Tetrahedron Letters No.60, pp. 5325-5328, 1969. Pergamon Press. Printed in Great Britain.

1,6-CYCLOADDITION OF CHLOROSULFONYL ISOCYANATE TO CYCLOHEPTATRIENE

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(Received in the USA 30 October 1969; received in the UK for publication 28 November 1969)

Product formation,[1,2] kinetics[3] and the prohibitions originally imposed by the Woodward-Hoffmann[4] selection rules have suggested a 1,2-step-wise electrophilic cycloaddition of chlorosulfonyl isocyanate (CSI) to certain olefins and allenes. Recently reported observations which include: (i) the lack of rearrangement noted in the cycloaddition of CSI to bridged bi- and tricyclic olefins,[5] (ii) the stereospecific cycloadducts formed on addition of CSI to cis- and trans-olefins,[6,7] and (iii) the initial formation of 2+2 cycloadducts between CSI and conjugated dienes,[8-11] coupled with the refined Woodward-Hoffmann selection rules[12] suggest, in these cases, the clear possibility of a near-synchronous process. Whether these cycloaddition reactions proceed inter alia via a 1,4-dipole aligned for bonding,[5] or in a sequential ring closure via an electronically unsymmetrical transition state[13,14] are to date, unresolved problems. Evidence is mounting, however, that β-lactam formation may precede rather than follow the generation of Graf's open 1,4-dipole.[1]

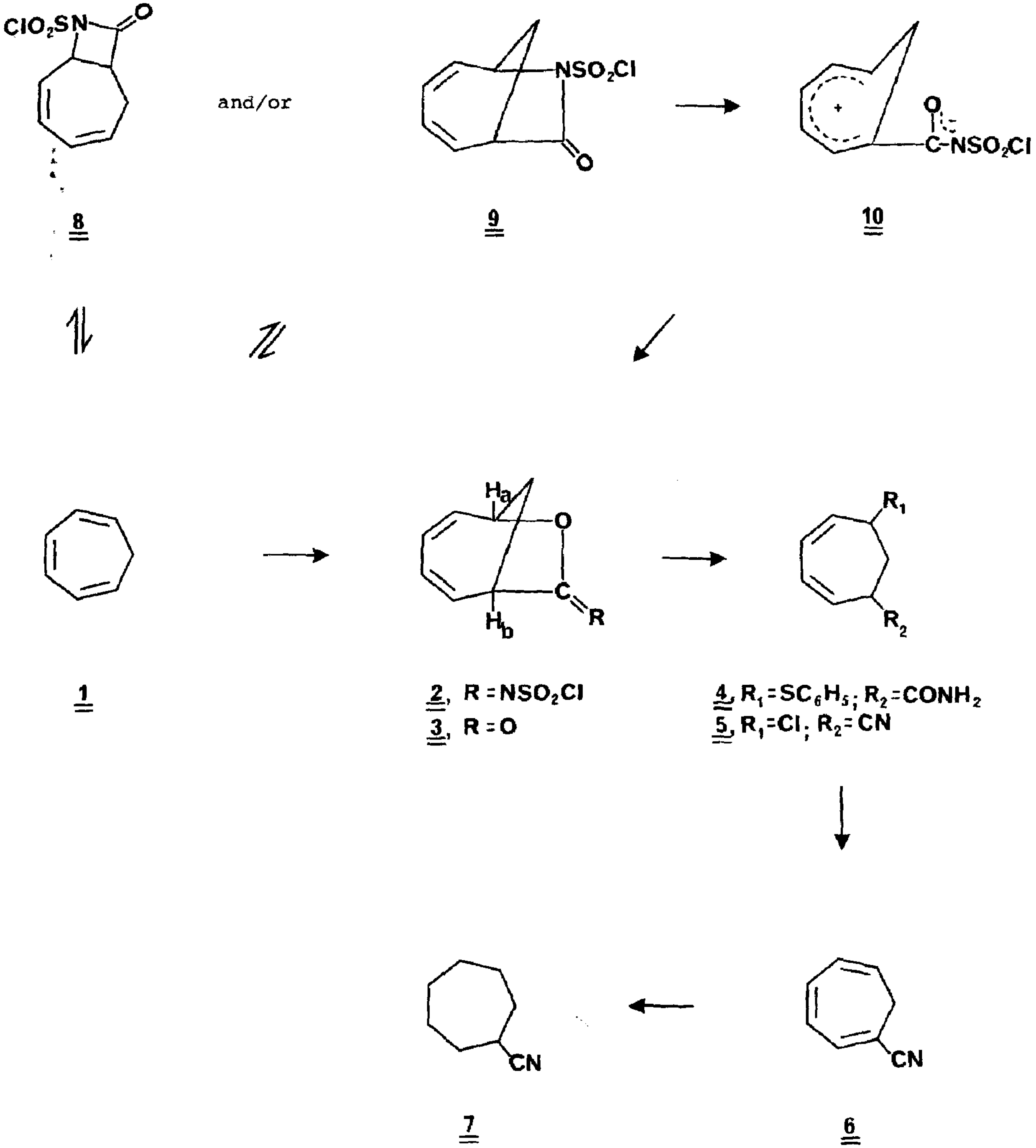
The formation of such 2+2 cycloadducts between CSI and olefins, conjugated dienes and allenes suggested the possibility of similar reactivity between CSI and conjugated trienes. We should like to report the first such case between CSI and cycloheptatriene (**1**) in which the singular 1,6-cycloaddition product (**2**) involves bonding exclusively to O.[15,16]

