[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Heterocyclic Vinyl Ethers. IX.[1] Substitution Reactions of *cis*- and *trans*-Bis-(phenylmercapto)-ethylene

BY WILLIAM E. PARHAM AND JACK HEBERLING[2]

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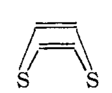
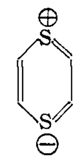
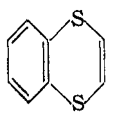
The syntheses of *cis*- and *trans*-bis-(phenylmercapto)-ethylene (IIIa and IIIb) are described. These products were characterized by their conversion into the corresponding sulfones, and by reaction of the latter with dienes. The reactions of IIIa and IIIb with N-methylformanilide and phosphorus oxychloride (the Vilsmeyer reaction) have been studied, and it has been shown that substitution occurs at the ethylenic system to give IV. These results are compared to reactions of the 1,4-dithiadiene ring system. The independent synthesis of IV from 1,1,3,3-tetraethoxy-2-bromobutane is further evidence that the ϵ-1 elimination of hydrogen halide from halomercaptals occurs by a process involving molecular rearrangement of sulfonium intermediates. New structures are suggested for products previously reported from similar reactions.

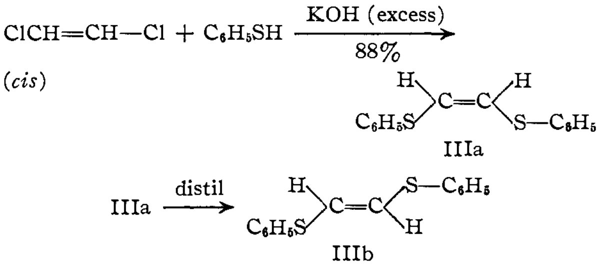
The fact that 1,4-dithiadiene (I) possesses a boat configuration[3] established the fact that the molecule is not appreciably stabilized by structures (such as Ia) which are dependent upon the closed ring system. It was concluded, therefore, that the unusual behavior[4,5] of the dithiadiene ring in benzo-1,4-dithiadiene (II), may be a result of the 1,2-bismercaptoethylene structure, and that open chain analogs of II might undergo electrophilic substitution preferentially at the ethylenic group. In order to test this hypothesis, a study has been made of the synthesis and properties of *cis*- and *trans*-1,2-bis-(phenylmercapto)-ethylene (III).


I


Ia


II

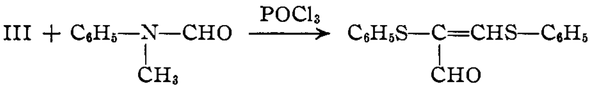
cis- and *trans*-1,2-bis-(phenylmercapto)-ethylene (III) were prepared as described in the following equations[6]



The *trans* isomer (IIIb, m.p. 64°) was characterized by conversion into the corresponding disulfone (m.p. 227°), and the latter was converted into the corresponding Diels–Alder adducts, by reaction with dimethylbutadiene and cyclopentadiene. The *cis* isomer, IIIa (m.p. 32°), was also characterized by conversion into its corresponding disulfone[7] (m.p. 90°). Reduction of either sulfone gave 1,2-bisphenylsulfonylethane.

The reactions of IIIa and IIIb with nitric acid[8] were first investigated; however, results were inconclusive and no homogeneous products were obtained. Attempts to distil the products of nitration resulted in decomposition with the loss of oxides of nitrogen. The loss of oxides of nitrogen suggested that nitration had occurred at the ethylenic linkage.[4]

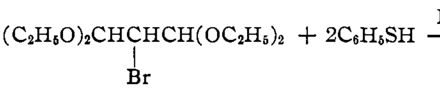
The reactions of IIIa and IIIb with N-methylformanilide and phosphorus oxychloride (Vilsmeyer reaction) were found to give essentially identical reaction products. These products were oils composed principally of an aldehyde. The corresponding dinitrophenylhydrazones and *p*-nitrophenylhydrazones, obtained in high yield[9] from the products derived from IIIa and IIIb, were shown to be identical by comparison of their melting points and mixed melting points. The composition of the hydrazones established the empirical formula $C_{15}H_{12}OS_2$ for the aldehyde.



$$\text{III} + C_6H_5\underset{\substack{|\\ CH_3}}{N}-CHO \xrightarrow{POCl_3} C_6H_5S-\underset{\substack{|\\ CHO}}{C}=CHS-C_6H_5$$

IV

Evidence that the structure of the aldehyde obtained from IIIa and IIIb was IV, was obtained by its independent synthesis as outlined in the equations



$$(C_2H_5O)_2CH\underset{\substack{|\\ Br}}{C}HCH(OC_2H_5)_2 + 2C_6H_5SH \xrightarrow{H^+}$$

V

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[1] This work was supported by the Office of Ordnance Research, Contract No. DA-11-022-ORD-571.

