also to determine if various functional groups can be oxidized in these solvents.

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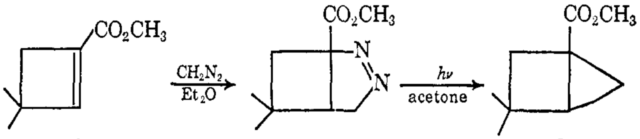
Substituted Bicyclo[2.1.0]pentanes

Sir:

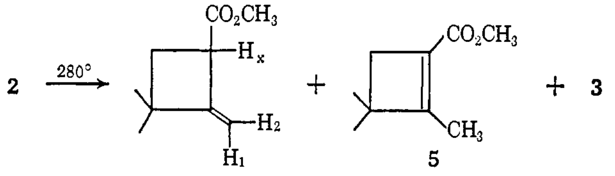
The pyrolytic or photolytic conversions of pyrazolines to cyclopropanes are valuable synthetic methods even though the mechanistic details of these reactions are still under active investigation.[1] These methods have been applied only to a limited extent to the preparation of fused ring cyclopropanes.[2-4] We wish to report a versatile high yield preparation of substituted bicyclo-[2.1.0]pentanes[5] using these methods.

Methyl 3,3-dimethylcyclobutene-1-carboxylate[6] (**1**) was converted to pyrazoline **2** in 93% yield by treatment with an excess of ethereal diazomethane at room temperature. The nmr spectrum of **2** exhibited the characteristic ABX pattern of a 3- or 5-substituted Δ^1-pyrazoline. Irradiation of **2** as a 1.5% solution in acetone[7] (irradiation in pentane solution produced a much more complex product mixture) caused an immediate evolution of nitrogen which was complete after 4 hr. Removal of solvent yielded a light yellow oil which consisted of 80% of one component by vpc analysis. Distillation (bp 34° (0.7 mm)) and final purification by gas chromatographic collection yielded ester **3** (ν_{CO} 1720 cm^{-1}) whose nmr spectrum exhibited three-proton singlets at 0.81, 1.26, and 3.57 ppm and two multiplets totaling five protons between 1.1 and 2.2 ppm. Hydrogenation of the ester[8] at room temperature using PtO_2–HOAc at 500 psi resulted in a slow uptake of hydrogen to produce methyl 3,3-dimethylcyclopentane-1-carboxylate whose nmr and mass spectra were identical with a sample prepared by a Favorskii reaction using 4,4-dimethylcyclohexanone.



1 2 3

In contrast to these photolytic results, pyrolysis of **2** yielded a three-major-component mixture containing **5** in largest quantity.[9]

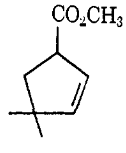


4 5

The structures of **4** and **5** follow clearly from spectral data. Compound **4** (ν_{CO} 1740 cm^{-1}, mol wt (mass spectroscopy) 154) showed proton resonance signals at 4.83 ppm (2 H, multiplet showing geminal and allylic coupling), the AB portion of an ABX centered at 2.0 ppm, a four-proton signal at 3.62 ppm (OCH_3 plus the X of the ABX pattern), and a six-proton singlet (perturbed) at 1.18 ppm. Compound **5** (ν_{CO} 1720 cm^{-1}) possessed an nmr spectrum containing signals at 1.12 (6 H, singlet), 3.62 (3 H, singlet), 1.85 (3 H, triplet, J = 2.0 cps), and 2.28 ppm (2 H, quartet, J = 2.0 cps).

This photolytic synthetic method is a general one. We have prepared 1-cyano-3,3-dimethylbicyclo[2.1.0]-pentane, 1-benzoyl-3,3-dimethylbicyclo[2.1.0]pentane, methyl-3,3,5-trimethylbicyclo[2.1.0]pentane-1-carboxylate (*exo*), methyl-3,3,5,5-tetramethylbicyclo[2.1.0]pentane-1-carboxylate, methyl-3-methylbicyclo[2.1.0]pentane-1-carboxylate, and methylbicyclo[2.1.0]pentane-1-carboxylate, among others, all in excellent yield. We have begun investigations of the chemical reactivity of these materials, particularly ring-opening reactions.