Thus, stirring equimolar amounts of **1** and CSI in methylene chloride solution for 6 hr at ambient temperature afforded the N-chlorosulfonyl iminoether 2[17] (87%, mp 85-86° from ether); ir (KBr) 6.25 (C=C) and 6.35 μ (C=N); uv (95% EtOH) 265 mμ[18] (ϵ 4000); nmr ($CDCl_3$) δ 6.18 and 6.15 (two peaks, 4 =CH), 5.50-5.20 (m, 1, H_a), 4.25-3.90 (m, 1, H_b) and 3.05-2.25 (m, 2, CH_2). Trace amounts (<1%) of a second compound ($\lambda^{neat}_{C=O}$ 5.60μ) suggests the presence of N-cyclized product 8/9 but all attempts to increase the yield or isolate the product were unsuccessful.

Further support for the structure of 2 was obtained by its hydrolysis with sodium hydroxide-acetone-water at -10° to lactone 3[17] (33%, bp 86-88°/0.2 mm); $\lambda^{film}_{C=O}$ 5.65μ; uv (95% EtOH) 265 mμ (ϵ 4900); nmr (neat) δ 6.10-6.05 (two peaks, 4, =CH), 4.90-4.70 (m, 1, H_a), 3.70-3.30 (m, 1, H_b) and 2.50-2.00 (m, 2, CH_2).

Admixture of three mole equivalents of thiophenol and 2 in acetone at -30° followed by slow addition of two mole equivalents of pyridine in acetone afforded, after a non-aqueous work-up, 5-carboxamido-7-mercaptophenyl-1,3-cycloheptadiene[17] (4, 37%, mp 121-122° from ether-hexane); ir (KBr) 2.97 and 3.15 μ (NH), 6.08 (C=O); nmr [$(CD_3)_2CO$] δ 7.60-7.15 (m, 5, C_6H_5), 7.00-6.75 (broad mound, 2, NH_2), 5.87 (s, 4, =CH), 4.40-4.15 (m, 1, CHCO), 2.65-2.35 (m, 1, CHS) and 2.15-1.90 (m, 2, CH_2). Finally, treatment of 2 with DMF for 3 hr at ambient temperature followed by aqueous hydrolysis led to a chlorocyanocycloheptadiene of probable structure 5[17] (40%, 86-87°/0.1 mm); ir (film) 4.48 μ (C≡N); nmr (neat) δ 5.91 (s, 4, =CH), 4.95-4.70 (m, 1, CHCN), 3.95-3.70 (m, 1, CHCl) and 3.55-2.30 (m, 2, CH_2). When 5 was allowed to stand for 24 hr at ambient temperature, hydrogen chloride was evolved. Distillation of the darkened product gave cyanocycloheptatriene 6[17] (bp 38-40°/0.1 mm), hydrogenation (PtO_2, 50 psi, 3 hr) of which afforded the known cycloheptylcyanide (7).[19]

