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2,3,4-TRITHIABICYCLO[4,3,1]DECA-6,8-DIENE. SULFURATION OF CYCLOHEPTATRIENE

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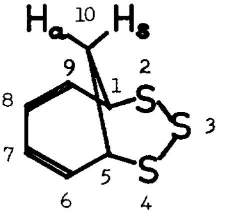
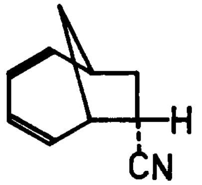
A number of reports in the literature describe reactions of olefins with elemental sulfur from which complex mixtures of sulfurated olefins result in various degrees [1]. The first examples, in which the sulfuration of unsaturated hydrocarbons gave trithia-hydrocarbons were the selective and stereospecific sulfuration of norbornyl olefins with S_8 in the presence of ammonia which produced exo-3,4,5-trithiatricyclo[5,2,1,$0^{2,6}$]decanes [2].

We now wish to report the reaction of elemental sulfur with cycloheptatriene which results in a selective 1,6-addition of an S_3-fragment to cycloheptatriene with the formation of 2,3,4-trithiabicyclo[4,3,1]deca-6,8-diene (1) with a 21% yield. This sulfuration proceeds using sulfolane as the preferred solvent at 70° and is strongly catalyzed by pyridine.



1



2

The reaction offers further evidence for the always inherent possibility that cycloheptatriene may undergo reactions of the [6+2]-addition type even under conditions which normally seem to favor the [4+2]-addition [3,4].

Amorphous sulfur is stirred in a mixture of sulfolane (1,2 l.), pyridine (20 ml) and cycloheptatriene (4 moles) at 70° for 72 hours. Additional pyridine (10 ml) is added in 24 hour intervals. Volatile material is removed in vacuo and residue treated with water and ether. Insoluble material is separated and 10,3 g of 1 isolated from the ether extraction. Additional 2,9 g are obtained from ether extraction of the polymer, total yield: 13,2 g (21%), m.p. 115-117°.

The structure of the new compound is derived from elemental analysis and supporting spectral data. The elemental analysis agrees with $C_7H_8S_3$, calcd: C 44,65% H 4,29% S 51,09%, found: C 44,85% H 4,33% S 50,71%. The mass spectral pattern exhibits a molecular peak at m/e = 188 (M) and further fragment peaks are at m/e=155 (M-SH), 124 (M=2S), 123 ($M-S_2H$), 92 ($C_7H_8^+$) and 91 (C_7H_7, base peak), UV(max, CH_3OH):243 (ε=4900),266 nm(ε=4070); IR(KBr): 3020 (=C-H), 1603 (C=C), 720 cm^{-1} (strongest band, out of plane deformation vibration of the cis-conjugated system).

The ^{13}C and ^{1}H NMR spectra (Table I) unequivocally prove that the molecule has a twofold symmetry element (mirror plane through C-10). The noise decoupled ^{13}C spectrum consists of 4 singlets; in the undecoupled spectrum three of these are split into doublets, and one into a triplet, with spacings characteristic for one bond C-H couplings. All signals show further small splittings due to long range C-H couplings.

The ^{1}H spectrum is of the type AA' BB' KK' YZ with well resolved multiplets for the equivalent proton groups. Some of the coupling constants can be extracted by first order analysis, their values are given in the last column of Table I. All couplings were confirmed by double resonance decoupling experiments. The assignment given for the protons on C-10 (H_s and H_a) follows from observation of a coupling interaction (J = 1.3 Hz) between the signals at 5.64 and 2.28. Only H_s fulfills the geometric condition (W-path) necessary for such a large four bond coupling.

Table I. ^{13}C- and ^{1}H-NMR spectral parameters for 1

C, H	^{13}C-spectrum ($CDCl_3$)		^{1}H-spectrum (C_6D_6)	
	(ppm)	^{1}J(C,H) Hz	(ppm)	J(H,H) Hz
7,8	126.85	155 ± 2	5.82	J (5,6) = J (1,9) = 6.0 Hz
6,9	134.14	162 ± 2	5.64	J (1,s) = J (5,s) = J (1,a) = J (5,a)
1,5	40.68	135 ± 2	2.98	= 3.7 Hz
10	29.26	130 ± 2	2.28 (H_s)	J (5,a) = 14.5 Hz
			1.58 (H_a)	J (6,s) = J (9,s) = 1.3 Hz

1 is also formed from cycloheptatriene and hexaatomic sulfur without catalyst in 11% yield. Reaction in other solvents such as pyridine, dimethylsulfoxide or dimethylformamide gave much inferior yields. The insoluble material (30 g) which remains after ether extraction of 1 is polymeric in nature, and agrees with $(C_7H_8S_3)_n$ calcd: C 44,65% H 4,29% S 51,09%, found: C 44,60% H 4,10% S 50,38%, MW($CHCl_3$): 1620.

The unsaturated, conjugated system of 1 does not react with tetracyanoethylene or dimethyl acetylendicarboxylate which reminds one of a similar unreactivity of 2 in Diels-Alder-reactions[3].

References:

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