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

CYCLOPROPANES. IV. ATTEMPTED SYNTHESIS OF A NITROCYCLOPROPYL SULFONE (1)

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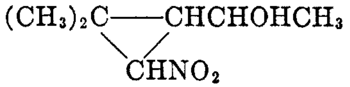
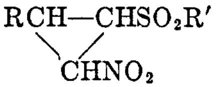
In a previous paper (2) a mechanism was proposed for the cleavage of 2-nitrocyclopropyl ketones by action of alkali, whereby 1,3-diketones or their derivatives result.

An essential feature of this mechanism was the requirement that the carbon atom adjacent to the one holding the nitro group be joined to an electron-attracting group, such as a ketone or ester group, for the nitrocyclopropylcarbinol (A) was found to be inert to the action of bases such as sodium methoxide.



A



B

$RCH_2COCH_2SO_2R'$

C

If the function of the carbonyl or ester group attached to the nitrocyclopropane ring is solely that of an electron-attracting group, then other electronegative groups should be able to perform the role of the carbonyl group and allow cleavage of the ring by action of alkalis. Kohler and Potter (3) have shown that sulfones are chemically similar to ketones when conjugated with an aliphatic double bond, and other workers also have demonstrated the electron-attracting properties of the sulfone group. Therefore, the synthesis of a nitrocyclopropyl sulfone, such as B, was undertaken; action of sodium methoxide upon such a substance should give the β-ketosulfone (C) if the analogy between the carbonyl and sulfone groups is valid. The primary purpose of the research was not achieved, for all the syntheses of the cyclopropyl sulfones failed at some critical step. However, the results obtained are interesting in themselves.

Two α,β unsaturated sulfones I and II, were prepared. Sulfone I, phenyl β-styryl sulfone, was prepared by the method described by Kohler and Potter (3) for preparation of p-tolyl β-styryl sulfone.

$RSO_2CH{=}CHR'$ $\quad$ $RSCH{=}CHR'$ $\quad$ $C_6H_5SO_2CH(C_6H_5)CH_2SO_2C_6H_5$ IV
I $R = R' = C_6H_5$ $\quad$ III $R = R' = C_6H_5$ $\quad$ $(C_6H_5SO_2)_2CHCH_2C_6H_5$ V
II $R = p\text{-}CH_3C_6H_4$; $R' = H$

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[1] Abstracted from a thesis by Horace R. Davis, Jr., presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph. D. degree, July, 1949. National Research Council Predoctoral Fellow, 1946–1949.

Thiophenol was added to phenylacetylene, producing a mixture of stereoisomers of phenyl β-styryl sulfide (III). It was not possible to obtain the sulfide in a crystalline form, nor to separate from the mixture any pure stereoisomers, as was possible in the case of *p*-tolyl β-styryl sulfide (3). Most of the product distilled at 155–160°/1 mm., and was apparently a mixture of the *cis-trans* isomers of III, but there was also a small amount of a material boiling at a somewhat higher temperature, 175–185°/1 mm. The lower-boiling material, when subjected to the action of hydrogen peroxide in acetic acid, gave a crystalline sulfone (I), but the yield was only 65% and the remainder, an oil, was probably a mixture of the stereoisomers of I. The higher-boiling material was likewise converted into a sulfone by action of hydrogen peroxide in acetic acid. This sulfone, a white crystalline solid, was inert toward neutral permanganate, and gave analytical values consistent with those required for either of the two disulfones, IV or V. These would result from the oxidation of the respective disulfides obtained by adding a second molecule of thiophenol to III in the two possible ways. The disulfone was only slightly soluble in aqueous sodium hydroxide (10%) and from this, it would appear that IV is the more probable structure, for Shriner, Struck, and Jorison (4) have shown that phenyl benzyl sulfone is only slightly soluble in alkali, whereas *bis*-(benzenesulfonyl)methane is readily soluble.

