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α-DIAZOBUTYRALDEHYDE: THE FIRST ALIPHATIC α-DIAZOALDEHYDE

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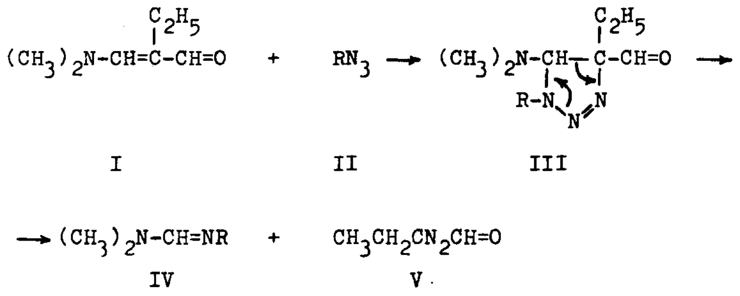
Although very much attention has already been devoted to aliphatic diazo compounds, no α-diazoaldehyde has yet been reported. We now wish to report the preparation of the first representative of this class, α-diazobutyraldehyde (V). The synthesis was accomplished by reaction of α-ethyl-β-dimethylaminoacraldehyde (I) (1) with certain reactive organic azides (II) (cf. Scheme 1).



Scheme 1

Direct introduction of the diazo group by means of an organic azide has for the first time been reported by Doering and DePuy (2); subsequently, the method was adapted to provide a general procedure for the synthesis of diazodiketones, diazodisulphones etc., in which the diazo group was directly introduced on an activated methylene group (3-6). The synthesis now reported sets out from the findings of Fusco and coworkers (7) who studied the reaction of enamines with organic azides; one of the reactions they found in the case of dialkylaminomethylenecarbonyl derivatives was the formation of diazoketones.

The formulae in Scheme 1 show the probable reaction sequence leading to the diazoaldehyde V, involving the fragmentation of the postulated unstable intermediate III, itself formed by a dipolar addition reaction. The procedure ows its succes to the fact that the diazoaldehyde does not come into contact with any reagents other than the starting compounds themselves and that the entire reaction is conducted in an inert aprotic solvent.

α-Diazobutyraldehyde is a yellow oil which may be distilled under reduced pressure at low temperatures; it can be kept at 0°C for several days without notable decomposition. The postulated structure is in accord with analytical as well as spectral data. The infrared spectrum exhibits characteristic bands for the diazo and the carbonyl groups, 2080 and 1655 cm^{-1}, respectively, and bands at 2750 and 2830 cm^{-1} assigned to the C-H stretching vibrations of the CH=O group. The maxima in the ultraviolet (249 mμ, log ε 4.00; 284 mμ, log ε 3.81; 383 mμ, log ε 1.51) are close to those of the isomeric propionyldiazomethane (8). α-Diazobutyraldehyde liberates nitrogen on treatment with dilute acids, or on addition of traces of copper.

The yields of the diazoaldehyde were found to depend mainly on the character of the group R in the organic azide. Apart from tosyl azide we have made use of pikryl azide and cyanogen azide. The optimum conditions and the scope and limitations of the present reaction are being investigated.

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