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REACTION OF BULLVALENE WITH TETRACYANOETHYLENE AND N-METHYLTRIAZOLINEDIONE

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Schröder et alii[1] have studied the reaction of bullvalene with tetracyanoethylene (TCNE): they isolated an adduct $C_{10}H_{10}$.TCNE in benzene while in acetonitrile the products obtained were not characterized and considered polymeric substances. Product $C_{10}H_{10}$.TCNE was postulated to have structure **3** allowing for other alternative structures. We have now studied the same reaction in various solvent and found that it gives rise in all cases to a mixture of three isomeric adducts **3**, **4** and **5**[2]. All the adducts were stable in the reaction conditions. The structures of the adducts were elucidated by X-rays analysis,[3] **3** and **4**, and spectral methods **3**, **4** and **5**[4]. Adduct **3**, m.p. 230-231°C (lit.[1] 226-227°C) shows $\nu^{Nuj}_{C\equiv N}$ at 2250 cm^{-1}, a 6 H multiplet at $\delta(CDCl_3)$ 6.20 - 5.40, a 2H multiplet at δ 3.87-3.51 and a 2 H multiplet at δ 3.23-3.10. By contrast **4**, m.p. 208-210°C, discloses a 4H multiplet at $\delta(CDCl_3)$ 6.35 - 5.55 and two 3H multiplet at δ 3.70-3.15 and 2.35 respectively. The IR spectrum shows $\nu^{Nuj}_{C\equiv N}$ at 2250 cm^{-1}. Adduct **5** shows a weak $\nu^{Nuj}_{C\equiv N}$ absorption at 2250 cm^{-1} and its structure is based on its NMR spectrum (100 MHz): $\delta(CDCl_3)$ 6.65 (1 H, dd, H_9, J_{19} =8.0 and $J_{9\,10}$ = 9.8 Hz), 6.55 (2H, dd, H_2 and H_8, J_{12} = 8.0 and J_{23} = 11.2 Hz), 5.84 (2H, dd, H_3 and H_7, J_{34} = 4.3 Hz), 5.74 (1 H, m, H_{10}), 3.67 (3 H, m, H_4, H_5 and H_6), 3.48 (1 H, apparent q, H_1)[5].

The data of the Table show that adduct **4** is favoured by polar solvents (CH_3CN, CH_3NO_2) whereas **3** is dominant in apolar solvents such as C_6H_{12} and CCl_4. A less defined relationship between solvent polarities and products distribution is observable with intermediate polarity solvents. However, particularly noticeable are the results in DMF where compound **5** was formed in high yield.

The most plausible reaction path to the products appears to involve an electrophilic attack of TCNE on bullvalene to give zwitterions **1** showing a Cope rearrangement equilibrium. The aromaticity of the bis-homotropilium ion **2** where the positive charge is readily dispersed, renders this intermediate the most likely in apolar solvents, while a longer lifetime for the other zwitterions in polar solvents, owing to better solvation and diminished Coulomb attraction of charge centers, appears to be responsible for the more complex rearrangement in the formation of **4**.

TABLE. Yields[a] of compounds 3,4,5.

Solvent	E_T[c]	Total yield (%)	Rel. yields (%)[b] 3	4	5
Nitromethane	46.3	90	13.5	74.5	12
Acetonitrile	46.0	70	18	66	16
Dimethylformamide	43.8	51	11	45	44
1,2-Dichloroethane	41.9	90	57	36	7
Methylene chloride	41.3	90	60	33	7
Chloroform	39.1	85	78.5	18.5	3
1,2-Dimethoxyethane	38.2	80	43	44	13
Ethyl acetate	38.1	85	56	35	9
Ethyl ether	34.6	75	75.5	21.5	3
Benzene	34.5	75	81.5	16.0	2.5
Carbon tetrachloride	32.5	85	82.5	16	≃1.5
Cyclohexane	31.2	66	82	17	≃1

[a] The reactions were carried out in sealed ampoules with a slight excess of TCNE at 85°C for 30 h the first eight entries, and 60 h the others. Products were separated by column chromatography (eluents cyclohexane: ethylacetate 7:3 and benzene). [b] Evaluated by GLC using 2 m x 4 mm columns packed with CGS 100-120 mesh coated with 3% OV17. The retention times were in the order $3 < 5 < 4$. The values represents the results of two runs. [c] Parameter of solvent polarity.[8]

Bullvalene was also reacted with a slight excess of N-methyltriazolinedione in ethylacetate at 60°C for 100 h, to give the sole adduct 6, m.p. 126-127°C (16%).[2] The structure of 6 was elucidated by IR and NMR (100 MHz) spectra: $\nu^{Nuj}_{C=O}$ 1765 and 1700 cm^{-1}; δ(CDCl$_3$) 6.66 (1H, dd, H_9, J_{19} = 9.0 and $J_{9\,10}$ = 10.0 Hz), 6.28 (2H, dd, H_2 and H_8, J_{12} = 9.4 and J_{23} = 11.0 Hz), 5.82 (2H, dd, H_3 and H_7, J_{34} = 4.8 Hz), 5.76 (1H, dd, H_{10}, $J_{5\,10}$ = 8.0 Hz), 4.72 (2H, dd, H_4 and H_6, J_{45} = 7.0 Hz), 3.50-2.90 (2H, m, H-1 and H-5), 3.04 (3H, s, Me)[5].