p-Tolyl vinyl sulfone II was prepared *via* the following sequence (R = *p*-tolyl):

$$\mathrm{RSH} + \mathrm{ClCH_2CH_2OH} \xrightarrow{\mathrm{NaOC_2H_5}} \mathrm{RSCH_2CH_2OH}$$

$$\xrightarrow{\mathrm{HCl}} \mathrm{RSCH_2CH_2Cl} \xrightarrow{\mathrm{H_2O_2}} \mathrm{RSO_2CH_2CH_2Cl} \xrightarrow{\mathrm{Et_3N}} \mathrm{II}$$

The yield of II from *p*-thiocresol was 67%; the yield of *p*-tolyl β-chloroethyl sulfide was 93%. This synthesis of *p*-tolyl β-chloroethyl sulfide involved a modification of the procedure of Steinkopf, Herold, and Stöhr (5); the procedure of Buckley, Charlish, and Rose (6) was used for conversion of the sulfide to the sulfone.

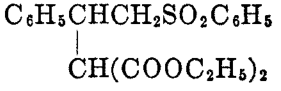
Although the addition of nitromethane to α,β-unsaturated sulfones has been reported (6) the products were not derived by simple addition of the reagents, but were formed from one molecule of nitromethane and three molecules of the sulfone; the condensing agent was 30% aqueous potassium hydroxide. Kohler (7) reported that nitromethane gave an excellent yield of a 1:1 addition product with benzalacetophenone when slightly more than one mole of sodium methoxide in methanol was used as the condensing agent. Under these conditions, the sulfone I failed to react with nitromethane or with the dipotassium salt of nitroacetic acid; a substantial amount of I was recovered unchanged. When only a catalytic amount of sodium methoxide was used, and the reaction was carried out at room temperature for 36 hours, there was obtained, in 40% yield, a product inert to neutral permanganate, which had the composition corresponding to that of VIa. Other catalysts were also tried in attempts to bring about addition of nitromethane to I, but without success. These included triethylamine, Triton-B,

$C_6H_5CH(R)CH_2SO_2C_6H_5$ VI $(p\text{-}CH_3C_6H_4SO_2CH_2CH_2)_2CHNO_2$ VIII
a. R = OCH_3; b. R = OC_2H_5; c. R = $N(CH_3)_2$
$p\text{-}CH_3C_6H_4SO_2CH_2CH_2CH_2NO_2$ VII $(p\text{-}CH_3C_6H_4SO_2CH_2CH_2)_3CNO_2$ IX

and the sodium derivative of nitromethane in dioxane or benzene. The failure of nitromethane to add to I was not a matter of steric hindrance, for other nucleophilic reagents—methanol, ethanol, dimethylamine, ethyl malonate—added easily.

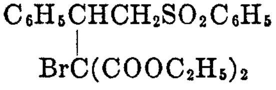
On the other hand, nitromethane added readily to the sulfone II. Using the conditions described by Kohler (7) for addition of the nitro compound to benzalacetophenone, the sulfone II gave, in 91% yield, the *bis* derivative VIII, and none of the mono derivative VII. The *bis* derivative VIII was inert to neutral permanganate, and soluble in 10% aqueous sodium hydroxide. When VIII was heated for 30 minutes in any polar solvent (ethanol, methanol, acetone), it was converted in 84% yield into the *tris* derivative IX, a substance insoluble in aqueous alkali.

Since nitromethane could not be added to the sulfones I or II to give a simple 1:1 adduct, attention was turned to the addition of malonic ester to I in the hope of obtaining a substance which could be converted by known methods into a sulfonylcarboethoxycyclopropane. Solid sodio malonic ester was shaken with a solution of I in benzene (3), and an excellent yield of addition product X was obtained after acidification. This material reacted slowly with bromine under ultraviolet light.



