ml of anhydrous pyridine and 7 ml (0.090 mol) of methanesulfonyl chloride was added. The solution was cooled (ice bath) for 1 hr and allowed to stand at ambient temperature for 3 hr. The reaction solution was diluted with 150 ml of benzene and washed successively with water, 10% HCl, H_2O, 5% Na_2CO_3, and H_2O. The benzene solution was dried (Na_2SO_4) and concentrated *in vacuo* leaving 21.3 g (68%) of a mixture of crude 2-bromo-1-(4′-trifluoromethylphenyl)ethanol methanesulfonates (**10**): nmr (CCl_4) 2.92 (m, 0.72), 3.55–3.73 (m, 0.35), 5.60–5.90 (m, 0.25), and 7.4–7.9 ppm (m, 1.00).[11] The crude mixture of methanesulfonates (21.3 g, 0.061 mol) was dissolved in 100 ml of *N*,*N*-dimethylformamide and 4.5 g (0.069 mol) of sodium azide was added. The solution was stirred for 26 hr at ambient temperature. The reaction solution was diluted with H_2O (500 ml) and extracted with petroleum ether (bp 35–40°) until the extracts were colorless. The combined extracts were dried (Na_2SO_4) and evaporated *in vacuo* leaving 16 g of red oil. The nmr spectrum of the crude product indicated that the reaction was incomplete. The crude product was again dissolved in *N*,*N*-dimethylformamide (80 ml) containing 0.9 g (0.014 mol) of sodium azide. After 18 hr the reaction was worked up as before yielding 13.0 g (100%) of crude 1-azido-4′-trifluoromethylstyrene (**4g**). The crude product was chromatographed on alumina with petroleum ether (bp 63–69°) as eluent yielding 10.5 g (63%) of 95% pure 1-azido-4′-trifluoromethylstyrene (**4g**): bp 40–45° (1.8 mm); nmr (CCl_4) 5.01 (d, 1, J = 2.5 Hz), 5.47 (d, 1, J = 2.5 Hz), and 7.41 ppm (s, 4); ir (CCl_4)

(7) An aliquot withdrawn from the mixture at this time contained **3a** and **4a** in a ratio 1.0:1.0; none of the starting dibromide **2a** could be detected. The azido bromide **3a** exhibits nmr δ (CCl_4) 3.45 (d, 2, J = 6.5 Hz), 4.67 (t, 1, J = 6.5 Hz), and 7.3 ppm (s, 5).

(8) The description of the nmr spectrum of **4a** as "two single sharp lines at τ 5.68 and 4.68 . . . " in ref 2 is apparently in error.

(9) E. T. McBee, S. Resconich, L. R. Belohlav, and H. P. Braendlin, *J. Org. Chem.*, **28**, 3579 (1963).

(10) W. T. Caldwell and G. C. Schweiker, *J. Amer. Chem. Soc.*, **75**, 5884 (1953).

(11) Since the product is impure, the integrated peak areas do not simplify to a ratio of whole numbers of protons.

2200, 2140, 2110, 1615, 1410, 1320, 1295, 1175, 1140, 1120, 1095, 1070, 1020, 910, 850, and 620 cm^{-1}. The impurity in the azidostyrene was assumed to be another 1-substituted styrene: nmr (CCl_4) 5.60 (d, 1, J = 2.1 Hz) and 5.80 ppm (d, 1, J = 2.1 Hz).

The partially purified 1-azido-4′-trifluoromethylstyrene (**4g**) (4.6 g, 0.0216 mol) was refluxed in toluene (300 ml) until the evolution of nitrogen ceased (1 hr). The toluene was evaporated *in vacuo* and the residue was distilled yielding 2.8 g (70%) of 2-(4′-trifluoromethylphenyl)-1-azirine (**5g**): bp 42–44° (1.2 mm); nmr (CCl_4) 1.74 (s, 2) and 7.6–8.2 ppm (m, 4); ir (CCl_4) 1750, 1735, 1620, 1420, 1325, 1180, 1140, 1110, 1070, 1020, 995, 850, and 600 cm^{-1}.

Anal. Calcd for $C_9H_6NF_3$: C, 58.30; H, 3.26; N, 7.55. Found: C, 58.12; H, 3.20; N, 7.33.

The azirine **5g** also contained about 4 mol % of the same impurity (1-substituted styrene) which was present in the azidostyrene **4g**. The impurity could not be removed by repeated recrystallization of the azirine **5g** from petroleum ether at −40°.

Registry No.—**3a**, 29847-04-9; **4a**, 16717-64-9; **4g**, 32654-71-0; **5a**, 7654-06-0; **5b**, 32687-32-4; **5c**, 32687-33-5; **5d**, 32687-34-6; **5e**, 32687-35-7; **5f**, 17631-26-4; **5g**, 32687-37-9; **7**, 709-63-7; **9**, 32687-39-1; **10**, 32687-40-4.

