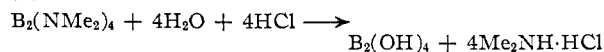


was prepared from tetra-(dimethylamino)-diboron in about 60% yield by low-temperature hydrolysis in hydrochloric acid solution as shown in the equation



Tetrahydroxydiboron prepared in this manner appears to be identical with that obtained by Wartik<sup>9</sup> from diboron tetrachloride. Excess boron trichloride was passed over 80.6 mg. of boron monoxide at 200–236° at 450 mm. pressure. Fractionation of the boron trichloride stream gave 0.192 mmole (13% conversion of boron monoxide) of diboron tetrachloride which had vapor pressures of 2.3 and 6 mm. at –45 and –30°, respectively. The reported vapor pressures of diboron tetrachloride at these temperatures are 2.3 and 6.8 mm.<sup>4</sup> The infrared spectrum of the material isolated was identical with that reported in the literature for diboron tetrachloride,<sup>10</sup> and its elemental analyses were satisfactory for this compound.

(9) T. Wartik and E. F. Apple, *J. Am. Chem. Soc.*, **80**, 6155 (1958).

(10) M. J. Linevsky, *et al.*, *ibid.*, **75**, 3287 (1953); D. E. Mann and L. Fano, *J. Chem. Phys.*, **26**, 1665 (1957).

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#### CESIUM FLUORIDE CATALYZED REARRANGEMENT OF PERFLUORODIENES TO PERFLUORODIALKYLACETYLENES

Sir:

We have found that reaction takes place between cesium fluoride and perfluorodienes at moderate temperatures in the absence of a solvent to yield perfluorodialkylacetylenes. We conclude that the reaction path consists of a series of  $\text{S}_\text{N}2'$  substitutions with fluoride ion as shown below with perfluoro-1,4-pentadiene. The greater stability indicated for the perfluoroalkylacetylenes as compared with the isomeric dienes is in contrast to the relative stabilities of corresponding hydrocarbons<sup>1</sup> and appears to be due to the presence of additional  $\text{CF}_3$ - and  $-\text{CF}_2$ - groupings. The ready conversion of terminal perfluoroolefins into internal olefins by fluoride ion supports this view.<sup>2</sup>

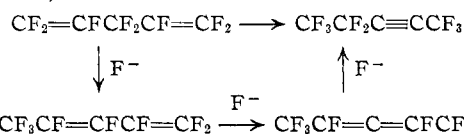
Perfluoro-1,3-butadiene, 4.4 g., and 6.0 g. of anhydrous cesium fluoride were heated in a sealed glass ampule at 150° for 0.5 hr. to yield 3.0 g., 68%, pure perfluoro-2-butyne,  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ , as shown by gas chromatogram,<sup>3</sup> infrared spectrum, and by chlorination to  $\text{CF}_3\text{CCl}_2\text{CCl}_2\text{CF}_3$ , m. p. 82.7–83.5°, reported m. p. 83–84°.<sup>4</sup> A similar reaction at 100° for 0.5 hr. yielded 83%  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  and 1% recovered  $\text{CF}_2=\text{CFCF}=\text{CF}_2$ . At room temperature after 100 days 76.4% pure  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  was isolated. At 200° with a 22 sec.

contact time over  $\text{CsF}$  22%  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  and 40%  $\text{CF}_2=\text{CFCF}=\text{CF}_2$  were recovered.

Recently, Christie, Tlumac, Dresdner and Young reported the preparation of perfluorobicyclopentane, b.p. 3.3–3.6°,<sup>7</sup> from perfluoro-1,4-pentadiene by passing the diene over cesium fluoride at 250°.<sup>5</sup> On repeating this reaction we find that the product, obtained in about 95% yield and purity with a 40 sec. contact time, is, in fact, perfluoro-2-pentyne, a result suggested to us by the rearrangement of perfluoro-1,3-butadiene described above.<sup>6,8</sup>