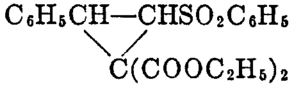
$$\begin{array}{l} C_6H_5CHCH_2SO_2C_6H_5 \\ \quad | \\ \quad CH(COOC_2H_5)_2 \end{array}$$

X



$$\begin{array}{l} C_6H_5CHCH_2SO_2C_6H_5 \\ \quad\quad | \\ \quad BrC(COOC_2H_5)_2 \end{array}$$

XI



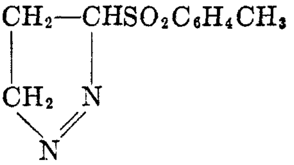
XII

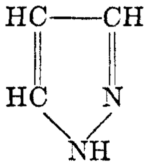
The same monobromo compound, XI was formed more rapidly, and in better yield, when the sodium derivative of X was brominated in benzene solution—a reaction which served to locate the bromine atom in XI.

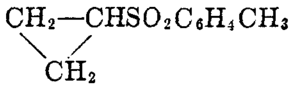
The bromo compound (XI) was inert to the action of fused potassium acetate in methanol, either at room temperature or at the boiling point of the solution. When XI was subjected to the action of 2,4,6-collidine at the boiling point (171–172°) for 25 minutes, bromine was removed, but the product was X and not the cyclopropane XII. Similarly, XI was reduced to X by action of triethylamine in ether at room temperature. In these reductions, ionic bromine was formed. Apparently, then, the sulfonyl group does not activate hydrogen atoms on the adjacent carbon atom sufficiently so that a cyclopropane ring may be closed by removal of the elements of hydrogen bromide, a reaction easy to bring about in the case of the analogous ketones.

Since the vinyl sulfone (II) was available, the synthesis of a sulfonyl cyclopropane (XV) *via* a pyrazoline was attempted (9). Diazomethane added readily to II in ether, to form the white, crystalline pyrazoline (XIII) in yields up to

64%. In analogy with the work of von Auwers (8), this pyrazoline is written as the Δ_1-isomer. When the pyrazoline (XIII) was heated with platinized asbestos,


XIII


XIV


XV

only 32% of the calculated amount of nitrogen was evolved, whether or not a small amount of potassium hydroxide was included in the mixture. At 185°, pyrazole (XIV) distilled from the mixture, and was obtained in yields up to 53%. The pyrazole was identified by its physical constants and by the melting point of the picrate. The reaction thus represents a cleavage of *p*-toluenesulfinic acid, rather than nitrogen, from the pyrazoline (XIII). *p*-Toluenesulfinic acid was not isolated from the reaction mixture. When the evolution of nitrogen and distillation of pyrazole from the pyrolysis mixture ceased, the pyrolysis was continued in a vacuum. A small amount of yellow oil distilled at 275°/1.5 mm. (bath temperature); this oil solidified on standing overnight. The material was insoluble in water and dilute acid, was extremely soluble in all organic solvents, and was inert to neutral permanganate. After purification by adsorption on alumina, it melted at 41–43° (*p*-thiocresol, m.p., 43°; disulfide, m.p., 46°), but the analytical values were not concordant nor consistent with those required by a cyclopropyl sulfone or any other compound that would be expected as a product of the reaction. The amount of this material was too small for further investigation.

EXPERIMENTAL PART[2]

Phenyl β-styryl sulfone (I). Thiophenol (15.4 g., 0.014 mole) was added dropwise, with stirring and cooling, to phenylacetylene (14.3 g., 0.014 mole); the mixture was stirred at room temperature for one hour and then distilled under reduced pressure from a modified Claisen flask. After a small forerun, the main fraction (22.9 g., 77%) was collected at 155–160°/1 mm.; this was followed by a third fraction boiling at 175–185°/1 mm. (1.2 g.). The main fraction was dissolved in acetic acid (50 cc.) and aqueous hydrogen peroxide (30%, 30 g., 0.27 mole) was added. A heavy oil separated; the flask was shaken intermittently for two hours, when the oil dissolved. The mixture was allowed to stand overnight. Water (150 cc.) was added and the mixture was cooled. The product, separating as an oil, soon crystallized. The solid (15.9 g., 65%, m.p., 71–74°) was removed and dried in a vacuum over potassium hydroxide. The analytical sample, crystallized from aqueous methanol, melted at 74–75°.

