allene it is 84 Hz.[8] In various fluorocyclopropanes $J_{\mathrm{HF}}^{\mathrm{gem}} \approx 60$ Hz,[9] and in fluoromethanes $J_{\mathrm{HF}} \approx 45$ Hz.[7] The large value of $J_{\mathrm{HF}}^{\mathrm{gem}}$ in 1 suggests an unusually large CFH bond angle.

The gas-phase infrared spectrum of 1 had the following principal features (band center in cm^{-1}, intensity, band shape): 3161, w, A; 3032, m, C; 1622, m, A; 1327, m, ?; 1200, s, A; 1060, m, B; 956, vs, A; 876, m, B; 660, s, C; and 456, m, A. The band at 3161 cm^{-1} and the less distinct feature to somewhat lower frequency are due to stretching of the CH bonds attached to the double bond. The 3032-cm^{-1} frequency is due to stretching of the methylene CH bond. The band at 1622 cm^{-1} is largely C=C stretching, and the intense band at 956 cm^{-1} is largely CF stretching. Thus, the infrared spectrum is also consistent with 1 being 3-fluorocyclopropene. In a separate paper we will present a complete vibrational assignment of 1 and its d_3 isotopomer based on Raman as well as infrared spectra.

We attempted to prepare the cyclopropenyl cation for Raman spectroscopy by reaction of 1 with BF_3 in liquid SO_2 at low temperature.[1] However, this reaction could not be controlled. In the first attempt the mixture glowed red and charred upon partial thawing. In another attempt the depth of color gave overwhelming fluorescence in Raman spectroscopy. However, a controlled reaction of 1 with BF_3 was achieved on a CsI crystal at low temperature to give $C_3H_3^+BF_4^-$ for use in infrared spectroscopy.[1] Frequencies of bands due to the $C_3H_3^+$ ion were in satisfactory agreement with the ones reported previously for the spectra of crystalline $C_3H_3^+SbCl_6^-$ and $C_3H_3^+AlCl_4^-$ in hydrocarbon mulls.[5]

Experimental Section

Warning: *Breslow and co-workers have noted the hazardous nature of chlorocyclopropenes.*[5] *Fluorocyclopropene is likely to be more hazardous due to its greater instability and the well-known toxicity of compounds containing monofluoro-substituted carbon atoms. We handled these materials other than the perchlorocyclopropene starting material in small amounts in enclosed systems.*

3-Chlorocyclopropene (2). Perchlorocyclopropene (3 g) (Aldrich Chemical Co.) was reduced to 2 with 17 g of tributyltin hydride (Alfa Products, Morton Thiokol, Inc.).[5] It is essential to remove residual diethyl ether from the tributyltin hydride by distillation in vacuo at room temperature before using this material in the reaction. 2 was separated from the reaction products by gas chromatography[5] and passed through a column packed with 2 cm of 3-Å molecular sieves, which had been dried at 100 °C under vacuum for 12 h. Passage through the molecular sieves removed water and reduced the amount of hydrogen chloride, which had formed during chromatography. Partial vaporization during slow warmup of the sample removed impurity acetylene and some more of the residual HCl. 2 was confirmed by its proton NMR spectrum (7.5_5 ppm, intensity 2; 4.2_5 ppm, intensity 1 at room temperature), although the reported splitting patterns in CCl_4 solution were not observed in $CFCl_3$ solution, even at temperatures as low as -90 °C.[10] Principal infrared bands of 2 in the gas phase were (band center in cm^{-1}, intensity, band shape): 3170, w, A.; 3139, w, B; 3028, m, C; 1631, s, A; 1265, s, A; 1179, m, A; 1140, s, A; 1033, s, B; 912, m, C; 867, m, B; 839, m, B; 713, vs, A; 590, s, C; and 348, s, B. Agreement with the frequencies of the reported spectrum of 2 in solution in CCl_4 in solution was only fair,[5] even when the frequencies of the liquid-phase Raman spectrum were compared.

3-Fluorocyclopropene (1). About 1 mmol of 2 as a gas was passed through a 2-cm length of a 1.3 g:1 g mixture of silver difluoride (Alfa Products) and potassium fluoride to give 1. The potassium fluoride was material that had been dried by heating at 175 °C under vacuum for 3 h. Glass wool plugs (20 cm) held the loosely packed solid mixture in place. The column was packed in a dry bag and then heated to 130 °C under vacuum for 12 h. During the heating some lighter color developed in the dark brown AgF_2. Typically, to achieve nearly quantitative conversion a sample was passed six times through the column by allowing material to vaporize in one tube while being condensed at liquid nitrogen temperature in another.

For successful gas-phase infrared spectroscopy in a demountable 10-cm minigas cell (Wilmad Glass Co.), it was essential to scrub all of the interior glass surfaces with a detergent and to use Krytox grease. Krytox, a Dupont product, is a polymer of perfluoropropylene oxide that is thickened with Teflon powder. Silicone grease, which is thickened with silica powder, is not a good grease for prolonged contact with 1. However, silicone grease, which darkens upon contact with 1, suffices for the vacuum system.

A good vacuum system was used for all of the sample handling after the synthesis of 2. The detector for the gas chromatography system was a thermal conductivity cell, which may have caused the HCl formation.