Pyrolysis[10] of **3** at 300° produced a nearly quantitative conversion to a 3:1 mixture of **6** and **7**.[11] Compound **6** (ν_{CO} 1740 cm^{-1}, mol wt (mass spectroscopy), 154) shows resonances at 1.05, 1.12, and 3.62 (each 3 H, singlets), 1.8–2.1 (2 H, multiplet), 3.3–3.7 (1 H, multiplet), and 5.35–5.7 ppm (2 H, multiplet). Compound **7** (ν_{CO} 1720 cm^{-1}, mol wt (mass spectroscopy) 154) possesses an nmr spectrum with resonances at 1.12 (6 H, singlet), 2.2–2.5 (4 H, multiplet), 3.67 (3 H, singlet), and 6.55 ppm (1 H, broadened singlet).



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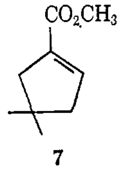

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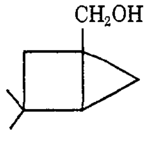

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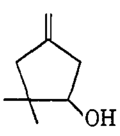

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[1] (a) T. V. Van Auken and K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, **84**, 3736 (1962); (b) D. E. McGreer, *et al.*, *Can. J. Chem.*, **43**, 1389, 1398, 1407 (1965); R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3768 (1965), and references cited therein; R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2587 (1966); P. Dowd, *ibid.*, **88**, 2589 (1966).

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[3] See G. W. Krakower and H. A. Van Dine, *J. Org. Chem.*, **31**, 3467 (1966), for a discussion of the advantages of the ylide approach over the pyrazoline approach in certain steroidal systems.

[4] P. G. Gassman and K. T. Mansfield, *J. Org. Chem.*, **32**, 915 (1967).

[5] R. B. Turner, "Kekule Symposium on Theoretical Organic Chemistry," Butterworth & Co. (Publishers) Ltd., London, 1959, p 67, reports a very high 55.1-kcal/mole heat of hydrogenation for bicyclo-[2.1.0]pentane, indicative of its high degree of ring strain.

[6] K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **29**, 801 (1964).

[7] Hanovia Type 673 A lamp using Pyrex apparatus.

[8] The mass spectrum of **3** exhibited a molecular ion at *m/e* 154 and intense fragment ions at *m/e* 139, 123, and 95 ($C_7H_{11}^+$, base peak). D. S. Weinberg and C. Djerassi [*J. Org. Chem.*, **31**, 3832 (1966)] have recently discussed the inherent stability of hydrocarbon ions derived from bicyclic compounds.

[9] Some mechanistic implications of these results are being studied further.

[10] M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2688 (1962); J. P. Chesick, *ibid.*, **84**, 3250 (1962). These papers report pyrolysis studies of bicyclo[2.1.0]pentane and 2-methylbicyclo[2.1.0]-pentane.

[11] Pyrolysis at higher temperatures produces much larger quantities (>70%) of **7**. Control experiments indicate **6** is not appreciably isomerized to **7** under these higher temperature conditions.

Ester **3** was reduced with lithium aluminum hydride to alcohol **8** whose nmr spectrum contained an AB pattern (2 H) centered at 3.5 ppm (J_{AB} = 12.0 cps), singlets (each 3 H) at 0.79 and 1.22 ppm, and a complex multiplet (5 H) extending from 0.5 to 1.9 ppm. Derivatives of **8** would be expected to solvolyze very rapidly to produce less strained isomers.[12] It is therefore not surprising that **8** is very rapidly destroyed upon exposure to traces of acid in aqueous dioxane and the isomer **9** is formed in nearly quantitative yield. The structure of **9** is defined by its spectral properties: mass spectral molecule ion at *m/e* 126 (*m/e* 168 for the acetate of **9**); infrared absorptions at 3340 (OH), 1655 (C=C), and 878 cm^{-1} (exocyclic C=C); nmr signals at 4.8 (2 H, characteristic pentuplet[13]), 3.68 (1 H, triplet), 2.0–2.7 (5 H, broad multiplet), and 0.92 ppm (6 H, singlet[14]).

One would expect the reactivity of the central bond[16] of bicyclo[2.1.0]pentanes to be altered depending on the nature of the bridgehead substituent. Our observation that treatment of **3** with *p*-TsOH in HOAc at 50° for 24 hr leads to no chemical change is in accord with the expected decrease in reactivity of this bond.

Several aspects of the solution and pyrolytic reactivity of substituted bicyclo[2.1.0]pentanes as well as the extension of the synthesis to other ring systems are presently under active investigation in our laboratories.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant No. 423-G).

