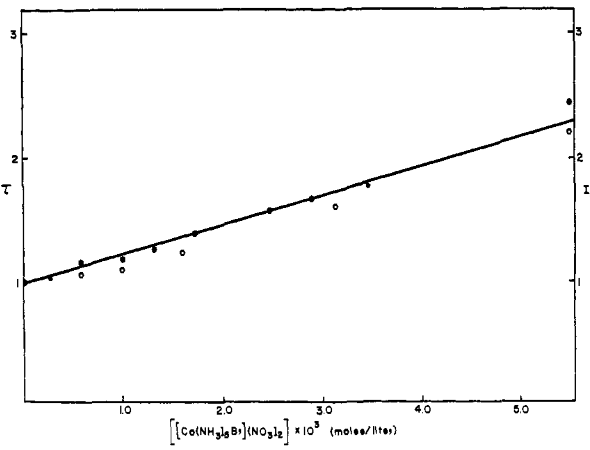


Figure 1. Quenching of ${}^3Ru(bipyr)_3{}^{2+}$ by $Co(NH_3)_5Br^{2+}$. ○: phosphorescence quenching, $I_0/I$, corrected for absorption of the exciting and the emitted light. ●: lifetime quenching, $\tau_0/\tau$, using the equipment cited in ref 1.

secondary reactions with radicals produced in the reduction of $Co(NH_3)_5X^{2+}$. Reduction *via* photoelectron production can be ruled out, however. $Ru(bipyr)_3{}^{2+}$ is ordinarily quite stable toward irradiation even under circumstances such that scavenging of any produced $e_{aq}^-$ should occur. For example, no reaction occurs in solutions saturated with $N_2O$, nor did flash photolysis of $Ru(bipyr)_3{}^{2+}$ in water show any transient absorbing at 700 nm with a half-life greater than 50 μsec (using the equipment of ref 4). Also, it has been found that $Ru(bipyr)_3{}^{3+}$ efficiently captures $e_{aq}^-$ to produce ${}^3Ru(bipyr)_3{}^{2+}$ [5] so that the reverse process is not likely.

As noted above, the possibility that the reaction is one of sensitization producing, say, a ${}^3CT$ cobalt complex which decomposes to Co(II) and a radical capable of oxidizing $Ru(bipyr)_3{}^{2+}$ cannot be ruled out. Results of the key experiment of direct irradiation of $Co(NH_3)_5Br^{2+}$ in the presence of (nonabsorbing) $Ru(bipyr)_3{}^{2+}$ are inconclusive because only an extremely small concentration of Ru(II) can be used.

An interesting aspect of the electron-transfer mechanism which we propose is that in the process a good reductant, ${}^3Ru(bipyr)_3{}^{2+}$, is transformed into a strong oxidant, $Ru(bipyr)_3{}^{3+}$. A necessary condition for the reaction to be observed may, therefore, be that the reduction of the substrate be irreversible, as is the case here.

Other substrates were found, with results as summarized in Table I. Species whose standard reduction potential is less than about +0.0 V are not reduced. The inference of the mechanism is that the standard potential for $Ru(bipyr)_3{}^{2+} \rightarrow {}^3Ru(bipyr)_3{}^{2+}$ may be as low as 1.2 V. The above figure of 1.2 V is, of course, quite approximate; not only are the half-wave potentials irreversible, but possibly major Nernst corrections have not been made. The interesting point remains that with further investigation it may be possible to obtain an experimental entropy of formation of excited state $Ru(bipyr)_3{}^{2+}$.

**Table I.** Reduction of Various Substrates by ${}^3Ru(bipyr)_3{}^{2+}$

| Substrate | $\phi_{Co^{2+}}$ [a] | $K_{SV}$, $M^{-1}$ | $\epsilon_{1/2}$, V (*vs.* sce)[b] |
|---|---|---|---|
| $Co(NH_3)_6{}^{3+}$ | Small | | −0.44 |
| $Co(NH_3)_5F^{2+}$ | 0.0003 | 0 | −0.33 |
| $Co(NH_3)_5Cl^{2+}$ | 0.063 | 100 | 0.28 |
| $Co(NH_3)_5Br^{2+}$ | 0.104 | 225 | 0.38 |
| $Co(HEDTA)Cl^-$ | ~0.2 | | |
| $Fe(C_2O_4)_3{}^{3-}$ | 0.1[c] | | |

[a] Determined for $1 \times 10^{-3}$ *M* complex. [b] From A. A. Vlček, *Discuss. Faraday Soc.*, **26**, 164 (1958). [c] $\phi_{Fe^{2+}}$.

