BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2894—2895 (1973)

Formation of Trithiocarbonate by the Reaction of 2,2-Diphenylethylenesulfonamide and Carbon Disulfide

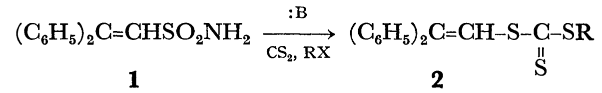
Kiyoshi HASEGAWA, Tadashi SASAKI,* and Syuzi HIROOKA
Department of Industrial Chemistry, Faculty of Engineering, Toyama University, Takaoka-shi 933
**Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464*

(Received December 6, 1972)

We have reported[1-3] on the syntheses and intramolecular Michael cycloaddition of $RCH{=}CHSO_2N{=}CX\text{-}S^-M^+$ ($R{=}H$, $R^1C_6H_4$; $X{=}SR^2$, OR^2, NHR^2, $N(R^2)_2$, S^-M^+). The reaction of 2,2-diphenylethylenesulfonamide **1** with carbon disulfide and alkyl halides afforded unexpected trithiocarbonates. This paper describes the mechanism of these new reactions studied by the use of the carbon disulfide-^{35}S tracer technique.

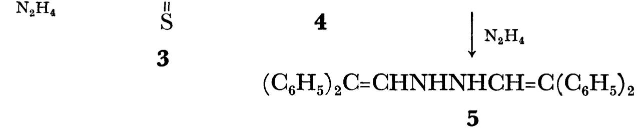
Results and Discussion

The reaction of **1** with carbon disulfide and alkyl halides in the presence of base in DMF or DMSO gave alkyl 2,2-diphenylvinyl trithiocarbonates **2** as yellow crystals, **1** being recovered by acidifying the alkaline filtrate. The results are summarized in Table 1. The IR spectrum of **2a** displayed the strongest band at 1065 cm^{-1} due to the C=S bond,[4] but no absorption due to the SO_2 group. The NMR spectrum of **2a** exhibited a peak of the methine proton at δ 7.71. The mass spectrum showed a molecular ion peak at m/e 302.0270 assignable to a molecular formula $C_{16}H_{14}S_3$. Final structural elucidation of **2** was accomplished by the following degradation. Treatment of **2** with excess hydrazine afforded thiocarbohydrazid **3**, mp 167—168 °C (lit,[5] 168 °C), alkanethiol **4**, and N,N'-bis(2,2-diphenylvinyl)hydrazine **5** which was formed from 2 mol of 2,2-diphenylvinylthiol and 1 mol of hydrazine.



$$(C_6H_5)_2C{=}CHSO_2NH_2 \xrightarrow[CS_2,\ RX]{:B} (C_6H_5)_2C{=}CH\text{-}S\text{-}\underset{\underset{S}{\|}}{C}\text{-}SR$$

1 2



$$2 \xrightarrow[N_2H_4]{} H_2NHN\underset{\underset{S}{\|}}{C}NHNH_2 + RSH + ((C_6H_5)_2C{=}CHSH)$$

3 4

$$\downarrow N_2H_4$$

$$(C_6H_5)_2C{=}CHNHNHCH{=}C(C_6H_5)_2$$

5

The yield of **2** increased with the amount of carbon disulfide and base added, but no further increase was observed when more than two equiv. of carbon disulfide and base were used. The reaction of **1** and carbon disulfide was quite rapid and a considerable yield (40%) of **2a** was obtained in a minute. The origin of three sulfur atoms in **2** were sought with carbon disulfide-^{35}S. Carbon disulfide-^{35}S was converted in to N,N,N',N'-tetramethylthiuram disulfide-^{35}S **6** by the usual method.[6] The specific activities of **6** and **2a** were found to be 25.84×10^5 dpm/mmol and 19.79×10^5 dpm/mmol, respectively. The fact that the relative ^{35}S atom ratio of **6** to **2a** was 4.00: 3.07 supports the mechanism that all the three sulfur atoms of **2** come from two moles of carbon disulfide. The trithiocarbonate formation was specific to the sulfonamide **1**. Neither N,N-dimethylsulfonamide nor 2-phenyl-2-methylethylenesulfonamide took part in it. The IR absorption peak at 2080 cm^{-1} due to the N=C=S bond was recognized in the reaction mixture of **1** and carbon disulfide. The following intramolecular rearrangement mechanism is proposed: (1) electrophilic attack of CS_2 on the N atom to form reactive **7**, (2) intramolecular S_N attack of thiolate anion on the 1-carbon atom with a loss of sulfinate anion, (3) cleavage of the C-S bond, (4) attack of CS_2 on the thiolate anion, and (5) alkylation.

