pene-derived and this can be accomplished formally by a single methyl shift of a unique cyclization of a geranyl–geraniol residue as illustrated in **3.** We have not been able to demonstrate the presence of any naturally occurring formamides, the suggested intermediates for diterpene isocyanide formation in another sponge[4] in this *Adocia* species. Other isocyanides have been extracted from the sponge and will be discussed in a subsequent publication.

Acknowledgments. The authors wish to thank Drs. W. Vetter and L. Chopard for valuable discussions.

Supplementary Material Available: A listing of structure factors and atomic coordinates (28 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. Cafieri, E. Fattorusso, S. Magno, C. Santacroce, and D. Sica, *Tetrahedron*, **29**, 4259 (1973).

(2) L. Minale, R. Riccio, and G. Sodano, *Tetrahedron*, **30**, 1341 (1974).

(3) E. Fattorusso, S. Magno, L. Mayol, C. Santacroce, and D. Sica, *Tetrahedron*, **30**, 3911 (1974).

(4) B. J. Burreson, C. Christophersen, and P. J. Scheuer, *Tetrahedron*, **31**, 2015 (1975).

(5) B. J. Burreson, P. J. Scheuer, J. Finer, and J. Clardy, *J. Am. Chem. Soc.*, **97**, 4763 (1975).

(6) A listing of structure factors and atomic coordinates is available. See paragraph at the end of paper regarding supplementary material.

(7) This stereoprojection was drawn by ORTEP, C. K. Johnson, (1965) ORNL-3794 Oak Ridge National Laboratory, Oak Ridge, Tenn.

J. T. Baker, R. J. Wells*
Roche Research Institute of Marine Pharmacology
Dee Why, N.S.W. 2099, Australia

W. E. Oberhänsli*
Department VI/Phy. F. Hoffmann-La Roche & Co.
Basel, Switzerland

G. B. Hawes
Department of Chemistry
James Cook University of North Queensland
Townsville, Queensland, 4811, Australia

Received February 2, 1976

Ozonolysis of Fluoroalkenes: the Synthesis, Conformation, and Microwave Spectrum of 3-Fluoro-1,2,4-trioxolane

Sir:

Simple derivatives of ethylene ozonide with halogen substitution directly on the ring have not been synthesized until recently. Gillies[1] has isolated the cis/trans difluoroethylene ozonide isomers from ozonolysis of 1,2-difluoroethylene in isobutane and observed little dependence of the ozonide cis/trans ratio on the initial alkene configuration. He also observed that in CH_3Cl, *cis*-1,2-difluoroethylene oxide and HFCO were major products along with lesser amounts of the ozonides and a trace of *cis*-1,2,3-trifluorocyclopropane. In related studies, the ozonolysis of 2,3-dibromo-2-butene[2,3] and C_2F_4[4] in solution gave only trace amounts of the ozonides while emission from CF_2 was observed upon gas phase ozonolysis of C_2F_4.[5] Such results raise the question as to what extent the normal ozonolysis mechanism[6] is applicable to halogenated alkenes.

In this note we report the identification of the ozonide of vinyl fluoride, $\mathrm{HF\overline{COOCH_2O}}$ (I) and preliminary results of cross ozonide formation and foreign aldehyde insertion with *cis*-1,2-$C_2H_2F_2$. I is also reported to have the twisted half-chair conformation observed for other ozonides[6d,7] with the fluorine in the axial position.