The forgoing work indicates the complexities of addition to bullvalene which was previously shown to react with chlorsulfonylisocyanate by a kinetically controlled perispecific 1,2-cycloaddition[6] while the adducts obtained with bromine, chlorine and methanol in the presence of acid derived by 1,4-perispecific additions of the electrophiles at the cyclopropylvinyl system.[7]

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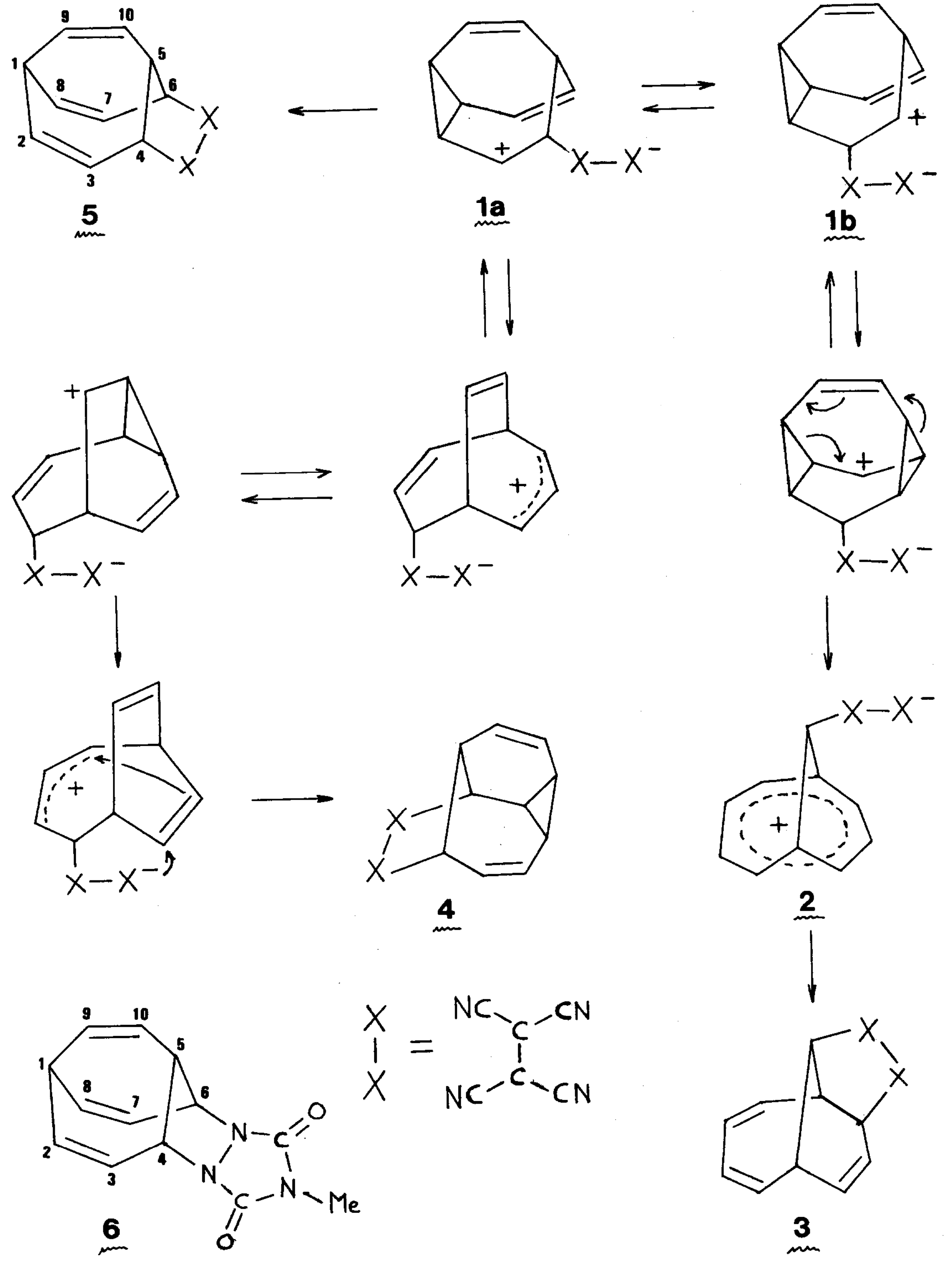
5
1a
1b
4
2
3
6
X–X⁻
X–X =
NC CN
NC CN
N–Me
O
1 2 3 4 5 6 7 8 9 10

References and Footnotes

1 H. P. Löffler, Th. Martini, H. Musso and G. Schröder, *Chem. Ber.*, **103**, 2109 (1970).

2 All compounds gave satisfactory C, H, N (± 0.3%) analyses.

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4 Compounds **4** and **5** show end absorption only in the UV spectrum.

5 The signals present additional fine splitting due to allylic coupling. Spin decoupling experiments allowed unambigous assignment of the protons. The spectra closely resemble those of analogous compounds reported in the literature[6].

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