Anal. Calcd. for $C_4H_3Cl_3$: C, 30.47; H, 1.90; Cl, 67.61. Found: C, 29.50, 29.43; H, 2.33, 2.19; Cl, 68.42, 68.50.

Tetrachloro-1,2,2,3-butene-3.—B. p. 41 to 42° at 7 mm.; n^{20}_D 1.5133; d^{20}_4 1.4602; MR calcd. 39.67; MR found, 39.91.

Anal. Calcd. for $C_4H_4Cl_4$: C, 24.74; H, 2.06; Cl, 73.19. Found: C, 25.49, 25.16; H, 2.23, 2.24; Cl, 72.66, 72.16.

Oxidation.—A sample (23 g.) of the tetrachlorobutene was oxidized with excess aqueous potassium permanganate. After filtration and treatment with sulfur dioxide the solution was extracted continuously with ether. Evaporation of the ether gave a liquid residue which distilled at 120 to 125° at 22 mm. It crystallized on cooling and after being washed with petroleum ether melted at 48 to 50°. Neutral equivalent found, 176.4; calcd. for trichloropropionic acid, 177.5.

Summary

Dichloro-2,3-butadiene-1,3 and trichloro-1,2,3-butadiene-1,3 have been prepared and their properties are described. The dichloro compound polymerizes more rapidly than chloroprene, the trichloro compound more slowly than chloroprene. The polymers are not rubber-like in either case. The chlorobutadienes now known may be arranged in the following order so far as their speed of spontaneous polymerization is concerned: $\beta,\gamma \gg \beta \gg \alpha,\beta,\gamma > \alpha \gg \alpha,\beta,\gamma,\delta$; and only the second member of the series (chloroprene) yields a definitely rubber-like polymer.

WILMINGTON, DELAWARE

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Acetylene Polymers and their Derivatives. XII. The Addition of Thio-*p*-cresol to Divinylacetylene

BY WALLACE H. CAROTHERS

The reaction of acetylene with itself to form an open-chain trimer was described in the first paper of this series.[1] This compound, which has the molecular formula C_6H_6, contains no true acetylenic hydrogen; on hydrogenation it yields *n*-hexane; and it differs from the already known dimethyldiacetylene (I). It was therefore assigned the structure divinylacetylene (V).[2] The formulas II, III and IV, which are equally con-

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(1) Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, **53**, 4197 (1931).

(2) This compound has perhaps been obtained in small amounts, though not completely characterized, by Farmer, Laroia, Switz and Thorpe, *J. Chem. Soc.*, 2948 (1927). See also Mignonac and de Saint-Aunay, *Compt. rend.*, **188**, 959 (1929).

Lespieau and Guillemonat in a recent publication [*Compt. rend.*, **195**, 245 (1932)] have described divinylacetylene under the title "A New Isomer of Benzene." Apparently they have entirely overlooked the paper of Nieuwland, Calcott, Downing and Carter referred to above. They also state that they have obtained about 12 cc. of (impure) vinylacetylene, of which hitherto only 1.4 g. has been prepared (referring to Willstätter and Wirth). It may, therefore, be of interest to state that in the laboratories and works of the du Pont Company many hundreds of kilograms of vinylacetylene and divinylacetylene have been prepared by the process of Nieuwland, Calcott, Downing and Carter.

sistent with the above indicated properties, may perhaps be rejected as inherently unlikely; but in connection with a detailed study of the acetylene trimer it seemed desirable to obtain direct and decisive experimental proof of the structure represented by formula V.

$$CH_3{-}C{\equiv}C{-}C{\equiv}C{-}CH_3 \quad \text{(I)}$$

$$CH_2{=}C{=}C{=}C{=}CH{-}CH_3 \quad \text{(II)} \qquad CH_2{=}C{=}C{=}CH{-}CH{=}CH_2 \quad \text{(III)}$$

$$CH_2{=}C{=}CH{-}CH{=}C{=}CH_2 \quad \text{(IV)} \qquad CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 \quad \text{(V)}$$

Efforts in this direction at first met with difficulties: the compound has a great tendency to combine with itself in the presence of polar reagents, and it does not readily yield well-defined derivatives capable of easy identification, but a solution of the problem was found in the reaction with thio-*p*-cresol.

