N-**Benzenesulfonyl-*N*-carboxymethyl-2,4-dimethyl-6-nitroaniline** (II) was prepared by the method of Adams and Gordon[13] as modified by Adams and Brower.[14]

Calorimetry.—The calorimeter used was similar to that already described by Arnett.[2] The errors reported with the heats of solution are 95% confidence limits. The relatively large errors are due to the extremely small temperature change resulting from the solution of 100 mg of sample in 175 ml of solvent. It was not practical to work with a larger sample size because of the slow rates of solution. In some solvents it was not possible to measure heats of solution because of the slow rates of solution.

Kinetics.—Resolved compound (0.1 g) was dissolved in 25 ml of solvent. Aliquots (2 ml) were placed in 12 13 × 100 mm Pyrex test tubes which were then flushed with nitrogen, sealed off, and placed in a constant-temperature bath. Temperature values known to within 0.1° were obtained with an N. B. S. calibrated thermometer. The 12 ampoules were removed in pairs over the course of the reaction and quenched by immersion in ice–water. After quenching the tubes were opened and the contents were placed in a polarimeter tube. A Rudolph photoelectric polarimeter (Model 520-M) equipped with a sodium vapor lamp was used to measure the optical rotation. Rates were measured at three different temperatures, usually 40, 60, and 80°. A least-squares program written by A. Ault of Cornell College was used to calculate the best values of $\Delta H^{\pm}$ and $\Delta S^{\pm}$ from the kinetic data. The errors listed are 95% confidence limits.

(13) R. Adams and J. R. Gordon, *J. Amer. Chem. Soc.*, **72**, 2458 (1950).
(14) R. Adams and K. R. Brower, *J. Amer. Chem. Soc.*, **78**, 663 (1956).

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Notes

Synthesis of Trineopentylamine

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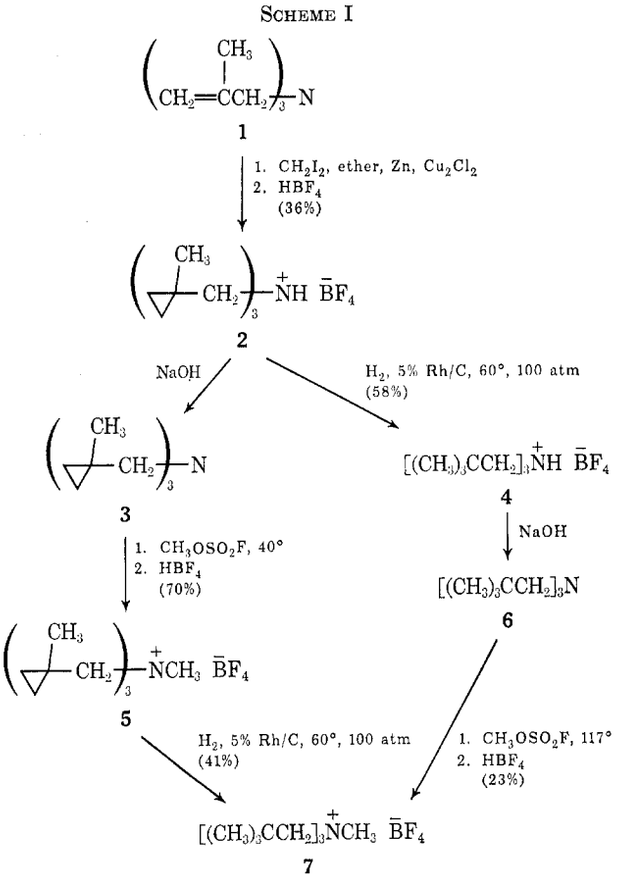
In attempts to prepare base-resistant quaternary ammonium ions, with tetraneopentylammonium ion as a fanciful goal, I have synthesized two new highly crowded tertiary amines, tris(1-methylcyclopropylmethyl)amine (**3**) and trineopentylamine (**6**), directly from tris(2-methylallyl)amine (**1**). The synthetic methods and results are summarized in Scheme I. Little effort has been made to optimize the yields.

