

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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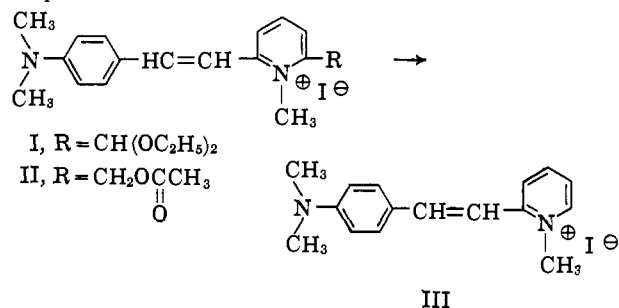
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An Unexpected Cleavage in the Pyridine Series

Sir:

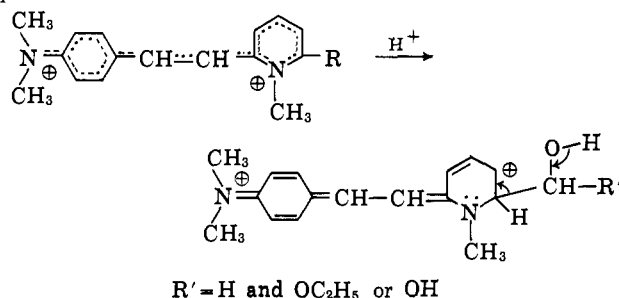
We have observed that an acetoxymethyl group and an aldehyde group, as the acetal, are cleaved from the pyridine nucleus under mild conditions.

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 III¹ 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.



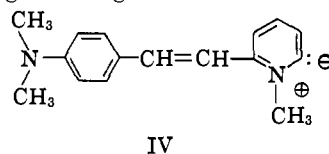
2-Acetoxymethyl-6-methylpyridine methiodide was treated with dimethylaminobenzaldehyde in ethanol and again a cleavage occurred, this time with loss of the acetoxymethyl group. Although stilbazole II was not isolated, it seems reasonable to believe that it was formed and subsequently cleaved in the reaction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

Previous work^{2,3} 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.^{1–3} Free-radical chain reaction of 1,6-heptadiene with 1-iodoperfluoropropane ($R_F I$), 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 $R_F I$ 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 $R_F I$ 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.⁴ It seems possible that approach of the large and strongly electronegative $R_F I$ to within bonding distance of the radical site on 1a may be hindered by the R_F 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 $R_F CH_2$ and iodine groups.⁵ Studies now under-

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