[2] From the Ph.D. Thesis of Jack Heberling, University of Minnesota, 1954.

[3] W. E. Parham, H. Wynberg, W. R. Hasek, P. A. Howell, R. M. Curtis and W. N. Lipscomb, THIS JOURNAL, **76**, 4957 (1954).

[4] W. E. Parham, T. M. Roder and W. R. Hasek, *ibid.*, **75**, 1647 (1953).

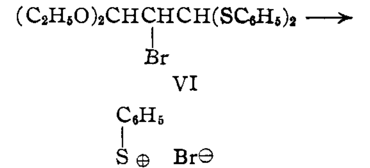
[5] W. E. Parham and J. Jones, *ibid.*, **76**, 1068 (1954).

[6] The synthesis and proof of structure of *cis*- and *trans*-III was discovered independently by W. E. Truce and R. McManimie (paper presented before the Organic Division of the American Chemical Society, Kansas City, 1954). Our work was essentially in accord with theirs; consequently only those details considered essential to this report will be considered in the text of this report. Our assignment of configuration to these isomers was made on the basis of the lower melting points observed for IIIa and its sulfone, as compared to IIIb and its sulfone. The isomerization noted for the Diels–Alder adducts of the lower melting sulfone to products identical to those obtained from the higher melting sulfone also supported the assignment of the *cis*-configuration to the former.

[7] Truce and McManimie[6] reported pure Diels–Alder adducts with the sulfones derived from either IIIa or IIIb. We were unable to obtain pure adducts with the *cis*-isomer. The products obtained from our *cis*-isomer isomerized during recrystallization, and after standing for three months had completely isomerized to products identical with those obtained from *trans*-III.

[8] Conditions employed were identical to those previously reported for the nitration of II. *Cf.*, ref. 4.

[9] In one case the reaction with 2,4-dinitrophenylhydrazine was studied quantitatively. A 74% yield (from IIIb) of the corresponding hydrazone was obtained.



$$(C_2H_5O)_2CH\underset{\displaystyle Br}{\underset{|}{C}}HCH(SC_6H_5)_2 \longrightarrow$$

VI

$$(C_2H_5O)_2CHCH\overset{\displaystyle \overset{C_6H_5}{\overset{|}{S^{\oplus}}}\ Br^{\ominus}}{—}CH—SC_6H_5 \xrightarrow{\text{pyridine}}$$

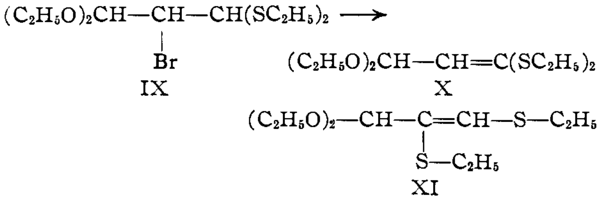
VII

$$(C_2H_5O)_2CH—\overset{\displaystyle \overset{S—C_6H_5}{|}}{C}=CH—S—C_6H_5 \xrightarrow{H_3O^+} \text{IV}$$

VIII

The 2,4-dinitrophenylhydrazone of the product obtained from VIII was identical (mixed m.p., ultraviolet and infrared spectra) with that obtained from the Vilsmeyer reaction product IV. This observation established, beyond any doubt, that the formylation of III occurred on the ethylenic group, and not on the benzene ring.

The elimination of hydrogen halide from IX has been reported[10] to give isomeric olefins when pyridine and when potassium *t*-butoxide is used



$$(C_2H_5O)_2CH—\underset{\displaystyle Br}{\underset{|}{CH}}—CH(SC_2H_5)_2 \longrightarrow$$

IX

$$(C_2H_5O)_2CH—CH=C(SC_2H_5)_2$$

X

$$(C_2H_5O)_2—CH—\underset{\displaystyle S—C_2H_5}{\underset{|}{C}}=CH—S—C_2H_5$$

XI

to effect dehydrohalogenation. Rothstein and Whitely[10] have suggested that these products are geometric isomers of X. The identity of the aldehyde derived from VIII with that derived from III is convincing evidence that molecular rearrangement occurred during the reaction of VI with pyridine. Such a rearrangement is in keeping with our previous work, and the conclusion that the elimination of hydrogen halide from α-halomercaptals, by an ϵ-1 process, is accompanied by molecular rearrangement involving sulfonium intermediates.[11] The elimination of hydrogen halide from IX by an ϵ-2 process should give the ketene mercaptal X[12]; consequently it is suggested that the geometric isomers previously obtained from IX are actually the position isomers X and XI.