**Acknowledgment.** These investigations were supported in part by Contract DA-ARO-D-31-124-G87 between the University of Southern California and the Army Research Office (Durham).

Harry D. Gafney, Arthur W. Adamson*
*Department of Chemistry, University of Southern California*
*Los Angeles, California 90016*
*Received May 17, 1972*

---

(4) W. L. Waltz and A. W. Adamson, *J. Phys. Chem.*, **73**, 4250 (1969).

(5) J. E. Martin, E. J. Hart, A. W. Adamson, H. D. Gafney, and J. Halpern, *J. Amer. Chem. Soc.*, in press.

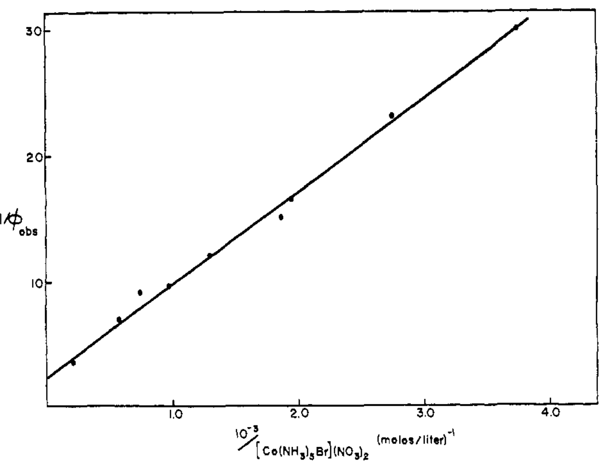


Figure 2. Effect of $Co(NH_3)_5Br^{2+}$ concentration on $\phi_{Co^{2+}}$.

---

## Geometry and Solvolysis of *exo-anti*-Tricyclo[3.1.1.0^{2,4}]heptan-6-yl *p*-Nitrobenzoate[1]

*Sir:*

Only two examples (compounds **1** and **2**)[2] demonstrate that the cyclopropane ring incorporated in a system homoconjugates symmetrically with a developing carbonium center, causing an enormous enhancement in rate of solvolysis. The ground-state geometry of the system is evidently a decisive factor contributing to this rate acceleration. We have completed solvolytic studies of the title compound **3a** and an X-ray analysis of **3b** (R = *p*-$BrC_6H_4CO$). The system has now been shown to possess a geometry similar to the one predicted for the maximum delocalization of the positive charge of the bicyclo[3.1.0]hex-3-yl cation.[3]

---

(1) The prefix anti denotes the anti orientation of the cyclopropane ring with respect to the substituted bridge.

(2) (a) J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969); H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (b) R. M. Coates and J. L. Kirkpatrick, *ibid.*, **92**, 4883 (1970), and references cited therein.

(3) R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965). We assume the interplanar angle between the cyclopropane and the main cyclopentane ring (see text) is the same both for **3b** and the bicyclo[3.1.0]hexane system.

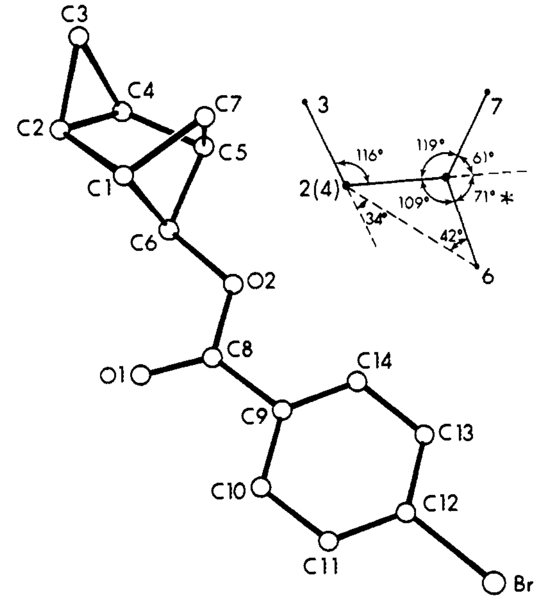
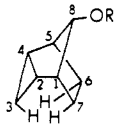
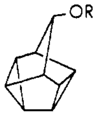