Spectroscopy. Infrared spectra were recorded on a Perkin-Elmer Model 580B spectrometer. NMR spectra were obtained on a Perkin-Elmer Model R12B instrument. NMR samples were prepared in sealed tubes with Me_4Si as proton reference and with $CFCl_3$ as the solvent and ^{19}F reference.

Acknowledgment. This research was supported by a Cottrell grant from Research Corporation and by National Science Foundation College Research Instrumentation grants (PRM-7911202 and PRM-8115415). The synthesis, characterization, and exploration of dehydrohalogenation of *cis*- and *trans*-1-chloro-2-fluorocyclopropane were done by Kenneth Felz and David S. Phillips. We are grateful for their contributions.

Registry No. 1, 72507-66-5; 2, 17336-56-0; $C_3H_3^+BF_4^-$, 12294-37-0; *cis*-1-chloro-2-fluorocyclopropane, 91444-06-3; *trans*-1-chloro-2-fluorocyclopropane, 91444-07-4.

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[8] As measured by us on a sample obtained by flash vacuum pyrolysis of *cis*-1-chloro-2-fluorocyclopropane. This material had the same infrared spectrum as was reported for 1-fluoroallene by Durig, J. R.; Li, Y. S.; Witt, J. D.; Zens, A. P.; Ellis, P. D. *Spectrochim. Acta* 1977, *33A*, 529–544.

[9] Agopovich, J. W.; Craig, N. C.; Gillies, C. W., unpublished.

[10] **Note added in proof**: The expected splitting pattern of a doublet and a triplet has now been observed for a sample, low in HCl impurity, in CCl_4 solution at -30 °C.

Studies on the Flash Vacuum Pyrolysis and Anomalous Course of Alkali Metal Promoted Reductions of 8-Methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-11-one

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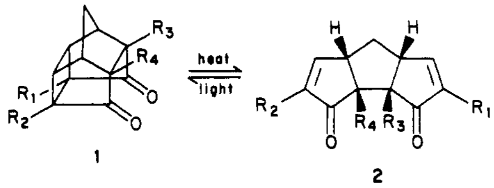
Thermal [2 + 2] cycloreversions of substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones 1 have been



studied extensively as a simple, general method for the synthesis of tricyclo[6.3.0.0^{2,6}]undecanes (i.e., linearly fused

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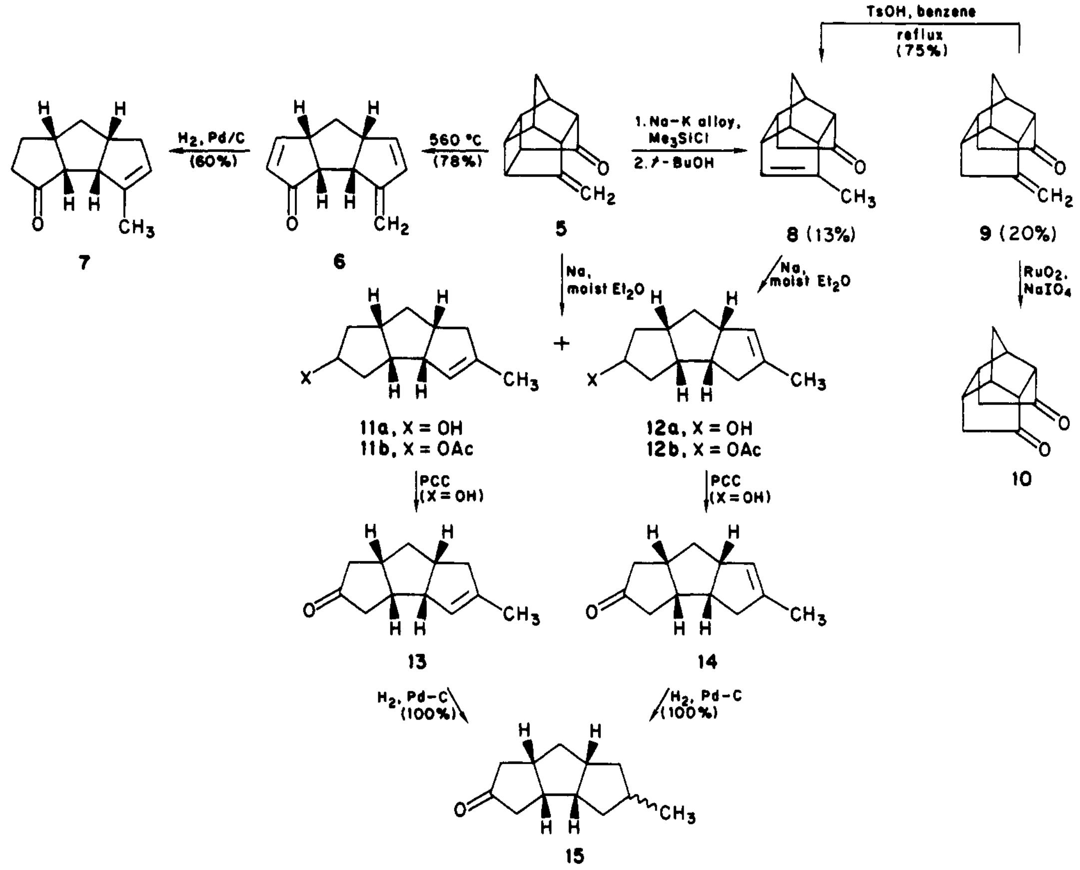
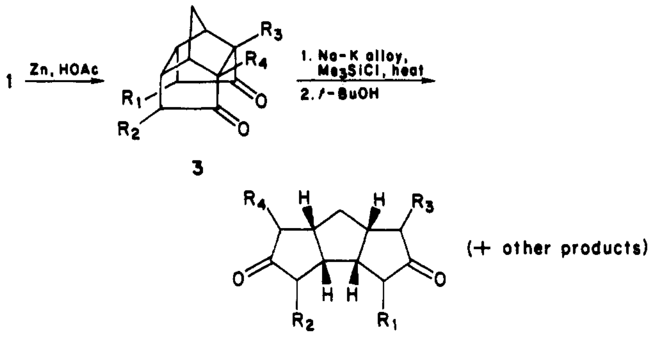
Scheme I



