acid. All of these arguments will be fully delineated in a forthcoming paper.

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(12) Alfred P. Sloan Fellow, 1963–1967.

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Preparation of Bis(fluoroxy)difluoromethane, $CF_2(OF)_2$

Sir:

The known existence of $CF_2(OF)_2$ as established by Thompson[1] of the 3M Company together with a knowledge of the usefulness of cesium fluoride as an aid to the formation of hypofluorites, as established by Ruff and Lustig,[2] suggested the possibility of preparing $CF_2(OF)_2$ by the fluorination of carbon dioxide. The procedure was tried and found to be very effective.

In a typical run, 0.298 g (6.78 mmoles) of carbon dioxide and 1.03 g (27.1 mmoles) of fluorine were condensed together from a 2310-ml glass vacuum line into a heavy-walled, 9-ml Monel metal bomb which contained 7.80 g of dry cesium fluoride at about −196°. The salt was used directly from a bottle of the "99% pure" compound by Alfa Inorganics, Inc. It was pulverized in a drybox and placed in the bomb which was then filled with gaseous fluorine under pressure and allowed to stand at room temperature for 1 day. The fluorine was then removed. After addition of the above amounts of carbon dioxide and fluorine, the bomb was closed and placed in a safety shield consisting of a piece of heavy-walled pipe. It warmed slowly and remained at room temperature for 3 days. The gases were then transferred to the vacuum line and found to have a volume corresponding to 20.1 mmoles (theory, 20.3 mmoles). When the gas was pumped slowly through a U-trap cooled by liquid nitrogen (−196°), fluorine was removed, and the material, which condensed in the trap, upon evaporation had a volume of 6.72 mmoles (theory, 6.78 mmoles) of gas. Fractional codistillation[3] gave one peak, indicating that the compound was pure. Successive fractions taken by evaporation had vapor densities expressed as molecular weights of 120.0, 119.2, and 120.8 (theory for $CF_2(OF)_2$, 120.0).

The reaction described above showed each molecule of product to contain (like CO_2) one atom of carbon. When a similar run was made using an excess of carbon dioxide, the fluorine was completely consumed, and substantially no material volatile at −196° remained in the bomb. This meant that oxygen was not produced and that a molecule of product (on the average) contained two atoms of oxygen. The product had the same volume as the carbon dioxide used in the process. Fractional codistillation separated the product into two fractions. Infrared spectra showed one to be carbon dioxide, and the other to be the same new compound that was produced by the reaction involving an excess of fluorine. Two moles of fluorine was consumed for every mole of product formed in the first reaction. This evidence clearly established the reaction to be

$$CO_2 + 2F_2 \xrightarrow[25^\circ]{CsF} CO_2F_4$$

The compound was not observed to freeze when chilled. It was a liquid at −183° and a glassy material, or very viscous liquid, at −196°. It reacted vigorously with an aqueous solution of potassium iodide liberating iodine. The infrared spectrum of the gas as observed through silver chloride windows using a Beckman IR-10 spectrometer had absorption bands (in μ) at 7.84 (vs), 8.01 (vs), 8.22 (vs), 8.30 (vs), 8.43 (vs), 10.6 (m), 10.7 (m), 10.8 (m), 10.9 (m), 11.0 (m), 14.5 (m), and 15.2 (m). Several weaker bands were also present.

The fluorine-19 nmr spectrum was obtained with a Varian Associates high-resolution, 40-Mc, nuclear magnetic resonance spectrometer with a Model No. V-4311 fixed-frequency radio frequency transmitter using $CFCl_3$ as an external standard. Two triplets of equal area were observed, centering at chemical shifts (from $CFCl_3$) of −155 and 88.5 ppm. The coupling constant, J, had a value of 39 cps. This spectrum is consistent with the structure $CF_2(OF)_2$.

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(1) P. G. Thompson, private communication.
(2) J. Ruff and M. Lustig, *Inorg. Chem.*, 3, 1422 (1964).
(3) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, 31, 618 (1959).