It has been shown by Posner[3] that vinyl compounds readily add thiophenols. In the case of styrene the reaction proceeds in accordance with the equation

$$C_6H_5CH{=}CH_2 + RSH \longrightarrow C_6H_5CH_2CH_2{-}S{-}R$$

Since the direction of addition alleged by Posner is exclusively the reverse of that required by well-known empirical generalizations and by currently popular electronic theories, the reaction was lately re-examined by Ashworth and Burkhardt with the result that Posner's conclusion was completely verified.[4] Thus for the purpose in view the thiophenols as reagents have the advantage that their mode of addition is thoroughly established. Moreover, neither heat nor catalysts are required to induce their reaction with reactive carbon double bonds.

Acetylene trimer (one mole) readily dissolved thio-*p*-cresol (two moles). When the fluid mixture was allowed to stand at the laboratory temperature during ten days it gradually set to a magma of thin, transparent, leaf-like crystals, and the odor of the thiocresol almost entirely disappeared. The reaction was powerfully accelerated by light, and when the mixture (40 g. of thiocresol and 12.5 g. of acetylene trimer) in a reagent bottle of soda glass was directly illuminated by a mercury arc, reaction was complete in about five hours. The yield of crystalline product was about 80% of the theoretical, and some unidentified oily material was formed.

After crystallization from alcohol and from acetic acid the reaction product melted at 74.5–75.5°. Its composition agreed with that required for di-(*p*-tolylthio)-1,6-hexine-3 (VI). The verification of this structure through reactions described below decisively establishes the structure of the acetylene trimer as divinylacetylene (V). In its reaction with thio-*p*-cresol the double bonds of divinylacetylene function independently of the

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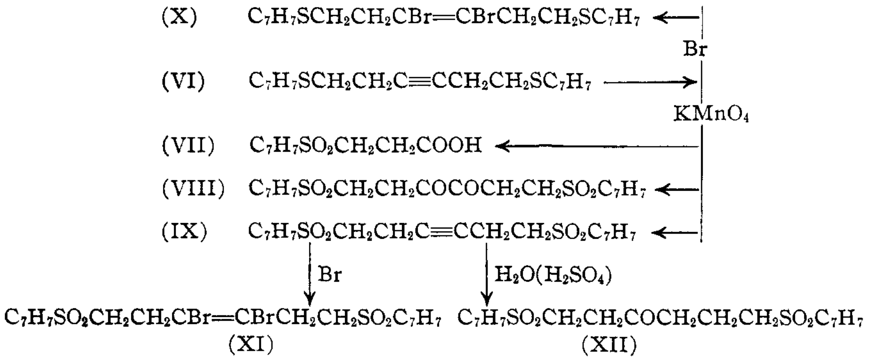
[3] Posner, *Ber.*, **38**, 646 (1905).

[4] Ashworth and Burkhardt, *J. Chem. Soc.*, 1791 (1928).

triple bond. As will be shown in future papers, however, this behavior is not typical: other reactions indicate conjugation between the ethylenic and acetylenic linkages.

Di-(*p*-tolylthio)-1,6-hexine-3 readily adds two atoms of bromine to form the dibromide X. The action of potassium permanganate leads to a series of oxidation products. When the di-(*p*-tolylthio)-1,6-hexine-3 is dissolved in chloroform and shaken with cold dilute sulfuric acid to which permanganate is added in portions, the acetylenic disulfone, IX, is obtained. When carbon tetrachloride is used as the solvent in this process oxidation proceeds further and one obtains the diketone, VIII. In acetone solution, alkaline permanganate causes rupture of the carbon chain with the formation of the already known β-*p*-tolylsulfonepropionic acid (VII). The acetylenic disulfone, IX, readily adds bromine to form the dibromide XI, and sulfuric acid converts it into the ketone XII.



(X) $C_7H_7SCH_2CH_2CBr{=}CBrCH_2CH_2SC_7H_7$

Br

(VI) $C_7H_7SCH_2CH_2C{\equiv}CCH_2CH_2SC_7H_7$

$KMnO_4$

(VII) $C_7H_7SO_2CH_2CH_2COOH$

(VIII) $C_7H_7SO_2CH_2CH_2COCOCH_2CH_2SO_2C_7H_7$

(IX) $C_7H_7SO_2CH_2CH_2C{\equiv}CCH_2CH_2SO_2C_7H_7$

Br $H_2O(H_2SO_4)$

$C_7H_7SO_2CH_2CH_2CBr{=}CBrCH_2CH_2SO_2C_7H_7$ (XI)

$C_7H_7SO_2CH_2CH_2COCH_2CH_2CH_2SO_2C_7H_7$ (XII)

Di-(*p*-tolylthio)-1,6-hexine-3 (VI).—M. p. 74.5–75.5°.—*Anal.* Calcd. for $C_{20}H_{22}S_2$: C, 73.60; H, 6.79; S, 19.65; mol. wt., 326.3. Found: C, 73.50; H, 7.18; S, 20.1; mol. wt. (in freezing benzene), 291, 299, 302, 308.

