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THE REACTION OF ACETYLENES WITH CHLOROSULFONYL ISOCYANATE

Emil J. Moriconi, John G. White, Richard W. Franck,
JoAnn Jansing, John F. Kelly, Ramon A. Salomone[1] and
Yasuo Shimakawa.

Department of Chemistry, Fordham University, New York, N.Y.

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*Since its discovery in 1952 by R. Graf, the extraordinary propensity of chloro*sulfonyl isocyanate (CSI) to add to carbon-carbon multiple bonds (alkenes, conjugated dienes, cumulenes, polyenes) has been continuously documented.[2,3] Its response to carbon-carbon triple bonds however has not been described to date.

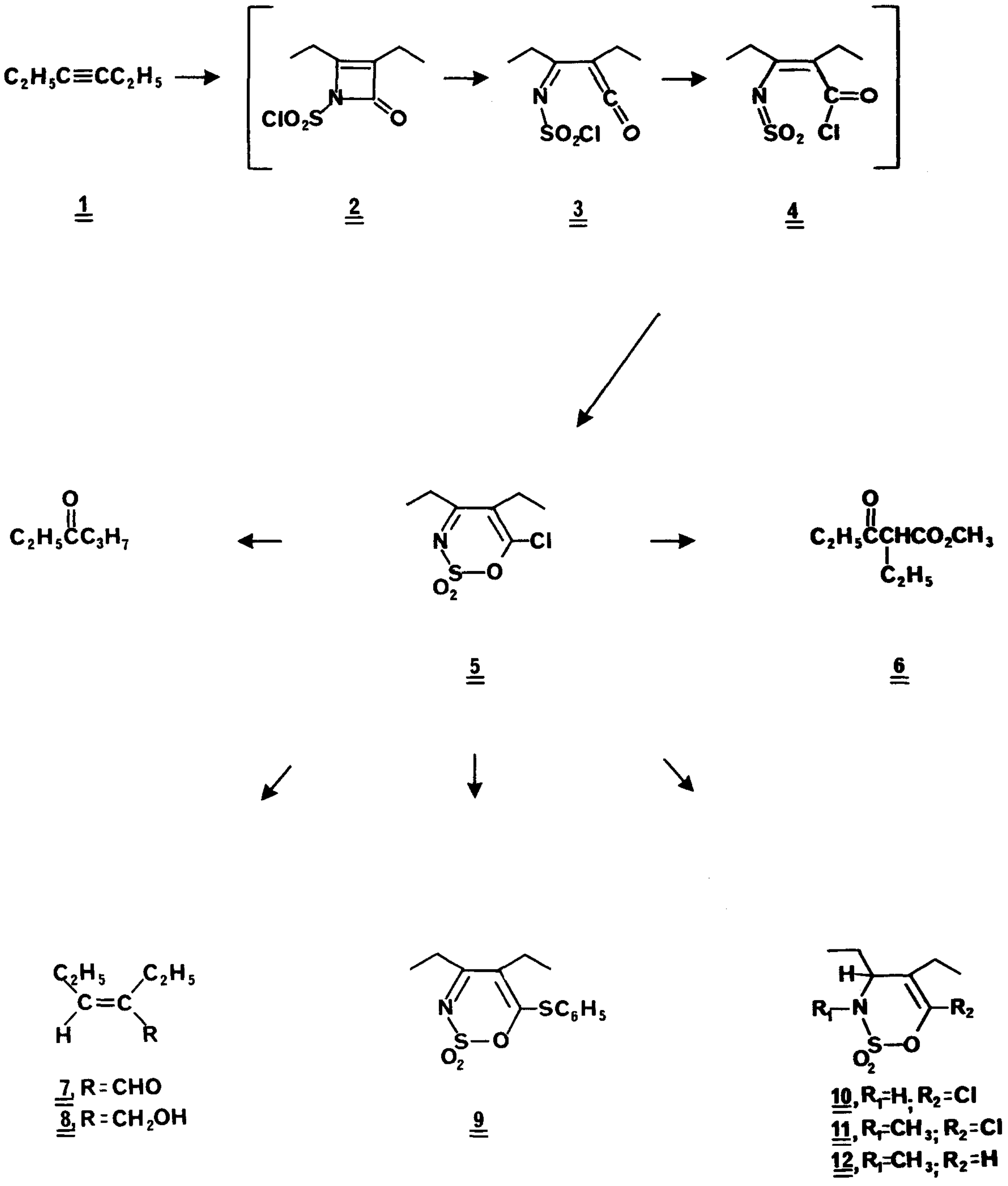
We wish now to report the result of our studies of the adducts of CSI with acetylenes. Using 3-hexyne (1) as an exemplary substrate, addition of freshly distilled CSI in methylene chloride solution to an equimolar quantity of 1 at ambient temperature led to 96% of the 1:1 adduct 5[4]: mp 54-55°; ν_{max}^{KBr} 1621 (C=C or C=N), 1385 and 1209 cm^{-1} (SO_2); $\lambda_{max}^{isooctane}$ 292 mμ (ε 5300); $\delta_{TMS}^{CDCl_3}$ 3.05-2.40 (m, 4H, $CH_3\underline{CH_2}$) and 1.45-1.00 (m, 6H, $\underline{CH_3}CH_2$). Aqueous hydrolysis of 5 afforded 3-hexanone (70%) while methanolysis gave methyl 2-ethyl-3-oxopentanoate (6, 60%). Reduction of 5 with two and four mole equivalents of $LiAlH_4$ afforded 2-ethyl-2-pentenal (7, 30%) and 2-ethyl-2-penten-1-ol (8, 36%), respectively. These results summarized in Scheme I showed that no rearrangement of carbon skeleton had occurred and that the carbon of CSI had become affixed to the acetylene function. The mass spectrum of 5 had *inter alia* a fragment m/e 124 which corresponds to the loss of SO_2Cl from the molecular ion. A contra-indication to this evidence for a sulfonyl chloride function was the replacement of chloride upon treatment of 5 with thiophenol-pyridine-acetone[5] with formation of phenylthio ether 9.[4] Reduction of 5 with 0.5 mole equivalent of $LiAlH_4$ led to the dihydro derivative 10[4] (81%): mp 58-59°; ν_{max}^{KBr} 3195 (NH), 1642 (C=C), 1364 and 1202 cm^{-1} (SO_2); $\delta_{TMS}^{CDCl_3}$ 5.00 (d, J=7 Hz, 1H, NH), 3.93 (X portion of an ABX pattern, 1H, J_{AB} = 5.5 Hz, $\Delta\nu_{AB}$ = 7.5 Hz, further split by NH, J = 7 Hz, =CHCH$_2$), 2.40-1.60 (m, 4H, CH_2CH_3) and 1.30-0.85 (m, 6H, CH_2CH_3). The mass spectrum of 10 had no M-SO_2Cl fragment but did show a fragment m/e 146 ($C_7H_{11}OCl$) corresponding to loss of $NHSO_2$.[6] The most informative evidence appeared in the nmr which revealed a new carbon-bonded proton which was coupled to both NH and the CH_2 of an ethyl group. Compound 10 was methylated with CH_3I, K_2CO_3 to afford an N-methyl derivative 11[4] (64%). Dehalogenation[7] of 11 with Li-t-BuOH gave 12[4] (93%) which displayed a vinyl H in the nmr at δ 6.30. These experiments show that the chlorine in 10 and 11 was bound to a vinyl carbon and that a C=N function in 5 was reduced. These facts can be accommodated in structures 5⟶10.[8]

