Tetrahedron Letters,Vol.26,No.46,pp 5635-5638,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

COMPETITIVE 1,2- AND 1,6-CYCLOADDITIONS OF DICHLOROKETENE TO BULLVALENE

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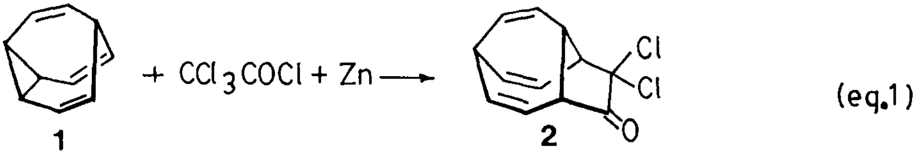
Summary: Dichloroketene cycloadds to bullvalene to give an unusual 1,6-cycloadduct. The mechanism of this reaction is probed by means of suitable control experiments.

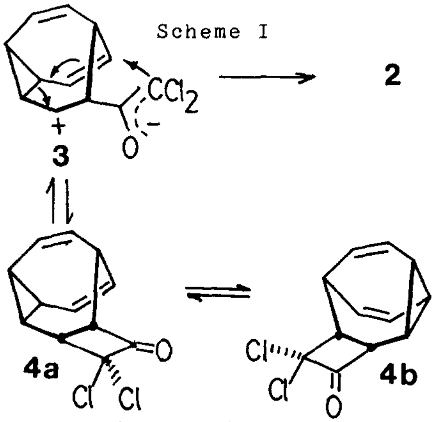
Bullvalene (1), with its cis-divinylcyclopropane moiety and fully fluxional structure, is capable of exhibiting diverse modes of cycloadditions. Dipolar cycloadditions of bullvalene to tetracyanoethylene (TCNE), triazolindione (TAD) and chlorosulfonyl isocyanate (CSI) have previously been reported.[1,2,3] In the latter case, irreversible heterolytic opening of the initial 1,2-adduct to give a 1,6-adduct was observed.[3] Whereas the reversible and dipolar nature of myriad CSI cycloadditions has been well established,[4,5,6,7] dichloroketene (DCK) has previously exhibited only [2+2] cycloadditions with carbocyclic olefins.[8,9,10,11] We describe here our results from reactions of dichloroketene with bullvalene. A new variant in DCK cycloadditions is revealed.

Slow addition of a solution of a slight excess of trichloroacetyl chloride in anhydrous ether to a slurry of activated zinc in an ether solution of bullvalene[12] (1) at room temperature, followed, after 12 h, by work-up and preparative TLC (SiO_2, n-pentane/CH_2Cl_2 95:5) afforded a colorless oil which gave satisfactory elemental analysis for the $C_{12}H_{10}C\ell_2O$ molecular formula. Its carbonyl absorption in the IR spectrum at 1770 cm^{-1} was indicative of an α, α-dichlorocyclopentanone. Its ^1H and ^{13}C NMR spectra[13] permitted an unequivocal assignment of its structure to that of the 1,6-cycloadduct 2 (eq. 1). The formation of 2 could be inter-



(eq.1)

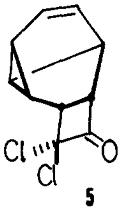
preted in terms of a two-step pathway involving the dipolar intermediate 3, which would cyclize to 2 with cyclopropylmethyl-homoally rearrangement (Scheme 1). An alternative mechanism would involve initial formation of a 1,2-cycloadduct 4 which would undergo either a thermal, or Lewis acid (in this case $ZnCl_2$) catalyzed ring opening to 3. Subsequent cyclization with skeletal rearrangement would give 2. Since neither of these mechanistic pathways had precedence in DCK additions to carbocyclic olefins,


Scheme I

further experiments were needed to probe the actual mechanism of this reaction. Toward that end, the addition of dichloroketene to bullvalene was repeated in the presence of equimolar amounts of $POCl_3$, which is known to complex a variety of Lewis acids, including $ZnCl_2$.[14] The product obtained from this reaction exhibited a carbonyl absorption at 1810 cm^{-1}, characteristic of α, α-dichlorocyclobutanones. Its ^{1}H NMR spectrum (400 MHz) was temperature dependent, as is typical of *cis*-fused bicyclo[5.1.0]-octa-2,5-diene systems.[3a,b] On the basis of a detailed analysis of the NMR spectrum, supported by double-resonance experiments, and comparison with the literature,[3a,b] it was conclusively shown that an equilibrium mixture of the 1,2-cycloadducts 4a and 4b was formed. The ^{13}C NMR spectrum showed eight lines (at 25.1 MHz), in full accord with the proposed fluxional structures. Although 4 could be purified by rapid column chromatography on SiO_2, longer exposure to silica gel or preparative TLC, as well as treatment with $ZnCl_2$ in diethyl ether resulted in quantitative rearrangement to 2.

