

and the anisotropic terms should be determined before a serious effort is made to explain the axial and equatorial coupling constants in terms of bonding.

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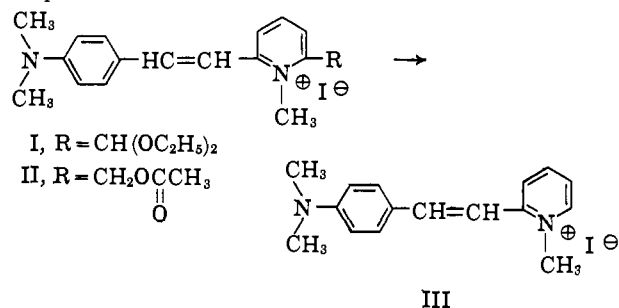
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### An Unexpected Cleavage in the Pyridine Series

Sir:

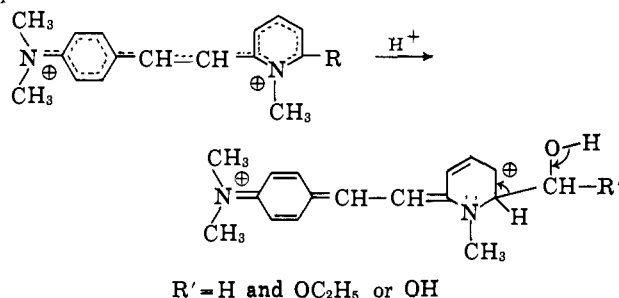
We have observed that an acetoxymethyl group and an aldehyde group, as the acetal, are cleaved from the pyridine nucleus under mild conditions.

The methiodide prepared from the diethyl acetal of 2-methyl-6-pyridinecarboxaldehyde reacted normally with *p*-dimethylaminobenzaldehyde to yield the expected stilbazole I. *Anal.* Calcd. for  $C_{21}H_{29}O_2NI$ : C, 53.82; H, 6.16; N, 5.85. Found: C, 53.85; H, 6.26; N, 6.07. However, attempts to hydrolyze the acetal linkage in dilute acid resulted in the loss of the group R to yield the known stilbazole III<sup>1</sup> with m.p. 269–270° alone or when mixed with an authentic sample; the infrared and ultraviolet spectra of the two samples were also identical.



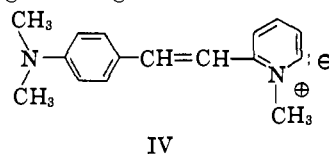
2-Acetoxymethyl-6-methylpyridine methiodide was treated with dimethylaminobenzaldehyde in ethanol and again a cleavage occurred, this time with loss of the acetoxymethyl group. Although stilbazole II was not isolated, it seems reasonable to believe that it was formed and subsequently cleaved in the reaction mixture as for compound I.

Previous work<sup>2,3</sup> has not suggested that 2-acetoxymethylpyridines or the acetals (or hemiacetals) of 2-pyridine aldehydes are unstable. Therefore, it seems likely that the *p*-dimethylaminophenyl group must in some way facilitate the cleavage reaction. A tentative mechanism for this reaction uses the electron pair of the dimethylamino group to increase the electron density of the pyridine ring so that protonation can take place.



- (1) A. P. Phillips, *J. Org. Chem.*, **12**, 333 (1947).  
(2) V. Boekelheide and W. J. Linn, *J. Am. Chem. Soc.*, **76**, 1286 (1954).  
(3) W. Mathes and W. Sauermilch, *Chem. Ztg.*, **80**, 475 (1956).

In order for this mechanism to explain the second cleavage it is necessary that the acetic acid resulting from the alcoholysis of the acetoxymethyl group be able to serve as a proton donor. A variation of this mechanism would allow the cleavage to occur before protonation, generating ion IV as an intermediate.



However, the dimethylaminophenyl group plays no part in this mechanism.

Further experiments to determine the scope of the reaction and to illuminate its mechanism further are in progress.

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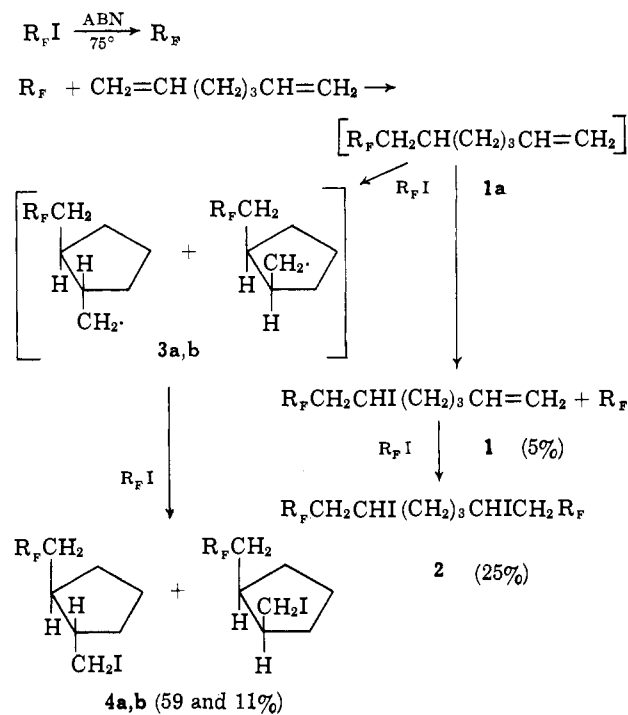
### Cyclization to a Five-Membered Ring in the Free-Radical Reaction of Iodoperfluoroalkanes with 1,6-Heptadiene

