CYCLO-ADDITION OF PERFLUOROISOBUTYLENE TO AZOMETHINES

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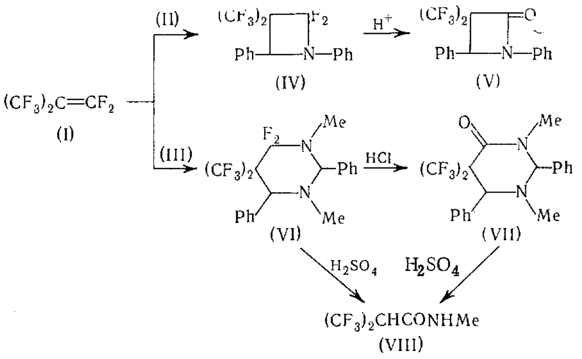
Cyclo-addition to perfluoroisobutylene (I) is a recent discovery [1] and was formerly considered impossible. This is understandable because the mechanism of such a reaction with polyfluoroethylenes and perfluoropropylene is usually of a radical character [2] and homolysis of (I) is impeded owing to the high polarization of the multiple bond. But it is just for this reason that cyclo-addition to (I) is possible by an ion mechanism; this is confirmed by formation of cyclobutane derivatives from (I) and enamines [3] The reaction of (I) with nitrobenzene [1] is also probably effected via a stage of cyclo-addition with subsequent conversion of oxazetidine to the anil of hexafluoroacetone and difluorophosgene.

We studied the reaction of (I) with benzalaniline (II) and benzalmethylamine (III):



Cyclo-addition to (I) can be represented via formation of the bipolar ion $(CF_3)_2\bar{C}-CF_2-\underset{R}{\overset{+}{N}}=CHPh \longleftrightarrow (CF_3)_2\bar{C}-CF_2-\underset{R}{\overset{+}{N}}CHPh$ (A), stabilization of which is determined by steric factors and the character of R. Where R = Ph, formation of A with cyclization to (IV) is observed only under severe conditions (200°C). Where R = Me, owing to the incomparably greater nucleophilicity of the nitrogen in (III) the reaction is effected without heating, with attack of A by the second molecule of azomethine and formation of a more favorable six-membered ring (VI). Clemens and Emmons [4] have described such "trimerization" for tert-alkylazomethines with ketene, and for azomethines with isocyanates and isothiocyanates, the latter also forming trimers with enamines. The structures of (IV) and (VI) have been confirmed by spectral data and a number of conversions. Acid hydrolysis of (IV) gave lactam (V), of which the structure also agrees with its pyrolytic decomposition at 300°C to bis(trifluoromethyl)ketene and benzalaniline. Mild hydrolysis of (VI) gives diazine (VII), while severe hydrolysis gives the methylamide of α-hydroperfluoroisobutyric acid (VIII), which is obtained under the same conditions from (VII). Delyagina et al. [3] described hydrolytic splitting of the C—C bond in the system $(CF_3)_2\underset{|}{C}-\underset{|}{C}H-N\langle$ under milder conditions. The $(CF_3)_2C$ group in this system has a pseudohaloid character and its detachment is facilitated by formation of the stable immonium ion.

In the PMR spectra of (IV), the signals from the atoms of hydrogen and the phenyl substituent are split owing to spin-spin interaction of H^1-F^{19} with the CH_2 group; this is confirmed by the absence of splitting in lactam (V) and also for protons of CH_3NCF_2 (VI) and CH_3NCO (VII) (Fig. 1). Splitting of the proton signal during heating and after sublimation of (VI) indicates conformation transition to the sterically more favor-

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able diequatorial position of the Ph groups and therefore a diaxial position of the protons, at which the interaction with F is maximal.

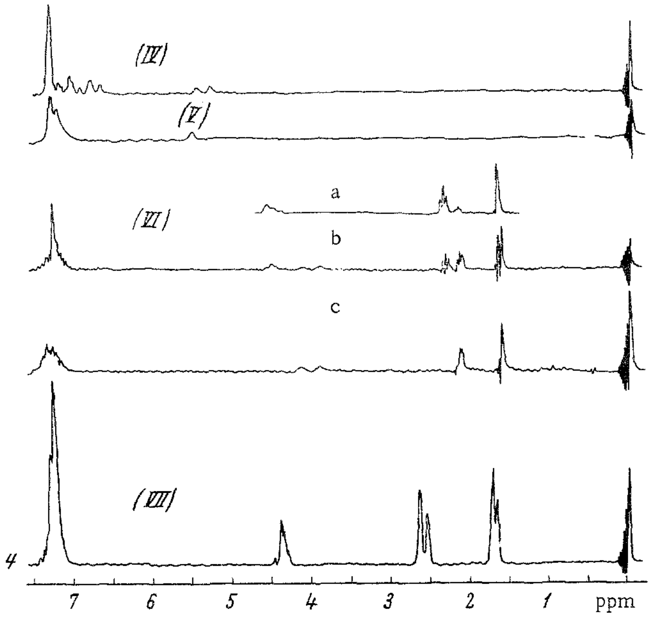

Fig. 1. PMR spectra of (IV)-(VII): a) after recrystallization from heptane; b) after heating to 50°; c) after sublimation.

