[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF FURMAN UNIVERSITY]

# Side-Chain Bromination[1]

BY JOHN R. SAMPEY, FRANK S. FAWCETT AND B. A. MOREHEAD

Although the photochemistry of side-chain bromination in sunlight and artificial radiation has received much attention,[2] no systematic study has been made of the differences in rates of photochemical bromination of more than just a few toluene derivatives. In the present paper we present the rates of side-chain bromination of twenty-six substituted toluenes. The extent of side-chain halogenation has been determined by a sodium acetate method of analysis. Some striking effects of solvents on the rates of bromination also have been observed.

**Bromination in Direct Sunlight.**—In a preliminary series of experiments an investigation was made of the ease of bromination in direct sunlight at room temperature. The compounds to be brominated were dissolved in chloroform, and slightly more than one mole of bromine dissolved in the same solvent was added slowly with stirring in bright sunlight. The following compounds decolorized the bromine in approximately the order listed, diphenylmethane reacting the fastest. All the products had lachrymatory properties. Diphenylmethane, mesitylene, hexamethylbenzene, *p*-, *m*-, *o*-xylene, toluene, *p*-, *m*-, *o*-chlorotoluene, *p*-, *m*-, *o*-bromotoluene, *p*-, *m*-, *o*-iodotoluene. The compounds which reacted with little or no bromine were: *o*-, *m*-, *p*-tolunitrile, *o*-, *m*-, *p*-nitrotoluene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, 4,4′-dinitrodiphenylmethane, and *p*-toluenesulfonyl chloride.

**Choice of Solvent.**—An attempt to measure quantitatively the rates of bromination was begun with chloroform as solvent, but it soon became evident that the solvent itself was being brominated. The extent of bromination of Reagent or C. P. grade of chloroform at 57° under two 300-watt bulbs was determined by adding 1.60 g. of bromine dissolved in 10.0 cc. of carbon disulfide, and placing the flask in a thermostat under a reflux condenser. The amount of bromination was determined by adding an excess of 15% potassium iodide solution, and titrating the liberated iodine with standard sodium thiosulfate solution. After heating one sample of chloroform for ten minutes, it was found that 22.6% of the bromine originally present had been taken up by the 20.0-cc. sample of chloroform, while another sample (20.0 cc.) from the same bottle reacted with 30.5% of the bromine present in twenty minutes. Two other bottles of C. P. chloroform were tested with the result that one showed 19.7% and the other 25.4% of the bromine had been consumed by heating 20.0 cc. samples for ten minutes.

When a 75-cc. sample of chloroform was washed with a 50-cc. portion of water, and the chloroform layer dried and redistilled, the loss of bromine was reduced to 5.6% Washing again with 50 cc. of water cut the bromine consumed by the chloroform to 2.4%, while washing a 75-cc. sample with ten 50-cc. portions of water resulted in no bromination of the solvent on heating for ten minutes.

When different samples of Reagent or C. P. grade of carbon disulfide were substituted for chloroform as solvent, the rates of bromination varied more than 100% under otherwise identical conditions. Samples (20.0 cc.) of the best grade of carbon disulfide made by a half a dozen different manufacturers were used as solvent for the bromination of a one-hundredth mole sample (1.71 g.) of *o*-bromotoluene by the method described below.

TABLE I

BROMINATION OF *o*-BROMOTOLUENE IN DIFFERENT SAMPLES OF CARBON DISULFIDE

Temperature, 57°; time, 15 minutes

| Sample | Bromination, % | Sample | Bromination, % |
|---|---|---|---|
| A | 19.8 | F | 44.0 |
| B | 20.7 | G | 45.4 |
| C | 21.3 | H | 49.0 |
| D | 27.6 | I | 52.8 |
| E | 42.7 | | |

Labels on the samples of carbon disulfide indicated the presence of only negligible amounts of hydrogen sulfide sulfides, sulfites, and sulfates in the solvent, but when the two grades showing the lower rates of bromination were shaken with metallic mercury, a black precipitate was formed. Vigorous shaking of these impure samples with several portions of mercury, followed by redistillation, yielded a solvent which gave consistently high rates of bromination. On the other hand, the addition of small amounts of sulfur to the purified grades of carbon disulfide markedly decreased the rates of side-chain bromination.[3] In all the rates reported in this paper the same sample of carbon disulfide was used.

Carbon tetrachloride of C. P. grade showed no bromination when heated in the thermostat with bromine. This solvent is seen to give much faster rates of bromination than carbon disulfide (Table II).

**Relative Rates of Bromination.**—The relative rates of bromination of the toluene derivatives in Table II were obtained by heating a one-hundredth mole sample dissolved in 20.0 cc. of purified carbon disulfide (or carbon tetrachloride) in a 300-cc. Pyrex Erlenmeyer flask attached by a ground-glass joint to a reflux condenser. The flask was immersed to a measured depth in an electrically controlled thermostat heated to 57° (or 10° for the faster

---

(1) Presented before the Organic Division of the American Chemical Society at the 99th meeting, April 10, 1940, Cincinnati, Ohio.

