Tetrahedron Letters No. 41, pp 3975 - 3978.
©Pergamon Press Ltd. 1978. Printed in Great Britain.

0040-4039/78/1008-3975$02.00/0

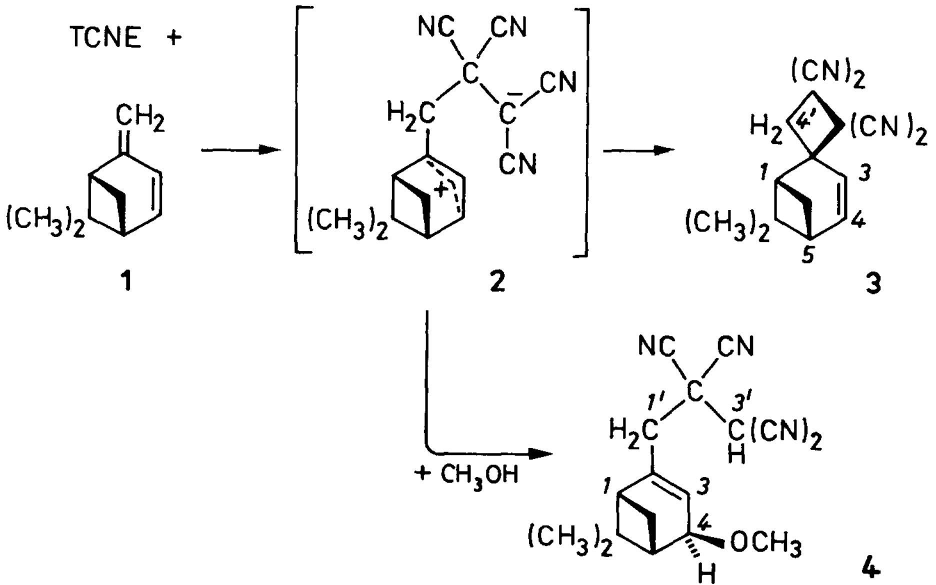
EVIDENCE FOR A ZWITTERIONIC INTERMEDIATE IN THE 2+2 CYCLOADDITION OF TETRACYANOETHYLENE TO A TRANS-FIXED 1,3-DIENE

Rolf Huisgen* and Joaquin Plumet Ortega

Institut für Organische Chemie der Universität, Karlstr. 23, 8000 München,
West Germany

Tetracyanoethylene (TCNE) belongs to the most active dienophiles in the Diels-Alder reaction.[1] Trans-fixed 1,3-dienes, however, combine with TCNE in 2+2 cycloadditions to give vinylcyclobutanes;[2,3] the second double bond effects an activation, since simple alkenes do not react with TCNE. The readiness of vinyl ethers to undergo 2+2 cycloadditions with TCNE was ascribed to charge separation in the rate-determining step;[4] an abundance of mechanistic criteria established a zwitterionic intermediate.[5]

Competitive 2+2 cycloaddition and ene reaction were observed for the interaction of polycyanoolefins with 3-methylenecyclohexenes and its methyl derivatives.[3,6] To prevent the ene reaction on the basis of Bredt's rule,



we chose verbenene (1) as a model for a mechanistic investigation; 1 is easily accesible from α- or β-pinene.[7]

The reaction of 1 with TCNE in benzene at 60°C (48 h) produced the crystalline 1:1 adduct 3, mp 160-161°C (dec.), in 75 % yield. NMR (d_6-acetone, 60 MHz): τ 3.22 (dd, $J_{3,4}$ = 9.0, $J_{4,5}$ = 6.7 Hz, 4-H), 3.93 (dd, $J_{3,5}$ = 2.0 Hz, 3-H), 6.52 (s, 4'-H_2), 8.55 and 9.05 (2 s, 2 CH_3); ($CDCl_3$): 6.98 and 7.04 (AB, J_{gem} = 12.8 Hz, 4'-H_2).

The disappearance of the charge transfer absorption (530 nm) of the reactants allowed the photometric measurement of the rate. The reaction of TCNE (0.005 - 0.013 M) with 10-14 equiv of 1 provided the pseudo first order rate constant from which k_2 ($l\ mol^{-1}sec^{-1}$, 25°C) was evaluated. In some solvents the CT absorption in the case of 1 was weak; here the stronger CT band (610 nm) involving anisole was measured.