triquinanes, 2).[1-8] Recently, *cis,syn,cis*-tricyclo[6.3.0.$0^{2,6}$]undecane-4,10-diones 4 have been prepared from



1 via sodium–potassium alloy reduction of a related tetracyclic intermediate, 3.[9] We now report the results of a study of the flash vacuum pyrolysis and alkali metal-promoted reduction of a related system, 5,[10] (see Scheme I).

As expected,[1-8] flash vacuum pyrolysis of 5 at 560 °C afforded the corresponding unsymmetrical triquinane 6 (78%). Interestingly, catalytic hydrogenation of 6 with 2 equiv of hydrogen resulted in 1,4-reduction of the conjugated diene system, affording 7 as the sole reduction product (60%).

By analogy with the behavior of 3,[9] reduction of 5 with excess sodium–potassium alloy in the presence of trimethylchlorosilane (Me_3SiCl) followed by quenching with *t*-butyl alcohol was expected to afford *cis,syn,cis*-10-methylenetricyclo[6.3.0.$0^{2,6}$]undecan-4-one, among other products. Instead of the expected result, two tetracyclic products, 8 and 9, were formed as products of this reaction (13% and 20% yield, respectively). The structure of 8 was established via analysis of its infrared, proton NMR, and ^{13}C NMR spectra. The structure of 9 was confirmed via its successful oxidation with $NaIO_4$–RuO_2, which afforded the corresponding tetracycloundecanedione 10, a known[11] compound. Interestingly, 9 could be isomerized to 8 in 75% yield by refluxing with *p*-toluenesulfonic acid in benzene solution for 2 h.

As part of our study of the chemistry of 5, we investigated its reaction with sodium in moist ether. The results of earlier studies on nonconjugated polycyclic enones suggested that this reaction might be capable of providing a route to substituted homopentaprismanes[12] via transannualr reductive cyclization of 5.[13,14] Instead, a reductive ring opening occurred, producing an intractible 1:1 mixture

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of tricyclic alcohols **11a** and **12a** (50%). Interestingly, reduction of **8** with sodium in moist ether also afforded a 1:1 mixture of alcohols **11a** and **12a** (see Experimental Section). The mixture of alcohols was acylated with acetic anhydride–pyridine; the resulting mixture of acetate esters **11b** and **12b** (71%) could be separated conveniently by careful column chromatography on silver nitrate impregnated silica gel. Acetates **11b** and **12b** were found to be unstable toward atmospheric oxygen and moisture.

Base-promoted hydrolysis of **11b** and **12b** afforded the isomerically pure alcohols (**11a** and **12a**, respectively, 89% yield). The stereochemistry of the C–OH bond in **11a** and in **12a** is not known. Oxidation of **11a** and **12a** with pyridinium chlorochromate (PCC) afforded the corresponding ketone in each case (**13** and **14**, respectively, 75% yield). Catalytic hydrogenation of either **13** or **14** afforded the same saturated tricyclic ketone, **15**, in essentially quantitative yield.[15]

A potentially important feature of this study is our ability to place vinylic methyl groups at different positions in a triquinane framework (as in, e.g., **7** and **13**) by elaboration of a common pentacyclic precursor, **5**. It is hoped that such relatively facile and regiospecific conversions will find application to the synthesis of polycyclopentanoid natural products.

Experimental Section

Melting points and boiling points are uncorrected. Proton NMR spectra (100 MHz) and ^{13}C NMR spectra (25 MHz) were obtained with a JEOL FX 100 NMR spectrometer. In all cases, signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer Model 297 infrared spectrophotometer. Ultraviolet spectra were recorded on a Shimadzu Model 200S ultraviolet spectrophotometer. Mass spectra were obtained with an AEI Model MS-50 mass spectrometer which was operated at 70 eV. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and at The National Chemical Laboratory, Pune, India.