Sir:

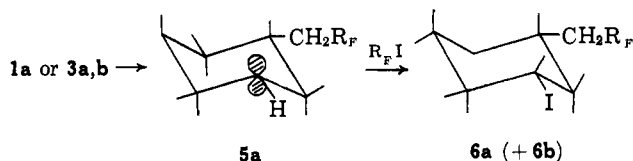
Cyclic polymerization of 1,6-heptadiene to saturated polymeric chains containing six-membered ring units has been reported.<sup>1–3</sup> Free-radical chain reaction of 1,6-heptadiene with 1-iodoperfluoropropane (R<sub>F</sub>I), initiated by 2 mole % of azobisisobutyronitrile, gave an olefinic monoadduct (1), a bisadduct (2), and two isomeric methylcyclopentane derivatives (4a,b) in the ratio of 84:16. Surprisingly, cyclization gave a five-membered ring rather than the anticipated cyclohexane derivatives. Gas chromatography (g.l.c.) showed no other products were formed. Analogous reaction of R<sub>F</sub>I with either 1,5-hexadiene or 1,7-octadiene, however, gave only the olefinic and saturated noncyclic adducts resulting from addition of one or two R<sub>F</sub>I molecules, respectively.

Cyclization of the perfluoroalkylheptenyl radical 1a exclusively to a methylcyclopentane structure indicates an unusual degree of kinetic control of products. Secondary radicals such as 1a or the cyclohexyl radical 5a are generally thought to be more stable than primary radicals such as 3a,b. Cyclohexane is known to be more stable than methylcyclopentane.<sup>4</sup> It seems possible that approach of the large and strongly electronegative R<sub>F</sub>I to within bonding distance of the radical site on 1a may be hindered by the R<sub>F</sub> group already present on the adjacent carbon. For radicals 3a,b this approach is to the fourth carbon removed; for 5a it is also to the fourth carbon, but steric and conformational effects in the cyclohexane system may serve to raise the energy and entropy of the transition state intermediate leading to 6a (or isomer) having bulky R<sub>F</sub>CH<sub>2</sub> and iodine groups.<sup>5</sup> Studies now under-

- (1) For reviews up to 1960, see (a) C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y. (1963), p. 446; (b) G. B. Butler, *J. Polymer Sci.*, **48**, 279 (1960); (c) C. S. Marvel, *ibid.*, **48**, 101 (1960).  
(2) (a) C. S. Marvel and E. J. Gall, *J. Org. Chem.*, **25**, 1784 (1960); (b) N. D. Field, *ibid.*, **25**, 1006 (1960).  
(3) S. G. Matsoyan, G. M. Pogoyan, R. K. Skripnikova, and A. V. Mushyegyan, *Vysokomolekul. Soedin.*, **5**, 183 (1963).  
(4) R. C. Lamb, D. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).  
(5) (a) N. O. Brace, *J. Org. Chem.*, **28**, 3093 (1963); (b) *J. Am. Chem. Soc.*, **84**, 3020 (1962); (c) *ibid.*, in press.

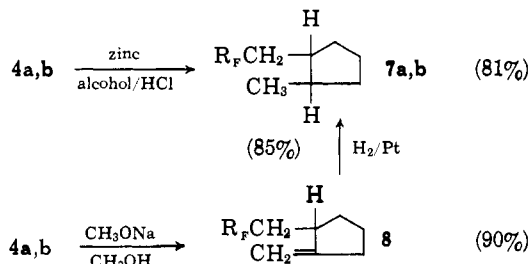


Not observed



way will seek further evidence relating to this problem and its obvious implications for cyclic polymerization and other radical rearrangements.

Evidence for *cis*- and *trans*-1-heptafluorobutyl-2-iodomethylcyclopentane structures for **4a,b** is as follows:<sup>6</sup> (1) zinc reduction of a 20:80 mixture of **4a,b** gave a 20:80 mixture of isomeric heptafluorobutyl-2-methylcyclopentanes<sup>7</sup> (**7a,b**); (2) dehydrohalogenation of **4a,b** gave a single olefin<sup>8</sup> **8**, which added hydrogen at 45 p.s.i. over a platinum catalyst, giving a 45:55 mixture of **7a,b**.