Solvent	10^5k_2
Dibutyl ether	0.96
Benzene	3.2
Anisole	21.8
Ethyl acetate	14.7
Chloroform	196
Dichloromethane	630
1,2-Dichloroethane	735

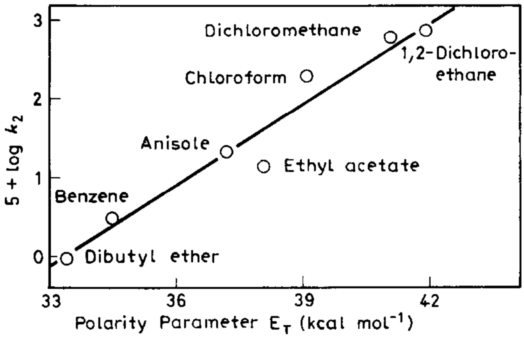


Figure 1

The great influence of solvent polarity on the rate constant is in accordance with the formation of the zwitterion 2 in the rate-determining step. The production of dark insoluble polymers prevented rate measurements in highly polar solvents like acetonitrile. Figure 1 shows a fairly linear relation (correlation coefficient r = 0.976) of k_2 with E_T,[8] an empirical parameter of solvent polarity. The slope of the straight line, R_E, amounts to 0.32, compared with 0.33, 0.30, and 0.31 for the TCNE cycloadditions to anethole, isobutenyl ethyl ether and 2,3-dihydro-4H-pyrane, respectively;[9] the latter cycloadditions proceed through oxonium zwitterions.[5] Extrapolation to media of higher and lower E_T allows one to calculate

$$k_2(\text{acetonitrile})/k_2(\text{cyclohexane}) = 54\ 000$$

for TCNE + 1, compared with experimental ratios of 29 000 for TCNE + anethole and 10 800 for TCNE + isobutenyl ethyl ether. In contrast, the Diels-Alder reaction of TCNE with anthracene is rather insensitive to solvent polarity;[10] k_2(acetonitrile)/k_2(benzene) $\approx$ 2 indicates a concerted cycloaddition without much charge separation in the early transition state.

The oxonium zwitterions from TCNE + enol ethers can be trapped with alcohols[11] or with electrophilic double bonds.[12] Is also the allyl type zwitterion 2 interceptable ? The 1:1 reaction of TCNE and 1 in methanol at 20°C was complete in 14 min, as the decolorization of the dark-red CT complex testified. The cyclobutane 3 and the methoxy compound 4, a methanol adduct of the zwitterion 2, were formed in a 1:4 ratio (NMR analysis). The colorless crystalline 4, mp 112-113°C, gave satisfactory elemental analyses and mol. weight. Its NMR spectrum ($CDCl_3$) reveals one vinyl-H at 3.95 (m), CH_3O at 6.58 (s), 1'-H_2 at 7.02 (s) and 6-$(CH_3)_2$ at 8.58 and 9.04 (s); the acidic 3'-H at 5.32 is exchanged by D_2O. The configurational assignment in formulae 3 and 4 is based on the approach from the least hindered side.

That indeed an intermediate of the 2+2 cycloaddition is trapped, is established by the slow reaction of the cyclobutane 3 with methanol at 20°C; after 12 h most of 3 was unchanged. After 81 h 72 % of a 1:2 adduct of 3 and methanol, mp 197 - 199°C (dec.), was isolated. The structure has not yet been established. The strong IR absorption for C=N at 1665 cm^{-1} leaves no doubt that at least one CH_3OH has reacted with a cyano group to yield the imido ester. Probably the 1:1:1 adduct 4 is not an intermediate on the path to the methanol bisadduct, because 4 was not converted to the bisadduct in methanol.

Thus, TCNE appears to furnish 2+2 cycloadducts with those olefinic compounds (enol ethers, 1,3-dienes, cyclopropylethylenes) which offer excellent stabilization of the cationic charge in a zwitterionic intermediate.

ACKNOWLEDGMENT. J.P.O. expresses his gratitude to the Alexander von Humboldt-Stiftung for a stipend.

REFERENCES

1. Review: H. Wollweber, "Diels-Alder-Reaktion", Georg Thieme Verlag, Stuttgart, 1972.
2. A.T. Blomquist and Y.C. Meinwald, J.Am.Chem.Soc., **81**, 667 (1959); J.K. Williams, ibid., **81**, 4013 (1959); R. Criegee, J. Dekker, W. Engel, P. Ludwig, and K. Noll, Chem.Ber., **96**, 2362 (1963).
3. P.D. Bartlett, Quart.Rev., Chem.Soc., **24**, 473 (1970).
4. J.K. Williams, D.W. Wiley, and B.C. McKusick, J.Am.Chem.Soc., **84**, 2210 (1962).
5. Review: R. Huisgen, Acc.Chem.Res., **10**, 117, 199 (1977).
6. R. Huisgen and R. Schug, J.Am.Chem.Soc., **98**, 7819 (1976).
7. G. Zweifel and C.C. Whitney, J.Org.Chem., **31**, 4178 (1966).
8. K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, Liebigs Ann.Chem., **666**, 1 (1963).
9. G. Steiner and R. Huisgen, J.Am.Chem.Soc., **95**, 5056 (1973).
10. P. Brown and R.C. Cookson, Tetrahedron, **21**, 1977 (1965).
11. R. Huisgen, R. Schug, and G. Steiner, Angew.Chem., Int.Ed.Engl., **13**, 80, 81 (1974).
12. R. Schug and R. Huisgen, J.C.S. Chem.Commun., 60 (1975).

(Received in UK 3 August 1978; accepted for publication 11 August 1978)