

A FACILE SYNTHESIS OF 2,3-DICYANOBUTADIENE-1,3 AND 2,3-DICARBOMETHOXYBUTADIENE-1,3

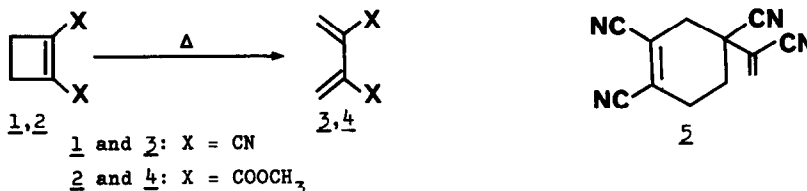
D. Belluš and C. D. Weis

Central Research Laboratories, Ciba-Geigy AG, 4002 Basel, Switzerland

(Received in UK 24 January 1973; accepted for publication 8 February 1973)

2,3-Dicyanobutadiene-1,3 (3) and 2,3-dicarbomethoxybutadiene-1,3 (4) have been prepared only in non-specific low yield syntheses; e.g. 3 is formed on pyrolysis of 2,3-diacetoxy-2,3-dicyanobutane at 400-500° (10% yield)¹, whilst 4 has been detected on pyrolysis of 1,2-dicarbomethoxycyclohexene at 750° (10% yield)² and dimethyl-1,2-dimethyl-1,2-diacetoxysuccinate at 490° (23% crude yield)¹.

Thermal ring opening in 1,2-dicarbomethoxycyclobutene (2)³ as a possible synthetic route to 4 has been reported to be unsuccessful in solution⁴. Heating of 1,2-dicyanocyclobutene (1)⁵ in mesitylene at 160° in the presence of polymerisation inhibitor led to the formation of dimer 5 (65% yield; mp. 124.5-5°; uv.(CH₃OH): 229-30 nm. (ε=12800); ir.(KBr): 3112,2242 and 2234 (-CN),1625 cm.⁻¹; nmr.(CDCl₃): δ=1.9-2.5 (m,2,CH₂), 2.75 + 3.05 (2xm,4,allylic protons), 6.38 (s,2,vinyl protons); ms.: m/e=208(M⁺)) and some polymeric materials.



We wish to report that ring-opening 1 → 3 can be achieved readily in the gas-phase; e.g. on distilling 1 under reduced pressure (0.5-0.01 torr) through a heated column (380-420°) filled with glass or ceramic beads⁶. In this manner monomeric 3 condenses in a cooled receiver as a crystalline solid. The small amount of insoluble polymer is removed by filtration of a chloroform or benzene solution of this solid and the pure 3 is obtained by precipitation with n-hexane (80-85% yield; colourless needles; mp. 118-20°⁷; uv.(CH₃OH): 226 nm. (ε=16800); ir.(KBr): 3114,2231,1592,1406,1388,1165,960,882 cm.⁻¹; nmr.(CDCl₃): δ=3.64 (d, J=7.0); ms.: m/e=104(M⁺)). Crystalline 3 slowly⁸ polymerized to yield highly crosslinked polymers without losing its original crystal form. In dimethylformamide solution, after addition of a small amount of dioxane, 3 gave a linear, non-crosslinked homopolymer, from which, after evaporation of solvent, transparent, elastic films were obtained. Without use of dioxane a jellied mass resulted^{9,10}.

Under the same pyrolytic conditions used for the ring opening $1 \rightarrow 3$, liquid monomeric 4 was readily obtained from 2 (above 90% yield; greater than 98% purity, estimated from nmr.; bp. $58-63^{\circ}/1.2$ torr; ir.(neat): 3126,1748,1638,1588,1190,1124 cm^{-1} ; nmr. (CDCl_3): $\delta=3.70+4.15$ (2xd, $J=1.2$, CH_2), 6.23 (s, CH_3); ms.: $m/e=170(\text{M}^+)$).

From these pyrolytic gas-phase reactions, which we have also observed with diethyl- (88% yield) and diallyl-cyclobutene-1,2-dicarboxylate (76% yield), we suggest that the above method may be a convenient synthetic route to derivatives of buta-1,3-diene-2,3-dicarboxylic acid.

3 is an electron-deficient diene and does not react with electron-deficient olefins such as maleic anhydride and fumaronitrile. However, 3 gives good yields of (4+2)-cycloadducts with olefins containing a strained double bond, and with electron-rich olefins¹¹. Thus, the cycloaddition reactions of 3 fit the seldom observed class of Diels-Alder reactions with "inverse electron demand"¹².

References and Footnotes

1. W.J.Bailey, R.L.Hudson and E.T.Yates, *J.Org.Chem.* 28, 828 (1963).
2. A.R.Barney and H.B.Stevenson (Du Pont), US pat. 2,870,196 (1959).
3. a) E.Lustig, E.P.Ragelis, N.Duy and J.A.Feretti, *J.Am.Chem.Soc.* 89, 3953 (1967) and references cited therein; b) R.N.McDonald and R.R.Reitz, *J.Org.Chem.* 37, 2418 (1972).
4. E.Vogel, *Ann.* 615, 14 (1958).
5. a) J.L.Greene, N.W.Standish and N.R.Gray (Standard Oil Co.), US pat. 3,275,676 (1966); b) J.L.Greene and M.Godfrey (Standard Oil Co.), US pat. 3,336,354 (1967).
6. E.g. ceramic beads 3×3 mm. used in distillation columns.
7. The bp. for 3 reported in ref. 1 does not correspond with our observations. Pure 3 partially dimerizes to yield 5 , partially sublimes but mainly polymerizes above its mp. under vacuum.
8. 100% yield of polymer in 3 months at -35° under oxygen-free nitrogen.
9. The authors are very much indebted to Dr. F.Lohse for the polymerisation experiments in dimethylformamide solutions.
10. Various attempts at radical or ionic homo- or co-polymerisation of 3 led to cross-linked, unworkable polymers.
11. D.Belluš, K.von Bredow, H.Sauter and C.D.Weiss, to be published.
12. J.Sauer, *Angew. Chem.* 79, 76 (1967).