Rearrangement as a Criterion for Triple Bond Participation in the Formolysis of Acetylenic Brosylates

Sir:

The intramolecular participation of an acetylenic bond with a center of developing positive charge, generated by the loss of a negative leaving group in a solvolysis reaction, leads, if classically described, to a vinylcarbonium ion. The possible intermediacy of such ions in a variety of reactions has received recent attention.[1]

Positive evidence for triple bond participation in a solvolysis reaction would be a rate acceleration[2] or the formation of rearrangement products involving the acetylenic bond.[2,3] Examples of rate acceleration are few, and their interpretation is complicated by the uncertainty in the magnitude of the inductive rate-retarding effect exerted by the acetylene group.[2] Several examples of rearrangements are known, all from closely related systems: sulfonate solvolysis in formic, acetic, or trifluoroacetic acids.[2,3] Thus, 3-pentyn-1-yl brosylate, heated at 60° for 17 days in formic acid buffered with sodium formate, gave 2-methylcyclobutanone and a trace of methyl cyclopropyl ketone as well as the normal solvolysis product.[3a]

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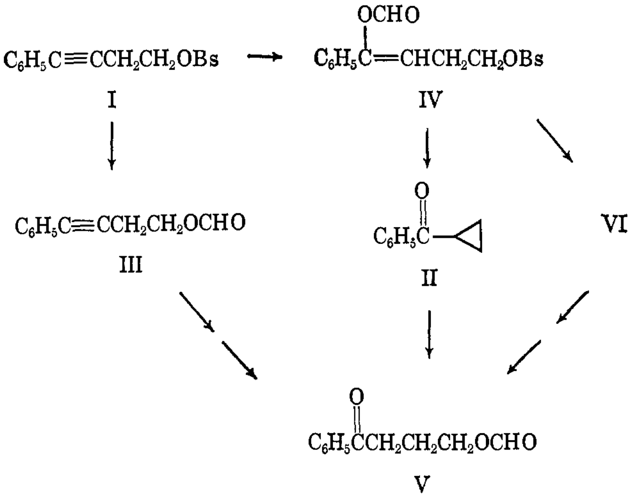
(1) D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *J. Am. Chem. Soc.*, 87, 2295 (1965); R. C. Fahey and D. J. Lee, *ibid.*, 88, 5555 (1966); P. E. Peterson and J. E. Duddey, *ibid.*, 88, 4990 (1966).
(2) P. E. Peterson and R. J. Kamat, *ibid.*, 88, 3152 (1966).
(3) (a) M. Hanack, J. Häffner, and I. Herterich, *Tetrahedron Letters*, 875 (1965); (b) M. Hanack and I. Herterich, *ibid.*, 3847 (1966); (c) W. D. Closson and S. A. Roman, *ibid.*, 6015 (1966).

We wish to report the investigation of the mechanism of the formolysis of 4-phenyl-3-butyn-1-yl brosylate (I), a system where rearranged product, phenyl cyclopropyl ketone (II), is observed,[4] and to suggest that the formation of this product does not necessarily result from direct triple bond participation in the solvolysis.

The solvolysis of I in formic acid, buffered by 1 equiv of pyridine[5] at 80°, gave II (30%) with a rate of formation of approximately 1×10^{-5} sec^{-1}. The measurement of rate constants in this system is complicated by the further reaction of II and the normal solvolysis product 4-phenyl-3-butyn-1-yl formate (III) with solvent to yield γ-formoxybutyrophenone (V). The addition of formic acid to the triple bond of III proceeds at a rate comparable to the solvolysis reaction. This addition bears directly on the question of triple bond participation, for if solvent can add to the triple bond of III, addition to I is also probable, and II might arise from participation of the double bond of the resulting enol formate (IV).