Figure 1. Perspective view of **3b**. Selected bond distances (ångströms) and angles (degrees) together with their standard deviations are: distances, C(1)–C(2), 1.56 (2); C(1)–C(6), 1.52 (2); C(1)–C(7), 1.52 (2), C(2)–C(3), 1.50 (2); C(2)–C(4), 1.53 (3); C(3)–C(4), 1.46 (2); C(4)–C(5), 1.59 (2); C(5)–C(6), 1.54 (2); C(5)–C(7), 1.52 (2); angles, C(1)–C(6)–C(5), 82 (1); C(1)–C(7)–C(5), 83 (1); C(6)–C(1)–C(7), 87 (1); C(7)–C(5)–C(7), 87 (1); C(1)–C(2)–C(4), 100 (2); C(5)–C(4)–C(2), 98 (2); C(2)–C(3)–C(4), 62 (1); C(3)–C(4)–C(2), 60 (1); C(4)–C(2)–C(3), 58 (1). Inset shows side view of the system.

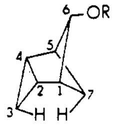


**1**, R = p-$NO_2C_6H_4CO$

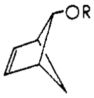


**2**

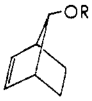
**5a**, R = H
**b**, R = p-$NO_2C_6H_4CO$



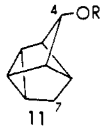
**3a**, R = p-$NO_2C_6H_4CO$
**b**, R = p-Br$C_6H_4CO$
**c**, R = $CH_3CO$
**d**, R = H



**4**



**10**



**11**

Reaction of *exo*-bicyclo[2.1.1]hex-2-en-5-yl acetate[4] with diazomethane in the presence of cuprous chloride[5] proceeded *stereoselectively* (*vide infra*) to afford a single compound **3c**[6] in quantitative yield. Acetate **3c** was in turn converted into **3a**, mp 83–84°,[6] and **3b**, mp 61–63°, *via* the corresponding alcohol **3d**, mp 62–63°. The X-ray crystallographic analysis of **3b** (*vide infra*) established the structures and stereochemistry of these esters (**3a–d**).

**X-Ray Analysis.** Compound **3b** crystallizes in the space group $P2_1/n$ with unit cell dimensions $a$ = 6.704 (1), $b$ = 12.087 (1), and $c$ = 15.577 (2) Å, $\beta$ = 94.12 (1)°, and four molecules per unit cell. X-Ray diffraction data were collected on a Picker manual four-circle diffractomer using Cu K$\alpha$ X-radiation ($0 < 2\theta < 100°$) to give 527 significant reflections which have been corrected for absorption and decomposition effects. The crystals were of low quality (from a diffraction viewpoint) and severe decomposition in the X-ray beam further reduced the quality of the intensity data. At this point it was quite clear that a diffraction study would yield results of low precision but this study was pursued since the gross stereochemistry was of interest. The structure was solved by heavy atom techniques and has been refined to a conventional $R$ factor of 0.072. In this refinement the bromine atom was allowed to vibrate anisotropically but lighter atoms were restricted to isotropic temperature factors in view of the paucity and low quality of the data.[6] Hydrogen atoms were placed at their calculated positions and their scattering included in the calculation of structure factors. No refinement of these hydrogen atoms was allowed. The overall stereochemistry and important interplanar angles of the molecule are shown in Figure 1 and bond lengths and angles are included in the caption. The figure shows that the cyclopropane ring is anti with respect to the substituted bridge. The inset demonstrates that the molecule is significantly distorted in the sense expected from the nonbonded interaction between C(3)–H and C(7)–H and that C(6) which carried the ester group is lifted by 71° from the plane defined by atoms C(1), C(2), C(4), and C(5). In view of our interest in the geometrical relationship between **3a** and the corresponding cation likely involved in the solvolysis, it is appropriate to describe briefly the result obtained by theoretical calculations. The potential energy curve of the 3-bicyclo[3.1.0]hexyl cation as a function of dihedral angle defined in the above manner shows an energy minimum in the region of 70–80°.[3]

