The quantitative data obtained are given in Table I.

TABLE I

| | Type of wood | Western Red Cedar | Douglas Fir | Western Hemlock |
|---|---|---|---|---|
| Lignin in starting materials | Klason lignin %[a] | 38 | 29.3 | 30.6 |
| | Klason lignin g. | 179 | 155 | 210 |
| Lignin in residual wood meal | Klason lignin % | 34.2 | 25.8 | 28.2 |
| | Klason lignin g. | 120 | 93 | 140 |
| Extracted oil (phenolic constituent) | from Aq. soln. g. | 4.63 | 4.9 | 8.02 |
| | from EtOH lignin g. | 0.82 | 2.9 | 1.44 |
| | total, g. | 5.45 | 7.8 | 9.46 |
| Distilled oils (phenolic constituent) | from Aq. soln. g. | 3.25 | 3.7 | 5.48 |
| | from EtOH lignin g. | 0.53 | 0.2 | ... |
| | total, g. | 3.78 | 3.9 | 5.48 |

[a] Yields are on an oven dry basis.

The alkaline phenolic extract was methylated with an ether solution of diazomethane[3] using 50% excess. After removal of the ether a clear yellow oil was obtained which, after crystallization had been induced by scratching, solidified completely. After repeated recrystallizations from petroleum ether a white crystalline product was obtained which melted at 81–82°. This was shown to be α-ethoxy-propioveratrone, by conversion of 0.5 g. of it into its 2,4-dinitrophenyl-hydrazone,[4] an orange-yellow precipitate which after crystallization from chloroform and then from petroleum ether melted at 140–141°.

Using the procedure developed by Hibbert and co-workers[5] for the separation of the syringyl and guaiacyl radicals, the former was shown to be absent.

## Summary

The ethanolyses of the western soft woods, red cedar, Douglas fir, and western hemlock, gave a phenolic fraction containing the veratryl group, as demonstrated by the isolation of α-ethoxy-propioveratrone, and none of the syringyl group.

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(3) E. A. Werner, *J. Chem. Soc.*, **115**, 1093 (1919).

(4) J. J. Pyle, L. Brickman and H. Hibbert, THIS JOURNAL, **61**, 2198 (1939).

(5) M. J. Hunter and H. Hibbert, *ibid.*, **61**, 2190 (1939).

VANCOUVER, B. C. RECEIVED AUGUST 12, 1940

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF FURMAN UNIVERSITY]

# Side-Chain Bromination. II. Negative Catalytic Effects

BY JOHN R. SAMPEY AND ELIJAH M. HICKS

In an earlier communication[1] attention was called to the negative catalytic effect of small amounts of sulfur present as impurities in C. P. and Reagent grades of carbon disulfide on the side-chain bromination of toluene derivatives. In the present paper data are presented on the rates of bromination with different amounts of sulfur present in both carbon disulfide and carbon tetrachloride as solvents. A few measurements are made also with changing sulfur concentration and different intensities of the artificial illumination.

**Negative Catalytic Effects of Sulfur.**—The relative rates of bromination in Table I were obtained as described in the previous paper. The carbon disulfide was carefully purified and was purer than that used previously, which accounts for the higher rates of bromination. The slower rate in carbon tetrachloride, on the other hand, is due to the fact that the bromination reported below was made with the reacting flask at a greater distance from the source of irradiation than that carried out in the earlier work. The brominations in Table I below were made with the Erlenmeyer flask exactly three inches (7.6 cm.) from the two 300-watt clear-glass Mazda lamps. Twenty cc. samples were measured in each run; the small amounts of sulfur reported in Column 2 were obtained by dilution of stronger solutions.

The striking negative catalytic effect of sulfur on the side-chain bromination is apparent from the fact that 0.01 mg. slows down the reaction, while 100 mg. practically stops the bromination of one-hundredth molar quantities of toluene and *p*-bromotoluene in both carbon disulfide and carbon tetrachloride. The sulfur effects on toluene and *p*-bromotoluene are roughly parallel in carbon disulfide; sulfur has a greater retarding action on side-chain bromination in carbon tetrachloride than in carbon disulfide.

**Photochemical Effects.**—The care which had to be exercised in placing the reaction flask exactly the same distance from the source of radiation in all our side-chain brominations sug-

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(1) Sampey, Fawcett and Morehead, THIS JOURNAL, **62**. 1839–1840 (1940).

