THE NITRODIFLUOROMETHYL GROUP

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Earlier we discovered the intramolecular condensation of the nitro group with an olefinic double bond, found in the δ , ε -position to the nitro group [1]; the condensation of the nitro group with an α,β double bond is also known [2]. It was interesting to ascertain whether the analogous reaction will also proceed with multiple bonds that are located in the γ , δ - and β,γ -positions. It seemed expedient to synthesize the starting compounds from nitroperfluoroacetone. The compound containing a γ, δ double bond (III) was synthesized by the condensation of nitroperfluoroacetone with ketene acetal. In contrast to the (I) oxetanes, which isomerize to unsaturated carbinols at 100°C [3], oxetane (II), which is obtained by the cycloaddition of ketene acetal to nitroperfluoroacetone, isomerizes even at -30° to the unsaturated alcohol (III)



We were unable to detect the intramolecular condensation products of the nitro group with the double bond on heating alcohol (III). From the reaction mixture, besides tar, were isolated difluoronitromethane and the hydrolysis product of trifluoromethyl β , β -diethoxyvinyl ketone (IV), namely trifluoromethylacetoacetic ester (V). The same decomposition is easily accomplished in the presence of catalytic amounts of K_2CO_3 (cf. [4]), and is a convenient method for the synthesis of trifluoromethyl β , β -diethoxyvinyl ketone

$$\begin{array}{c} F_{3}C & CH & OR \\ C & O & C \\ HO & CF_{2}-N-O & OR \end{array} \leftarrow \times - (III) \xrightarrow{K_{2}CO_{3}}{-HCF_{2}NO_{2}} CF_{3}C-CH=C & OR & O \\ HO & CF_{2}-N-O & OR & O & OR \\ (IV) & (V) & (V) \end{array}$$

The ester of β -trifluoromethyl- β -nitrodifluoromethylacrylic acid could serve as the compound containing the β, γ double bond. A convenient method for the synthesis of β,β -bis(trifluoromethyl)acrylic acid is the isomerization of bis(trifluoromethyl)- β -propiolactone [5], but this method could not be applied to the synthesis of trifluoromethylnitrodifluoromethyl lactone: heating lactone (VI) with BF₃ etherate yielded not the unsaturated acid, but the ester of the β -hydroxy acid (VII). The same ester can also be obtained by the esterification of the condensation product of nitroperfluoroacetone with malonic acid (cf. [6])



Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2742-2744, December, 1972. Original article submitted October 13, 1971.

• 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00. We were able to obtain the unsaturated ester (VIII) by the condensation of nitroperfluoroacetone with ethoxyacetylene. The initially formed cycloadduct (IX) was recorded by means of the NMR spectra, which, similar to its hexafluorodimethyl analog [7], isomerizes even at room temperature to a mixture of the cisand trans-isomers of the α,β -unsaturated ester



The ethyl ester of β -trifluoromethyl- β -nitrodifluoromethylacrylic acid (VIII) remains unchanged on prolonged heating at 140-150°.

Thus, for the objects available to us, and under conditions in which intramolecular condensation of the nitro group with δ , ε double bonds took place, we were unable to accomplish the intramolecular condensation of the nitro group β , γ and γ , δ double bonds.

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-10 instrument, while the NMR spectra (δ , ppm) were taken on a Perkin-Elmer R-12 spectrometer (HMDS was used as the internal standard). The ¹⁹F NMR spectra were taken on a Hitachi spectrometer (56.46 MHz) (external standard CF₃COOH), and the chemical shifts are given in parts per million from CF₃COOH.

 $\begin{array}{l} \underline{\beta}, \beta-\text{Diethoxyvinyltrifluoromethylnitrodifluoromethylcarbinol (III).} & \text{To 6.9 ml of nitroperfluoroacetone} \\ \text{at} - 30^\circ \text{ was added 6 g of ketene diethyl acetal.} & \text{The mixture was allowed to stand at the same temperature} \\ \text{for 2 h. Vacuum-distillation gave 14.1 g (88\%) of (III), bp 72-73^\circ (2 mm).} & \text{Found: C 35.73; H 4.09; F 30.33;} \\ \text{N 4.50\%. } C_9H_{12}O_5\text{NF}_5\text{.} & \text{Calculated: C 35.06; H 3.89; F 30.84; N 4.54\%.} & \text{Infrared spectrum: 1600 (NO_2), 1675} \\ \text{(C=C); 3360 cm^{-1} (OH).} & \text{NMR spectrum: } \delta_{\text{CH}_3}1.22 \text{ and } 1.33 (two triplets); \\ \delta_{\text{OCH}_2}3.88 \text{ and } 4.08 (two quartets); \\ J_{\text{CH}_2-\text{CH}_3}6.6 \text{ Hz; } \delta_{\text{CH}}5.77 (\text{singlet}); \\ \delta_{\text{OH}}3.62 (\text{singlet}). & \text{The IR and NMR spectra of the sample taken from the reaction mixture at - 30^\circ and of the product obtained after distillation were identical.} \end{array}$

