ate poisoned with 40% by weight of lead acetate.[20] The temperature was controlled by means of a cooling coil. After the theoretical amount of hydrogen was absorbed, the reaction mixture was filtered and distilled through a Todd column at a 10:1 reflux ratio to yield III (92 g., 94%), b.p. 70–71°/40 mm., $n^{25}{}_{\rm D}$ 1.4512. Heilbron[19] reported b.p. 86–87°/100 mm., $n^{19}{}_{\rm D}$ 1.4052.

Anal. Calcd. for $C_6H_{10}O$: hydrogen no., 2.0. Found: hydrogen no., 1.99, 2.00.

1,3,5-Hexatriene (I).—A Pyrex tube (29 mm. i.d.) was packed with alumina for a length of 10 in. (Harshaw Chemical Co. 0104T—surface area, 80 sq. m./g.). A preheat zone of 6 in. of glass beads was used and a thermocouple well (4 mm. o.d.) was placed in the center of the tube before the catalyst was added. The exit line from the system was through a Dry Ice–cooled trap to a vacuum pump which was set to maintain a pressure of 30 mm. The catalyst was dried at 400° before use by passing a stream of nitrogen through the system. III (98 g., 1.0 mole) was distilled into the evacuated system over a period of 1 hr. The temperature in the catalyst zone was maintained at 300–315°. The products condensed in the Dry Ice–cooled trap were melted, the water separated and the organic layer distilled at 30 mm. and 0°. Only I (92–95% pure) distilled and the unchanged hexadienol remained in the distillation pot. The yield of I was 75% per pass and was 90–95% ultimate.

Crude I was recrystallized four times from methanol at −80°, washed with water, dried over magnesium sulfate, and flash distilled at 30 mm. into a Dry Ice–cooled trap, to give a product with a freezing temperature of −8.46°.

At a dehydration temperature of 350° over alumina at 30 mm. pressure, the yield of I was 70%, 50% at 400°, and 37% at 425°. Varying the contact time from 0.2 sec. to 1.5 sec. at 300° and 75 mm. pressure had essentially no effect on yield of product. Dehydration at reduced pressure gave a higher purity crude product than dehydration at atmospheric pressure. Comparable purities of the crude were 90% at 30 mm. pressure and 60% at 750 mm. pressure. Comparison of a silica–alumina catalyst (Davison Chemical—87% silica + 13% alumina) with an alumina catalyst indicated a preference for alumina. The silica–alumina gave a low purity crude product, 26% to 72%, whereas a crude of 90% purity was obtained with an alumina catalyst under optimum conditions.

Alternate Preparation of I. Dehydration of 2,5-Hexadien-1-ol.—The intermediate 5-hexen-2-yn-1-ol was prepared from propargyl alcohol and allyl chloride by the method of Kurtz[21]; yield 47%, b.p. 71–77°/11 mm., $n^{22}{}_{\rm D}$ 1.4770.

Anal. Calcd. for C_6H_8O: hydrogen no., 3.0. Found: hydrogen no., 2.94.

5-Hexen-2-yn-1-ol (165 g., 1.72 moles) was hydrogenated at room temperature over a catalyst consisting of 5% palladium-on-calcium carbonate poisoned with 40% by weight of lead acetate.[20] Before hydrogenation, it was necessary to treat the 5-hexen-3-yn-1-ol with sponge nickel (2 g.) at room temperature to remove an impurity which markedly slowed hydrogenation. The hydrogenate was filtered and distilled to yield 2,5-hexadien-1-ol (157 g., 93%), b.p. 76–78°/25 mm., $n^{22}{}_{\rm D}$ 1.4615 and a residue (10 g.).

Anal. Calcd. for $C_6H_{10}O$: hydrogen no., 2.0. Found: hydrogen no., 1.98, 2.0.

The 2,5-hexadien-1-ol was dehydrated to I over alumina in a manner similar to that which we have described for dehydration of III. The yield of crude I from 98 g. (1.0 mole) of 2,5-hexadien-1-ol was 45.5 g. Recycling of unchanged hexadienol gave an ultimate yield of 69% of a product which had purity of 80 mole %.