The resonance stabilization of the diphenylmethylcarbanion **8** provides an important driving force which causes the thiolate anion attack on the 1-carbon atom. When DMF was removed *in vacuo* from the basic reaction mixture before alkylation, yellow hygroscopic crystals **12** ($\nu_{C=S}$ 1040, and 990 cm^{-1}) and a viscous oil ($\nu_{N=C=S}$ 2080 cm^{-1}) were obtained. This seems to be mainly composed of **11**, though it could not be

TABLE 1. $(C_6H_5)_2C{=}CH\text{-}S\text{-}C({=}S)\text{-}SR$ **2**

Compd	R	Yield (%)	Mp (°C)	Found (%)			Calcd (%)		
				C	H	S	C	H	S
2a	CH_3	57	110—111	63.78	4.62	31.45	63.53	4.67	31.80
2b	C_2H_5	57	87—88	64.37	4.98	29.93	64.55	5.10	30.35
2c	n-C_3H_7	44	40—41	65.50	5.39	29.14	65.44	5.49	29.06
2d	n-C_4H_9	44	36—37	66.09	5.74	27.51	66.27	5.85	27.88

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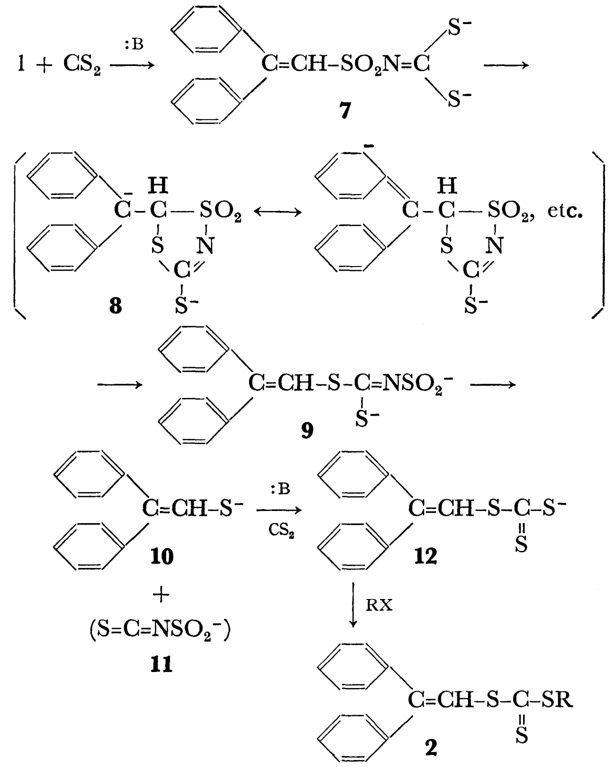

purified. Even when **1** and carbon disulfide were allowed to react for a minute followed by alkylation, **2** was the only product. This supports the view that conversion of **7** into **12** may proceed faster than the formation of **7**. The present rearrangement reaction seems to be a new case in which Smiles-type rearrangement can occur at a methine carbon atom⁷⁾ conjugated with two phenyl groups.

Experimental

All melting points are uncorrected. Specific activities of the labelled compounds were counted with a TEN-GSL-163 liquid scintillation counter using a mixture of POPOP and PPO (0.005 g and 0.4 g in 100 ml of toluene) as a scintillator.

Specific Activity of Carbon Disulfide-^{35}S Stock Solution. Radioactive carbon disulfide (2.7 mCi of ^{35}S in 15 mg) was transferred into unlabelled carbon disulfide (10 ml) by means of a vacuum line. Approximately 0.5 ml of this solution was diluted with unlabelled carbon disulfide (10 ml) to provide the stock solution used in reactions leading to labelled products. *N,N,N′,N′*-Tetramethylthiuram disulfide-^{35}S was prepared from the carbon disulfide-^{35}S stock solution by the usual method⁶⁾ and its specific activity was measured.

Liquid Scintillation Counting. The radioactivity of each sample in count per minute (cpm) was measured three times with different weighing, disintegration value per minute (dpm) being obtained in reference to the quenching calibration curve.

2,2-Diphenylethylenesulfonamide 1. In an analogous manner to that described by B. M. Culbortson⁸⁾ for the synthesis of 2-phenylethylenesulfonamide, 1,1-diphenylethylene (48.0 g, 0.266 mol) was treated with sulfuryl chloride (60 g, 0.445 mol) in DMF (60 ml) to give 13.5 g (17%) of 2,2-diphenylethylenesulfonyl chloride. The sulfonamide was prepared in 79% yield from crude sulfonyl chloride in benzene and 28% aqueous ammonia. Recrystallization from water gave colorless crystals, mp 136—137 °C. IR (KBr): 3340 and 3240 (NH_2), 3030 (=CH), 1585 (C=C), 1310 and 1130 (SO_2) cm^{-1}. NMR (DMSO-d_6): δ 6.92 (s, 1H, =CH), 6.96 (s, 2H, NH_2), and 7.34 ± 0.10 (m, 10H, diphenyl). Mass spectrum (75 eV) *m/e* (rel. intensity): 89 (33, $C_6H_5C^+$), 93 (8, $C^+HSO_2NH_2$), 102 (10, $C_6H_5C{=}C^+H$), 152 (20, $2C_6H_4^+$), 165 (14) and 167 (15, $(C_6H_5)_2C^+\pm H$), 178 (100, $(C_6H_5)_2C{=}C^+$), 179 (70, $(C_6H_5)_2C{=}CH^+$), 195 (23, M^+-SO_2), and 259 (53, M^+).

