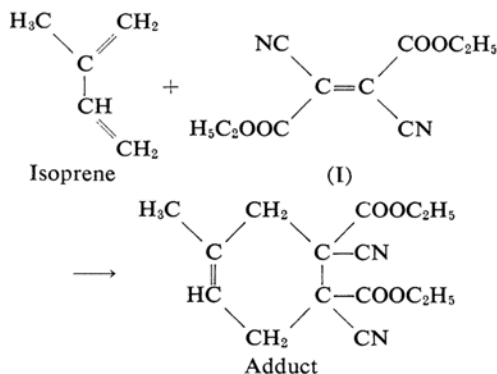


Studies on trans-Dicyanodiethoxycarbonyl ethylene. III. Diels-Alder Reaction

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Knowledge in various addition reactions of tetracyanoethylene¹⁾ and the properties of *trans*-dicyanodiethoxycarbonyl ethylene (I) described in the previous papers²⁾ suggest that I might also undergo Diels-Alder additions with



conjugated dienes with unusual ease. However, such vigorous and exothermic reactions as expected were not observed in the additions of I with conjugated dienes. Namely, the addition of I with cyclopentadiene proceeded in tetrahydrofuran slowly at room temperature. Furthermore, to obtain a condensation product of I with butadiene or isoprene, it was necessary to heat them in an autoclave under pressure at 180~190°C for several hours.

In the reaction with cyclopentadiene, the reaction mixture showed a transient yellow color, which would be attributed to the formation of a π -complex between I and cyclopentadiene.

The proposed structures of the adducts were supported by the infrared absorption spectra and the elemental analyses.

Experimental

Adduct with Isoprene.—A mixture of 4 g. (0.06 mol.) of isoprene and 13 g. (0.06 mol.) of I in

1) W. J. Middleton et al., *J. Am. Chem. Soc.*, **80**, 2783 (1958).

2) Parts I and II: K Kudo, *This Bulletin*, **35**, 1490, 1730 (1962).

100 ml. of benzene was heated in an autoclave at 180~188°C for 5 hr. After cooling, benzene was removed by vacuum distillation to obtain the syrupy residue which changed to crystals. The crystals were collected by filtration, washed with benzene-petroleum benzine, and recrystallized to give 17 g. (100%) of 1-methyl-4,5-dicyano-4,5-diethoxycarbonylcyclohexene, m. p. 77~79°C, as colorless crystals.

Found: C, 62.30; H, 6.36; N, 9.73. Calcd. for $C_{15}H_{18}O_4N_2$: C, 62.05; H, 6.25; N, 9.65%.

Its infrared absorption spectrum had bands at 2252 cm^{-1} ($C\equiv N$) and at 1761 cm^{-1} ($C=O$).

Adduct with Butadiene.—A mixture of 13 g. (0.06 mol.) of I and 100 ml. of benzene in a flask was chilled to -40°C. The flask was tarred, charged with 3.2 g. (0.06 mol.) of butadiene by distillation, and placed in an autoclave. The mixture was heated at 170~190°C for 5 hr. After cooling, benzene was removed by distillation and the residue solidified. After recrystallization from benzene-petroleum benzine, there was obtained 11 g. (70%) of 4,5-dicyano-4,5-diethoxycarbonylcyclohexene, m. p. 109~110°C, as colorless crystals.

Found: C, 61.11; H, 5.76; N, 10.15. Calcd. for $C_{14}H_{16}O_4N_2$: C, 60.86; H, 5.84; N, 10.14%.

Its infrared absorption spectrum had a $C\equiv N$ band at 2247 cm^{-1} and a $C=O$ band at 1757 cm^{-1} .

Adduct with Cyclopentadiene.—A mixture of 6.5 g. (0.03 mol.) of I and 20 ml. of tetrahydrofuran in a flask was chilled to 0°C. The flask was tarred, charged with 2.3 g. (0.03 mol.) of cyclopentadiene by distillation, capped, and allowed to stand at

room temperature for 24 hr. The mixture was evaporated to expel benzene at room temperature and the residue crystallized to give 8 g. (90%) of the adduct, m. p. 70~71°C, as colorless crystals.

Found: C, 62.40; H, 5.34; N, 9.52. Calcd. for $C_{15}H_{16}O_4N_2$: C, 62.49; H, 5.59; N, 9.72%.

Its infrared absorption spectrum had a $C\equiv N$ band at 2247 cm^{-1} and a $C=O$ band at 1761 cm^{-1} .

Adduct with Anthracene.—A mixture of 13 g. (0.06 mol.) of I and 8 g. (0.06 mol.) of anthracene was heated at 130~150°C for 5 min. After cooling, the mixture was crystallized by trituration with acetone to give 12 g. (57%) of the adduct, m. p. 168~169°C, as colorless crystals.

Found: C, 72.20; H, 5.01; N, 7.37. Calcd. for $C_{24}H_{20}O_4N_2$: C, 71.98; H, 5.03; N, 7.00%.

Its infrared absorption spectrum had a $C\equiv N$ band at 2242 cm^{-1} and a $C=O$ band at 1764 cm^{-1} .

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