Acknowledgment.—The authors are indebted to the following Koppers Company Research Department personnel; Mr. R. Mainier, Mrs. B. McKinstry, and Mr. M. Hamming for infrared, ultraviolet, and mass spectrographic data; and Dr. G. R. Atwood for cryoscopic analyses.

---

(20) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(21) P. Kurtz, U. S. Patent 2,884,464,

Carbonyl and Thiocarbonyl Compounds. VII.[1a] A New Method for the Direct Synthesis of Ethylene Sulfides

N. LATIF[1b] AND I. FATHY

Organic Chemistry Department, National Research Center, Cairo, U.A.R.

Received October 17, 1961

The ethylene sulfides, epithiotetraphenylethane, II, epithiobidiphenyleneethane, III, dispiro(xanthene-9,2′-thiirane-3′,9″-xanthene), IVa, and dispiro(thioxanthene-9,2′-thiirane-3′,9″-thioxanthene), IVb, are directly synthesized, in excellent yields, by the reaction of elemental sulfur with the corresponding diazoalkanes. A reaction mechanism, based on the formation of a biradical, is suggested. The reaction of 9-diazoxanthene with thioketones and of thiofluorenone with diazoalkanes is described.

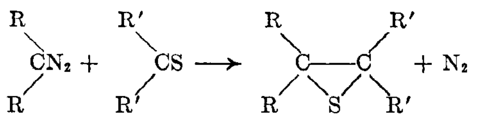
The successful application of ethylene sulfides in industry and biology directed the attention of various investigators to study the chemistry of this group of compounds. Various aromatic and heterocyclic ethylene sulfides are now usually prepared by the reaction of diazoalkanes with thioketones[2] according to scheme A. However, the instability of some of these thioketones, such as thiofluorenone, and the difficulty of their preparation, limits the general usefulness of this method.

In the present investigation, the authors have found that symmetrical ethylene sulfides of the general formula I can be directly produced by the

---

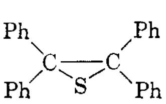
(1) (a) Part VI of this series, *J. Org. Chem.*, **27**, 846 (1962); (b) Present address during this year: Carnegie Institute of Technology, Pittsburgh Pa.

(2) *Cf.* (a) B. Eistert in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, 1948, p. 513; (b) A. Schönberg in Houben-Weyl, "Methoden Der Organischen Chemie. IX.," George Thieme Verlag, Stuttgart, 1955, p. 158.

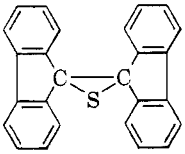


I. R = R'
Scheme A

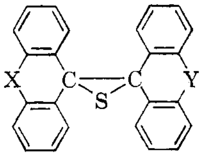
reaction of diazoalkanes with elemental sulfur. For example, when diphenyldiazomethane, 9-diazofluorene, 9-diazoxanthene, or 9-diazothiaxanthene is allowed to react with elemental sulfur in ether, the ethylene sulfides, epithiotetraphenylethane (II) epithiobidiphenyleneethane (III), dispiro(xanthene-9,2′-thiirane-3′,9′′-xanthene) (IVa), and dispiro-(thioxanthene-9,2′-thiirane-3′,9′′-thioxanthene) (IVb), are produced, respectively. The reaction takes place readily at room temperature, and the products are obtained in excellent yields.



II



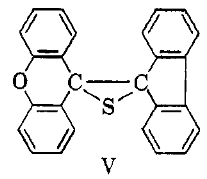
III



IVa. X = Y = O
b. X = Y = S
c. X = O, Y = S

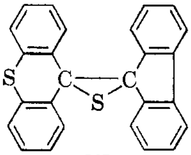
The speed of the reaction depends on the nature of the diazoalkane used. Thus while it is most rapid in the case of 9-diazoxanthene and is almost complete within about thirty minutes, a twenty-four-hour period is required in the case of 9-diazofluorene. Compound II was previously prepared by the action of diphenyldiazomethane on thiobenzophenone,[3] and the sulfide IVb from 9-diazothiaxanthene and thiaxanthione.[4] It is found that compounds III and IVa can be prepared in a similar manner; the first by the reaction of 9-diazofluorene with thiofluorenone, and the second by the action of 9-diazoxanthene on xanthione. The constitution of both products is based, besides analytical data, on analogy[1,3,4] and on the fact that when their xylene solutions are boiled with copper powder, dibiphenyleneethylene and dixanthylene are produced, respectively.