Experimental

cis-1,2-**Bis-(phenylmercapto)-ethylene** (IIIa).—A solution of pure *cis*-1,2-dichloroethylene (5.21 g., 0.054 mole, b.p. 59.54° (740 mm.), $n^{25}D$ 1.4461, d^{25}_4 1.2739) in ethanol (58 ml.) was added, with stirring, to a solution of potassium hydroxide (10.4 g., 0.185 mole), thiophenol (11.6 g., 0.105 mole) and ethanol (160 ml.). The resulting solution was heated at the reflux temperature for five hours, the solvent was then removed at reduced pressure and the resulting residue was diluted with water and extracted with ether. The ether was dried (magnesium sulfate) and removed giving 11.39 g. (88.8% yield) of *cis*-1,2-bis-(phenylmercapto)-ethylene (m.p. 32–32.5 from ethanol).

Anal. Calcd. for $C_{14}H_{12}S_2$: C, 68.8; H, 4.92. Found: C, 68.48; H, 4.87.

IIIa was not obtained when the reaction was carried out with only two equivalents of base. Diphenyl disulfide was the only product isolated.

When the reaction was carried out with a commercially available equilibrium mixture of *cis*- and *trans*-dichloroethylene, the yield of IIIa was 47.2%.

cis-1,2-**Bis-(phenylsulfonyl)-ethylene**.—The procedure used for the oxidation of IIIa was similar to that described for the oxidation of 1,2-bis-(tolylmercapto)-ethylene.[13] The product (76% yield, m.p. 81–90°) melted at 89.5–90° after recrystallization from ethanol.

Anal. Calcd. for $C_{14}H_{12}S_2O_4$: C, 54.52; H, 3.92. Found: C, 54.63; H, 3.60.

trans-1,2-**Bis-(phenylmercapto)-ethylene** (IIIb).—The procedure used was similar to that previously described by Snyder and Hallada[14] and Cusa and McCombie,[15] and was essentially identical to that described above for the *cis* isomer. The product, obtained in 88% yield from *cis*-1,2-dichloroethylene, was distilled at reduced pressure which caused isomerization of the *cis* to the *trans* isomer. The yield of IIIb (b.p. 150–155° (0.24 mm.)) was 47–52% when an equilibrium mixture of *cis*- and *trans*-dichloroethylene was employed as starting material.

Anal. Calcd. for $C_{14}H_{14}S_2$: C, 68.8; H, 4.92. Found: C, 68.65; H, 5.12.

When *trans*-1,2-dichloroethylene (b.p. 46.25° (731 mm.), $n^{25}D$ 1.4423, d^{25}_4 1.2455) was used as starting material, only diphenyl disulfide was obtained. The reaction mixture was heated for 21 hours, and then analyzed for ionic chloride ion. The weight of silver chloride obtained corresponded to 1.12% reaction.

trans-1,2-**Bis-(phenylsulfonyl)-ethylene**.—The disulfone of IIIb (73% yield, m.p. 226.5–227° (from ethanol)) was prepared as described for the corresponding *cis* isomer.

Anal. Calcd. for $C_{14}H_{12}S_2O_4$: C, 54.52; H, 3.92. Found: C, 54.74; H, 4.11.

The reduction of the disulfones obtained from IIIa and IIIb (Pd–C, in ethanol, 40 p.s.i. of hydrogen) gave 1,2-bis-(phenylsulfonyl)-ethane (m.p. and mixed m.p. 183.5–184.5°). The reported m.p. is 179.5–180°.[16]

Diels–Alder Adducts with *trans*-**1,2-Bis-(phenylsulfonyl)-ethylene**.—The procedure was similar to that of Snyder and Hallada.[14]

1. **With 2,3-Dimethyl-1,3-butadiene**.—A mixture of the *trans*-sulfone (0.56 g., 1.82 mmoles), freshly distilled dimethylbutadiene (5.05 g., 61.5 mmoles), picric acid (*ca.* 5 mg.), and dry benzene (12 ml.) was heated at the reflux temperature for 20 hours. The crude product (0.51 g., 69%) was recrystallized from ethanol to give *trans*-4,5-bisphenylsulfonyl-1,2-dimethyl-1-cyclohexene (white powder, m.p. 163–164°).

Anal. Calcd. for $C_{20}H_{27}S_2O_4$: C, 61.51; H, 5.68. Found: C, 61.36; H, 5.73.