Anal. Calc'd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95.
Found: C, 68.88, H, 5.09.

1-Phenyl-1,2-dibenzenesulfonylethane (IV). The high-boiling fraction from the above distillation (1.2 g.) was dissolved in acetic acid (10 cc.), aqueous hydrogen peroxide (30%, 4 g.) was added, and the mixture was processed as described above for I, except that the mixture obtained by dilution with water (25 cc.) was extracted with benzene (10 cc.). The

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[2] Microanalyses by R. W. Amidon, J. S. Buckley, Jr., and William Cummings.

benzene extract was filtered and the filtrate was diluted with petroleum ether (15 cc., b.p., 60–68°). The granular solid was removed, washed with petroleum ether, and crystallized from benzene-petroleum ether. It weighed 0.24 g.; m.p. 141.5–142.5°.

Anal. Calc'd for $C_{20}H_{18}O_4S_2$: C, 62.15; H, 4.69.
Found: C, 62.19; H, 4.89.

The sulfone I (2.44 g., 0.01 mole) and nitromethane (0.73 g., 0.012 mole) were dissolved in dry methanol (20 cc.), and a solution of sodium (0.3 g., 0.013 gram-atom) in dry methanol (5 cc.) was added rapidly. The temperature was maintained at 40–50° for 30 minutes; then acetic acid (0.8 g.) was added and the mixture was cooled. The white crystalline solid was removed and washed with dilute methanol. It weighed 1.95 g. (80%) and melted at 72–73°, alone or when mixed with authentic I. The sulfone I (1.22 g.) and the dipotassium salt of nitroacetic acid (1.8 g.) were heated to 40–50° in ethanol (10 cc.) and water (6 cc.) for a few minutes; the solution was then allowed to stand overnight. Addition of acetic acid (1 cc.) produced evolution of carbon dioxide. Water (10 cc.) was added and the solid was removed. It was unchanged I, m.p. and mixed m.p. 73–74°.

1-Phenyl-1-methoxy-2-benzenesulfonylethane (VIa). Nitromethane (0.73 g., 0.012 mole) and the sulfone I (2.44 g., 0.01 mole) were dissolved in dry methanol (20 cc.), and a solution of sodium (0.1 g., 0.003 mole) in dry methanol (5 cc.) was added. The solution was allowed to stand at room temperature for 36 hours after which it was acidified with hydrochloric acid (1 cc.) and diluted with water (25 cc.). The aqueous layer was decanted and the residual oil was dissolved in benzene (10 cc.). The solution was diluted with petroleum ether (15 cc., b.p. 60–68°) and cooled. The solid was removed, washed with petroleum ether, and dried. It weighed 1.1 g. (40%) and melted at 68–74°. The analytical sample, crystallized from aqueous methanol (75%), melted at 84.5–86°. The substance was inert toward permanganate, and contained no nitrogen.

Anal. Calc'd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84.
Found: C, 65.48; H, 5.96.

1-Phenyl-1-dimethylamino-2-benzenesulfonylethane (VIc). The sulfone I (2.44 g., 0.01 mole) was dissolved in dry ethanol (10 cc.). Solid dimethylamine hydrochloride (0.89 g., 0.011 mole) was added, followed by a solution of sodium (0.23 g., 0.01 gram-atom) in dry ethanol (10 cc.). The mixture was allowed to stand at room temperature for 42 hours. Sodium chloride was removed, and the filtrate was cooled. The solid (0.9 g., 30%, m.p., 119–127°) was removed and dried. (Filtrate, see below.) It was almost completely soluble in dilute acid and only faintly unsaturated toward permanganate. A sample for analysis was prepared by dissolving the material in acid, filtering the solution, and neutralizing the filtrate. The solid was washed with water and crystallized successively from ethanol, benzene-petroleum ether, and methanol. It then melted at 133.5–134°.