Oxidation of Di-(*p*-tolylthio)-1,6-hexine-3 (VI) to *p*-Tolylsulfonepropionic Acid (VII).—Ten grams of di-(*p*-tolylthio)-1,6-hexine-3 suspended in 100 cc. of pure acetone in a bottle was constantly stirred and maintained below 32° while 41 g. of powdered potassium permanganate was added during two and a half hours. The permanganate was rapidly reduced. The manganese dioxide was removed by filtration and washed with acetone and water; the filtrates were evaporated, dissolved in water, treated with decolorizing carbon, filtered and acidified. The semi-crystalline precipitate was dissolved in a mixture of ether and chloroform, and the filtered solution was extracted with aqueous sodium bicarbonate solution. The aqueous solution was acidified. The precipitated solid (4 g.) melted at 102–113°. After crystallization from alcohol and then from water it was obtained in the form of needles melting at 110–113°.[5]

Anal. Calcd. for $C_{10}H_{12}O_4S$: neutral equivalent, 228. Found: 234.

Partial Oxidation of Di-(*p*-tolylthio)-1,6-hexine-3 (VI). Formation of Di-(*p*-tolylsulfone)-1,6-hexandione-3,4 (VIII).—To 3.2 g. of di-(*p*-tolylthio)-1,6-hexine-3 in 30 cc. of carbon tetrachloride, 100 cc. of 3 *N* sulfuric acid was added and then ice and

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(5) Kohler and Reimer [*Am. Chem. J.*, **31**, 175 (1904)] describe β-*p*-tolylsulfonepropionic acid as needles melting at 110–113°. It is partially decomposed by repeated crystallization from boiling water

powdered potassium permanganate in small portions with constant shaking. About 6.5 g. of permanganate was consumed. The mixture was decolorized with aqueous sodium bisulfite. A white solid, which was suspended in the mixture, was filtered off, dissolved in chloroform, and precipitated with petroleum ether. After crystallization from ethylene chloride, glacial acetic acid, and butyl acetate, it was obtained in the form of fine, yellowish needles which softened at 197–200° and melted at 200–201°.

Anal. Calcd. for $C_{20}H_{22}O_6S_2$: C, 56.85; H, 5.22. Found: C, 56.37, 56.74; H, 5.23, 5.37.

This material was insoluble in ether, petroleum ether, ligroin, benzene, and carbon tetrachloride; readily soluble in warm chloroform and ethylene chloride. It reacted with phenylhydrazine to form a crystalline derivative melting above 215°.

Partial Oxidation of Di-(*p*-tolylthio)-1,6-hexine-3 (VI). Formation of Di-(*p*-tolylsulfone)-1,6-hexine-3 (IX).—Three grams of di-(*p*-tolylthio)-1,6-hexine-3 in 40 cc. of chloroform together with 100 cc. of 3 *N* sulfuric acid was vigorously shaken in a stoppered bottle while ice and powdered potassium permanganate were added in small portions until a purple color persisted in the mixture. A total of 6.7 g. of potassium permanganate was applied. The mixture was treated with sulfur dioxide to dissolve the precipitated manganese dioxide. The aqueous layer was discarded and the chloroform layer was washed with dilute alkali and water, dried, filtered and evaporated. Crystallization of the solid residue from dilute acetic acid gave 2.4 g. of white crystals melting at 150–158°; recrystallized from butyl acetate; needles, m. p. 157–158°; insoluble in boiling carbon tetrachloride.

Anal. Calcd. for $C_{20}H_{22}O_4S_2$: C, 61.50; H, 5.68; S, 16.43. Found: C, 61.60, 61.48; H, 5.85, 6.17; S, 16.54, 16.68.

Action of Bromine on Di-(*p*-tolylsulfone)-1,6-hexine-3 (IX). Formation of Di-(*p*-tolylsulfone)-1,6-dibromo-3,4-hexene-3 (XI).—In 10 cc. of 0.13 *M* bromine in chloroform, 0.38 g. of di-(*p*-tolylsulfone)-1,6-hexine-3 was dissolved. The mixture was illuminated by a 40-watt Mazda lamp for fifteen minutes. About 40 cc. of petroleum ether was added and the crystalline precipitate was recrystallized from butyl acetate; m. p. 172.5–173.5°.