Mechanistically, we suggest an electrophilic, near-synchronous process[13] leading to 1,2- (8) and/or 1,6-cycloaddition (9) product(s). Thermal and irreversible ring opening of either/both would lead to the true, charge-separated dipolar intermediate 10 which stabilizes itself by recyclization to the thermodynamically more stable 2.


ClO_2SN
O
and/or
NSO_2Cl
O
O
$C-NSO_2Cl$
+
8
9
10
H_a
O
C
R
H_b
R_1
R_2
1
2, R = NSO_2Cl
3, R = O
4, $R_1 = SC_6H_5$; $R_2 = CONH_2$
5, $R_1 = Cl$; $R_2 = CN$
CN
CN
7
6

Experiments to distinguish between these various near synchronous process of CSI cycloaddition to 2 and 6π systems, and rational extensions to 10 and 14π systems are currently under investigation.

REFERENCES

1) R. Graf, Angew. Chem. internat. Edit., 7, 172 (1968).

2) E.J.Moriconi and J.F.Kelly, J.Org.Chem., 33, 3036 (1968).

3) K.Clauss, Liebigs Ann.Chem., 722, 110 (1969).

4) R.Hoffmann and R.B. Woodward, J.Am.Chem.Soc., 87, 2046 (1965).

5) E.J.Moriconi and W.C. Crawford, J.Org.Chem., 33, 370 (1968).

6) E.J.Moriconi and J.F. Kelly, Tetrahedron Lett., 1435 (1968).

7) H.Bestian, H.Biener, K.Clauss and H.Heyn, Liebigs Ann.Chem., 718, 94 (1969).

8) E.J.Moriconi and W.C. Meyer, Tetrahedron Lett., 3823 (1968).

9) Th.Haug, F.Lohse, K.Metzger and H.Batzer, Helv.Chim.Acta., 51, 2068 (1968).

10) P.Goebel and K.Clauss, Liebigs Ann.Chem., 722, 122 (1969).

11) These 1,2-cycloaddition products thermally rearrange to 1,4-cycloadducts probably via step-wise ring opening to a true resonance-stabilized 1,4-dipolar intermediate, and recyclize to O and/or N.

12) R.B.Woodward, Lecture at IUPAC Symposium on Valence Isomerism, Karlsruhe, Sept.10,1969; R.B.Woodward and R.Hoffmann, Angew.Chem.,in press.

13) E.J.Moriconi, Mechanisms of Reactions of Sulfur Compounds, Vol.3, in press (1969).

14) R.Gompper, Angew.Chem., 81, 348 (1969); Angew Chem.internat.Edit., 8, 312 (1969).

15) T.W.Doyle and T.T. Conway, Tetrahedron Lett., 1889 (1969).

16) L.A. Paquette, S. Kirschner and J.R. Malpass, J.Am.Chem.Soc., 91, 3970 (1969).

17) All new compounds reported herein were analyzed for C, H and N, and satisfactory analyses (± 0.3%) were obtained.

18) Strong evidence for dienic conjugation.

19) Compounds 2 and 3 have been synthesized via the same reaction sequence and characterized independently by G.Schröder and S.Meyer, Institut für Organische Chemie, 75 Karlsruhe; private communication.

Acknowledgement. - This contribution is supported by Public Health Service Research Grants identified as 5 RO1 AI08063-01-03 from the National Institute of Allergy and Infectious Diseases.