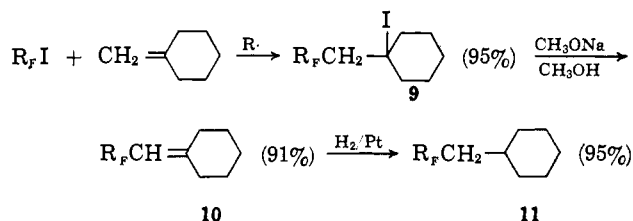
(6) The cyclic isomer mixture (**4a,b**), b.p. 92–93° (5.5 mm.),  $n_D^{25} 1.4295$ – $1.4309$ , was analyzed by g.l.c., but could not be separated by distillation. G.l.c. analyses were done with a Perkin-Elmer vapor fractometer using a polypropylene glycol column (Perkin-Elmer "R" column) at 150°. *Anal.* Calcd. for  $C_{10}H_{12}F_7I$ : C, 30.63; H, 3.09; F, 33.9; I, 32.4. Found: C, 30.9; H, 3.1; F, 34.0; I, 32.0. Olefinic monoadduct **1** (b.p. 65° (4.2 mm.),  $n_D^{25} 1.4160$ ), had an infrared absorption (C=C) band at 6.00 and at 10.10  $\mu$ , and the same analysis.

(7) **7a,b**, b.p. 97° (138 mm.),  $n_D^{25} 1.3562$ . *Anal.* Calcd. for  $C_{10}H_{12}F_7$ : C, 45.12; H, 4.92; F, 50.0. Found: C, 45.6; H, 5.0; F, 50.0. A fraction containing 90% of isomer with retention time of 16.7 min. at 80° was arbitrarily called **7b**; **7a** was separated by gas chromatography, with retention time of 13.4 min.

(8) **8**, b.p. 97° (144 mm.),  $n_D^{25} 1.3638$ . *Anal.* Calcd. for  $C_{10}H_{11}F_7$ : C, 45.46; H, 4.20; F, 50.34. Found: C, 45.6; H, 4.2; F, 50.2. Infrared absorption bands at 6.00 and at 11.30  $\mu$  with an overtone band at 5.62  $\mu$  strongly indicates  $CH_2=CR_1R_2$  rather than  $RCH=CHR$  for **8**.

Infrared and n.m.r. spectra<sup>9</sup> were consistent with structures **4a,b**, **7a,b**, and **8**. There was no proton resonance at  $-4.50$  p.p.m. (relative to tetramethylsilane at 60 Mc.) in **4a,b**, characteristic for  $-CHI$  as in iodocyclohexane,<sup>10</sup> but a resonance pattern at  $-3.25$  p.p.m. (*two*-proton area) was obtained as found for 1-iodobutane.<sup>11</sup> A methyl proton resonance split into a doublet ( $J = 7$  c.p.s.) at  $-0.85$  p.p.m. appeared only in **7b**; in **7a** the methyl peak was at  $-1.10$  p.p.m. Mass spectra of **7a** and **7b** were identical; the principal peak had mass of 56, and next in abundance was 41, consistent with reported spectra for methyl- or dimethylcyclopentanes.<sup>12</sup> Zinc reduction of **6a,b** should have given only one product; dehydrohalogenation ought to have given two olefins, which on hydrogenation could give only one product.

Additional evidence was obtained by synthesis of the anticipated heptafluorobutylcyclohexane (**11**).



The infrared spectrum of **11** was completely different from that of **7a,b** and consistent with a cyclohexane ring. There was no  $CH_3C-$  band at 7.24  $\mu$  and no methyl proton resonance in the n.m.r. spectrum. The mass spectrum of **11** gave a base peak of mass 83, as found for other alkylcyclohexanes.<sup>12</sup>

Reaction of  $R_F I$  with biallyl ether gave a product mixture analogous to 1,6-heptadiene; biallyl cyanamide and diethyl 1,6-heptadiene-4,4-dicarboxylate gave apparently only cyclic monoadducts. An investigation into the scope of this unusual cyclization reaction is underway, and a complete description of these reactions will be published shortly.

(9) The author is indebted to Dr. R. K. Miller for infrared spectra and to T. E. Beukelman for n.m.r. spectra reported herein.

(10) W. C. Neikam and B. P. Dailey, *J. Chem. Phys.*, **38**, 445 (1963).

(11) Varian Associates, "NMR Spectra Catalog," spectrum No. 71. Compare with spectrum No. 72 (2-iodobutane).

(12) The author is indebted to Dr. F. Kitson, who obtained time-of-flight mass spectra of compounds separated by g.l.c. and aided in interpretation of the results.

CONTRIBUTION NO. 361

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### Carbene Insertion into the Carbon-Mercury Bond. Formation of Stable Dichlorocarbene Insertion Products which Undergo an Unusual Thermal Breakdown

Sir:

Although Reutov<sup>1</sup> has reported an insertion of dichlorocarbene into a mercury-chlorine bond, the product has been shown more recently to have resulted from a simple nucleophilic displacement of chloride by the trichloromethyl anion.<sup>2</sup>

We wish to report the first observation of dichlorocarbene (ground electronic state<sup>3</sup>) insertion into one carbon-mercury bond of several simple *sym*-dialkyl-

(1) O. A. Reutov and A. N. Lovtsova, *Dokl. Akad. Nauk SSSR*, **139**, 622 (1961), and references cited therein.

(2) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **84**, 1757 (1962).

(3) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).