Anal. Calc'd for $C_{16}H_{19}NO_2S$: C, 66.40; H, 6.62; N, 4.84.
Found: C, 66.29; H, 6.62; N, 4.76.

1-Phenyl-1-ethoxy-2-benzenesulfonyl ethane (VIb). The above filtrate remaining after removal of the crude dimethylamino compound was diluted with water (20 cc.) and cooled. The solid (1.81 g., 62%) was removed and dried in a vacuum. It melted at 88–90°; after crystallization from benzene-petroleum ether (1:2, b.p., 60–68°), and then from ethanol, the substance melted at 101–102°. It was not soluble in dilute acid, and was inert toward permanganate.

Anal. Calc'd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25.
Found: C, 66.42; H, 6.36.

p-Tolyl vinyl sulfone (II). Sodium (7.6 g., 0.33 mole) was dissolved in ethanol (120 cc.) and *p*-thiocresol (40 g., 0.32 mole) was added to this solution, followed by addition of ethylene chlorohydrin (25.9 g., 0.32 mole) in four portions. The temperature was maintained at 45–55° for 30 minutes, then hydrochloric acid (200 cc.) was added and the mixture was heated on the steam-bath for 1½ hours, during which time a heavy yellow oil separated. Ethanol (75 cc.) was removed by distillation; the distillate was diluted with water and extracted twice with ether. The residue left after distillation of the ethanol was diluted with water (100 cc.) and extracted with ether. The extracts were combined with the extracts of the distillate and dried (sodium sulfate). The ether was removed and the residue was distilled under reduced pressure. *p*-Tolyl β-chloroethyl sulfide (55 g., 93%) was collected at 147–151°/22 mm. (This substance is a strong vesicant and proper precautions must be observed in handling it.) The sulfide was dissolved in acetic acid (150 cc.) and the solution was refluxed while aqueous hydrogen peroxide (30%, 200 g., 1.76 moles) was added. Refluxing was continued for two hours, then the mixture was cooled (5°), diluted with water (400 cc.), and kept at 5° for 30 minutes. The solid was removed, washed with water, and dried in a vacuum over potassium hydroxide. The sulfone was dissolved in ether (100 cc.) and a solution of triethylamine (60 cc.) in ether (100 cc.) was added. The white solid was removed, washed twice with ether (50 cc.), and the ether washings were combined with the filtrate. The ether was removed; the residual brown oil solidified when it was shaken with water. The solid was removed, washed with water, and crystallized from ethanol (150 cc.). The product (25 g.) melted at 65–66°; reported 66° (6). Additional material (14 g.) melting at 64–65° was obtained by diluting the mother liquor with water. The over-all yield for the four steps was 67%.

Bis-(2-p-toluenesulfonylethyl)nitromethane (VIII). The sulfone (II) (1.82 g., 0.01 mole) and nitromethane (0.73 g., 0.012 mole) were dissolved in dry methanol (20 cc.). The solution was warmed to 40° while a solution of sodium (0.3 g., 0.013 mole) in dry methanol (10 cc.) was added. The solution was maintained at 40–50° for 10 minutes, and was then acidified with acetic acid (1 cc.), cooled, diluted with water (3 cc.), and set aside at 0° for 2 hours. The solid was removed, washed with aqueous methanol (50%), and dried. It weighed 1.95 g. (91%) and melted at 121–131°. The analytical sample, crystallized twice from benzene-petroleum ether (1:2), melted at 134–137°. The substance was inert toward permanganate, and was soluble in aqueous sodium hydroxide (10%).

Anal. Calc'd for $C_{19}H_{23}NO_6S_2$: C, 53.63; H, 5.45; N, 3.29.
Found: C, 53.87; H, 5.55; N, 3.27.