TABLE I

NEGATIVE CATALYTIC EFFECTS OF SULFUR ON SIDE-CHAIN BROMINATION

| Time, min. | Sulfur added, mg. | Bromination, % |
|---|---|---|
| | Toluene in $CS_2$ at 57° | |
| 5 | None | 89.8 |
| 5 | None | 91.2 |
| 20 | 1000 | None |
| 20 | 100 | 1.9 |
| 20 | 100 | 2.8 |
| 20 | 10 | 29.3 |
| 20 | 10 | 28.9 |
| 5 | 1 | 40.4 |
| 5 | 0.1 | 82.9 |
| 5 | .01 | 86.1 |
| 5 | .01 | 88.5 |
| | *p*-Bromotoluene in $CS_2$ at 57° | |
| 10 | None | 91.7 |
| 10 | None | 92.2 |
| 10 | 10 | 8.5 |
| 10 | 10 | 8.3 |
| 10 | 1 | 39.9 |
| 10 | 0.2 | 74.3 |
| 10 | .1 | 83.7 |
| 10 | .1 | 82.4 |
| 10 | .01 | 91.5 |
| | Toluene in $CCl_4$ at 57° | |
| 1 | None | 87.2 |
| 5 | 100 | 4.8 |
| 5 | 10 | 14.9 |
| 5 | 1 | 50.5 |
| 1 | 0.1 | 52.4 |
| 2.5 | .1 | 80.6 |

gested experiments to determine the magnitude of this variable on the rates. In Table II the photochemical effects are shown for both carbon disulfide, sulfur free, and for two concentrations of the negative catalyst in this solvent on the bromination of *p*-bromotoluene.

TABLE II

PERCENTAGE OF BROMINATION OF *p*-BROMOTOLUENE IN FIVE-MINUTE EXPOSURES TO 600 WATTS AT DIFFERENT DISTANCES, WITH AND WITHOUT SULFUR

| Sulfur, mg. | Distance 1 inch | Distance 3 inches | Distance 6 inches |
|---|---|---|---|
| None | 77.6 | 62.0 | 53.1 |
| 10 | 4.7 | 3.4 | .. |
| 0.1 | 66.1 | 56.2 | 40.8 |

With 300 watts at 7.6 cm. the bromination was 52.3% without sulfur, and 41.2% with 0.1 mg. Attention is called to the observation, previously made, that with both Mazda lamps turned off only 1.5% bromination of toluene occurred in eight minutes.

Recognition is gladly extended to Dr. E. Emmet Reid for his interest in this investigation.

## Summary

1. Measurements have been made on the negative catalytic effect of sulfur on the rates of side-chain bromination of one-hundredth molar quantities of toluene and *p*-bromotoluene in carbon disulfide and carbon tetrachloride.

2. Concentrations of 0.01 mg. of sulfur caused a definite decrease in the rates, while approximately 100 mg. of sulfur blocked side-chain bromination.

3. Marked differences in the rates of bromination accompanied changes in the intensity of the irradiation.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

# Some Reactions of Unsaturated Nitro Compounds Derived from Terephthalaldehyde

BY DAVID E. WORRALL

Some years ago Thiele[1] prepared a small quantity of dinitrodivinylbenzene and from it, made one derivative. With this exception, no work has been done previously on unsaturated nitro compounds containing more than one functional group. In the present investigation several unsaturated systems containing two nitrovinyl groups were examined. The results thus far obtained are in accord with the conventional reactions of unsaturated nitro compounds.

## Experimental

**1,4-Bis-(β-bromo-β-nitrovinyl)-benzene (II).**—Approximately 18 g. of crude dinitrodivinylbenzene (I) resulted from the action of 0.1 gram mole of terephthalaldehyde on nitromethane in the presence of alcoholic sodium hydroxide.[2] Nitromethane proved to be an admirable solvent for I which was relatively insoluble in most of the common organic solvents. The tetrabromide was obtained by bromination of 4 g. of I in chloroform, followed by evaporation to dryness and extraction with cold alcohol. A small portion crystallized from nitromethane–alcohol mixture as

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[1] Thiele, *Ber.*, **32**, 1295 (1899).

[2] "Organic Syntheses," Vol. 9, p. 66.