NEW REARRANGEMENT IN THE o-CARBOMETHOXYDIAZOACETYLPYRIDINE SERIES

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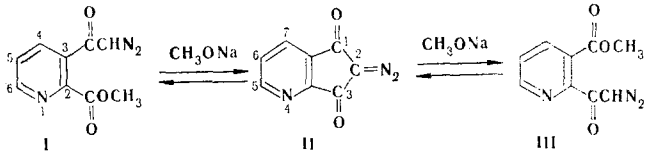
We have observed that a rearrangement occurs in the reaction of o-carbomethoxydiazoacetylpyirdines with sodium methoxide; the product of this rearrangement is the isomeric diazo ketone.

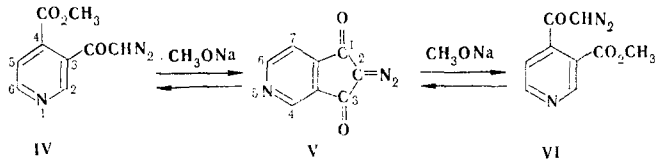
Thus diazo ketone I at room temperature in methanol in the presence of 5% CH_3ONa solution is converted to the isomeric diazo ketone III. In turn, the addition of sodium methoxide to a methanol solution of III leads to the formation of diazo ketone I.



I II III

2-Diazo-4-azaindan-1,3-dione (II) is present in the reaction mixtures in both cases. Equilibrium is established after 48 h, and the percentages of diazo ketones I-III in the reaction mixture are 7.5, 7.5, and 85%, respectively.

The mutual rearrangement of β,γ-isomeric diazo ketones IV and VI proceeds under similar conditions; in this case the percentages of IV-VI in the equilibrium mixture are 37.5, 7.5, and 55%, respectively (according to the PMR data).



IV V VI

Diazo ketone I was obtained by the method in [1], and isomeric III, IV, and VI were similarly obtained.

Diazo ketone I was obtained in 67% yield and had mp 68°C. IR spectrum: 2097, 1725, 1600 and 1555 cm^{-1}. PMR spectrum ($CDCl_3$): 8.81 (1H, q, 6-H, J_{65} = 4.5 Hz, J_{64} = 1.5 Hz), 7.92 (1H, q, 4-H, J_{45} = 7.5 Hz, J_{46} = 1.5 Hz), 7.59 (1H, q, 5-H, J_{54} = 7.5 Hz, J_{56} = 4.5 Hz), 5.82 (1H, s, CH), and 4.08 ppm (3H, s, $COOCH_3$).

Diazo ketone III was obtained in 78% yield and had mp 51°C. IR spectrum: 2085, 1725, 1600, and 1550 cm^{-1}. PMR spectrum: 8.70 (1H, q, 6-H, J_{65} = 4.5 Hz, J_{64} = 1.5 Hz), 7.92 (1H, q, 4-H, J_{45} = 7.5 Hz, J_{46} = 1.5 Hz), 7.55 (1H, q, 5-H, J_{54} = 7.5 Hz, J_{56} = 4.5 Hz), 6.06 (1H, s, CH), and 4.03 ppm (3H, s, $COOCH_3$).

Dizao ketone IV was obtained in 65% yield as an oil. IR spectrum: 2105, 1735, 1620, 1585, and 1555 cm^{-1}. PMR spectrum: 8.80 (1H, d, 6-H, J_{65} = 4.5 Hz), 8.77 (1H, s, 2-H), 7.60 (1H, d, 5-H, J_{56} = 4.5 Hz), 5.80 (1H, s, CH), and 3.93 ppm (3H, s, $COOCH_3$).

Diazo ketone VI was obtained in 37% yield as an oil. IR spectrum: 2110, 1730, 1625, 1590, and 1555 cm^{-1}. PMR spectrum: 9.09 (1H, s, 2-H), 8.80 (1H, d, 6-H, J_{65} = 4.5 Hz), 7.32 (1H, d, 5-H, J_{56} = 4.5 Hz), 5.63 (1H, s, CH), and 3.93 ppm (3H, s, $COOCH_3$).

Compound II was obtained in 7.5% yield and had mp 152°C. IR spectrum; 2130, 1730, 1700, and 1575 cm^{-1}. PMR spectrum; 9.14 (1H, q, 5-H, J_{56} = 4.5 Hz, J_{57} = 1.5 Hz), 8.28 (1H, q, 7-H, J_{76} = 7.5 Hz, J_{75} = 1.5 Hz), and 7.77 ppm (1H, q, 6-H, J_{67} = 7.5 Hz, J_{65} = 4.5 Hz).

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Compound V was obtained in 7.5% yield as an oil. IR spectrum: 2125, 1730, 1690, and 1590 cm^{-1}. PMR spectrum: 9.27 (1H, s, 2-H), 8.80 (1H, d, 6-H, J_{65} = 4.5 Hz), and 7.69 ppm (1H, d, 5-H, J_{56} = 4.5 Hz).

The results of elementary analysis of the compounds obtained for the C, H, and N content were in agreement with the calculated values.

LITERATURE CITED

1. K. Miescher and H. Kägi, Helv. Chim. Acta, 24, 1471 (1941).