Several features of the synthesis may be of general interest. (1) A modified Simmons–Smith reaction,[1] the triple cyclopropanation of **1**, proceeds readily in the presence of a tertiary amine in 36% yield. (2) Hydrogenations of hindered cyclopropanes **2** and **5** proceed under milder conditions with rhodium than with the previously used[2] palladium catalyst. With 5% palladium on carbon, hydrogenations of **2** and **5** at 100 atm required temperatures of 130–150° and gave poorer yields of less pure **4** and **7**. As with other 1,1-dialkylcyclopropanes, catalytic hydrogenation of **2** and **5** occurs exclusively at the unsubstituted cyclopropane bond.[3] (3) Tertiary amines and tetraalkylammonium ions were handled whenever possible as their tetrafluoroborate salts, which are in general more stable and easier to crystallize than the free amines or the halide salts.[4] Trifluoromethanesulfonates may serve as well as tetrafluoroborates for this purpose.[5]

SCHEME I



The highly crowded nature of amines **3** and **6** is demonstrated by their resistance to alkylation. Only methyl fluorosulfonate, at 40 and 117° respectively, gave reasonable yields of their corresponding methyl-

(1) R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, **35**, 2057 (1970).
(2) A. L. Schultz, *J. Org. Chem.*, **36**, 383 (1971).
(3) C. W. Woodworth, V. Buss, and P. v. R. Schleyer, *Chem. Commun.*, 569 (1968).
(4) H. O. House, E. Feng, and N. P. Peet, *J. Org. Chem.*, **36**, 2371 (1971).
(5) K. Rousseau, G. C. Farrington, and D. Dolphin, *J. Org. Chem.*, **37**, 3968 (1972).

trialkylammonium salts, **5** and **7**. Attempts to methylate **3** and **6** with methyl iodide, methyl *p*-toluenesulfonate, and trimethyloxonium tetrafluoroborate all failed or gave much lower yields. All attempts to alkylate **3** and **6** with groups larger than methyl failed. Some of these experiments are reported briefly in the microfilm edition.

Experimental Section[6]

Materials.—Tris(2-methylallyl)amine (**1**) was prepared from 2-methylallyl chloride (Eastman) and aqueous ammonia,[7] bp 84–88° at 15 Torr (lit.[8] bp 83–85° at 15 Torr). Methyl fluorosulfonate (Aldrich) was distilled and stored over CaH_2 at −20°. Technical 2-methoxyethanol was distilled. *p*-Toluenesulfonyl chloride was purified.[9] All other chemicals were reagent grade and were used as obtained without further purification.

Tris(1-methylcyclopropylmethyl)ammonium Tetrafluoroborate (2).—A mixture of 58.8 g of zinc dust, 81.3 g of Cu_2Cl_2, and 150 ml of anhydrous ethyl ether was stirred for 30 min at reflux. A solution of 17.9 g of **1** and 10 ml of ethyl ether was added slowly, and 102.8 g of CH_2I_2 (Eastman) was added dropwise over 45 min. After 21 hr at reflux the mixture was cooled and poured into a mixture of 800 ml of saturated aqueous NH_4Cl and ice. The layers were separated, and the aqueous suspension was washed with 4 × 200 ml portions of ether. The combined ether extract was dried over $MgSO_4$ and distilled through a 30-cm Vigreux column until 150 ml of yellow solution remained. To the ethereal solution 9.7 g of 48–50% aqueous HBF_4 was added slowly with stirring. The resulting precipitate was collected, air dried, and crystallized from methanol–ethyl acetate to give 11.0 g (35.6%) of **2**:[10] white needles; mp 227–228.5° dec (gas evolution); pmr ($CDCl_3$) δ 0.63 (12 H, AA′BB′), 1.24 (9 H, s), 3.28 (6 H, d, J = 6 Hz). The pmr spectrum showed a trace of 2-methylallyl groups (<3% of the area of 1-methylcyclopropylmethyl groups) and showed no sign of ^+N–H. A second crop was obtained from acetone–ethyl acetate: 2.1 g, mp 224.5–226° dec.

Tris(1-methylcyclopropylmethyl)amine (3).—A 1.19-g sample of **2** was shaken with 6 ml of 1 *M* NaOH and extracted with 10 ml of 30–60° petroleum ether. The organic solution was dried over K_2CO_3 and distilled on a steam bath through a 15-cm Vigreux column. Cooling of the residual liquid formed white solid **3**:[11] 0.85 g; mp 35–41°; pmr (CCl_4) δ 0.25 (12 H, br s), 1.16 (9 H, s), 2.23 (6 H, s). The pmr spectrum also showed a trace of residual petroleum ether, but this slightly impure material was used for subsequent experiments because further attempted removal of petroleum ether by evacuation and by passing a stream of N_2 over the solid resulted in much loss of **3** by sublimation. A sample sublimed at 25° and 1 atm for 7 days from the bottom to the upper walls of a sealed flask had mp 46–46.5°.