**Solvolysis.** In 60% aqueous dioxane **3a** solvolyzed with the liberation of 0.76 equiv of *p*-nitrobenzoic acid and provided *endo*-tricyclo[3.2.0.0$^{2,7}$]heptan-4-ol (**5a**)[6] (*ca.* 70% yield) and the corresponding *p*-nitrobenzoate[6] (**5b**) (*ca.* 20%). These products were identified as such by independent synthesis. Oxidation of *exo*-tricyclo-[3.2.0.0$^{2,7}$]heptan-4-ol (**6**)[7] with $CrO_3$–Pyr afforded the corresponding ketone **7**,[6] which was then reduced with $NaBH_4$ to the alcohol **8** epimeric to **6**. Compound **8** and its *p*-nitrobenzoate (**9**) were identical with **5a** and **5b**, respectively. The solvolysis of **3a** in the above solvent system was followed titrimetrically and provided the following kinetic parameters (corrected for internal return):[8] $k(121.56 \pm 0.03°) = (1.30 \pm 0.08) \times 10^{-4}$ sec$^{-1}$, $k(101.55 \pm 0.03°) = (2.66 \pm 0.13) \times 10^{-5}$ sec$^{-1}$; $\Delta H^{\ddagger} = 22.5$ kcal/mol, $\Delta S^{\ddagger} = -10$ eu; $k(25.0°) = 7.79 \times 10^{-11}$ sec$^{-1}$.

Contrary to the naive prediction based on the geometry defined by the X-ray analysis, compound **3a** solvolyzes approximately ten times slower than **1**. In a related solvolytic study[9] it was shown quite recently (after receipt of our original manuscript) that compound **11** was 10–1000 times less reactive than **2** and

---

(4) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969).

(5) R. E. Pincock and J. I. Wells, *J. Org. Chem.*, **29**, 965 (1964).

(6) Spectral data of all new compounds, tables of fractional coordinates, and structure amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-8239. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(7) R. K. Lustgarten, *J. Amer. Chem. Soc.*, **93**, 1275 (1971).

(8) H. Hart and J. M. Sandri, *ibid.*, **81**, 326 (1959).

(9) R. M. Coates and K. Yano, *Tetrahedron Lett.*, 2289 (1972). We feel that the systems **2** and **11** utilized by these authors to test the ring size effect involve an obvious, additional factor to complicate the interpretation, compared with the present pair of compounds **1** and **3a**; **2** (pentacyclo) and **11** (tetracyclo) would differ significantly in rigidity and the strain energy required for a similar change of the critical relative geometry of the incipient cation center and cyclopropane in the process of ionization would not be of the same magnitude for the two systems.

this result was interpreted on the basis of "several reinforcing and opposing factors." As the cause of deceleration, it is pointed out further that the presence of the C(7) methylene bridge in **11** must increase the strain energy associated in the ionization, thus destabilizing the transitions tate and the resulting trishomocyclopropenyl cation intermediate.[9] Since the present system **3a** is missing such a bridge, one must seek other explanations for the slow rate of **3a** compared with **1**. If one considers the difference between angle [C(1)–C(6)–C(5)] of **3a** and angle [C(1)–C(8)–C(5)] of **1**,[10,11] it appears that the anchimeric assistance provided by the cyclopropane participation in the solvolysis of **3a** would be at least of the same order of magnitude as that estimated for **1** and very likely would be slightly more.[11] Thus, as the X-ray analysis of **3a** demonstrates the anomolous distortion of the system, the critical interplanar angle (*vide supra*) of system **1** could possibly be just as large as that of **3a** again due to the internal van der Waals interactions between C(3)–H and C(6)–H and C(7)–H of **1**.[12] Unfortunately, crystallographic data of **1** are not available. Finally, brief comments should be made on the chemical properties of **4**. As earlier noted,[4] the solvolysis rate of **4** is large ($5 \times 10^3$) as compared with its homolog, *anti*-bicyclo[2.2.1]hept-2-en-7-ol ester (**10**) (*cf.* $k(\mathbf{3a})/k(\mathbf{1}) = 0.1$). This accelerated solvolytic reaction of **4** and other observations such as the *stereoselective* addition (anti to the substituted bridge) of a methylene group (*vide supra*) and diazomethane (pyrazoline formation)[13,14] to **4** suggest that C(5) of **4** may be unsymmetrically bent toward the double bond unexpectedly and sufficiently to bring about these seemingly unusual experimental results.

**Acknowledgment.** The authors are grateful to the National Research Council of Canada for financial support.

---

(10) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

(11) C. S. Foote, *ibid.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854 (1964). The ketone **12** corresponding to **3d** was prepared by Oppenauer oxidation and exhibited a $\nu_{\max}$ at 1788 cm$^{-1}$ (CCl$_4$). If the Foote-Schleyer equation is still applicable to these strained systems, then the anchimeric assistance calculated for the solvolysis of **2a** is *ca.* 500 larger than that for **1**.