Anal. Calcd. for $C_{20}H_{22}O_4S_2Br_2$: Br, 29.06. Found: 28.87, 28.92.

Action of Sulfuric Acid on Di-(*p*-tolylsulfone)-1,6-hexine-3 (IX). Formation of Di-(*p*-tolylsulfone)-1,6-hexanone-3 (XII).—One gram of di-(*p*-tolylsulfone)-1,6-hexine-3 was dissolved in 10 cc. of cold concd. sulfuric acid. The colorless solution was allowed to stand for fifteen minutes and was then poured into 50 cc. of water. The resulting white precipitate was crystallized twice from alcohol; m. p. 134–135°.

Anal. Calcd. for $C_{20}H_{22}O_5S_2$: S, 15.77. Found: S, 16.41.

Action of Bromine on Di-(*p*-tolylthio)-1,6-hexine-3 (VI). Formation of Di-(*p*-tolylthio)-1,6-dibromo-3,4-hexene-3 (X).—Di-(*p*-tolylthio)-1,6-hexine-3 in dilute chloroform solution was allowed to stand for a few minutes with an excess of standard bromine, and the excess bromine was then titrated with standard thiosulfate. Approximately 1.05 moles of bromine was consumed by one mole of di-(*p*-tolylthio)-1,6-hexine-3.

To 1.6 g. of di-(*p*-tolylthio)-1,6-hexine-3 in 15 cc. of chloroform, 20 cc. of *N* bromine in chloroform was added. The solution was allowed to stand for five minutes. It was then shaken with 2 *N* thiosulfate solution, washed with water, dried with sodium sulfate, filtered and evaporated. From the residual oil, colorless crystals gradually separated. These were isolated and recrystallized from a mixture of alcohol and ether as transparent columns, m. p. 46–47.50°.

Anal. Calcd. for $C_{20}H_{22}S_2Br_2$: Br, 32.85. Found: Br, 32.98, 33.07.

Summary

The divinylacetylene described in a previous paper reacts with thio-*p*-cresol to form a crystalline derivative whose structure as di-(*p*-tolylthio)-1,6-hexine-3 is demonstrated by its oxidation to the known β-*p*-tolylsulfonepropionic acid. The following transformation products of the new derivative are described: di-(*p*-tolylthio)-1,6-dibromo-3,4-hexene-3, di-(*p*-tolylsulfone)-1,6-hexandione-3,4, di-(*p*-tolylsulfone)-1,6-hexine-3, di-(*p*-tolylsulfone)-1,6-dibromo-3,4-hexene-3, di-(*p*-tolyl-sulfone)-1,6-hexanone-3.

WILMINGTON, DELAWARE

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The Catalysis of Air Oxidations by Iron Salts, Phosphates and Pyrophosphates[1]

BY EMERY J. THERIAULT, C. T. BUTTERFIELD AND P. D. MCNAMEE

It is clear that the case for the rôle of iron, copper, manganese and other suggested carriers of oxygen in biological oxidations could be considerably strengthened if catalysts containing these elements were to be prepared and made to perform *in vitro* the same type of oxidations which are apparently accomplished by living cells. Such a model of biocatalytic oxidation should satisfy the essential conditions that the *P*H value, the salt concentration and the temperature of the liquid medium fall within the normal physiological range. Thus the oxidations accomplished at the *P*H values reached by sodium hydroxide, calcium hydroxide and even by sodium carbonate, while of considerable interest in themselves, are of a different order from those under consideration. Likewise the oxidations accomplished by the more energetic oxidizing agents such as potassium permanganate in alkaline solution or by Fehling's solution, are of remote interest to the present discussion. Within these limitations, the iron phosphate model of biocatalytic oxidation proposed by Spoehr[2] still remains as an outstanding example.

In several respects the claims made by Spoehr for his catalytic agent are truly remarkable. The iron pyrophosphate mixture itself is readily prepared from inorganic materials and its action on a variety of organic materials is supposedly pronounced at *P*H values ranging from 6.8 to 8.8 even at body temperatures. The conclusions reached by Spoehr were apparently confirmed by Degering and Upson[3] and by Degering,[4] although

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[1] Presented at the New Orleans Meeting of the American Chemical Society, April, 1932.

[2] Spoehr, THIS JOURNAL, **46**, 1494–1502 (1924).

[3] Degering and Upson, *J. Biol. Chem.*, **94**, 423 (1931).

[4] Degering, *ibid.*, **95**, 409 (1932).