After purification,<sup>3</sup>  $\text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_3$  was characterized by: b.p. 3–4°, weak  $\lambda_{\text{max}}$  at 4.27, 4.38, 4.92  $\mu$ , strong Raman  $\lambda_{\text{max}}$  2300  $\text{cm}^{-1}$ <sup>11</sup>; reported b.p. 7.5° with weak  $\lambda_{\text{max}}$  at 4.9  $\mu$ .<sup>12</sup> Chlorination gave  $\text{CF}_3\text{CCl}_2\text{CCl}_2\text{CF}_2\text{CF}_3$ , b.p. 150°,  $n_{\text{D}}^{20}$  1.3861  $d_{20}^{20}$  1.853 (Cl, calcd. 40.1; found 40.0%); reported b.p. 145–147°,  $n_{\text{D}}^{24}$  1.3838,  $d_{28.5}^{28.5}$  1.8238.<sup>12</sup>

Reaction takes place very easily between liquid perfluoro-1,4-pentadiene and cesium fluoride. From 3.35 g. of  $\text{CF}_2=\text{CFCF}_2\text{CF}=\text{CF}_2$ <sup>13</sup> and 6.0 g. of  $\text{CsF}$  heated at 80° for 0.5 hr. were recovered 2.3 g., 68%,  $\text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_3$  and 0.20 g., 6%, mixed pentadienes. The intermediate dienes were isolated<sup>3</sup> from a reaction at 45° for 8 hr. and shown to have properties consistent with the structures and reaction sequence given below. From 5.6 g. of  $\text{CF}_2=\text{CFCF}_2\text{CF}=\text{CF}_2$  and 4.0 g. of  $\text{CsF}$  were recovered 0.27 g., 4.8%, of  $\text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_3$ ; 0.47 g., 8.4%,  $\text{CF}_3\text{CF}=\text{C}=\text{CFCF}_3$ , b.p. 17°,  $\lambda_{\text{max}}$  4.94  $\mu$ , tetrachloride, b.p. 151–152°,  $n_{\text{D}}^{20}$  1.3853; 1.22 g., 21.7%,  $\text{CF}_3\text{CF}=\text{CFCF}=\text{CF}_2$ , b.p. 28.4°,  $\lambda_{\text{max}}$  5.60 and 5.78  $\mu$ , tetrachloride, b.p. 151–152°,  $n_{\text{D}}^{20}$  1.3798.



Perfluoro-1,5-hexadiene, b.p. 59.6°,<sup>9</sup> on treatment with  $\text{CsF}$  also yields an acetylenic product, b.p. 27–28°, consisting of two compounds, presumably  $\text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_2\text{CF}_3$  and  $\text{CF}_3\text{CF}_2\text{C}\equiv$

(5) W. H. Christie, F. N. Tlumac, R. D. Dresdner and J. A. Young, Abstracts of Papers, 138th Meeting, Amer. Chem. Soc., New York, N. Y., Sept. 1960, p. 18-M.

(6) The above workers have confirmed our conclusion regarding the formation of  $\text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_3$ . We are grateful to them for details of their experiments and for a comparison sample of their product.<sup>7</sup>

(7) Private communications from R. D. Dresdner and J. A. Young.

(8) Attempts to prepare perfluorobicyclopentane by thermal cyclization of perfluoro-1,4-pentadiene, following the procedure utilized by Fainberg and Miller to prepare perfluorobicyclo[2.2.0]hexane from perfluoro-1,5-hexadiene,<sup>9</sup> have yielded perfluorocyclopentane as the major and thermally stable product.<sup>10</sup> This reaction requires shift of a fluorine atom and probably takes place with the intermediate formation of perfluorobicyclopentane.

(9) A. H. Fainberg and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **79**, 4170 (1957).

(10) P. R. Resnick, Ph.D. Thesis, Cornell University, February, 1961.

(11) We are indebted to R. E. Hester for the Raman spectra.

(12) A. L. Henne and K. A. Latif, *J. Am. Chem. Soc.*, **76**, 610 (1954).

(13) Preparation:  $\text{CClF}_2\text{CClF}_2\text{CF}_2\text{CClF}_2\text{COONa} \xrightarrow{270-290^\circ} \text{CClF}_2\text{CClF}_2\text{CF}_2\text{CF}_2\text{CF}_2$

$\xrightarrow{\text{Zn/EtOH}} \text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_2\text{CF}_3$ , b.p. 33.5–34.0° (725 mm.),  $n_{\text{D}}^{20}$  1.2911,  $d_{20}^{20}$  1.5184. Chlorination yielded  $\text{CClF}_2\text{CClF}_2\text{CF}_2\text{CClF}_2\text{CF}_2$ , b.p. 153.7° (742 mm.),  $n_{\text{D}}^{20}$  1.3744,  $d_{20}^{20}$  1.7902.

