

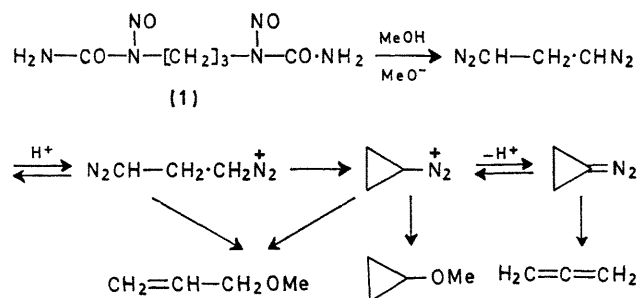
Methanolysis of 1,1-Bis(diazomethyl)cyclopropane

By WOLFGANG KIRMSE* and BERND BRINKMANN

(Abteilung für Chemie der Ruhr-Universität, 463 Bochum, Germany)

Summary Most of the products of the methanolysis of 1,1-bis(diazomethyl)cyclopropane arise by independent decomposition of the two diazomethyl groups, but one product (**11**) is probably formed *via* the spirocyclic diazonium ion (**10**).

THE formation of methoxycyclopropane (50%) and allene (18%) among the products of the alkaline cleavage of *NN'*-trimethylene-bis-*N*-nitrosoarea (**1**) has been attributed to the intervention of diazocyclopropane and cyclopropyl-diazonium ions¹ (Scheme 1). Under similar conditions

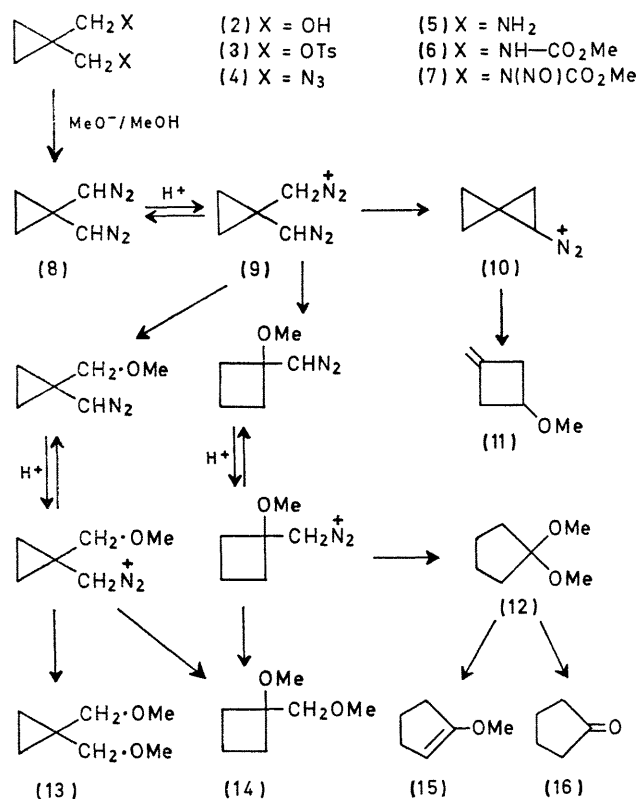


SCHEME 1

Products of the Alkaline Cleavage of (7) and the Solvolysis of (3) (%)

| | (11) | (12) | (13) | (14) | (15) | (16) |
|--|------|------|------|------|------|------|
| (7) MeOH-Na ₂ CO ₃ | 14.6 | 19.8 | 3.6 | 7.2 | 44.4 | 0.4 |
| (7) 5N-NaOMe | .. | 13.9 | 16.7 | 6.9 | 8.6 | 36.5 |
| (3) 2N-NaOMe | .. | 1.0 | — | 43.8 | 44.5 | — |

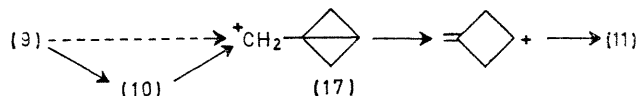
compound (7), prepared by the sequence (2) → (7), afforded compounds (11—16) (Scheme 2 and Table). Compounds (12), (13), and (14) were identified by comparison with authentic samples obtained by methylation (NaNH₂-MeI)



SCHEME 2

of (2) and 1-hydroxymethylcyclobutan-1-ol,² and by acetalization (methyl orthoformate) of cyclopentanone, respectively. 1-Methoxycyclopentene (15) and cyclopentanone (16) arise from (12) during the work-up and g.l.p.c.

separation. The formation of compounds (12)—(16) is due to the independent decomposition of the two diazomethyl groups of (8) *via* diazonium ions. 3-Methylenecyclobutanol



SCHEME 3

was the major product of the nitrous acid deamination of spiropentylamine.³ The spectral data of (11) were virtually identical (except for the OMe signals) with those reported for 3-methylenecyclobutanol.

The mechanism of the spiropentylamine deamination was shown by D-labelling to involve rearrangements of the

cyclopropylmethyl type⁴ (Scheme 3). The key intermediate (17) is accessible from (9) either by ring closure to give the spirocyclic diazonium ion (10) or, less likely, by 1,3 elimination. The solvolysis of (3) which cannot involve a spirocyclic intermediate, afforded only traces of (11). The solvolysis involved direct displacement and cyclopropylmethyl-cyclobutyl rearrangement to an almost equal extent, but cyclobutylmethyl-cyclopentyl rearrangement was not observed.

The formation of (11) from (7) suggests the intermediacy of spirocyclic diazonium ions (10), produced by the ring closure of (9). The absence of spirocyclic derivatives and of allenes among the products indicates a more rapid decomposition of (10), as compared with the cyclopropyl-diazonium ion generated from (1).

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