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[13] Varian Handbook of NMR Spectra, Spectrum 132 (methylenecyclopentane).

[14] The methyl groups in an authentic sample of 2,2-dimethylcyclopentanol which we prepared[15] also appeared as a singlet at 0.91 ppm.

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[16] P. G. Gassman and K. Mansfield, *Chem. Commun.*, 391 (1965); R. T. LaLonde and L. S. Forney, *J. Am. Chem. Soc.*, **85**, 3767 (1963); R. T. LaLonde, *ibid.*, **87**, 4217 (1965).

[17] National Institutes of Health Predoctoral Fellow, 1966–1967.

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The Thiolochromium(III) Ion

Sir:

Although HS$^-$ would seem to command interest as a ligand, if for no other reason than to compare it to its congener OH$^-$, little is known about its properties when coordinated to a metal ion. A possible reason for the limited attention it has received may be that, owing to the tendency of most metal ions to form insoluble sulfides, the preparation of complexes containing the thiolo group, HS, may be made difficult. By taking advantage of the property which Cr^{2+} has to capture groups on being oxidized, we have been able to prepare and characterize CrSH^{2+}. The CrSH^{2+} ion (almost certainly thiolopentaaquochromium(III)) is formed by a variety of sulfur-containing oxidizing agents acting on Cr^{2+}. With PbS, Ag$_2$S, or S$_2$O$_3^{2-}$ the yield is low. Of the oxidizing agents tried, the highest yield was obtained using polysulfide as oxidant.

The polysulfide solution was prepared by dissolving 0.04 mole of Na$_2$S and 0.04 g-atom of sulfur in water and diluting to 1 l. A 25-ml portion of this solution was slowly introduced, under nitrogen, into 40 ml of an acid solution of Cr(II) containing 3 mmoles of Cr(ClO$_4$)$_2$ and 3 mmoles of HClO$_4$. The color change, from blue to green, is instantaneous. The solution was stirred vigorously by means of a magnetic stirrer. Nitrogen was bubbled through the solution during the addition of the polysulfide to expel the H$_2$S which is formed in the reaction. Finally O$_2$ was introduced to oxidize the excess of Cr(II). When this procedure was followed, no elementary sulfur was precipitated. The resulting green solution was passed through a Dowex 50X2 cation-exchange column. Sodium perchlorate was used as eluent. A 0.5 *M* solution eluted a sharp brownish green band which was followed by a colorless band of Zn^{2+} (introduced into the chromous solution during its preparation from chromic perchlorate by means of a Zn amalgam). A gray band of hexaaquochromium(III) was eluted by a 1 *M* solution, and a sharp green band, containing polynuclear chromium species of a charge greater than 3, remained on the column. Yields of CrSH^{2+} from 10 to 20% were obtained by this method.

The composition of the complex contained in the sharp brownish green band was verified by oxidation with excess bromine followed by fuming with nitric acid and precipitation as BaSO$_4$. Chromium was determined[1] spectrophotometrically as chromate at 372 mμ. The ratio of Cr to S found was 1.02. The oxidation number of the sulfur ligand was determined by oxidation with a standard iodine solution. Elementary sulfur is formed as in the iodometric determination of free H$_2$S. Two equivalents (actually 2.06) of iodine was consumed for each mole of complex.

The absorption spectrum of the new ion has three maxima in the visible–near-ultraviolet region, 574 mμ (ϵ 27), 434 (43), and 259 ($\sim$7000), and is not affected by increasing the acidity from pH 2 to 0. The ion-exchange behavior of the complex ion is typical for a +2 ion, indicating that the anion HS$^-$ and not the H$_2$S molecule is coordinated to the metal ion. The strongly acidic nature of coordinated H$_2$S (which is completely dissociated even in 1 *M* acid) is to be expected by comparison to its congener H$_2$O. The first dissociation constant of water is increased by coordination to chromium(III) from 2×10^{-16} to 10^{-4} in the hexaaquo ion.[2] Hence it is not surprising that H$_2$S with a dissociation constant of 10^{-7} [3] will behave as a strong acid when replacing a water molecule in the hexaaquo ion.

CrSH^{2+} has a remarkable stability at room temperature. When kept under nitrogen, the half-life for the aquation reaction at pH 2 and 25° is 55 hr. The rate does not change much when (H$^+$) is increased to 1 *M*. In the presence of air the ligand is slowly oxidized to

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[3] L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 216.