Methyltris(1-methylcyclopropylmethyl)ammonium Tetrafluoroborate (5).—A solution of 24.4 mmol of **3** and 46.5 mmol of methyl fluorosulfonate in 10 ml of CH_2Cl_2 was refluxed for 4.7 hr under N_2. The resulting dark CH_2Cl_2 solution was poured into 50 ml of water, extracted, washed with 50 ml of 1 *M* aqueous NaOH (which changed its color to beige), and washed with 4 × 25 ml portions of 3 *M* aqueous HBF_4. The combined aqueous wash solutions were extracted with 10 ml of CH_2Cl_2, and the combined CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated to a beige solid. Crystallization from methanol–ethyl acetate gave 5.48 g (70%) of **5**:[10] white needles; mp 188.5–189.5° dec (gas evolution); pmr ($CDCl_3$) δ 0.70 (12 H, AA′BB′), 1.33 (9 H, s), 3.40 (6 H, d, J = 6 Hz), 3.47 (3 H, s). A second crop was obtained: 0.76 g, mp 186–187° dec.

Trineopentylammonium Tetrafluoroborate (4).—To a solution of 5.05 g of **2** in 175 ml of 2-methoxyethanol in a glass liner was added 4.99 g of 5% rhodium on carbon (Engelhard Industries). The mixture was rocked for 48 hr at 60° and 100 atm of H_2. The catalyst was removed by gravity filtration and washed with methanol. The filtrate was evaporated to ~10 ml. Addition of 50 ml of ethyl ether and filtration of the resulting mixture gave crude white solid, 4.3 g, mp 191–199°, which was a mixture of two compounds having *tert*-butyl peaks in the pmr. A slurry of the crude solid in 15 ml of CH_2Cl_2 was filtered to give a solution of **4** and an insoluble solid which was not identified. Evaporation of the filtrate gave white solid, 3.51 g, mp 215–220°, which was crystallized three times from ethyl acetate to give **4**:[10] 2.97 g (58%); mp 221–224°; pmr (CH_2Cl_2) δ 1.15 (27 H, s), 3.34 (6 H, d, J = 5 Hz).

Trineopentylamine (6).—By the method described for conversion of **2** to **3**, 0.97 g of **4** was converted to liquid **6** contaminated with a trace of petroleum ether. Pure samples of **6**[10] for elemental analysis and spectra were collected by preparative glpc on a 10 ft × 0.25 in. column of 20% Apiezon L on 60–80 Chromosorb W at 190°: pmr (CH_2Cl_2) δ 0.93 (27 H, s), 2.21 (6 H, s); mass spectrum (Varian-MAT CH-5, 70 ev) *m/e* 227 (M^+), 212, 170 (base peak), 100, 71.

Methyltrineopentylammonium Tetrafluoroborate (7). A.—A mixture of 6.24 g of **5**, 5.9 g of 5% rhodium on carbon, and 250 ml of 2-methoxyethanol in a glass liner was rocked for 24 hr at 60° and 100 atm of H_2. The catalyst was removed by gravity filtration and washed with methanol. The filtrate was evaporated to a solid, which was crystallized from methanol–ethyl acetate to give **7**:[10] 2.62 g (41%); fine white flakes; mp 237–239°; pmr ($CDCl_3$) δ 1.25 (27 H, s), 3.32 (3 H, s), 3.44 (6 H, s).

B.—A solution of 0.474 g of **6**, 1.17 g of methyl fluorosulfonate, and 1.0 ml of CH_2Cl_2 was sealed in a heavy-wall glass tube and heated 2.5 hr at 117°. The contents of the tube were poured into 6 ml of 1 *M* aqueous HBF_4 and extracted with 6 × 1 ml portions of CH_2Cl_2. The combined CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated to a white paste, which was extracted with 3 ml of 1 *M* aqueous NaOH and 3 × 2 ml portions of 30–60° petroleum ether. The combined petroleum ether solution contained much unreacted **6** according to its pmr spectrum. The white solid which remained suspended in the aqueous phase during the petroleum ether extractions was isolated by filtration (0.29 g) and crystallized from methanol–ethyl acetate to give **7**, 0.144 g (23%), white needles, mp 234–237° dec, whose pmr spectrum was identical with that of **7** prepared by method A.

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Supplementary Material Available.—A supplementary experimental section will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-3614-73.

(6) All temperatures including melting points and boiling points are uncorrected. Pmr spectra were obtained on Varian A-60A and HA-100 spectrometers. Microanalyses were performed by J. Nemeth and associates.

(7) G. B. Butler and B. M. Benjamin, *J. Chem. Educ.*, **28**, 191 (1951).

(8) M. Tamele, C. J. Ott, K. E. Marple, and G. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

(9) S. W. Pelletier, *Chem. Ind. (London)*, 1034 (1953).

(10) Satisfactory elemental analysis for C, H, and N (±0.3%) was obtained for this compound. The data appears in a supplementary table of this paper in the microfilm edition.

(11) No elemental analysis was obtained for this compound.

Synthesis of 2-Methylene-4-thiazolidinones

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In recent synthetic work it was anticipated that the base-catalyzed condensation of α-mercapto esters with ethyl cyanoacetate would give 2-amino-3-carbethoxy-4-