(12) Obviously we are assuming that the energy required for ionization increases as the ground-state geometry of a system departs from that of the corresponding cation which is ideally stabilized by the cyclopropane participation.

(13) S. Masamune and P. Vokov, unpublished results.

(14) Also see, W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969).

**S. Masamune,* R. Vukov, M. J. Bennett, J. T. Purdham**
*Department of Chemistry, University of Alberta*
*Edmonton, Alberta, Canada*

*Received June 12, 1972*

---

## Mixed Charge Exchange–Chemical Ionization Reactant Gases in High-Pressure Mass Spectrometry

*Sir:*

Electron-impact ionization mass spectra often lack abundant ions of high mass. For this reason other methods of ionization such as chemical ionization[1,2] are gaining acceptance as complements to electron-impact ionization. Chemical ionization mass spectrometry requires a reactant gas from which reactant ions are formed by electron-impact ionization and ion–molecule reactions.[1,2] A single reactant gas is generally used in the chemical ionization source. A discussion of two-component reactant gas systems limited to mixtures of charge exchange and chemical ionization reactant gases is presented herein. For illustrative purposes the two gases selected are helium, a charge-exchange reactant gas, and water vapor, a chemical ionization reactant gas.

Helium charge-exchange mass spectra measured under chemical ionization conditions[1,2] have been reported[3,4] to be similar to electron-impact ionization mass spectra. Gaseous mixtures made up of helium and water vapor may be varied so that the mass spectrum of the substance under examination will show peaks characteristic of charge-exchange ionization, of chemical ionization, or of both. Spectra which show peaks from both modes of ionization are referred to herein as simultaneous charge exchange–chemical ionization mass spectra.[5] Mass spectra of methyl 6,10,14-trimethylpentadecanoate (**1**), the methyl ester of a naturally occurring isoprenoid fatty acid,[6] are shown in Figure 1 to illustrate changes in mass spectra with variations in reactant gas mixtures.

The mass spectra (Figure 1) were measured with a modified[7] QUAD 300 quadrupole mass spectrometer. The sample (**1**) was vaporized directly into the high-pressure ion source held at *ca.* 0.5 Torr and 200°. The helium flow rate was 1.2 ml/min and the water content of the gaseous mixture was varied from 0 (Figure 1a and b) to 6 (Figure 1c)[8] to 13%[8] (Figure 1d). The sample (**1**) concentration was the same for all spectra.

Figure 1a shows the mass spectrum of **1** taken with the electron-impact ion source in series[7] with the high-pressure ion source. The helium charge-exchange mass spectrum of **1** (Figure 1b) is comparable although not identical. Both electron-impact and helium charge-exchange mass spectra of **1** show, for example, characteristic peaks at *m/e* 74 and 222 and a molecular ion peak (*m/e* 298) of such low abundance as to be hardly detectable. By contrast, the simultaneous mass spectrum (Figure 1c) shows an abundant $(\mathrm{M}+1)^+$ at *m/e* 299, one of the two most abundant ions in the chemical ionization mass spectrum (Figure 1d), which clearly points to the molecular weight (298) of **1** while retaining the peaks (*e.g.*, *m/e* 74 and 222) characteristic of electron-

---

(1) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).

(2) For recent reviews, see (a) B. Munson, *Anal. Chem.*, **43**, 28A (1971); (b) G. P. Arsenault in "Biochemical Applications of Mass Spectrometry," G. R. Waller, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 817–832.

(3) D. M. Schoengold and B. Munson, *Anal. Chem.*, **42**, 1811 (1970).

(4) R. L. Foltz, 19th Annual Conference on Mass Spectrometry, Atlanta Ga., May 1971, p 142.

(5) The paper by D. F. Hunt and J. F. Ryan III, *Anal. Chem.*, **44**, 1306 (1972), which appeared at the time this communication was submitted for publication discusses the use of argon–water to obtain simultaneous charge exchange–chemical ionization mass spectra without a mention of any other aspect of the use of mixtures of charge exchange and chemical ionization reactant gases.

(6) R. C. Murphy, M. V. Djuricic, S. P. Markey, and K. Biemann, *Science*, **165**, 695 (1969).

(7) G. P. Arsenault, J. J. Dolhun, and K. Biemann, *Anal. Chem.*, **43**, 1720 (1971).

(8) The water-vapor concentration necessary for either simultaneous charge exchange–chemical ionization mass spectra or chemical ionization mass spectra depends on the ion source pressure, the nature of the charge exchange reactant gas, and the mass discrimination inherent to the instrument being used.