(1) D. D. Wagman, C. W. Beckett, J. E. Kilpatrick, K. S. Pitzer, E. J. Prosen and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **35**, 467 (1945); **42**, 225 (1949).

(2) W. T. Miller, Jr., J. H. Fried and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

(3) Gas chromatographic separations and analyses were carried out with dioctyl phthalate on Chromosorb-W at room temperature.

(4) A. L. Henne, J. B. Hinkamp and W. J. Zimmerschied, *J. Am. Chem. Soc.*, **67**, 1906 (1945).

$\text{CCF}_2\text{CF}_3$ , but less readily than  $\text{CF}_2=\text{CFCF}_2$ - $\text{CF}=\text{CF}_2$  owing to the accumulation of relatively stable intermediates.

The above results not only establish a new type of fluoroolefin rearrangement but demonstrate the feasibility of carrying out fluoride ion reactions involving attack on unsaturated carbon in the absence of a solvent under heterogeneous conditions at moderate temperatures. This type of reaction technique with cesium fluoride will be of considerable value in overcoming some of the difficulties previously encountered in bringing about reactions of fluoride ion with carbon-fluorine compounds.<sup>2</sup>

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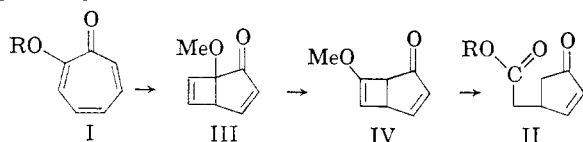
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RECEIVED FEBRUARY 13, 1961

**PHOTOISOMERIZATIONS IN THE  $\alpha$ -TROPOLONE SERIES: THE MECHANISTIC PATH OF THE  $\alpha$ -TROPOLONE TO 4-OXO-2-CYCLOPENTENYLACETIC ACID CONVERSION**

Sir:

It has been reported<sup>1</sup> that ultraviolet irradiation of an aqueous solution of  $\alpha$ -tropolone (Ia) gives the acid IIa and more recently that a similar irradiation of tropolone methyl ether (Ib)<sup>2,3</sup> gives the ester IIb. Various mechanisms have been considered for these transformations<sup>1-3</sup> and we now present evidence which clearly defines the mechanistic pathway from I to II.



a, R = H; b, R = Me

Irradiation<sup>1</sup> of a methanolic solution of Ib in a Pyrex vessel gave photoisomers III (224 m $\mu$ , 5.82 $\mu$ ) and IV (223 m $\mu$ , 5.84 $\mu$ ), separated by vapor phase chromatography. Pyrolysis of III (440°) gave  $\alpha$ -tropolone methyl ether (Ib), indicating only valence tautomeric changes, and pyrolysis of IV (420°) gave 3-methoxytropone<sup>4</sup> (hydrobromide, m.p. 118°), indicating a rearrangement. Hydrogenation of IV over palladium-charcoal gave a tetrahydro derivative (5.75  $\mu$ ; 2,4-dinitrophenylhydrazones, m.p. 170–172°). The n.m.r. spectra of III (2.75 and 4.33  $\tau$ ,  $\beta$  and  $\alpha$  proton; 3.62 and 3.90  $\tau$ , cyclobutene protons; 6.40  $\tau$ , methoxyl proton; 6.74  $\tau$ , ring juncture proton) and of IV (2.42 and 4.07  $\tau$ ,  $\beta$  and  $\alpha$  proton; 5.07  $\tau$ , cyclobutene proton; 6.40  $\tau$ , ring juncture protons; 6.52  $\tau$ , methoxyl protons) clearly estab-

lished the assigned structures. IV upon irradiation in water or on treatment with dilute aqueous acid gave keto ester IIb. The sequence I, III, IV, II for the reaction was established by v.p.c. analysis of aliquots removed during irradiation in methanol. As I decreased, III began to appear and more slowly IV was formed. Continued irradiation left only IV which after the addition of water decayed to II.