In this respect it is worth mentioning that 9-diazoxanthene is one of the diazo compounds which has not been investigated before as to its reaction with thioketones. In addition to its reaction with xanthione, it is found that it also reacts with thiaxanthione and with thiofluorenone to give the corresponding ethylene sulfides IVc and V in almost quantitative yields. These were previously obtained by the action of 9-diaxothiaxanthene and 9-diazofluorene, respectively, on xanthione.[4] The preparation of 9-diazoxanthene has been recently described by the authors.[5]

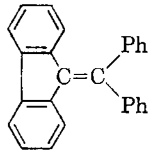


V

In addition to the above-mentioned reactions of thiofluorenone, it is found that it reacts also with 9-diazothiaxanthene producing the corresponding ethylene sulfide VI, which was previously obtained by the reaction of 9-diazofluorene with thiaxanthione.[4] However, it reacts with diphenyldiazomethane giving directly the ethylene VII. The latter is identical with the product obtained by Kaufmann[6] from the condensation of benzophenone dichloride with fluorene.

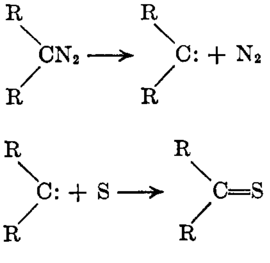


VI



VII

Concerning the mechanism of the reaction between diazoalkanes and elemental sulfur with direct production of the corresponding ethylene sulfides, it is assumed that this takes place by the initial decomposition of the diazoalkane to give a biradical. The latter then coordinates with sulfur giving the corresponding thioketone which reacts directly with another molecule of the diazoalkane producing the ethylene sulphide as shown in Scheme B. The possibility of the initial formation of biradicals in the reactions of diazoalkanes has been proposed by Badger.[7] The reaction of free radicals with elemental sulfur has been reported by Schlenk[8] when he found that the latter reacts with triphenylmethyl to give a mixture of sulfides. Also in favor of the suggested mechanism is the fact that the reaction is catalyzed by the action of sunlight, and that in some cases the corresponding ethylene is produced together with the ethylene sulfide. Thus, for example, in the reaction of diphenyldiazomethane with sulfur, tetraphenylethylene, and tetraphenylethylene sulfide are both produced.



---

(3) H. Staudinger and J. Siegwart, *Helv. Chem. Acta*, **3**, 833 (1920).

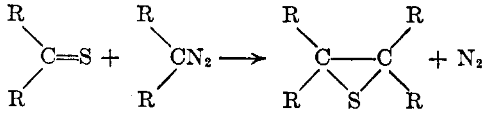
(4) Schönberg *et al.*, *J. Am. Chem. Soc.*, **81**, 2259 (1959).

(5) N. Latif and I. Fathy, *Can. J. Chem.*, **37**, 863 (1959).

(6) V. Kaufmann, *Ber.*, **29**, 75 (1896).

(7) G. M. Badger and B. J. Christie in "Current Trends in Heterocyclic Chemistry," Butterworths Scientific Publication, London, 1958.

(8) Von W. Schlenk, *Ann.*, **394**, 182 (1912).



Scheme B

It is found also that the diazoalkanes themselves decompose in the presence of sunlight giving the corresponding ethylenes. For example, dibiphenyleneethylene is produced from 9-diazofluorene, and dixanthylene from 9-diazoxanthene when the diazo compounds are exposed to sunlight.

Experimental

Reaction of 9-Diazofluorene with Thiofluorenone.—To a solution of 9-diazofluorene (1.1 g.) in dry ether (20 ml.) was added a solution of thiofluorenone (1.1 g.) in the same solvent (15 ml.). A vigorous reaction with evolution of gas took place. The solid separated during the reaction was filtered off, washed with ether, and crystallized from benzene to give III (1.5 g.) in colorless crystals, m.p. 162–163° (red melt). It gives a pale green color with concentrated sulfuric acid.