Flash Vacuum Pyrolysis of 5. The flash thermolysis of **5** was performed in a quartz tube in the manner which has been described in an earlier publication.[2] The column was equilibrated to 560 ± 10 °C (internal column temperature), and the substrate (**5**) was slowly sublimed through the column by heating at 90–100 °C. The condensate was deposited in the delivery tube and was purified subsequently by bulb-to-bulb distillation; pure **6** was thereby obtained in 78% yield as a colorless oil, bp 105 °C (0.5 mm). Compound **6** was found to be extremely sensitive to light and to atmospheric oxygen and moisture: ^{1}H NMR ($CDCl_3$) δ 1.8–2.3 (m, 2 H), 3.1 (m, 1 H), 3.48 (m, 3 H), 4.9 (s, 1 H), 5.04 (s, 1 H), 5.8 (m, 3 H), 7.3 (dd, J_1 = 6 Hz, J_2 = 3 Hz, 1 H), ^{13}C NMR ($CDCl_3$) δ 32.40 (t), 49.84 (d), 50.43 (d), 53.95 (d), 55.42 (d), 109.08 (t), 132.86 (d), 134.21 (d), 142.25 (d), 153.12 (s), 166.90 (d), 209.65 (s); IR (neat) 3090 (w), 3050 (w), 2950 (m), 2800 (w), 1710 (s), 1640 (w), 1590 (w), 1450 (w), 1340 (m), 1320 (w), 1180 (m), 1160 (m), 870 (m), 775 (m) cm^{-1}; UV λ_{max}^{MeOH} 224 (ϵ 16 500); mass spectrum (70 eV), *m/e* (relative intensity) 172.0885 (molecular ion, 100.00), 160.1250 ($C_{12}H_{16}$, 15.65), 143.0860 ($C_{11}H_{11}$, 15.40), 129.0703 ($C_{10}H_9$, 54.26), 128.0627 ($C_{10}H_8$, 24.19), 117.0700 (C_9H_9, 15.74), 116.0620 (C_9H_8, 14.20), 115.0547 (C_9H_7, 18.17), 96.0573 (C_6H_8O, 22.01), 93.0700 (C_7H_9, 31.08), 91.0548 (C_7H_7, 37.44), 80.0627 (C_6H_8, 36.86), 79.0547 (C_6H_7, 26.19), 78.0472 (C_6H_6, 24.75), 77.0396 (C_6H_5, 15.03), 66.0479 (C_5H_6, 15.71), 65.0403 (C_5H_5, 13.13).

Anal. Calcd for $C_{12}H_{12}O$: M_r 172.0888. Found (high-resolution mass spectrometry): M_r 172.0885.

Hydrogenation of 6. A solution of **6** (200 mg, 1.16 mmol) in ethyl acetate (5 mL) was hydrogenated over 10% palladized charcoal catalyst (20 mg) at a hydrogen pressure of 12 psig for 1 h. The catalyst was removed by filtration, and the filtrate was concentrated in vacuo. The oily residue was purified by column chromatography on silica gel (80% benzene–petroleum ether eluent) to afford **7** as a colorless oil. Distillation of this oil under reduced pressure afforded pure **7**: bp 120 °C (0.5 mm); ^{1}H NMR ($CDCl_3$) δ 1.0 (m, 1 H), 1.3 (m, 2 H), 1.8 (s, 3 H), 2.0–3.0 (m, 8 H), 3.28 (m, 1 H), 5.2 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.75 (q), 25.72 (t), 37.90 (t), 39.55 (t), 39.78 (t), 44.53 (d), 44.76 (d), 56.54 (d), 58.59 (d), 125.04 (d), 140.62 (s), 219.60 (s); IR (neat) 3030 (w), 2980 (s), 1730 (s), 1440 (m), 1400 (w), 1360 (w), 1260 (m), 1140 (m), 790 (w) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensitivity) 176.1202 (molecular ion, 26.03), 96.0575 (C_6H_8O, 100.00), 93.0703 (C_7H_9, 13.08), 91.0549 (C_7H_7, 11.78), 83.0499 (C_5H_7O, 18.04), 81.0703 (C_6H_9, 17.77), 79.0549 (C_6H_7, 17.48), 77.0394 (C_6H_5, 10.07).

Anal. Calcd for $C_{12}H_{16}O$: M_r 176.1202. Found (high-resolution mass spectrometry): M_r 176.1202.

Reduction of 5 with Na–K Alloy. To a flame-dried 250-mL, three-necked flask equipped with a water condenser and a nitrogen inlet were added freshly cut sodium metal (330 mg, 0.014 mol), freshly cut potassium metal (1.67 g, 0.042 mol), and dry toluene (100 mL). The resulting mixture was heated and stirred vigorously until a fine dispersion was formed. After being cooled to room temperature, a solution of **5** (1.0 g, 5.8 mmol) in dry toluene (15 mL) and chlorotrimethylsilane (10 mL, excess) were added sequentially under nitrogen to the reaction flask, and the reaction mixture was refluxed under nitrogen for 1.5 h. The reaction mixture was then cooled and filtered through Celite under a nitrogen blanket into a receiving flask which contained *t*-butyl alcohol (10 mL). The filtrate was then concentrated in vacuo, affording a viscous oil. This oil was purified via column chromatography on silver nitrate impregnated silica gel (25 g, 5% ethyl acetate–benzene eluent). Compound **8** was the first product to be eluted under these conditions (130 mg, 13%); recrystallization from petroleum ether afforded analytically pure **8** as a colorless microcrystalline solid: mp 48–49 °C; ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 3 H), 1.64 (s, 2 H), 2.0 (s, 2 H), 2.4 (m, 4 H), 2.7 (s, 1 H), 2.92 (s, 1 H), 5.4 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.32 (q), 34.00 (t), 39.74 (d), 42.15 (t), 46.67 (d), 51.60 (d), 54.60 (d), 55.42 (d), 59.60 (d), 130.04 (d), 147.65 (s), 219.92 (s); IR (KBr) 3040 (w), 2950 (s), 2860 (w), 1735 (s), 1440 (m), 1400 (m), 1240 (w), 1130 (m), 830 (m) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 174.1044 (molecular ion, 100.00), 159.0809 ($C_{11}H_{11}O$, 7.29), 146.1094 ($C_{11}H_{14}$, 11.17), 131.0860 ($C_{10}H_{11}$, 41.92), 117.0702 (C_9H_9, 17.50), 105.0705 (C_8H_9, 8.15), 93.0703 (C_7H_9, 57.08), 92.0363 (C_7H_8, 29.33), 91.0549 (C_7H_7, 32.47), 80.0628 (C_6H_8, 23.80), 77.0396 (C_6H_5, 16.70).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10; M_r 174.1045. Found: C, 83.05; H, 8.37; M_r 172.1044 (high-resolution mass spectrometry).

