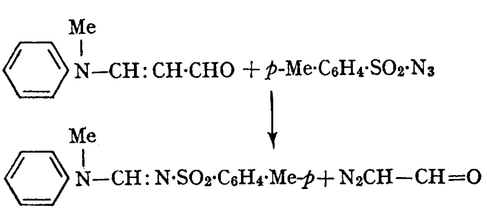
Diazoacetaldehyde as a Source of Formylcarbene: a New Carbene Species

By Z. ARNOLD

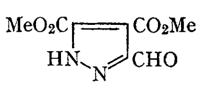
(*Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Science, Prague*)

RECENTLY we synthesised α-diazo-aldehydes, $R{\cdot}CN_2{\cdot}CH{=}O$ (R = alkyl),[1] a class of compounds till then unknown. With a slight modification of this method, we have now prepared the first member of this series, diazoacetaldehyde. Kaplan and Meloy[2] reported that this compound can be detected by n.m.r. spectroscopy in the crude residue obtained from the reaction between diazomethane and formyl fluoride, but they did not succeed in isolating the diazoaldehyde in a pure state. We have found that diazoacetaldehyde can be prepared (*ca.* 70% yield) by heating β-*N*-methylanilinoacraldehyde with excess of toluene-*p*-sulphonyl azide *in vacuo* to about 70—80° (Scheme 1). Diazoacetaldehyde distils off as soon as it is formed, which is important as its stability is limited at elevated temperatures. (Caution! Even pure diazoacetaldehyde detonates very violently when over-heated and great care is required in handling it!)

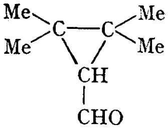


The product can be purified by rectification *in vacuo* (bath temperature not > 50°) or by extraction *e.g.*, by dissolving it in water, filtering, and extracting into methylene chloride. The product thus obtained is a yellow liquid, boiling at about 40°/10 mm. Hg (bath temperature), n_D^{20} 1·5263, d_{20} 1·159. It is soluble in water and most organic solvents, but insoluble in nonpolar hydrocarbons. It can be stored for several weeks at −70° without noticeable decomposition.*

Owing to the instability of diazoacetaldehyde in both acidic and alkaline medium we were unable to prepare simple aldehyde derivatives. Diazoacetaldehyde reacts with methyl acetylenedicarboxylate[3] to give a compound, m.p. 167—169°, which is 3-formyl-4,5-dimethoxycarbonylpyrazole (I) or its tautomer, 5-formyl-3,4-dimethoxycarbonylpyrazole. [I.r. spectrum: ν(CH=O) 1685 ν(NH) 3360, ν(CO) 1745 cm.$^{-1}$; Semicarbazone, m.p. 229—233·5°.]



(I)



(II)

In contrast to the widely studied alkoxycarbonyl- and keto-carbenes,[4] no successful attempts to produce formylcarbene have yet been reported. We found that, in the presence of catalysts used for

---

* A detailed spectral study of diazoacetaldehyde will be published separately.

producing carbenes from the corresponding diazo-compounds, diazoacetaldehyde decomposes quite readily and this decomposition reaction in tetramethylethylene has been studied. In addition to some polymeric material and some gaseous products in which the presence of keten has been proved, a neutral fraction has been isolated containing the desired product, tetramethylcyclopropanecarboxaldehyde (II). The quantity and the composition of the neutral portion is strongly dependent on the catalyst used. For the production of the cyclopropane derivative, copper acetylacetonate[5] proved to be the most efficient—with this catalyst the yield of (II) was 25% as shown by v.p.c. The cyclopropane derivative (II) gives a semicarbazone, m.p. 161—164°; on oxidation it gives the known tetramethylcyclopropanecarboxylic acid.[6] The n.m.r. spectrum (in $CDCl_3$) of the aldehyde (II) contains two signals at τ 8·66 (6H) and τ 8·82 (6 H), corresponding to two types of methyl group, one proton at τ 0·55 (1 H) coupled with one proton hidden under the signal of the methyl groups at τ 8·7 (J = 6·0 c./sec.).

Thus diazoacetaldehyde can serve as a source for producing formylcarbene. The chemical behaviour of this species observed so far, *i.e.*, both the addition reaction yielding the cyclopropane derivative and the rearrangement to keten resemble that of the keto-carbenes. These and other aspects of the chemistry of diazoaldehydes and formylcarbenes are under study.

(*Received, February* 13*th*, 1967; *Com.* 133.)

---

[1] J. Kučera and Z. Arnold, *Tetrahedron Letters*, 1966, 1109.

[2] F. Kaplan and G. K. Meloy, *J. Amer. Chem. Soc.*, 1966, **88**, 950.

[3] R. Huisgen, *Angew. Chem.*, 1963, **75**, 604.

[4] W. Kirmse, "Carbene Chemistry," Academic Press, New York and London, 1964.

[5] R. Huisgen, G. Binch, and L. Ghosez, *Chem. Ber.*, 1964, **97**, 2628.

[6] A. P. Meshcheryakov and I. E. Dolgii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1960, 931 (*Chem. Abs.*, 1961, **54**, 24436).