2. **With Cyclopentadiene**.—A solution of the *trans*-sulfone (0.22 g., 0.714 mmole), and dry benzene (10 ml.) was mixed with a solution of cyclopentadiene (1.6 g., 2.42 mmole) and dry benzene (5 ml.), and the resulting mixture was allowed to stand at room temperature for 40 hours. The reaction mixture was cooled and *trans*-4,5-bis-(phenylsulfonyl)-3,6-endomethylene-1-cyclohexene (0.1 g., 37.4%, m.p. 257–259°) was collected. The adduct melted at 257–258° after recrystallization from benzene–ethanol.[17]

Anal. Calcd. for $C_{19}H_{18}S_2O_4$: C, 60.94; H, 4.84. Found: C, 60.82; H, 4.95.

Diels–Alder Adducts with *cis*-**1,2-Bis-(phenylsulfonyl)-ethylene**.—The procedure was the same as that described for the *trans* isomer.

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[10] E. Rothstein and R. Whitely, *J. Chem. Soc.*, 4012 (1953).

[11] W. E. Parham, J. W. Heberling and H. Wynberg, THIS JOURNAL, **77**, 1169 (1955).

[12] In ϵ-2 eliminations, a hydrogen atom is removed in the rate-determining step. This process should involve the more acidic mercaptal hydrogen atom in IX. *Cf.* E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., N. Y., 1950, p. 108 ff. C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1950, Chapter 8.

[13] E. Fromm and E. Siebert, *Ber.*, **55**, 1014 (1922).

[14] H. R. Snyder and D. P. Hallada, THIS JOURNAL, **74**, 5595 (1952).

[15] N. W. Cusa and H. McCombie, *J. Chem. Soc.*, 767 (1937).

[16] R. Otto, *Ber.*, **17**, 1272 (1884).

[17] W. E. Truce and R. McManimie, THIS JOURNAL, **75**, 1672 (1953), report the melting point of this product to be 169–170°. Their method of preparation was similar to ours, but involved a 17 hour reflux period. Our product was recovered unchanged from a benzene solution after a 17-hour reflux period.

1. **With 2,3-Dimethyl-1,3-butadiene.**—The product (60%) melted at 144–147°, but could not be obtained with a constant melting point; it then was stored in the solid state, and after three months melted at 162.5–164.5°. Isomerization of the product to *trans*-4,5-bis-(phenylsulfonyl)-1,2-dimethyl-1-cyclohexene had occurred (mixed m.p. 160.5°).

2. **With Cyclopentadiene.**—The product (98% yield) melted at 240–249° dec. The solid could not be recrystallized to constant melting point and, after standing for three months in the solid state, isomerized to the *trans* adduct (m.p. and mixed m.p. with the *trans* adduct 250–252.5°).

The Vilsmeyer Reaction with *trans*-1,2-Bis-(phenylmercapto)-ethylene (IIIb).—Freshly distilled N-methylformanilide (4.68 g., 34.4 mmoles) and phosphorus oxychloride (5.34 g., 34.8 mmoles) were mixed (protected from moisture), and allowed to stand for one hour. Molten *trans*-1,2-bis-(phenylmercapto)-ethylene (7.87 g., 32.1 mmoles), was then added and the mixture was allowed to stand at room temperature for 24 hours. The reaction mixture now was poured into cold water (300 ml.) and the resulting mixture was stirred for one-half hour and then extracted with chloroform. The chloroform extract was washed (water, dilute bicarbonate, water) and dried (magnesium sulfate), and the solvent was removed at reduced pressure. Attempts to crystallize the residue (9.78 g.) resulted in the isolation of small quantities of IIIb. Attempts to isolate IV as a bisulfite adduct were unsuccessful.

Reaction of the residue with acidic 2,4-dinitrophenylhydrazine[18] gave an immediate precipitate of **the 2,4-dinitrophenylhydrazone of IV.** The yield of hydrazone melting at 187–194° was 74%. The pure hydrazone melted at 200–201° (ethyl acetate).

Anal. Calcd. for $C_{21}H_{16}N_4O_4S_2$: C, 55.74; H, 3.56; N, 12.38. Found: C, 55.50; H, 3.66; N, 12.38.

Reaction of the residue with *p*-nitrophenylhydrazine[18] gave, with difficulty, the *p*-nitrophenylhydrazone of IV (m.p. 141–142°, from chloroform).

Anal. Calcd. for $C_{21}H_{17}N_3O_2S_2$: C, 61.89; H, 4.21. Found: C, 61.81; H, 4.27.