Continued gradient elution of the chromatography column with 10% ethyl acetate-benzene eluent afforded **9** (200 mg, 20%). An analytically pure sample of **9** was obtained via repeated recrystallization from dichloromethane–petroleum ether mixed solvent. Compound **9** was thereby obtained as a colorless microcrystalline solid: mp 75–76 °C; ^{1}H NMR ($CDCl_3$) δ 1.6–1.88 (m, 2 H), 2.0–3.0 (m, 10 H), 4.95 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.76 (t), 34.16 (d), 38.92 (t), 39.98 (t), 42.03 (d), 46.61 (d), 49.84 (d), 53.72 (d), 59.06 (d), 109.30 (t), 151.94 (s), 220.40 (s); IR (KBr) 3060 (w), 2950 (m), 2790 (w), 1735 (s), 1660 (m), 1450 (m), 1405 (w), 1305 (w), 1175 (m), 1135 (m), 900 (m), 880 (s) cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 83.00; H, 8.19.

Compound **9** could be isomerized to **8** by the following procedure. To a solution of **9** (40 mg, 0.23 mmol) in dry benzene (10 mL) was added a catalytic amount of *p*-toluenesulfonic acid, and the resulting solution was refluxed for 2 h. The resulting mixture was cooled to room temperature, diluted with benzene, and then washed with saturated aqueous sodium bicarbonate solution. The organic layer was dried (anhydrous Na_2SO_4) and filtered, and the filtrate was concentrated to afford a colorless oil. The oil was purified by column chromatography on silica gel (5 g, benzene eluent). Pure **8** (30 mg, 75%), which was identical in all respects with the material isolated via column chromatography of the product of sodium–potassium alloy reduction of **5** (described

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[15] The position of the carbon–carbon double bonds in **11** and **12** was not determined in the present study. Therefore, the structures corresponding to **11** and **12** may be either as indicated in the scheme or the structural assignments may be reversed. However, our study establishes that **13** and **14** are derived from **11a** and **12a**, respectively, and it establishes that catalytic hydrogenation of both **13** and **14** afford the same reduction product, **15**.

above), was thereby obtained. Continued elution of the chromatography column afforded unreacted **9** (5 mg).

Tetracyclo$[6.3.0.0^{4,11}.0^{5,9}]$undecane-2,7-dione (10).[16] Compound **5** (10 mg, 0.057 mmol) was dissolved in a mixture of acetonitrile (0.8 mL), carbon tetrachloride (0.8 mL), and water (1.2 mL). To this mixture was added sequentially sodium metaperiodate (140 mg, 0.65 mmol) and ruthenium oxide (2.0 mg, 0.015 mmol), and the resulting mixture was stirred vigorously at room temperature for 1.5 h. Dichloromethane (10 mL) was added to the reaction mixture, and the organic layer was then separated from the aqueous layer. The aqueous layer was extracted with dichloromethane (5 mL). The combined organic layers were dried (anhydrous Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo, affording a black residue. The crude product was dissolved in ether and passed rapidly through a Celite pad. The ethereal filtrate was concentrated in vacuo, and the residue was recrystallized from toluene, thereby affording **10** as a colorless microcrystalline solid, mp 255 °C dec (lit.[11] mp 255 °C dec). The infrared spectrum of **10** thus produced was identical in all respects with that which has been resported previously.[11]

