Cycloaddition of Diazoesters to Norbornadiene, and Rapid Cycloreversion of the Adduct; Effect of Transition-metal Complexes

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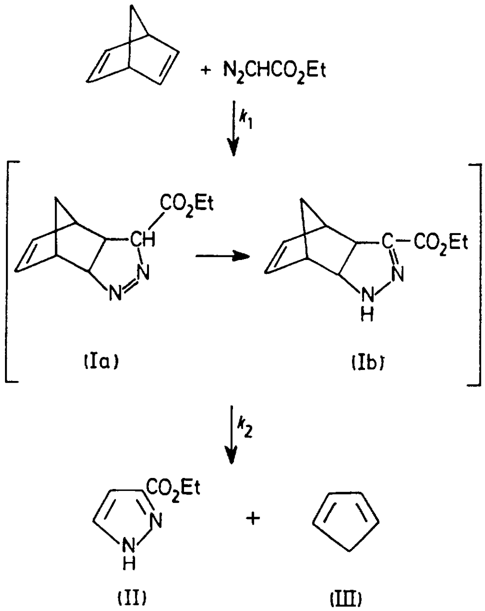
Summary Norbornadiene reacts with diazoesters with formation of 3- or 5-ethoxycarbonylpyrazole (II) and cyclopentadiene (III); this is the first example of a mild cycloreversion of a 1,3-dipolar adduct obtained from a diazoalkane, and metal carbonyl complexes accelerate the 1,3-dipolar addition of the diazoester to the double bond.



Copper derivatives have been mainly used to catalyse the reaction of diazo-compounds.[1] Some time ago we reported that palladium and rhodium salts were effective catalysts for cycloadditions to olefins[2] and nitriles[3] as well as insertion reactions into polar bonds[4] of alkoxycarbonylcarbenes generated from diazoacetic esters. A few cycloreversions of 1,3-dipolar adducts are known[5] but we describe here the first cycloreversion of a 1,3-dipole adduct obtained from a diazoalkane, and the accelerating effect of iron and cobalt carbonyls on the 1,3-dipolar cycloaddition.

In the reaction of ethyl diazoacetate with norbornadiene, only the pyrazole (II) and cyclopentadiene (III)‡ were isolated (in 95—100% yield) under a variety of conditions [25 °C, 4 weeks, no solvent; 80 °C, 4 h, C_6H_6; 25 °C, $Fe(CO)_5$, 3 days; 25 °C, $Co_2(CO)_8$, 3 days]. After 3 days at 25 °C in the absence of metal carbonyls these products were not

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‡ Compounds (I) and (III) were identified by comparison with authentic samples, while other products were identified by elemental and spectral analyses. In the experiments with benzene as solvent, concentrations were *ca.* 0·05M, while a molar ratio of metal carbonyl to the compound of 1:50 to 1:20 was used in the experiments with carbonyl catalysts.

detected, indicating catalysis of the reaction by the carbonyls. Since the adducts (Ia) and (Ib) could not be detected by chromatography at any stage of the reaction with the carbonyls ($k_2 >> k_1$), the 1,3-dipolar step must be the one which is catalysed. This assumption was confirmed by studying the reaction of styrene with ethyl diazoacetate where $[Co_2(CO)_8]$ has a slight accelerating role on the formation of ethyl 5-phenyl-Δ^2-pyrazoline-3-carboxylate.

The precise role of the catalyst is not yet fully established but evidence of complex formation between the metal and ethyl diazoacetate was obtained from ^1H n.m.r. spectra in C_6D_6 (1 p.p.m. downfield shift of the CH proton).

The reported reaction must be exceptionally favoured since with norbornadiene and diphenyldiazomethane or diazomethane stable pyrazolines are formed,[6] and decomposition to pyrazole derivatives does not occur even in the presence of metal carbonyls. In the reaction of ethyl diazoacetate with norbornene (25 °C, 1 week, no solvent), cycloreversion of the 1,3-dipolar adduct was not observed, as expected, since it is symmetry-forbidden, retro-Diels–Alder reactions being typically (4 + 2) reactions. The Δ^2-pyrazoline analogous to (Ib) is formed instead, in 75% yield. In the reaction of norbornadiene with ethoxycarbonyl azide, the triazoline analogous to (Ib) is formed after 3 days at 25 °C with no solvent, but the corresponding aziridine is formed if this reaction is carried out at 80 °C in benzene for 4 h.

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[1] W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971.

[2] R. Paulissen, A. J. Hubert, and Ph. Teyssié, *Tetrahedron Letters*, 1972, 1465.

[3] R. Paulissen, Ph. Moniotte, A. J. Hubert, and Ph. Teyssié, *Tetrahedron Letters*, 1974, 3311.

[4] R. Paulissen, H. Reimlinger, E. Hayez, A. J. Hubert, and Ph. Teyssié, *Tetrahedron Letters*, 1973, 2233.

[5] H. Kwart and K. King, *Chem. Rev.*, 1968, **68**, 415; J. M. Vandensavel, G. Smets, and G. L'Abbé, *J. Org. Chem.*, 1973, **38**, 675

[6] R. Fleischmann, Ph.D. Thesis, Universität München, 1957.