REACTIONS OF CARBENES WITH DIAZOCOMPOUNDS, V* A NEW CUMULENE SYNTHESIS

Hans Reimlinger and Robert Paulissen**
Union Carbide European Research Associates, B - 1180 Brussels, Belgium
and University of Liège, Institut de Chimie Organique

(Received in UK 9 June 1970; accepted for publication 2 July 1970)

Some years ago we found that halocarbenes react with diazoalkanes to form 1,1-dihaloethylenes (1). In the meantime this reaction has been applied to other carbenes and several diazocompounds for the preparation of 1,1-dihaloethylenes (2), 1-halo-1-aryl-ethylenes (2), unsymmetrical azines (3), thiovinyl ethers (4), 1-halo-1-arylmercapto-ethylenes (4), bis [phenylmercapto]cyclopropanes (4), haloacetylenes (5) or dichlorovinyl dialkyl phosphates (6). Other 1,3-dipoles have so far been used only in one case (7) for the preparation of N-(dichloromethylene)-amines from azides and dichlorocarbene.

We have now extended this type of reaction to vinylidene carbenes 2 (8) which are formed from derivatives of ethynylcarbinols 1 in the presence of a base and which have been trapped by olefins to give ethylidene cyclopropanes (8).

The formation of carbene $\underline{2}$ in the presence of a diazocompound in an inert solvent gives rise to the synthesis of the corresponding cumulenes $\underline{3a} - \underline{e}$.

Applying the same procedure as described for the preparation of 1, 1-dihalo-ethylenes (2) moderate yields of 3 are obtained. The known cumulenes 3a (9) (10), 3b (10) (11) and 3c (10) (12) (21%, 26%, and 16% respectively) were identified by their physical properties. The two new cumulenes have been obtained in small yields: 3d (7%), m.p. $214-215^{\circ}$. Anal. Calcd. for $C_{26}H_{16}S:C$, 86.64; H, 4.48; S, 8.88%. Found: C, 86.02; H, 4.60; S, 8.84%. chloroform 251, 277, and 474 nm (ϵ , 37100, 26700, and 44300). V_{max}^{KBr} 2030, 1440, 1350, and 722 cm⁻¹.

3e (5%), m.p. 180°. Anal. Calcd. for C₂₂H₂₂: C, 92.25; H, 7.75%; Found: C, 92.30; H, 7.67%.

 $\lambda_{\rm max}^{\rm dioxane}$ 234, 249, 258, 298, 313, and 326 nm (ϵ ,39300, 21060, 28910, 33550, 39260, and 41410). $\nu_{\rm max}^{\rm KBr}$ 2961, 2850, 1949, 1206, and 895 cm⁻¹.

All attempts to reduce the undesired decomposition of the diazoalkane by the base have so far been unsuccessful.

- For the previous paper in this series, see ref. 4.
- In part fulfilment of the requirements for the degree of Docteur en Science Chimique of the University of Liège.

REFERENCES

- 1. H. Reimlinger, Angew. Chem. 73, 153 (1962).
- 2. H. Reimlinger, Chem. Ber. 97, 339 (1964); A. Schönberg and E. Fresse, Tetrahedron Letters 1964, 2575.
- 3. H. Reimlinger, Chem. Ber. 97, 3503 (1964).
- 4. H. Reimlinger, Chem. and Ind. 1966, 1682.
- H. Reimlinger, presented at the Annual Meeting of GdCH in Heidelberg 1963, abstracted in Angew. Chem. 75, 1122 (1963); S. P. McManus, J. T. Carroll and C. L. Dodson, J. Org. Chemistry 33, 4272 (1968).
- 6. D. Seyferth, P. Hilbert and R.S. Marmor, J. Amer chem. Soc. 89, 4811 (1967).
- 7. J.E. Baldwin and J.E. Patrick, Chem. Commun. 1968, 968.
- 8. H.D. Hartzler, J. Amer. chem. Soc. 83, 4990 (1961).
- 9. K. Brand, Ber. dtsch. chem. Ges. 54, 1987 (1921).
- 10. R. Kuhn and H. Fischer, Chem. Ber. 92, 1849 (1959).
- 11. R. Kuhn and J. Jahn, Chem. Ber. 86, 759 (1953).
- 12. E. Bergmann, W. Hoffmann and D. Winter, Ber. dtsch. chem. Ges. 66, 46 (1933).