Reduction of 5 with Sodium in Moist Ether. Diethyl ether and water were shaken together in a separatory funnel and the (moist) ether layer was withdrawn. Compound **5** (1.0 g, 5.8 mmol) was dissolved in the moist ether (100 mL), and finely cut pieces of sodium metal (4.0 g, 0.17 mol) were added gradually during 1 h. The resulting mixture was stirred at room temperature for 8 h with occassional addition of a few drops of water. At the conclusion of the reaction, unreacted sodium metal was removed by filtration, and the organic layer was separated from the aqueous phase. The organic layer was washed successively with water and with saturated brine solution, dried (anhydrous Na_2SO_4), and filtered, and the filtrate was concentrated in vacuo to afford a viscous oil. The oil was placed on a chromatography column composed of silver nitrate impregnated silica gel (25 g) and eluted with 60% benzene–petroleum ether mixed solvent. The first material to be eluted was recovered **5** (50 mg, 5%). Continued elution afforded a mixture of alcohols **11a** and **12a** (500 mg, 500%) which could not be separated further chromatographically. Separation of these materials was achieved by first converting them to a mixture of the corresponding acetate esters **11b** and **12b**, which could be separated conveniently by column chromatography on silver nitrate impregnated silica gel; subsequent base-promoted hydrolysis of the individual isomers **11b** and **12b** afforded the corresponding isomerically pure alcohols **11a** and **12a**, respectively (vide infra). **11a**: ^1H NMR ($CDCl_3$) δ 1.0–1.5 (m, 2 H), 1.6 (s, disappeared upon addition of D_2O to the NMR tube, 1 H), 1.7 (s, 3 H), 1.8–3.0 (m, 9 H), 3.2 (m, 1 H), 4.24 (m, 1 H), 5.16 (s, 1 H); IR (neat) 3350 (s), 3040 (w), 2940 (s), 1650 (w), 1440 (m), 1340 (w), 1080 (m), 1040 (m), 810 (w) cm^{-1}. Compound **11a** was further characterized by conversion to the corresponding ketone (**13**, vide infra). **12a**: ^1H NMR ($CDCl_3$) δ 1.0–1.5 (m, 4 H), 1.6 (s, disappeared upon addition of D_2O to the NMR tube, 1 H), 1.7 (s, 3 H), 1.8–2.6 (m, 6 H), 2.8 (m, 1 H), 3.1 (m, 1 H), 4.28 (m, 1 H), 5.3 (s, 1 H); IR (neat) 3350 (s), 3050 (w) 2940 (s), 1660 (w), 1440 (m), 1340 (w), 1080 (m), 810 (m) cm^{-1}. Compound **12a** was further characterized by conversion to the corresponding ketone (**14**, vide infra).

Reduction of 8 with Sodium in Moist Ether. Compound **8** (40 mg, 0.23 mmol) was dissolved in moist ether (20 mL), and finely cut pieces of sodium metal (200 mg, 0.0087 mol) were added gradually during 0.5 h. The resulting mixture was stirred at room temperature for 3 h with occassional additional of a few drops of water. At the conclusion of the reaction, unreacted sodium metal was removed by filtration, and the organic layer was separated from the aqueous phase. The organic layer was washed successively with water and with saturated brine solution, dried (anhydrous Na_2SO_4), and filtered, and the filtrate was concentrated in vacuo to afford a viscous oil. The oil was chromatographed in silica gel (10 g, benzene eluent). After a brief forerun consisting of minor impurities, a 1:1 mixture of alcohols **11a** and **12a** was collected (18 mg, 45%) whose ^1H NMR and IR spectra were identical in all respects with the corresponding spectra of the mixture of products (**11a** and **12a**) obtained via sodium–moist ether reduction of **5** (vide supra).

Synthesis of Acetate Esters 11b and 12b. To a mixture of alcohols **11a** and **12a** (500 mg, 2.81 mmol) in pyridine (5 mL) was added acetic anhydride (1 mL, excess), and the resulting mixture was heated at 100 °C for 2.5 h. The reaction mixture was then cooled to room temperature, diluted with ice water, and extracted with ether. The organic layer was washed successively with dilute hydrochlorid acid solution, saturated aqueous sodium bicarbonate solution and saturated brine solution, dried (anhydrous Na_2SO_4), and filtered, and the filtrate was concentrated in vacuo to afford a mixture of acetate esters **11b** and **12b** (500 mg, 90%). The product mixture was separated by column chromatography on silver nitrate impregnated silica gel (25 g, 10% benzene–petroleum ether eluent). Compound **11b** was the first product to elute under these conditions. A pure sample of **11b** (220 mg, 35.6%) was obtained via bulb-to-bulb distillation under reduced pressure: bp 130 °C (0.5 mm); ^1H NMR ($CDCl_3$) δ 1.0–1.6 (m, 4 H), 1.7 (s, 3 H), 2.0 (s, 4 H), 2.1–2.8 (m, 6 H), 3.2 (m, 1 H), 5.14 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.73 (q), 21.07 (q), 33.76 (t), 36.52 (d), 41.39 (t), 42.56 (d), 43.56 (t), 44.33 (t), 45.21 (d), 53.25 (d), 77.85 (d), 125.9 (d), 138.4 (s), 170.6 (s); IR (neat) 3020 (w), 2930 (s), 1730 (s), 1640 (w), 1440 (m), 1360 (m), 1340 (m), 1240 (s), 1020 (m), 890 (w), 830 (w) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 220.1461 (molecular ion, 12.19), 178.1357 ($C_{12}H_{18}O$, 14.50), 160.1250 ($C_{12}H_{16}$, 43.39), 145.1018 ($C_{11}H_{13}$, 10.05), 131.0860 ($C_{10}H_{11}$, 17.38), 119.0860 (C_9H_{11}, 20.22), 105.0705 (C_8H_9, 9.05), 94.0775 (C_7H_{10}, 38.00), 93.0702 (C_7H_9, 75.52), 80.0624 (C_6H_8, 100.00), 67.0554 (C_5H_7, 12.04).

Anal. Calcd for $C_{14}H_{20}O_2$: M_r 220.1464. Found (high-resolution mass spectrometry): M_r 220.1461.