Tris-(2-p-toluenesulfonylethyl)nitromethane (IX). The *bis*-compound (VIII) (0.45 g.) was warmed for 30 minutes in ethanol (40 cc.). The solution was cooled and the solid (0.36 g., m.p., 195–197°) was removed and crystallized from ethanol (100 cc.). It melted at 197–198°, and was insoluble in aqueous sodium hydroxide (10%).

Anal. Calc'd for $C_{28}H_{33}NO_8S_3$: C, 55.33; H, 5.47; N, 2.31.
Found: C, 55.42; H, 5.70; N, 2.36.

Ethyl 1-carboethoxy-2-phenyl-3-benzenesulfonylpropionate (X). A solution of the sulfone (I) (4.88 g., 0.02 mole) was added to a suspension of ethyl sodiomalonate (from ethyl malonate, 3.8 g., 0.024 mole and sodium, 0.5 g., 0.022 gram-atom) in benzene (20 cc.). The mixture was shaken for 24 hours, filtered, and the filtrate was washed with dilute hydrochloric acid and water. Removal of the benzene left an oil which solidified when cooled; weight, 7.85 g. (97%); m.p. 101–104°. After crystallization three times from ethanol, the substance melted at 110–110.5°.

Anal. Calc'd for $C_{21}H_{24}O_6S$: C, 62.36; H, 5.98.
Found: C, 62.60; H, 6.14.

Ethyl 1-carboethoxy-1-bromo-2-phenyl-3-benzenesulfonylpropionate (XI). *A*. Bromine (1.3 g., 0.008 mole) in carbon tetrachloride (20 cc.) was added to a solution of the malonic ester (X) (3.03 g., 0.0075 mole) in carbon tetrachloride (70 cc.). There was no evolution of hydrogen bromide when the solution was warmed, or when a drop of acetone was added. Evolution of hydrogen bromide began only after the solution was exposed to ultraviolet light; irradiation was continued for 6 hours. The solution was washed with aqueous sodium bisulfite and then with water, the solvent was removed, and the residue was crystallized from benzene-petroleum ether (1:2). The product (2.93 g., 81%) melted at 93–95°; after recrystallization from methanol, it melted at 96–97°.

Anal. Calc'd for $C_{21}H_{23}BrO_6S$: C, 52.18; H, 4.80.
Found: C, 52.14; H, 4.99.

B. A clear, filtered, benzene solution of the enolate of X was prepared as described above from sodium (0.76 g., 0.033 mole), ethyl malonate (5.90 g., 0.037 mole), and the sulfone (I) (7.32 g., 0.03 mole). To this was added a solution of bromine (5.27 g., 0.033 mole) in carbon tetrachloride (40 cc.). The color of the bromine rapidly faded. The solution was allowed to stand overnight and was then processed as described under A above. The product weighed 11.73 g. (81%) and melted at 93–96°, alone or when mixed with a sample prepared by method A.

The bromomalonate XI (1 g.) was dissolved in 2,4,6-collidine (10 cc.) and the solution was refluxed for 25 minutes. Within 5 minutes the solution became black and a granular solid was deposited. The solution was decanted from the solid material into benzene; the solid was washed with benzene and dissolved in water. This aqueous solution gave a strongly positive test for bromide ion. The combined benzene filtrates and washings were washed successively with dilute hydrochloric acid, aqueous sodium carbonate, and water. The benzene was removed and the residue was crystallized from benzene-petroleum ether (1:4). The white crystalline solid (0.5 g., 60%) melted at 98–103°. This material was deposited from benzene onto a column (18 × 110 mm.) of alumina (Alcoa, 80–200 mesh). A faint yellow band appeared in the middle of the column. The material was eluted with benzene-ether (4:1) until this band was within 15 mm. of the bottom of the column. The solvent was removed from the eluate and the residue was crystallized from benzene-petroleum ether (1:4). The product weighed 0.25 g. and melted at 109.5–110° alone or when mixed with authentic X. Essentially the same results were obtained in a duplication of this experiment, substituting triethylamine for the collidine. The bromomalonic ester XI (200 mg.) in methanol (5 cc.) was boiled with fused potassium acetate (0.5 g.) and then allowed to stand overnight. No potassium bromide was formed, and from the mixture only unchanged XI could be isolated.