To test this hypothesis I was heated at 50° for 15 min in anhydrous formic acid containing 1 equiv of benzenesulfonic acid. The nmr spectrum of the reaction solution (Figure 1b) showed two triplets at τ 4.14 and 4.43 attributed to the vinyl protons of the geometric isomers of IV, and a triplet at τ 4.2 from two of the protons of compound VI, whose structure has not yet been assigned. This treatment converted 75% of I to IV and VI in a ratio of 5:2. When 2 equiv of pyridine was added to the nmr sample (Figure 1c), the triplet assigned to VI disappeared, and absorption at τ 6.82, characteristic of the $-CH_2C(=O)-$ group, appeared. This sample was held at 80 ± 1° in a heated nmr probe and the reaction followed by repeated integral scans.[6] Phenyl cyclopropyl ketone (II, 85% based on initial IV) was formed at a rate ten times that in the buffered system, $k = 1 \times 10^{-4}$ sec^{-1}. No appreciable change was observed in the concentration of V or remaining I during the time that the reaction was followed: 5 hr or approximately two half-lives. A concomitant decrease in the absorption of the vinyl protons in IV was observed. The spectrum of the "infinity" sample (IV was completely reacted but I remained), Figure 1d, showed the four methylene protons of the cyclopropyl ring at τ 8.8. These facts are consistent with Scheme I.

Scheme I



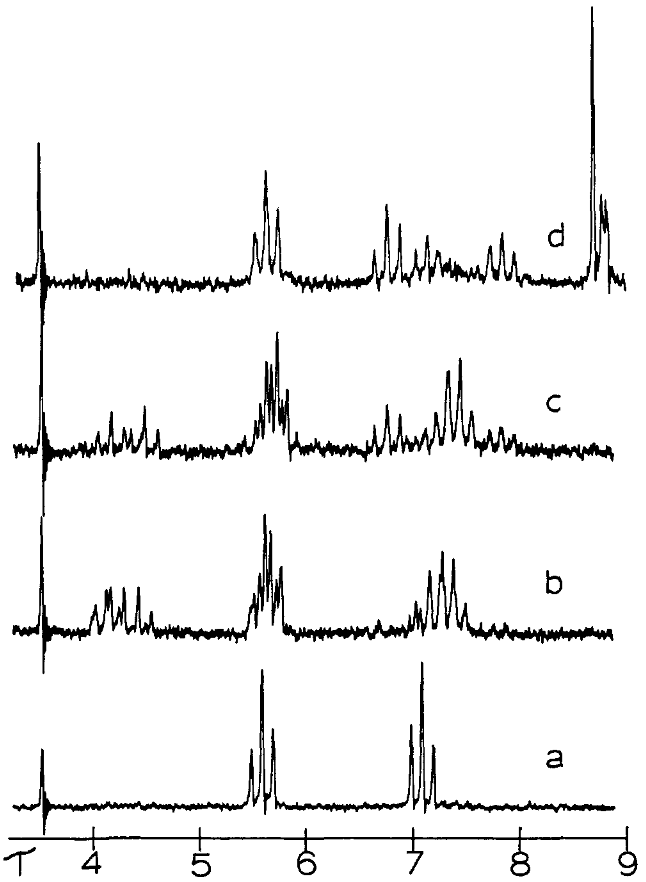


Figure 1. The nmr spectra of the formolysis of I at various stages of completion. The sharp line at τ 3.54 in all spectra is the high-field ^{13}C satellite of the carbonyl proton in the formic acid solvent. (a) Formic acid solution of I; (b) after the addition of benzenesulfonic acid and heating at 50° for 15 min; (c) after the addition of 2 equiv of pyridine; (d) after heating the buffered solution for 12 hr.

These experiments show that the enol formate, IV, reacts to form the rearrangement product, II, in a reaction which is an order of magnitude faster than the reaction of the acetylenic brosylate, I, in the same solvent system. Since the formation of IV from I is almost certain during the solvolysis of I in the buffered solvent, some, and perhaps all, of the phenyl cyclopropyl ketone must result from participation of the double bond of IV. In addition, induction periods of about 5 hr for the formation of II and about 20 hr for the formation of V are observed in the buffered reaction. This is consistent with a series of first-order reactions which has a slow first step, as proposed in Scheme I.

In summary, we suggest that the formation of rearrangement products, at least in the system at hand, does not constitute compelling proof for triple bond participation during solvolysis in strongly acidic solvents.

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[4] The formation of phenyl cyclopropyl ketone in a similar solvolysis has been indirectly reported in ref 3b, but no details are available.

[5] Pyridine has been shown to be a useful buffer in the formolysis of olefinic tosylates: K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 1331 (1965). Similar results were obtained in the present investigation using sodium formate buffer.

[6] The Varian A-60A nmr spectrometer used in these measurements was purchased with funds supplied by the National Science Foundation.