In view of the thermal stability of 4 (no rearrangement was observed in refluxing diethylether or neat at 80° in the absence of free $ZnCl_2$) it can safely be deduced that the 1,6-adduct 2 stems from a concerted [2+2] cycloaddition of dichloroketene to bullvalene giving 4, followed by $ZnCl_2$-catalyzed, irreversible passage of 4 to 2.[15]

Interestingly, other 4,8-bridged homotropylidenes, such as semibullvalene and barbaralane gave with dichloroketene (in the presence or absence of $POCl_3$) exclusively the corresponding 1,2-adducts, 5[13] and 6[13], respectively (Fig 1). The reason why 5 and 6 do not undergo a similar isomerization to the corresponding 1,6-adducts can be traced to the *exo*-orientation (distal to the remote double bond) of the α, α-dichlorocyclobutanone ring in these adducts. Suitably substituted semibullvalenes and barbaralanes (e.g., barbaralone ethylene acetal) should give *endo* adducts due to steric hindrance on the *exo*-face. This aspect is currently being investigated, as is the mechanism of the rearrangement of 4 to 2.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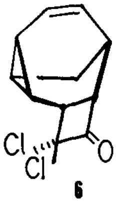
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Fig.1

Acknowledgment. I gratefully acknowledge financial support of this research by the donors of Petroleum Research Fund, administered by the American Chemical Society. I am also indebted to Professor A. de Meijere, University of Hamburg, for supplying a sample of bullvalene, and Professor L. A. Paquette, Ohio State University, for a 100 MHz ^1H NMR spectrum of the bullvalene-CSI adduct.

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(13) Spectral data of the adducts: 2 (81%) IR (Film): 3040, 2960, 2930, 1770, 1420, 1280 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$): δ_{TMS} = 6.47 (m,1H); 6.09-6.27 (m, 2H); 5.59-5.82 (m, 3H); 3.69 (m, 1H); 3.54 (m, 1H); 3.38 (m, 1H); 3.19 (m, 1H); ^{13}C NMR (25.1 MHz, CDCl$_3$): δ_{TMS} = 199.61, 142.16, 134.61, 126.13, 125.19, 123.73, 88.34, 51.69, 43.70, 34.34, 33.05.
Adducts 4a 4b (79%) IR (Film): 3030, 2925, 1810, 1440 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$); δ_{TMS} = 5.79 (m, 2H); 4.54 (m, 2H); 4.27 (dd, ^3J = 11.90, 6.41 Hz, 1H); 3.22 (dd, ^3J = 11.90, 3.66 Hz, 1H); 3.19 (m, 2H); 2.62 (ddd, ^3J = 8.65, 8.55, 3.66 Hz, 1H); 2.25 (ddd, ^3J = 8.85, 8.55, 6.41 Hz, 1H); ^{13}C NMR (25.1 MHz, CDCl$_3$); δ_{TMS} = 196.16, 127.83, 127.53, 88.2, 54.66, 47.08, 20.39, 20.87.
Adduct 5 (74%) IR (Film): 3060, 2955, 1815, 1605, 1350, 1320 cm^{-1}. ^{1}H NMR (100 MHz, CDCl$_3$): δ_{TMS} = 5.65 (dd, ^3J = 5.50, 1.83 Hz, 1H); 5.51 (dd ^3J = 5.50, 1.22 Hz, 1H); 3.95 (d, ^3J = 6.10 Hz, 1H); 3.51 (dd, ^3J = 5.49, 2.14 Hz, 1H); 3.32 (d, ^3J = 6.10 Hz, 1H); 2.66 (q, ^3J = 6.11 Hz, 1H); 2.04 (m, 2H); ^{13}C NMR (25.1 MHz, CDCl$_3$): δ_{TMS} = 195.29, 134.38, 127.95, 87.29, 72.87, 51.51, 50.36, 34.10, 32.46, 31.31.
Adduct 6 (69%) Mp. 85-86 (n-hexane); IR (KBr): 3055, 2930, 1810, 1615, 1450, 1250 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$): δ_{TMS} = 5.98-5.83 (m, 2H); 3.77 (dd, ^3J = 10.68, 3.66 Hz, 1H); 3.16 (d, ^3J = 10.68 Hz, 1H); 2.62 (m, 1H);1.92 (d, ^2J = 13.35 Hz, 1H); 1.28-1.71 (m, 4H); ^{13}C NMR (25.1 MHz, CDCl$_3$): δ_{TMS} = 196.45, 127.54, 126.60, 89.10, 55.58, 43.94, 28.37, 19.59, 16.26, 15.74, 13.51.

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(15) A referee suggested that the conversion of 4 to 2 could also be a Lewis-acid catalyzed [1,5]-shift without the intermediacy of 3.

(Received in USA 10 September 1984)