Found: C, 64.71; H, 4.92; N, 5.34; S, 12.38%. Calcd for $C_{14}H_{13}NO_2S$: C, 64.86; H, 5.05; N, 5.40; S, 12.35%.

Labelled Trithiocarbonate from 1, Carbon Disulfide-^{35}S and Methyl Iodide. To a stirred solution of **1** (0.78 g, 3.0 mmol) in DMF (8.0 ml) were added carefully sodium hydroxide (0.24 g, 6.0 ml) in water (0.5 ml) and then a carbon disulfide-^{35}S stock solution (0.57 g, 7.5 mmol) at room temperature. The orange-yellow reaction mixture was stirred for 2 hr. Methyl iodide (0.51 g, 3.6 mmol) was then added drop by drop at 20—30 °C. The yellow reaction mixture was stirred for 2 hr at 20—30 °C, and poured into ice water (100 ml), and the resulting alkaline solution was left to stand overnight. The yellow crystals were collected and thoroughly washed twice with 20 ml portions of 1M sodium hydroxide solution to give 0.50 g (55%) of **2a**. Recrystallization from methanol gave yellow crystals. The alkaline filtrate was acidified with concentrated hydrochloric acid to recover 0.27 g (35%) of **1**. The IR, NMR, and mass spectra of unlabelled trithiocarbonate are given below. IR (KBr): 3020 (=CH), 1595 (C=C), 1065 (C=S), 815, 755 and 690 cm^{-1}. NMR ($CDCl_3$): δ 2.80 (s, 3H, CH_3), 7.34 (m, 10H, diphenyl), and 7.71 (s, 1H, =CH). Mass spectrum (75 eV) *m/e* (rel. intensity): 91 (100, C^+SSCH_3), 152 (7, $2C_6H_4^+$), 165 (15) and 167 (7, $(C_6H_5)_2C^+\pm H$), 178 (28, $(C_6H_5)_2C{=}C^+$), 179 (11, $(C_6H_5)_2C{=}CH^+$), 210 (21, $(C_6H_5)_2C{=}CS^+$), 211 (31, $(C_6H_5)_2C{=}CHS^+$), 226 (15, M^+-CS_2), 255 (4, M^+-SCH_3), and 302.0270 (43, calcd molecular weight, 302.0257).

Reaction of 2 with Hydrazine. Methanethiol was evolved when a solution of **2a** (1.46 g, 4.8 mmol) and 80% hydrazine hydrate (0.75 g, 15 mmol) in ethanol (50 ml) was refluxed for 3.5 hr. The reaction mixture was cooled overnight. Light pink precipitates (0.33 g, 65%) of **3** were obtained. Evaporation of the ethanol from the basic filtrate *in vacuo* left a yellow oily product which was acidified with sulfuric acid under cooling to afford a soft solid. It was triturated with ether to yield colorless crystals. Recrystallization from benzene–petroleum ether gave 0.64 g (69%) of **5**, mp 156—157 °C. IR (KBr): 3400 (weak, NH), 3020 (=CH), 1630 (NH), 1590 (C=C), 1490, 1450, 750, 740, and 690 cm^{-1}. NMR ($CDCl_3$): δ 5.02 (d, 2H, 2=CH), 8.25 (d, 2H, 2NH, $J_{CHNH}=7.5$ Hz), and 7.27 (m, 20H, phenyl). Mass spectrum (75 eV) *m/e*: 388 (M^+).

Found: C, 86.56; H, 6.06; N, 7.45%. Calcd for $C_{28}H_{24}N_2$: C, 86.56; H, 6.23; N, 7.21%.

The authors wish to thank Prof. Shigeru Oae, Osaka City University, for recommendation of the isotope experiment and encouragement throughout this work. Thanks are also due to Dr. Seizi Kozuka, Dr. Naomichi Furukawa and Mr. Yoshiyuki Tsuchida, Osaka City University, for direction in the experiment and valuable discussions, Mr. Osamu Shiokari for assistance in the preparation of some compounds, and Dr. Eizo Nakano, Nagoya University, for use of the liquid scintillation counter.

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8) B. M. Culbortson and S. Dietz, *J. Chem. Soc., C*, **90**, 992 (1968).