I was synthesized by ozonolysis of vinyl fluoride in isobutane or CH_3Cl at −95° using standard techniques.[6d] The major volatile products were I and ethylene ozonide (about 5:1 in CH_3Cl) along with HFCO, H_2CO, and HCOOH. Not all products have been identified yet; whether 1,2-difluoroethylene ozonide, fluoroethylene oxide, or cyclopropanes are obtained requires further investigation. I was partially isolated at −95° by trap to trap distillation and further purified by VPC.[8] It was identified by its mass spectrum, ir, and microwave (MW) spectrum.[9,10]

I has also been isolated upon ozonolysis of mixtures of C_2H_4 (or *cis*-$C_2H_2D_2$) and *cis*-1,2-$C_2H_2F_2$ in CH_3Cl (−95°) or mixtures of H_2CO and *cis*-1,2-$C_2H_2F_2$ in isobutane (−45°). For the former reaction, the yield of the monofluoro cross ozonide was small (5–10%). The latter reaction was efficient enough to synthesize $\mathrm{HF\overline{COOCH_2{}^{18}O}}$ using labeled H_2CO (^{18}O, ~55%). The enriched ozonide was identified by its MW spectrum (cf. below). No MW spectrum for $\mathrm{HF\overline{CO^{18}OCH_2O}}$ could be assigned suggesting that insertion produced enrichment predominantly at the ether site.

Although further work is obviously desired, it is reasonable to propose from these preliminary experiments that formation of I from C_2H_3F and by aldehyde insertion and cross ozonide reactions with *cis*-$C_2H_2F_2$ very likely involves a Criegee mechanism. This could occur by the combination of the H_2COO zwitterion (or diradical)[11] plus HFCO (path A) and/or the HFCOO zwitterion plus H_2CO (path B). The synthesis involving H_2CO insertion (in isobutane) argues strongly that HFCOO must be considered a viable precursor (path B). The cross ozonide synthesis of I ($C_2H_4 + C_2H_2F_2$) can be rationalized by either pathway alone or both competing; since difluoroozonides are also formed from $C_2H_2F_2$[1] it seems likely that both pathways are occurring.

The production of I from C_2H_3F is also possibly occurring via both pathways. Thus, the identification of ethylene ozonide (a cross ozonide) implies both pathways; however, an ambiguity remains since the other cross ozonide (the difluoro) has not yet been identified. Therefore the possibility can not yet be eliminated that with C_2H_3F, path A predominantly leads to I and that the H_2CO necessary to produce ethylene ozonide arises from decomposition reactions rather than path B.

In summary, formation of fluorinated ozonides from C_2H_3F and $C_2H_2F_2$ can be rationalized by a Criegee mechanism; the existence of the HFCOO precursor is more clearly established as an intermediate from $C_2H_2F_2$ than from C_2H_3F. Also, it is not clear from this work what relevance these conclusions have towards rationalizing the more unusual products obtained[1] from ozonolysis of $C_2H_2F_2$.

The conformation of I was established by assignment of the MW spectrum of the normal isotopic species, $\mathrm{HF\overline{COOCH_2{}^{18}O}}$ and *cis*-$\mathrm{HF\overline{COOCHDO}}$.[10] The rotational constants can be readily correlated with the O_p–O_p twisted half-chair conformation reported for other ozonides but only if the fluorine occupies the axial site.[6d,7] Using structural parameters from ethylene ozonide (and $d(C\text{–}F) = 1.33$ Å), the rotational constants for the eq and ax isomers of the normal species were predicted to be respectively (in MHz): 8046, 3589, 2721 and 6610, 4030 and 3231. The observed constants[10] argue strongly for the axial conformer.

The rotational constants for the ^{18}O species are consistent with substitution at the ether site. The observed coordinates (Å) for this atom[12] are $a = 0.120$, $b = 1.162$, and $c = 0.211$. This is within 0.02–0.05 Å of values predicted with the assumed structural parameters noted above but differs by 0.25–0.80 Å for enrichment at the $O_p(CH_2)$ site. Similar good agreement between the model and data serves to identify the assigned deuterium species as the cis-D isomer. Several tentative transitions for the trans-D species have also been observed, but this assignment was not completed before sample depletion.

No transitions for the equatorial fluorine conformer were assigned although a search was made for them. It is clear that the axial conformer is the predominant form. This is in contrast to the preference for the equatorial site by methyl groups in other ozonides.[6d] This contrast seems attributable to the anomeric effect and has analogies in other haloheterocyclic systems.[13-16]

Acknowledgment. The authors are grateful to the National Science Foundation for the support of this work.