The Vilsmeyer Reaction with *cis*-1,2-Bis-(phenylmercapto)-ethylene (IIIa).—The experiment was essentially identical to that described above for the *trans* isomer. Essentially identical results were obtained (m.p. and mixed m.p. of the 2,4-dinitrophenylhydrazone of the product 199–200°).

1,1,3,3-Tetraethoxy-2-bromopropane (V).—This material (b.p. 109–112° (4 mm.), 51% yield, $n^{25}\text{D}$ 1.4399) was prepared according to the directions of Rothstein and Whitely.[10] The 1,3-diphenylimine derivative melted at 143–144° (reported[10] 145°).

Independent Synthesis of the 2,4-Dinitrophenylhydrazone of IV.—The procedure used by Rothstein and Whiteley[10] for the reaction of 1,1,3,3-tetraethoxy-2-bromopropane with ethyl mercaptan was followed.

Concentrated hydrochloric acid (1 ml.) was added to a cold (ice-bath) solution of 1,1,3,3-tetraethoxy-2-bromopropane (1 g., 3.34 mmoles), thiophenol (0.75 g., 6.68 mmoles) and acetic acid (2 ml.). The mixture was allowed to stand in an ice-bath for two hours, and was then diluted with water and extracted with ether. The ether extract was washed (water) and dried (magnesium sulfate), and the ether was removed at reduced pressure. Pyridine (3 ml.) was added to the residue, and the resulting solution was heated on a steam-bath for one-half hour. The reaction mixture was allowed to stand overnight at room temperature, and was then diluted with water and extracted with ether. Ether was removed from the dry (calcium chloride) ether extract affording 0.74 g. of residue. The 2,4-dinitrophenylhydrazone, readily prepared[18] from the residue containing the acetal, melted at 197.5–199.5 after recrystallization from ethyl acetate. A mixed melting point with the corresponding hydrazone obtained from III was 197–200°. The infrared and ultraviolet spectra of the various samples of 2,4-dinitrophenylhydrazone of IV were essentially identical.

Attempted Nitration of III.—The procedure used was identical with that previously reported for the nitration of benzo-1,4-dithiadiene.[4] The yellow oil, which separated after the nitration mixture was added to ice, solidified and was separated by filtration. The solid remelted at room temperature. Attempts to isolate a solid product by crystallization failed. The product decomposed with the elimination of oxides of nitrogen, upon attempted distillation at reduced pressure.

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[18] R. C. Fuson and R. Shriner, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, third edition, p. 229.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Ring Expansion during the Reaction of Indenylsodium and Chloroform

BY WILLIAM E. PARHAM AND HARRY E. REIFF[1]

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The reaction of chloroform with indenylsodium in indene gives 2-chloronaphthalene (10% yield), and a product formulated as a chloroazulene.

The Reimer–Tiemann reaction is used conventionally for the introduction of the aldehyde group into certain aromatic compounds, usually phenolic substances, capable of forming relatively stable anions. Frequently side reactions occur which lead to the formation of a variety of nonaldehydic products and/or polymeric substances Thus, in the Reimer–Tiemann reaction with phenols, dichloromethylcyclohexadienones and orthoformic esters have been formed,[2] while reaction of pyrrole and indole with chloroform and base has given rise to, respectively, 3-chloropyridine[3] and 3-chloroquinoline,[4] in addition to the expected aldehydes. A rational explanation for the production of these products lies in the postulation[5] of dichlorocarbene (II) as an intermediate, and the existence of such an intermediate in the basic hydrolysis of chloroform has strong kinetic support.[5]

It seemed reasonable to expect that the ring expansion noted for derivatives of pyrrole would obtain for certain cyclic olefins which form anions, and this has been shown to be the case. When a mixture of indene and the sodium salt of indene was treated with chloroform, a tarry reaction product resulted from which 2-chloronaphthalene

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[1] National Science Foundation fellow 1954–1955.

[2] K. von Auwers and G. Keil, *Ber.*, **35**, 4207 (1902); J. E. Driver, THIS JOURNAL, **46**, 2090 (1924).

[3] G. L. Ciamician and M. Dennstedt, *Ber.*, **14**, 1153 (1881); **15**, 1172 (1882); O. Bocchi, *Gazz. chim. ital.*, **30**, I, 89 (1900); G. Plancher and U. Ponti, *Atti. accad. naz. Lincei*, [5] **18**, II, 473 (1909).

[4] G. Plancher and O. Carrasco, *ibid.*, [5] **13**, I, 575 (1904); G. Magnanini, *Gazz. chim. ital.*, **17**, 249 (1887).

[5] J. Hine, THIS JOURNAL, **72**, 1438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).