Anal. Calcd. for $C_{26}H_{16}S$: C, 86.66; H, 4.44; S, 8.88. Found: C, 86.32; H, 4.56; S, 8.65.

Action of Copper Powder on III.—To a boiling solution of III (0.5 g.) in xylene (20 ml.), 0.5 g. of copper powder was added and the mixture was refluxed for 1 hr. The reaction mixture was then filtered while hot, evaporated to dryness, and a few milliliters of acetone was added to the oily residue. The scarlet red crystals separated (0.42 g.) were shown to be dibiphenyleneethylene (melting point and mixed melting point).

Reaction of 9-Diazoxanthene with Xanthione.—Xanthione (1 g.) was added in small portions to a solution of 9-diazoxanthene (1 g.) in dry ether (20 ml.). A vigorous reaction with evolution of gas took place after each addition. A new portion of the thione was only added when the reaction from a previous addition had subsided. When all the thione had been added, a colorless product separated. This was filtered off, washed with acetone, and crystallized from the same solvent to give IVa (1.7 g.) in colorless crystals, m.p. 206–207°. It gives an orange-yellow color with concd. sulfuric acid.

Anal. Calcd. for $C_{26}H_{16}O_2S$: C, 79.59; H, 4.08; S, 8.16. Found: C, 79.7; H, 4.2; S, 7.78.

When IVa was treated with copper powder as above, dixanthylene was produced.

Reaction of 9-Diazoxanthene with Sulfur.—Powdered sulfur (0.1 g.) was added to a solution of 9-diazoxanthene (1 g.) in dry ether (20 ml.). The immediate mild reaction with evolution of gas which took place was accelerated by occasional gentle shaking. On standing for 30 min., the green color of the solution almost disappeared, and an almost colorless, crystalline product separated. This was filtered off and extracted with boiling acetone. The acetone extract was filtered, concentrated, and cooled. The colorless crystals which separated (0.7 g.) were shown to be IVa (undepressed when admixed with an authentic sample prepared by the action of 9-diazoxanthene on xanthione).

Reaction of 9-Diazofluorene with Sulfur.—To a solution of 9-diazofluorene (2 g.) in dry ether (30 ml.), powdered sulfur (0.2 g.) was added. The reaction mixture was kept at room temperature with occasional shaking for 48 hr. The colorless crystalline product which separated was filtered off and extracted with boiling acetone. The acetone extract was filtered, concentrated, and left to cool. The colorless crystals which separated (1.2 g.) were shown to be III (undepressed when admixed with an authentic sample prepared by the action of 9-diazofluorene on thiofluorenone).

Photochemical Reaction between 9-Diazofluorene and Sulfur.—A mixture of 9-diazofluorene (0.5 g.) and powdered sulfur (0.1 g.) in dry benzene (10 ml.) was exposed to sunlight for 3 hr. in a carbon dioxide atmosphere in a Pyrex glass tube. When the reaction mixture was worked up as above, III (0.06 g.) was obtained.

In a parallel experiment carried out in the dark, III could not be isolated and 9-diazofluorene was practically recovered unchanged.

Reaction of 9-Diazothiaxanthene with Sulfur.—A mixture of the diazo compound (0.5 g.) and powdered sulfur (0.1 g.) in dry ether (30 ml.) was kept at room temperature for 12 hr. The ether was then driven off under reduced pressure and the residue extracted with boiling acetone. The acetone extract was filtered while hot, concentrated, and left to cool when IVb (0.3 g.) separated in colorless crystals, m.p. above 360° (its infrared spectrum is identical with that of an authentic sample prepared by the action of 9-diazothiaxanthene on thiaxanthione).