References and Notes

(1) C. W. Gillies, *J. Am. Chem. Soc.*, **97**, 1276 (1975).
(2) K. Griesbaum and J. Bruggerman, *Chem. Ber.*, **105**, 3638 (1972).
(3) K. Griesbaum and J. Bruggerman, *Adv. Chem. Ser.*, **No. 112**, 50 (1972).
(4) F. Gozzo and G. Camaggi, *Chim. Ind. (Milan)*, **20**, 197 (1968).
(5) R. S. Sheinson, F. S. Toby, and S. Toby, *J. Am. Chem. Soc.*, **97**, 6593 (1975).
(6) (a) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **14**, 745 (1975); (b) R. W. Murray, *Acc. Chem. Res.*, **1**, 313 (1968); (c) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Am. Chem. Soc.*, **90**, 1822 (1968); (d) R. P. Lattimer, R. L. Kuczkowski, and C. W. Gillies, *J. Am. Chem. Soc.*, **96**, 348 (1974).
(7) C. W. Gillies and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **94**, 6337 (1972).
(8) Several explosions occurred during workup of the reaction products. They occurred when handling shock sensitive solid residues, while venting some samples, and upon syringing the products isolated in a −78° trap for GC analyses. The GC inlet was then modified to accept gases directly from the vacuum line. A 15% Dow 710 silicone column was used at slightly elevated temperatures (~30°).
(9) Mass spectrum (intensities in parentheses): 94 (0.35), 66 (0.25), 65 (0.02), 64 (0.07), 62 (0.08), 49 (0.05), 48 (0.2), 47 (0.1), 46 (0.9), 45 (0.15), 44 (1.0). IR (prominent Q branch listed, ±5 cm^{-1}): 3010 (vw), 2910 (w), 1390 (w), 1350 (w), 1300 (vw), 1112 (vs), 1078 (s), 1050 (s), 1005 (m).
(10) The number of MW transitions assigned followed by A, B, C (in MHz): normal species, 24 transitions, 6774.0, 3916.3, 3122.7; ^{18}O-ether, 11 transitions, 6534.6, 3912.9, 3071.7; cis-D, 6 transitions, 6582, 3791, 3040.
(11) W. R. Wadt and W. A. Goddard, III, *J. Am. Chem. Soc.*, **97**, 3004 (1975).
(12) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).
(13) R. U. Lemieux, *Pure Appl. Chem.*, **25**, 527 (1971).
(14) E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, **11**, 739 (1972).
(15) C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4**, 39 (1969).
(16) S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffman, *J. Am. Chem. Soc.*, **95**, 3806 (1973).

R. P. Lattimer, U. Mazur, R. L. Kuczkowski*
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

Received April 13, 1976

Discandium and Dititanium, Their Synthesis and Optical Spectra in Low Temperature Argon Matrices

Sir:

Besides the reaction of titanium atoms and benzene,[1] which at 10–70 K yields the electron rich 16-electron complex bis(benzene)titanium(0), little else is known about the reactivity of the early transition elemental vapors towards other reactive partners. Indeed, the even more fundamental question, as to the fate of these metal atomic vapors when cocondensed at low temperatures in the presence of a nonreactive partner, remains to be ascertained. This kind of information is crucial for designing efficient syntheses using metal vapor techniques.[2]

In a continuing effort to try to understand the intricate details associated with the surface and bulk diffusion properties and aggregation processes of metal atoms when cocondensed with reactive as well as inert partners at low temperatures,[2,3] we have recently turned our attention to the highly active metals on the left of the transition block.

Our preliminary studies with $Sc(4s^23d^1)$ and $Ti(4s^23d^2)$ have revealed a surprisingly facile matrix dimerization process in Ar. In this brief report we would like to present our optical data for the Sc/Ar and Ti/Ar systems as a function of total metal concentration which serve to identify, for the first time, matrix isolated Sc_2 and Ti_2.

