REACTION OF DIAZOMETHANE WITH SOME α-SUBSTITUTED ACRYLATES

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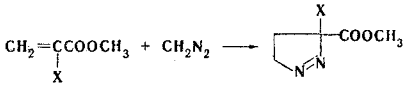
The reaction of methyl α-methoxy-, α-acetoxy-, and α-chloroacrylate with diazomethane proceeds in conformity with the −M orienting effect of the ester group. The resulting Δ^1-pyrazolines are converted to 3(5)-carbomethoxypyrazole at room temperature (the reaction proceeds more readily on heating).

Acrylates react with diazomethane in such a way that the methylene group of the nucleophile adds to the β-carbon atom [1]. Cycloaddition occurs most readily when there is an electron-acceptor group [2, 3] in the α position or when there is a substituent that has a weak electron-donor effect [4, 5] in the β position. On the other hand, when there is a grouping with a strong +M effect in the β position, the reaction does not proceed at all [2, 4]. Little study has been devoted to the addition of diazomethane to acrylates that have substituents with a +M effect in the α position [1, 6].

We have investigated the reaction of diazomethane with methyl α-methoxyacrylate, methyl α-acetoxyacrylate, and methyl α-chloroacrylate (I-III). The addition proceeded smoothly at room temperature, while the reaction with esters II and III proceeded even in the cold. The primary products of the cyclization are Δ^1-pyrazoline derivatives:

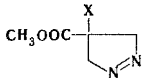


I-III IV-VI

I, IV $X = CH_3O$; II, V $X = CH_3COO$; III, VI $X = Cl$

Pyrazolines IV-VI are unstable, and we were able to isolate only IV by means of vacuum distillation. It is known that 3,3-disubstituted Δ^1-pyrazolines are isomerized with difficulty to Δ^2-pyrazolines [7] and can be isolated by distillation [6] and that IR-spectroscopic methods make it possible to distinguish between Δ^1- and Δ^2-pyrazolines [8]. The IR spectrum of IV contained a band with a maximum at 1565 cm^{-1}, which is characteristic for the stretching vibrations of the $N = N$ bond, and bands at $\sim$1590 and 3300 cm^{-1} ($\nu_{C=N}$ and ν_{N-H}, respectively) were not detected.

The other direction of addition would have led to 4,4-disubstituted Δ^1-pyrazolines.



In fact, the latter are not formed, since 3(5)-carbomethoxypyrazole (VII) was obtained in the process of spontaneous splitting out of HX, which occurred even at room temperature. Similar reactions have been observed previously in a study of the reaction of diazomethane with some β-chlorovinyl ketones [9] and β- and α-substituted acrylates [4-6].

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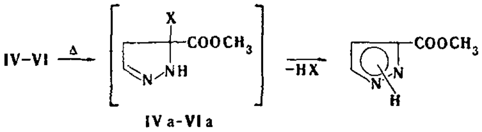

Catalytic amounts of acids, for example, acetic acid, considerably accelerated the conversion of IV and V to X, while the conversion of VI proceeded extremely vigorously at 50-70° in the absence of acids. The ability to split out H−X fragments was in agreement with the known data on the thermal stability of organic compounds that have the indicated substituents, and decreased in the order VI > V > IV.

Thus nucleophilic addition to multiple bonds that have two substituents with opposite M effects and identical I effects attached to one carbon atom occurs readily and leads to products strictly in accordance with the −M orienting effect of the ester group.

EXPERIMENTAL

The IR spectra were recorded with a UR-10 spectrophotometer.

3-Methoxy-3-carbomethoxy-Δ^1-pyrazoline (IV). A solution of 4.4 g (0.105 mole) of diazomethane [11] in 160-180 ml of ether was added at room temperature to a solution of 11.6 g (0.1 mole) of I [10] in 20 ml of dry ether, after which the mixture was allowed to stand for 24-30 h. The solvent and unchanged reagents were removed in vacuo, and the residue was distilled at a bath temperature of 90-95° to give 13.5 g (86%) of IV with bp 75-77° (1 mm) and n_D^{20} 1.4578. Found: C 45.9; H 6.2; N 18.0%; mol. wt. (cryoscopically), 155. $C_6H_{10}N_2O_3$. Calculated: C 45.5; H 6.3; N 17.7%; mol. wt. 158. In contrast to the reaction with I, the reaction of diazomethane with II [12] and III [13] was carried out in the cold, and the residue after removal of the solvent and unchanged reagents was not distilled because of the thermal instability of Δ^1-pyrazolines V and VI. Workup gave 18.0 g (96%) of V and 15.3 g (94%) of VI.

3(5)-Carbomethoxypyrazole (VII). A few drops of acetic acid were added to a solution of 0.1 mole of IV or V in 30 ml of benzene, and the mixture was stirred and heated on a water bath at 50-95° for 4 h. The precipitate was removed by filtration, washed with benzene, and dried to give 9.5-10.2 g (75-85%) of VII with mp 139.2-139.8° (from ether). A mixture of this product with the known pyrazole [14] melted without depression. In the case of pyrazoline VI, no more than 0.01-0.03-mole portions were used, and the mixture was heated at 50-70°.

LITERATURE CITED

1. P. Vatsulik, Chemistry of Monomers [Russian translation], Vol. 1, Inostr. Lit., Moscow (1960), p. 465.
2. I. A. D'yakonov, Zh. Obshch. Khim., 17, 67 (1947).
3. S. Mohan and J. S. Sandu, J. Indian Chem. Soc., 48, 305 (1971).
4. D. T. Witjak and M. C. Lu, J. Org. Chem., 33, 4451 (1968).
5. D. T. Witjak and B. K. Sinha, J. Org. Chem., 35, 501 (1970).
6. Yu. A. Kotikyan, P. V. Petrovskii, B. L. Dyatkin, and I. L. Knunyants, Zh. Organ. Khim., 7, 1363 (1971).
7. R. Elderfield (editor), Heterocyclic Compounds [Russian translation], Vol. 5, Inostr. Lit., Moscow (1961), p. 59.
8. B. V. Ioffe, Khim. Geterotsikl. Soedin., 1089 (1968).
9. A. N. Nesmeyanov and N. K. Kochetkov, Dokl. Akad. Nauk SSSR, 77, 65 (1951).
10. J. W. Baker, J. Chem. Soc., 521 (1942).
11. Organic Syntheses [Russian translation], Vol. 2, Inostr. Lit., Moscow (1949), p. 174.
12. T. M. Laakso and C. C. Unruh, Ind. Eng. Chem., 50, 1119 (1958).
13. W. Sorenson and T. Campbell, Preparative Methods of Polymer Chemistry, Wiley (1968).
14. N. K. Reimlinger, Ber., 93, 1857 (1960).