The nature of the shift of the methoxyl group was defined clearly by study of 4-methyl and 6-methyltropolone methyl ether. Under similar conditions, the 4-methyl isomer (Va) gave valence tautomer VIa (230 m $\mu$ , 5.85  $\mu$ ) and subsequently rearranged to VIIa (226 m $\mu$ , 5.93 $\mu$ ). The n.m.r. spectrum of the valence tautomer VIa shows a one-proton doublet at 3.80  $\tau$  ( $\alpha$ -proton), a one-proton quartet at 2.36  $\tau$  ( $\beta$ -proton), a one-proton peak at 6.32  $\tau$  (bridgehead proton), a three-proton

peak at 8.12  $\tau$  ( $\text{CH}_3-\text{C}=\text{C}-$ ), a one-proton peak at 4.07  $\tau$  (cyclobutene proton) and a three-proton peak at 6.58  $\tau$  ( $\text{OCH}_3$ ). The rearranged photoproduct VIIa shows a pair of doublets at 4.34 and 2.55  $\tau$  ( $\alpha$ - and  $\beta$ -protons), a three-proton singlet

at 8.60  $\tau$  ( $\text{CH}_3-\text{C}-$ ), a one-proton peak at 5.07  $\tau$

(cyclobutene proton), a three proton-peak at 6.45  $\tau$  ( $\text{OCH}_3$ ) and a one-proton peak at 6.95  $\tau$  (bridgehead proton). The 6-methyl isomer Vb first went to VIb (229 m $\mu$ , 5.89  $\mu$ ) and then to VIIb (223 m $\mu$ , 5.89  $\mu$ ). The valence tautomer VIb shows peaks

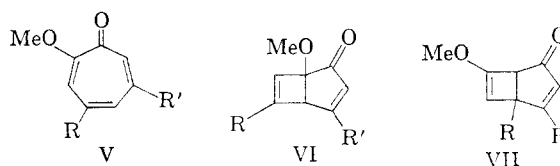
at 4.15  $\tau$  ( $\alpha$ -proton), 7.88  $\tau$  ( $\text{CH}_3-\text{C}=\text{C}-\text{C}=\text{O}$ ), 6.32  $\tau$  (bridgehead proton), 3.62 and 3.21  $\tau$  (cyclobutene protons) and 6.57  $\tau$  ( $\text{OCH}_3$ ). The rearranged photoproduct VIIb shows peaks at 4.25

$\tau$  ( $\alpha$ -proton), 7.94  $\tau$  ( $\text{CH}_3-\text{C}=\text{C}-\text{C}=\text{O}$ ), 6.68 and 6.42  $\tau$  (bridgehead protons), 4.91  $\tau$  (cyclobutene hydrogen), and 6.33  $\tau$  ( $\text{OCH}_3$ ). Both VIIa and VIIb upon acid treatment or irradiation in water yielded the ester analog of II. The ester X shows a pair of doublets at 4.00 and 2.43  $\tau$  ( $\alpha$ - and  $\beta$ -protons), a three proton singlet at 8.70  $\tau$

( $\text{CH}_3-\text{C}-$ ), a two-proton singlet at 7.50  $\tau$  (methyl-

ene adjacent to the ester carbonyl), a peak at 6.37  $\tau$  ( $-\text{OCH}_3$ ) and a pair of one-proton doublets at 7.65 and 7.84  $\tau$  (methylene adjacent to the ketone carbonyl).

The direction of the shifts of the methyl and methoxyl in going from the tropolone structure to the bicyclic structure of type IV or VII can be accounted for in the following manner. The first step is the formation of the expected valence tauto-



a, R = CH<sub>3</sub>, R' = H  
b, R = H, R' = CH<sub>3</sub>

(1) W. G. Dauben, K. Koch and W. E. Thiessen, *J. Am. Chem. Soc.*, **81**, 6087 (1959).

(2) E. J. Forbes and R. A. Ripley, *Chem. and Ind. (London)*, 589 (1960).

(3) W. G. Dauben and K. Koch, Abstracts of International Symposium on Chemistry of Natural Products, Sydney, Australia, 1960, p. 51.

(4) R. B. Johns, A. W. Johnson and M. Tisler, *J. Chem. Soc.*, 4605 (1954).