The formation of 5 can be rationalized by the sequence of cycloaddition (2),[2,3] electrocyclic ring opening to the ketene-imine-N-sulfonyl chloride (3),[9] 1,5-sigmatropic halogen shift[10] (4) and electrocyclic ring closure[11] to adduct 5. The mass spectrum of 5 can then be explained by invoking a reversal of 5 to intermediate 3 under electron impact or thermal conditions in the mass spectrometer.

Despite these satisfactory rationalizations, there remained the possibility that 5 had an undetermined structure which rearranged to 10 under the conditions of the $LiAlH_4$ reduction. Thus an X-ray crystallographic analysis of 5 was undertaken.

The crystals were monoclinic with a = 7.97 ± 0.01, b = 14.55 ± 0.02, c = 17.77 ± 0.02 Å, β = 92.2 ± 0.1°. Systematically absent spectra, $h0\ell$ with ℓ odd and $0k0$ with k odd, indicated the space group $P2_1/c$ with 8 molecules per unit cell or 2 molecules per crystal asymmetric unit. The structure was solved by a combination of Patterson and heavy atom methods. It was refined to a conventional R of 0.119, using

SCHEME I


C2H5C≡CC2H5
1
ClO2S
N
O
2
N
SO2Cl
C
O
3
N
SO2
C=O
Cl
4
N
S
O2
O
Cl
5
O
C2H5CC3H7
O
C2H5CCHCO2CH3
C2H5
6
C2H5
C2H5
C=C
H
R
7, R=CHO
8, R=CH2OH
N
S
O2
O
SC6H5
9
H
R1
N
S
O2
O
R2
10, R1=H, R2=Cl
11, R1=CH3; R2=Cl
12, R1=CH3; R2=H

1370 independent, visually estimated reflection intensities by Fourier and least square methods with individual isotropic temperature factors. The averages of the bond distances in the two independent molecules are given in Fig. 1 in Å and are in excellent agreement with those expected for **5**. The atomic positions in the ethyl groups are the least certain because of high thermal motion in these regions. The corresponding distances in the two independent molecules differ on the average by 0.02 Å and have a maximum deviation of 0.03 Å.