Reaction of Diphenyldiazomethane with Sulfur.—Half a gram of powdered sulfur was added to a solution of diphenyldiazomethane (2 g.) in dry ether (25 ml.), and the reaction mixture was left for 12 hr. at room temperature. The reaction mixture became almost colorless and a crystalline product separated. This was filtered off and extracted several times with boiling methyl alcohol. The alcoholic extracts were filtered while hot, concentrated, and left to cool. The colorless crystalline product which separated was recrystallized from acetone in colorless crystals, m.p. 223–224°, which proved to be tetraphenylethylene (m.p. and mixed m.p.). The ethereal mother liquor from the main reaction mixture was evaporated to dryness under reduced pressure, and a few milliliters of methyl alcohol was added to the residue. The colorless crystals which separated were filtered off, washed with methyl alcohol, and crystallized from the same solvent to give II in colorless crystals, m.p. 178° (undepressed when admixed with an authentic sample prepared by the action of diphenyldiazomethane on thiobenzophenone).

Reaction of 9-Diazoxanthene with Thiaxanthione.—To a solution of 9-diazoxanthene (1 g.) in dry ether (30 ml.) thiaxanthione (1 g.) was added in small portions. A vigorous reaction took place immediately accompanied by the separation of a pale yellow, crystalline product. This was filtered off, washed with acetone, and crystallized from the same solvent to give IVc (1.6 g.) in colorless crystals, m.p. 208° (undepressed when admixed with an authentic sample prepared by the reaction of 9-diaxothiaxanthene with xanthione). It gives an orange-red color with concd. sulfuric acid.

Anal. Calcd. for $C_{26}H_{16}OS_2$: C, 76.47; H, 3.92; S, 15.68. Found: C, 76.75; H, 4.02; S, 14.5.

When a solution of IVc (0.2 g.) in xylene was boiled with copper powder, the corresponding ethylene was obtained as colorless crystals, m.p. 295° (undepressed when admixed with an authentic sample[4]).

Anal. Calcd. for $C_{26}H_{16}OS$: C, 82.97; H, 4.25; S, 8.51. Found: C, 82.82; H, 4.20; S, 7.63.

Reaction of 9-Diazoxanthene with Thiofluorenone.—Thiofluorenone (1 g.) was added to a solution of 9-diazoxanthene (1 g.) in dry ether (20 ml.). The colorless product which separated was filtered off, washed with ether, and crystallized from acetone to give V in colorless crystals, m.p. 198° (violet melt—undepressed when admixed with an authentic sample prepared by the reaction of 9-diazofluorene with xanthione). The substance gives a violet color with concd. sulfuric acid; yield almost quantitative.

Anal. Calcd. for $C_{26}H_{12}OS$: C, 82.97; H, 4.25; S, 8.5. Found: C, 82.96; H, 4.16; S, 8.26.

Reaction of 9-Diazothiaxanthene with Thiofluorenone.—A solution of thiofluorenone (1.5 g.) in dry ether (20 ml.) was allowed to react with an ethereal solution of 9-diazothiaxanthene (1 g.). The product which separated was washed with acetone and crystallized from benzene to give VI in colorless crystals, m.p. 240° (undepressed when admixed with an authentic sample prepared by the reaction of 9-diazofluorene with thiaxanthione). The product and the authentic sample have identical infrared spectra. It gives a pink color with concd. sulfuric acid.

Reaction of Diphenyldiazomethane with Thiofluorenone.—Thiofluorenone (1.5 g.) was added to a solution of diphenyldiazomethane (1.7 g.) in dry ether (30 ml.). The solid which separated was filtered off, and crystallized from acetone to give VII in colorless crystals, m.p. 227–228° (undepressed when admixed with an authentic sample prepared by the reaction of benzophenone dichloride with fluorene). The product and the authentic sample have identical infrared spectra.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.54; H, 5.45. Found: C, 94.57; H, 5.52.

Action of Sunlight on 9-Diazoxanthene.—A solution of 9-diazoxanthene (1 g.) in dry ether (30 ml.) was exposed to sunlight in a carbon dioxide atmosphere for 6 hr. The pale yellow crystalline product which separated (0.8 g.) was filtered off, crystallized from xylene, and proved to be dixanthylene (melting point and mixed melting point).

When the above experiment was carried out using 9-diazofluorene, dibiphenyleneethylene was produced.

Reactions of Styrene Dimers

B. B. CORSON, W. J. HEINTZELMAN, H. MOE, AND C. R. ROUSSEAU

Koppers Co., Inc., Monomer Fellowship at Mellon Institute, Pittsburgh 13, Pa.