Our experimental techniques and apparatus have been described elsewhere.[4] The crucial aspect of the method involves the precise control and measurement of the rate of metal atom deposition onto the cooled optical window. This was achieved with the aid of a quartz crystal microbalance incorporated into the furnace-cryostat assembly.[5]

Monatomic scandium and titanium (99.99%) were generated by directly heating a thin filament (0.010 in.) of the metal. Argon was deposited at a rate of 2.2 mmol h^{-1}. Uv-visible spectra were recorded on a standard Unicam SP8000 instrument in the range 200–700 nm, the sample being condensed onto a NaCl plate cooled to 10 K by means of an Air Products Displex refrigerator.

Scandium. Several authors have reported on the electronic spectra of atoms trapped in low temperature matrices, which generally show lines shifted to higher energy than in the spectra of the gaseous atom.[2,6] The electronic spectrum of atomic Sc isolated in a low temperature matrix has not previously been published, although Weltner et al.[7] in their work on matrix isolated ScO briefly mention that two lines at 3896 and 3748 Å could be attributed to absorptions of Sc atoms.

When Sc atoms were cocondensed with Ar at high dilutions ($Sc/Ar \simeq 1/10^5$) the optical spectrum shown in Figure 1A was obtained. Table I lists the observed frequencies together with the corresponding gas phase absorptions from a $^2D_{3/2}$ ground state.[8] Noteworthy is the blue shift of the order of 500–1000 cm^{-1} for all absorptions of the isolated atom compared with those for the atom in the gas phase. For high energy transitions this shift can be as large as 3000–5000 cm^{-1} so that for absorptions with energies larger than 40 000 cm^{-1}, no correlation with the gas phase data was attempted.

When the rate of metal deposition at constant gas deposition

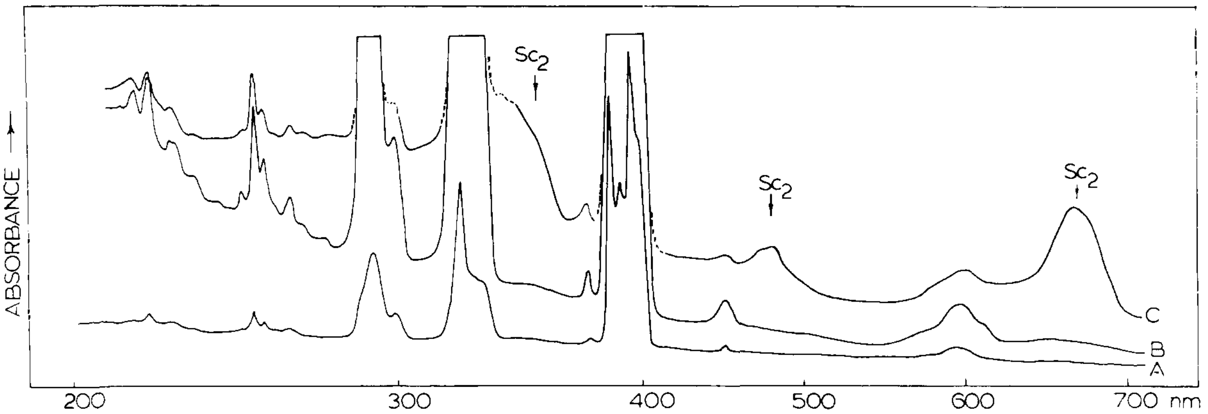

Figure 1. The uv-visible spectrum of (A) atomic Sc isolated in solid Ar at 10 K at high dilutions ($Sc/Ar \simeq 1/10^5$), (B) the same as (A) but on 5× scale expansion, and (C) the same total metal concentration as (B) but deposited at $Sc/Ar \simeq 1/10^4$ showing the growth of absorptions attributable to Sc_2 (also on 5× scale expansion).