Trifluoromethyl β,β-Diethoxyvinyl Ketone (IV). A mixture of 6.2 g of (III) and a catalytic amount of K_2CO_3 was heated at 110-140°. The difluoronitromethane was distilled off, and was identified by GLC. Vacuum-distillation of the residue gave 3.8 g (90%) of the unsaturated ketone (IV), bp 112-113° (7 mm); mol. wt. 212 (mass-spectrometrically). Found: C 45.15; H 5.26; F 26.44%. $C_8H_{11}O_3F_3$. Calculated: C 45.28; H 5.18; F 26.88%. Infrared spectrum: 1560, 1575, 1690 cm⁻¹. NMR spectrum: δ_{CH_3} 1.32 (triplet); δ_{OCH_2} 4.14 (broad quartet); δ_{CH} 4.86 (singlet). ¹⁹F NMR spectrum: ~ 0 (singlet).

Ethyl Ester of Hydroxynitroperfluoroisopropylacetic Acid (VII). To a solution of 5.2 g of malonic acid in 8 ml of pyridine was added 8.9 g of nitroperfluoroacetone in drops. After 0.5 h the reaction mixture was poured into chilled dilute HCl solution and then extracted with ether. The ether was distilled off, and to the residue were added 20 ml of absolute alcohol and 0.5 ml of conc. H₂SO₄. After refluxing for 25 h, the mixture was poured into water and the obtained oil was washed with water, dried, and distilled. We obtained 6.2 g (48%) of ester (VII), bp 79-80° (7 mm). Found: C 29.52; H 2.75; F 32.34; N 6.33%. C₇H₈O₅ · NF₅. Calculated: C 29.52; H 2.85; F 33.1; N 4.9%. NMR spectrum: δ_{CH_3} 1.3 (triplet), δ_{OCH_2} 4.3 (quartet), $J_{CH_2-CH_3}$ 6.6 Hz; δ_{CH_2} 2.9 and 3.3 (AB system), J_{H-H} 17.4 Hz; δ_{OH} 7.1 (singlet). ¹⁹F NMR spectrum: 0 (CF₃, X₃ component of AEX₃ system as a doublet of doublets); J 9.6 and 14.5 Hz; +12.3, +15.4, +18.2, +21.3 (A and B components of ABX₃ system).

A mixture of 6.5 g of lactone (VI) and 5.2 g of BF_3 etherate was heated at 80° for 6 h. Vacuum-distillation gave 2.4 g of the unreacted lactone (VI) (identified by GLC) and 3.75 g of ester (VII), which was identical with that obtained above (GLC).

Ethyl Ester of β -Trifluoromethyl- β -nitrodifluoromethylacrylic Acid (VIII). To 2.6 ml of nitroperfluoroacetone in 25 ml of absolute ether at -60° was added 1.4 g of ethoxyacetylene. A sample was taken immediately, from which the ether was distilled in vacuo. The NMR spectrum of the sample disclosed the presence of oxetene (IX), δ_{CH_3} 0.86 (triplet), δ_{OCH_2} 3.57 (quartet), $J_{CH_2-CH_3}$ 6.6 Hz, δ_{CH} 4.12. Vacuum-distillation gave 4.6 g (89%) of (VIII), bp 46-49° (9 mm). Found: C 32.30; H 2.49; F 36.94%. $C_7H_6O_4NF_5$. Calculated: C 31.94; H 2.26; F 36.12%. Infrared spectrum: 1615, 1700, 1760 cm⁻¹. NMR spectrum: δ_{CH_3} 0.97 and 1.02 (two triplets), δ_{OCH_2} 4.00 and 4.06 (two quartets), δ_{CH} 6.51 and 6.69 (two singlets).

CONCLUSIONS

We synthesized a number of saturated and unsaturated compounds containing the nitrodifluoromethyl group.

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