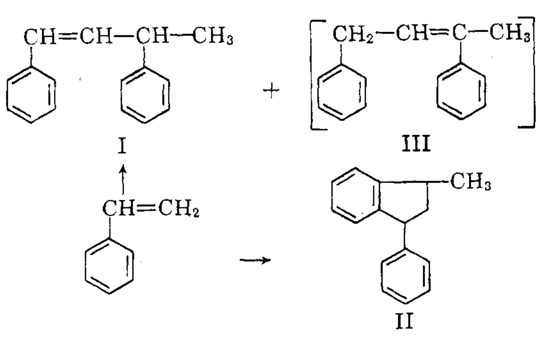
Received December 19, 1960

The dimerization of styrene and the structures of its dimers have been described, but little has been reported on their chemical reactions. We have reinvestigated the dimerization of styrene, the isomerization of the linear dimer (1,3-diphenyl-1-butene) to the cyclic dimer (1-phenyl-3-methylindane), and studied several chemical reactions of the dimeric styrenes. We have also shown that the linear dimer contains a small amount of isomeric 1,3-diphenyl-2-butene.

Chemical modification of the higher polymers of styrene has been studied extensively,[1] but very little work has been reported on the chemical reactions of the dimeric styrenes.[2]

The dimerization of styrene by means of sulfuric acid, silica gel, and phosphoric acid absorbed on activated char has been reported[3–8]; also the isomerization of linear styrene dimer (1,3-diphenyl-1-butene) to cyclic dimer (1-phenyl-3-methylindane) by means of sulfuric acid.[3,5,6] We have reinvestigated both of these processes, using several acidic catalysts.

Styrene can be converted in 83–85% yield to an isomer mixture of linear (I) and cyclic (II) dimers by means of aqueous sulfuric and phosphoric acids. The over-all yield of dimer and higher is 96–98%, the higher polymer being essentially trimer.



Styrene is dimerized in sulfuric acid at lower acid concentrations than phosphoric acid, but the latter is more easily separated from the product. By proper choice of conditions the isomer composition of the dimer can be varied from about 10% linear–90% cyclic to about 90% linear–10% cyclic (Table I).

In one experiment, twelve successive batches (fifty volumes) of styrene were dimerized with one volume of 85.8% phosphoric acid, the composition of the dimer being 45% linear–55% cyclic. The acid was as active at the end of the experiment as at the beginning. Phase separation of dimer from phosphoric acid is fast and clean, whereas with sulfuric acid troublesome emulsions are often encountered.

Linear dimer can be isomerized to cyclic dimer by means of various acidic catalysts—*e.g.*, alumina–silica, Filtrol, 100% phosphoric acid, polyphosphoric acid, and phosphoric acid absorbed on activated char. This isomerization is accompanied by the production of varying amounts of higher polymers.

A convenient method of isomerization is to heat a mixture of linear dimer and phosphoric acid under a distilling column at 20 mm. and take off distillate at such rate that the head temperature does not exceed the boiling point (180°) of the cyclic dimer. Starting with 100% linear dimer, a 94% yield of a 25% linear–75% cyclic dimer mixture was obtained.

Gas-liquid chromatography was found to be the

[1] J. A. Blanchette and J. D. Cotman, Jr., *J. Org. Chem.*, **23**, 1117 (1958).

[2] P. E. Spoerri and M. J. Rosen, *J. Am. Chem. Soc.*, **73**, 2095 (1951).

[3] R. Stoermer and H. Kootz, *Ber.*, **61**, 2330 (1928).

[4] J. Risi and D. Gauvin, *Can. J. Research*, **14B**, 255 (1936).

[5] P. E. Spoerri and M. J. Rosen, *J. Am. Chem. Soc.*, **72**, 4918 (1950).

[6] M. J. Rosen, *J. Org. Chem.*, **18**, 1701 (1953).

[7] A. Muller and K. Kormandy, *J. Org. Chem.*, **18**, 1237 (1953).

[8] B. B. Corson, J. Dorsky, J. E. Nickels, W. M. Kutz, and H. I. Thayer, *J. Org. Chem.*, **19**, 17 (1954).