EXPERIMENTAL

The PMR spectra were measured in an INM-3H-60 apparatus in CCl_4; the internal standard was HMDS. The infrared spectra were determined in a UR-10 and a Hitachi EPI-S2. The mass spectra were determined in an MKh-1303 apparatus at 30 eV.

1,4-Diphenyl-2,2-difluoro-3,3-bis(trifluoromethyl)azetidine (IV). We heated 20 g of benzalaniline and 28 g of perfluoroisobutylene in a steel capsule for 20 h at 190-200°. The unreacted perfluoroisobutylene was driven off by heating to 90°. The crude product-28.5 g (70 %) of (IV); the mp was 83-85°. Found %: C 53.57; H 2.75; N 3.85, F 39.77. $C_{17}H_{11}NF_8$. Calculated %: C 53.50; H 2.88; N 3.68; F 39.95. Compound (IV) was unchanged by boiling with 10 % alcoholic alkali for 5 h.

1,4-Diphenyl-3,3-bis(trifluoromethyl)azetidine-2-one (V). We heated 10 g of azetidine (IV), 15 ml of water, 27 ml of concentrated H_2SO_4, and 3 g of silica gel for 4 h at 100°. The cooled mixture was poured into water, the precipitated oil was extracted with ether and washed with bicarbonate. After distillation of the ether, the crude product was recrystallized from hexane. We obtained 5.3 g (56.5%) of β-lactam (V); the mp was 89-91°. Found %: C 56.80; H 3.13; N 3.99; F 31.60. $C_{17}H_{11}ONF_6$. Calculated %: C 56.94; H 3.06; N 3.90; F 31.76. The infrared spectrum was as follows: $\nu_{C=O}$ 1770 cm^{-1} (in petroleum jelly).

Total mineralization of fluorine occurred when (V) was boiled with 10% alcoholic alkali for 4 h, and also with treatment with liquid ammonia at 20° for 2 days.

We heated 0.5 g of (IV), 8 ml of alcohol, and 8 ml of concentrated HCl in a sealed capsule at 100° for 10 h; this gave 0.3 g of (V) with an mp of 87-89°.

1,3-Dimethyl-2,4-diphenyl-5,5-bis(trifluoromethyl)-6,6-difluorohexahydro-1,3-diazine (VI). We mixed 8 g of benzalmethylamine and 15 g of perfluoroisobutylene at −78° and left the mixture overnight in a sealed capsule at room temperature. After removal of the excess perfluoroisobutylene, the white crystalline product was sublimed in vacuum. We obtained 5 g (34%) of (VI); the mp was 85-86°. Found %: C 55.21; H 4.08. $C_{20}H_{18}N_2F_8$. Calculated %: C 54.79; H 4.13.

Mass spectrum: M^+ absent; m/e (%): 361 (M-77) 8.8%; 211 (15.3); 191 (48.7); 172 (31.6); 119 (65); 118 (100); 109 (35); 106 (71); 105 (65.8); 91 (14); 78 (30); 77 (85.5); 69 (11); 51 (39.5); 42 (28.5).

We heated 1 g of (VI) with 10 ml of 50% H_2SO_4 at 100° for 3 h. Product (VIII) was purified by sublimation in vacuum; the mp was 152°. Mass spectrum: m/e 209 (M^+) 100%; m/e 179 $[(CF_3)_2CHC\equiv O^+]$ 12%; m/e 69 ($CF_3^{\ +}$) 13%; m/e 58 ($O=C=N^+HCH_3$) 88%.

1,3-Dimethyl-2,4-diphenyl-5,5-bis(trifluoromethyl)hexahydro-1,3-diazine-6-one (VII). A quantity of 1 g of (VI) was heated with concentrated HCl, diluted with water, and extracted with heptane. We obtained 0.6 g of (VII); the mp was 115-116°. Found %: C 58.28; H 4.94. $C_{20}H_{18}ON_2F_6$. Calculated %: C 57.69; H 4.35. Infrared spectrum: $\nu_{C=O}$ 1685 cm^{-1} (in CCl_4).

Under the same conditions as the previous experiment, 0.3 g of (VII) was quantitatively converted to (VIII); the mp was 152°.

CONCLUSIONS

Perfluoroisobutylene can participate in cyclo-addition with azomethines.

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