3-p-Toluenesulfonylpyrazoline (XIII). Ethereal diazomethane [from N-nitrosomethylurea, 5 g., aqueous potassium hydroxide (40 cc., 40%), and ether, 50 cc.] was added to *p*-tolyl vinyl sulfone (II) (3.64 g., 0.02 mole) in ether (50 cc.). The solution was allowed to stand for 24 hours at room temperature; the ether was then removed under reduced pressure. The residue was crystallized from ether-petroleum ether (2:1). The product weighed 2.85 g. (64%) and melted at 86–93°. The analytical sample, crystallized twice from ether-petroleum ether, melted at 96–98°.

Anal. Calc'd for $C_{10}H_{12}N_2O_2S$: C, 53.55; H, 5.40; N, 12.49.
Found: C, 53.09; H, 5.60; N, 12.03.

The crude pyrazoline XIII (2 g., 0.01 mole, m.p., 86–93°) and platinized asbestos (0.1 g.) were placed in a 10-ml. flask connected to a receiver and immersed in a metal-bath. At 130°, nitrogen was evolved; the bath temperature was gradually raised to 275°. At 185° (thermometer in the reaction mixture) a clear white liquid distilled; the distillate solidified when cooled. This solid, pyrazole (XIV), weighed 0.32 g. (53%), melted at 68–69°, and formed a picrate melting at 161–162° (10). The volume of nitrogen evolved was 64 cc. (32%). When evolution of nitrogen and distillation of pyrazole ceased, the flask was heated at 275° (bath temperature) and under reduced pressure (1.5 mm.). The yellow, oily distillate crystallized on standing overnight at room temperature. The solid was dissolved in ether, the solution was washed with dilute hydrochloric acid, and dried (sodium sulfate). The solvent was removed and the yellow oily residue was crystallized from petroleum ether (5 cc., b.p., 60–68°). The product weighed 75 mg. and melted at 39–41°. It was inert toward permanganate. The substance was dissolved in benzene-petroleum ether (10 cc., 1:1) and deposited on a column (8 × 60 mm.) of alumina (Alcoa, 80–200 mesh). The column was eluted with benzene-ether (5:1) and the solvent was removed from the eluate. The product, a yellow waxy solid, weighed 52 mg., and melted at 41–43°. The analytical values for this material were not concordant and did not agree with those required by the cyclopropane structure XV.

Anal. Calc'd for $C_{10}H_{12}O_2S$ (XV): C, 61.19; H, 6.17.
Calc'd for $C_{14}H_{14}S_2$(ditolyl disulfide) C, 68.3; H, 5.7.
Found: C, 68.69, 69.79; H, 6.44, 6.42.

SUMMARY

1. Two α,β-unsaturated sulfones, phenyl β-styryl sulfone (I) and *p*-tolyl vinyl sulfone (II) have been prepared.

2. Although nitromethane could not be added to phenyl-β-styryl sulfone (I) under a variety of conditions, this sulfone readily added methanol, ethanol, dimethylamine, and malonic ester.

3. Ethyl 1-carboethoxy-2-phenyl-3-benzenesulfonyl propionate (X), formed from the sulfone I and sodio ethyl malonate, was converted into the α-bromomalonic ester. No cyclopropane could be prepared from the bromo compound; potassium acetate was without action, and collidine or triethylamine merely removed the bromine atom reductively to give X.

4. Nitromethane reacted readily with *p*-tolyl vinyl sulfone (II), but the reaction involved two or three molecules of the sulfone. No 1:1 addition product could be obtained.

5. Action of diazomethane upon *p*-tolyl vinyl sulfone (II) gave 3-p-toluenesulfonylpyrazoline smoothly and in good yield, but pyrolysis of the pyrazoline gave pyrazole as the only pure product. No cyclopropyl sulfone could be obtained.

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