Continued elution of the chromatography column with 10% benzene–petroleum ether mixed solvent afforded **12b** (220 mg, 35.6%). A pure sample of **12b** was obtained via bulb-to-bulb distillation under reduced pressure: bp 130 °C (0.5 mm); ^1H NMR ($CDCl_3$) δ 1.0–1.6 (m, 2 H), 1.68 (s, 3 H), 2.0 (s, 4 H), 2.9–3.1 (m, 9 H), 4.8–5.3 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.38 (q), 21.31 (q), 33.52 (t), 37.34 (t), 39.04 (d), 39.57 (t), 44.15 (t), 44.73 (d), 46.56 (d), 53.43 (d), 77.14 (d), 129.9 (d), 138.5 (s), 170.8 (s); IR (neat) 3020 (w), 2950 (s), 2850 (w), 1735 (s), 1630 (w), 1440 (m), 1370 (m), 1350 (m), 1240 (vs), 1020 (m), 970 (w), 900 (w), 810 (w) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 220.1462 (molecular ion, 13.47), 178.1356 ($C_{12}H_{19}O$, 19.36), 160.1250 ($C_{12}H_{16}$, 49.21), 145.1016 ($C_{11}H_{13}$, 15.60), 131.0858 ($C_{10}H_{11}$, 22.86), 119.0859 (C_9H_{11}, 12.77), 117.0704 (C_9H_9, 12.63), 105.0706 (C_8H_9, 14.17), 93.0702 (C_7H_9, 84.64), 92.0620 (C_7H_8, 18.48), 91.0548 (C_7H_7, 28.99), 80.0624 (C_6H_8, 100.00), 67.0554 (C_5H_7, 12.92).

Anal. Calcd for $C_{14}H_{20}O_2$: M_r 220.1464. Found (high-resolution mass spectrometry): M_r 220.1462.

Hydrolysis of Acetate Esters 11b and 12b. To a solution of the acetate ester (**11b** or **12b**, 140 mg, 0.64 mmol) in methanol (5 mL) was added finely powdered potassium hydroxide pellets (140 mg, 2.5 mmol). The resulting mixture was stirred at room temperature for 2 h. At the conclusion of the reaction, the mixture was poured into water and extracted with ether. The organic layer was washed with saturated brine solution and then dried (anhydrous Na_2SO_4) and filtered, and the filtrate was concentrated to afford the corresponding alcohol (**11a** or **12a**, respectively, 100 mg, 89%); the crude product was purified via bulb-to-bulb distillation under reduced pressure, bp 130 °C (0.5 mm).

Pyridinium Chlorochromate Oxidation of Alcohols 11a and 12a. To a magnetically stirred suspension of pyridinium chlorochromate (125 mg, 0.57 mmol) in dichloromethane (10 mL) was added a solution of the alcohol (**11a** or **12a**, 100 mg, 0.56 mmol) in dichloromethane (5 mL). The resulting mixture was stirred vigorously at room temperature for 4 h and the filtered by being passed through a short chromatography column packed with silica gel (10 g). The eluate was concentrated in vacuo, affording the corresponding ketone (**13** or **14**, respectively, 75 mg, 75%). In each case, the product ketone was purified via bulb-to-bulb distillation under reduced pressure, bp 130 °C (0.5 mm). **13**: ^1H NMR ($CDCl_3$) δ 0.8–1.4 (m, 2 H), 1.7 (s, 3 H), 1.8–3.0 (m, 9 H), 3.34 (m, 1 H), 5.1 (s, 1 H); ^{13}C NMR δ 16.73 (q), 39.98 (t), 40.09 (t), 42.56 (d), 43.15 (t), 43.15 (t), 43.56 (d), 43.85 (d), 54.25 (d), 125.1 (d), 140.7 (s), 221.1 (s); IR (neat) 3040 (w), 2940 (s), 1735 (s), 1650 (w), 1450 (m), 1405 (m), 1140 (m) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 176.0 (molecular ion, 21.1), 95

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[16] Carlsen, P. H.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936.

(23.8), 94 (26.0), 93 (61.4), 80 (25.0), 79 (27.1), 31 (100.0), 29 (50.2).

Anal. Calcd for $C_{12}H_{16}O$: M_r 176.1202. Found (high-resolution mass spectrometry): M_r 176.1201.

The following spectra data were obtained for **14**: ^1H NMR ($CDCl_3$) δ 0.8–1.3 (m, 2 H), 1.68 (s, 3 H), 1.8–3.0 (m, 9 H), 3.3 (m, 1 H), 5.28 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.26 (q), 37.45 (d), 39.28 (t), 39.57 (t), 42.39 (d), 44.44 (t), 44.62 (d), 45.67 (t), 52.72 (d), 129.8 (d), 139.0 (s), 220.6 (s); IR (neat) 3040 (w), 2940 (s), 1735 (s), 1650 (w), 1440 (m), 1410 (m), 1140 (m), 1020 (m), 820 (m) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 176 (molecular ion, 43.6), 147 (23.4), 106 (50.2), 95 (84.3), 94 (38.9), 93 (56.9), 91 (49.4), 82 (21.7), 80 (31.8), 79 (44.4), 77 (28.7), 41 (37.9), 39 (26.2), 31 (100.0), 29 (59.5).

Anal. Calcd for $C_{12}H_{16}O$: M_r 176.1202. Found (high-resolution mass spectrometry): M_r 176.1205.