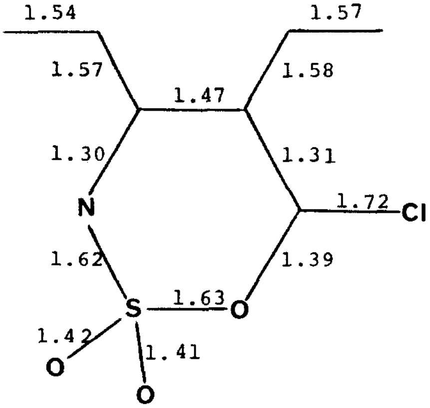


Figure 1. Bond lengths of adduct **5**.

Analogous alkyne: CSI adducts of varying sensitivity to air, moisture and polymerization but of similar chemical reactivity have been obtained with symmetrical dialkylacetylenes (2-butyne and 4-octyne), phenylacetylene, phenylmethylacetylene and diphenylacetylene. [These as well as the complete X-ray data will be reported in a full paper.] Additional research in the chemistry of the unusual heterocyclic system (**5**)[12] is in progress.

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1) Department of Chemistry, Massachusetts Institute of Technology, National Institutes of Health Postdoctoral Trainee, 1967-1969 (GM 015230).

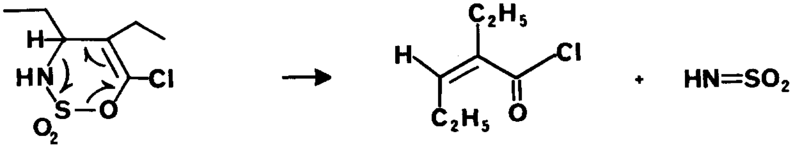
2) R. Graf, Angew. Chem., **80**, 179 (1968); Angew.Chem.internat.Edit., **7**, 172 (1968).

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

4) Satisfactory elemental analyses (± 0.3%) were obtained for all new compounds, and spectral data supported structure assignments.

5) This reagent combination does not yield substitution products with NSO_2Cl functions but serves to convert it to NH while producing SO_2, pyridine hydrochloride and diphenyl disulfide.

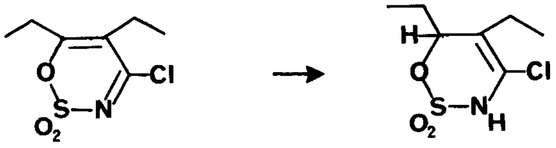
6) Both fragments are derived from the six-membered ring via a retro-Diels-Alder rearrangement. The high resolution spectrum shows the correct composition for these two ions:



10 m/e 146 m/e 79

7) P.G. Gassman and P.G. Pape, J.Org.Chem., **29**, 160 (1964).

8) The isomeric six-membered heterocycles I ⟶ II were considered less likely because the magnitude of J_{NH-CH} in **10**.



I **II**

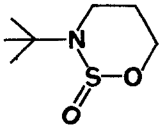
9) J.E. Baldwin and M.C. McDaniel, J.Am.Chem.Soc., **90**, 6118 (1968).

10) Possible examples of 1,7-, 1,3- and 1,6-sigmatropic chloride shifts are found, respectively, in: E. Baciocchi, A. Ciana, G. Illuminati and C. Pasini, ibid., **87** 3953 (1965); G. Antinori, E. Baciocchi and G. Illuminati, J.Chem.Soc., (B) 373,

1969; G. Guroff, J.W. Daly, D.M. Jerima, J. Renson, B. Witkop, S. Udenfried, Science, 151, 1524 (1967).

11) E.N. Marvell, G. Caple, T.A. Gosink, G. Zimmer, J.Am.Chem.Soc., 88, 619 (1966). It should be noted that cyclization of 4 to 5 requires a rotation about the acyl carbon single bond.

12) The only example of this atomic arrangement known to us is III: J.A. Deyrup and C.L. Moyer, J.Org.Chem., 34, 175 (1969).



III

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