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Stereochemistry of Tropane Quaternizations[1]

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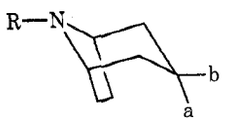
In 1964, MacGillavry and Fodor[3] reported the results of an X-ray diffraction study of an *N*-ethyltropinium bromide which indicated that the major products from reactions of *N*-ethylnortropine (**1b**) and tropine (**1a**) with methyl and ethyl iodide, respectively,



1, a = OH; b = H **a**, R = CH_3
2, a = H; b = OH **b**, R = C_2H_5
3, a, b = O **c**, R = $PhCH_2$
4, a = b = H

are formed by equatorial attack. Three years later, a group at Sheffield[4] questioned MacGillavry and Fodor's results and suggested that these major quaternization products, as well as the main products from other quaternizations of tropanes and 3-substituted tropanes,[5] are formed by axial attack. The following year, Fodor, Medina, and Mandava[6] reported that empirical correlations of nmr chemical shifts of exo α hydrogens indicated that the main products from reactions of tropine and pseudotropine (**2a**) with ethyl iodide are formed by different stereochemical pathways, namely, equatorial attack on tropine and axial attack on pseudotropine.[7] In that same year, two of us[11a] and Fodor and Mandava[11b] reported that hydrolysis of the lactone formed from pseudotropine bromoacetate gave the same *N*-carboxymethylpseudotropinium bromide as is formed by hydrolysis of the main product from quaternization of pseudotropine (**2a**) with ethyl bromoacetate. Because the lactone was formed by inter- rather than intramolecular reaction,[8] these results[11] led to the *erroneous conclusions* (1) that the *N*-carboxymethylpseudotropinium bromides were formed by axial attack on nitrogen and, therefore, (2) that the structural assignments originally made by Fodor, Koczka, and Lestyán[5] to the ethoxycarbonylmethylation products were incorrect.

Results described here and in a recent paper by Fodor and coworkers[8] establish conclusively that the predominant pathway for ethylation as well as methylation (or deuteriomethylation), alkoxycarbonylmethylation, and other quaternizations of tropine (**1a**), pseudotropine (**2a**), tropinone (**3a**), and several related compounds is by equatorial attack.

The major product from pseudotropine (**2a**) and ethyl bromide was obtained in >98% purity (nmr) by two crystallizations from methanol of the 74:26 mixture of diastereomers with δ_{NCH_3} 3.12 and 2.98 ppm, respectively.[12] The crystals are orthorhombic, space group *Pbca*, with unit cell dimensions a = 11.93, b = 14.15, c = 13.32 ± 0.004 Å, d_{obsd} (flotation) 1.45, d_{calcd} 1.45, Z = 8. A crystal was ground to a sphere of diameter 0.31 mm, and intensities were measured on a Picker automatic diffractometer using Ni-filtered Cu Kα radiation (λ 1.5418) and the θ–2θ scan mode to a value of 2θ = 133°. Out of 1952 measured reflections, 1648 were considered to be observed. The data were corrected for absorption effects (μR = 0.784) in addition to the usual data treatment. The position of the bromine atom was found from a three-dimensional Patterson map. A Fourier summation phased on the bromine atom immediately revealed the

(1) Supported in part by Grant CA-05528 from the National Cancer Institute, U. S. Public Health Service.

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(3) C. H. MacGillavry and G. Fodor, *J. Chem. Soc.*, 597 (1964); see also P. Benci, C. H. Stam, and C. H. MacGillavry, *Tetrahedron Lett.*, 243 (1971).

(4) D. R. Brown, R. Lygo, J. McKenna, J. M. McKenna, and B. G. Hutley, *J. Chem. Soc. B*, 1184 (1967).

(5) G. Fodor, K. Koczka, and J. Lestyán, *Magy. Kem. Foly.*, **59**, 242 (1953); *J. Chem. Soc.*, 1411 (1956).

(6) G. Fodor, J. D. Medina, and N. Mandava, *Chem. Commun.*, 581 (1968).

(7) This incorrect tentative conclusion concerning the stereochemistry of quanternization of pseudotropine with ethyl iodide resulted from misassignment of the band due to the hydroxyl group to the equatorial methyl group. In the solvent used for examination of the nmr spectra of the diastereomeric *N*-ethylpseudotropinium salts, the two *N*-methyl bands are coincident. Our results and those of Fodor, *et al.*,[8] confirm the conclusion reached by Closs[9] in 1959 that exo α hydrogens of N substituents in the equatorial configuration of tropane and 3-substituted tropane salts are more shielded than when in the axial configuration. The opposite is generally the case for piperidine salts.[10]

(8) G. Fodor, R. V. Chastain, Jr., D. Frehel, M. J. Cooper, N. Mandava, and E. L. Gooden, *J. Amer. Chem. Soc.*, **93**, 403 (1971). We thank Professor Fodor for informing us of their results prior to publication.

(9) G. L. Closs, *ibid.*, **81**, 5456 (1959).

(10) For examples, see (a) T. M. Moynehan, K. Schofield, R. A. Y. Jones, and A. R. Katritzky, *J. Chem. Soc.*, 218 (1962); (b) H. O. House and C. G. Pitt, *J. Org. Chem.*, **31**, 1062 (1966); (c) A. T. Bottini and M. K. O'Rell, *Tetrahedron Lett.*, 429 (1967).

(11) (a) C. C. Thut and A. T. Bottini, *J. Amer. Chem. Soc.*, **90**, 4752 (1968); (b) N. Mandava and G. Fodor, Abstracts, 51st Annual Conference of the Chemical Institute of Canada, Vancouver, B. C., June 1968, p 56.

(12) Both samples had mp >300°. The melting point is a poor criterion of purity for salts of **1a** and **1b**. *Cf.* S. P. Findlay, *J. Amer. Chem. Soc.*, **75**, 3204 (1953); G. Fodor, *Acad. Chim. Acad. Sci. Hung.*, **5**, 379 (1955). See also K. Zeile and W. Schulz, *Chem. Ber.*, **88**, 1078 (1955).