Hydrogenation of 13 and 14. A solution of either **13** or **14** (10 mg, 0.56 mmol) in ethyl acetate (2 mL) was hydrogenated over 10% palladized charcoal catalyst (2 mg) at a hydrogen pressure of 12 psig for 40 min. The reaction mixture was filtered to remove catalyst, and the filtrate was concentrated in vacuo to afford **15** (10 mg, 100%) which was purified via bulb-to-bulb distillation under reduced pressure: bp 130 °C (0.5 mm); ^1H NMR ($CDCl_3$) δ 1.2 (d, 3 H, J = 6 Hz), 1.6–3.0 (m, 15 H); IR (neat) 2945 (s), 2870 (w), 1740 (s), 1460 (m), 1410 (m), 1380 (w), 1160 (m) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 178 (molecular ion, 17.4), 95 (27.3), 82 (48.6), 81 (24.9), 41 (20.3), 31 (100.0), 29 (55.9).

Anal. Calcd for $C_{12}H_{18}O$: M_r 178.1358. Found (high-resolution mass spectrometry): M_r 178.1358.

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Registry No. **5**, 87830-51-1; **6**, 91632-94-9; **7**, 91632-95-0; **8**, 91632-96-1; **9**, 91632-97-2; **10**, 25282-60-4; **11a**, 91632-98-3; **11b**, 91632-99-4; **12a**, 91633-00-0; **12b**, 91633-01-1; **13**, 91633-02-2; **14**, 91633-03-3; **15**, 91633-04-4.

Desiccant Efficiency in Solvent and Reagent Drying.[1,2] 9. A Reassessment of Calcium Sulfate as a Drying Agent

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Anhydrous calcium sulfate (Drierite) has been applied to the problem of solvent desiccation for over 50 years[3] and has received general endorsement[4] as an efficient and generally applicable low cost drying agent. However, many of the extravagent claims[5] made for the efficiency of this product are based on very early results,[3,6] and in our recent studies,[7–10] where calcium sulfate has been examined alongside other desiccants it has been found to have only very modest efficiency. Thus Drierite approaches the foot of the "drying league" in a recent[9] evaluation of 12 desiccants for the drying of wet ether extracts and is similarly placed in studies of the drying of benzene, dioxane, acetonitrile,[7] various dipolar aprotic solvents[8], and amines.[10] However, in our earliest studies[7,8,10] in an attempt to attain uniform and hence comparable experimental conditions desiccants were activated at 300–320 °C for 15 h before use. Since it is possible that such activation conditions may have had a deleterious effect on the activity of the calcium sulfate[11] and in view of the widespread utilization of this product it appeared pertinent to reevaluate its desiccant potential. This paper thus centers on a reappraisal of Drierite as a desiccant for solvent drying with particular attention being payed to the effect of activation temperature. Comparison with two other important desiccants, viz., calcium chloride and molecular sieves, is also made.

Table I. Effect of Calcium Sulfate Activation Temperature on Its Efficiency in Dioxane Drying[a]

activation temperature, °C	residual solvent water content, ppm			
	1 h	6 h	24 h	72 h
no activation	1700	1140	540	240
100	1820	1460	1190	1130
150	2000	1230	485	240
200	1690	1080	500	250
225	1950	1200	535	250
250	1770	1290	660	310
300	1930	1430	970	970

[a] Initial water content = 2500 ppm; desiccant loading = 5% w/v; desiccant samples activated overnight (16 h).

Table II. Effect of Calcium Chloride Activation Temperature on Its Efficiency in Dioxane Drying[a]

activation temperature, °C	residual solvent water content, ppm			
	1 h	6 h	24 h	72 h
no activation	1820	1020	430	350
150	1840	1230	420	290
225	1700	1090	370	290
300	1750	1040	385	325

[a] Initial water content = 2500 ppm; desiccant loading = 5% w/v; desiccant samples activated overnight (16 h).

Results and Discussion

Influence of Desiccant Activation Temperature. Dioxane was choosen for initial tests as it is moderately

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[2] Part 8: Burfield, D. R.; Hefter, G. T.; Koh, S. P. *J. Chem. Technol. Biotechnol.* **1984**, *34A*, 187.

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[4] See: (a) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley; New York, 1967; p 107, 1103. (b) Vogel, A. I. "Vogel's Textbook of Practical Organic Chemistry"; Longmans: London, 1978; p 139. (c) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon: Oxford, 1980; p 23.

[5] For example: "The last detectable traces of water are removed by Drierite from any liquid which is sufficiently fluid to make intimate contact with the porous solid" and "Regular Drierite is unsurpassed for the drying of organic liquids in the liquid or vapour phase. Moisture residue after treatment with Drierite is so low it cannot be measured, leaving the organic liquid truly anhydrous". Quoted in; Hammond, W. A. "Drierite"; W. A. Hammond Company: Xenia, OH.

[6] Thus calcium sulfate was surpassed only by barium oxide, magnesium perchlorate, and calcium oxide in evaluations based on gas drying efficiency reported by: Bower, J. H. *J. Res. Natl. Bur. Stand.* **1934**, *12*, 241.

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[9] Burfield, D. R.; Smithers, R. H. *J. Chem. Educ.* **1982**, *59*, 703.

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[11] Thus it has been shown[11a] that calcium sulfate heated above 400 °C rehydrates only slowly and it has been suggested[11b] that the transition to the inactive form occurs at around 313 °C. (a) Glasenapp, M. *J. Soc. Chem. Ind., London* **1908**, *27*, 858. (b) Chassevent, L. *Liebigs Ann. Chem.* **1927**, *7*, 43.