(2) Andrich and LeBlanc, *Z. wiss. Photochem.*, **15**, 148–164, 183–196, 197–223 (1915); Bruner, *Bull. Internl. l'acad. sci. Cracovie*, 181 (1902); 691–730 (1907); 221–238 (1909); 322–333 (1909); 560–593 (1910); Holleman, *Rec. trav. chim.*, **26**, 1–54 (1907); **27**, 435–454 (1908); **33**, 183–191 (1914); Lauer, *Ber.*, **69B**, 978–985 (1936); Swensson, *Z. wiss. Photochem.*, **20**, 206–218 (1921).

(3) A further study of solvent effects is being made.

compounds). Two 300-watt clear-glass Mazda lamps were placed at a fixed distance above the flask, and when the contents had reached the temperature of the bath, 10.0 cc. of a standard bromine solution in carbon disulfide (or carbon tetrachloride) was added through the condenser. There was 1.60 g. of bromine in every 10.0 cc. of this solution. Its strength was checked frequently during the runs. At the end of a definite length of time, the lights were switched off, and 20 cc. of a 15% solution of potassium iodide was added quickly, the solution cooled, and the liberated iodine titrated against standard sodium thiosulfate solution. Blanks were run to determine the small amount of bromine lost during the manipulations.

The photochemical nature of the bromination may be seen by comparing the rate of only 1.5% bromination of toluene when the lights were turned off, with the value of 88.7% bromination in Table II.

TABLE II

RELATIVE RATES OF BROMINATION OF SUBSTITUTED TOLUENES

| Substituent | Time, min. | Bromination, % | Substituent | Time, min. | Bromination, % |
|---|---|---|---|---|---|
| | | In $CS_2$ at 57° | | | |
| None | 8 | 88.7 | *p*-I | 20 | 41.8 |
| None | 8 | 86.2 | *m*-I | 20 | 20.0 |
| *p*-Cl | 10 | 78.7 | *o*-I | 20 | 13.1 |
| *m*-Cl | 10 | 28.1 | *p*-CN | 20 | 26.2 |
| *o*-Cl | 10 | 36.3 | *m*-CN | 20 | 13.7 |
| *o*-Cl | 10 | 38.8 | *o*-CN | 20 | 5.6 |
| *p*-Br | 20 | 97.5 | *p*-$NO_2$ | 20 | 16.9 |
| *m*-Br | 20 | 68.7 | *m*-$NO_2$ | 20 | 10.8 |
| *o*-Br | 20 | 58.1 | *o*-$NO_2$ | 20 | 4.4 |
| | | In $CCl_4$ at 57° | | | |
| None | 1 | 100 | 2,4,6-Trinitro | 20 | None |
| *p*-$ClO_2S$ | 8 | 91.9 | *m*-COOH[a] | 6 | 87.0 |
| 2,4-Dinitro | 20 | 5.6 | *o*-COOH | 6 | 27.0 |
| | | In $CS_2$ at 10° | | | |
| None | 20 | 26.7 | *p*-$CH_3$ | 20 | 90.0 |
| α-Phenyl | 5 | 80.0 | *m*-$CH_3$ | 20 | 76.3 |
| Pentamethyl | 10 | 87.5 | *o*-$CH_3$ | 20 | 83.1 |
| 3,5-Dimethyl | 10 | 86.9 | | | |

[a] *p*-Toluic acid was insoluble even in 60 cc. of carbon tetrachloride at 57°.

The sample of *m*-chlorotoluene was thought to be impure, because the ortho isomer was brominated faster than the meta, but a Parr bomb analysis of the former gave 27.9% chlorine (calculated 28.0%), and repeated distillations did not change the rate of bromination.

**Analysis for Side-Chain Bromine.**—To determine the amount of bromine in the side-chain after the brominations were made, the following procedure was employed.

The carbon disulfide or carbon tetrachloride layer was separated and washed with distilled water until free from bromide ion; the solvent was evaporated under reduced pressure, and the last traces of solvent removed by drawing air through the distilling flask for five minutes; a dried, weighed sample was refluxed for three hours with a large excess of anhydrous sodium acetate in absolute alcohol; the resulting solution was acidified with 6 *N* nitric acid, and after the addition of a measured excess of standard silver nitrate solution, the excess was back-titrated with standard ammonium thiocyanate solution.

The validity of this sodium acetate method of removing side-chain bromine was established by the analysis of a number of samples of *p*-nitrobenzyl bromide of known purity.

TABLE III

TEST ANALYSES OF *p*-NITROBENZYL BROMIDE BY SODIUM ACETATE METHOD

| % Bromine found | % Bromine found |
|---|---|
| 36.93 | 36.95 |
| 36.94 | 36.79 |
| 36.60 | 37.14 |
| 36.90 | |

Average found 36.89% Calculated 37.03%

Applying the sodium acetate method of analysis to the compounds brominated in Table II confirmed the belief that the bromination took place largely in the side-chain.

TABLE IV

PERCENTAGE OF TOTAL BROMINE FOUND IN THE SIDE-CHAIN

| Compound | % $Br_2$ Found | Compound | % $Br_2$ Found |
|---|---|---|---|
| *p*-Bromotoluene | 96.1 | *p*-Iodotoluene | 109.0[a] |
| *m*-Bromotoluene | 93.4 | *p*-Nitrotoluene | 85.2 |
| *p*-Chlorotoluene | 94.0 | *p*-Tolunitrile | 94.8 |

[a] Analysis of *p*-iodotoluene showed some iodine was removed from the ring by the sodium acetate method.

Acknowledgment is made of the many helpful suggestions of Dr. E. Emmet Reid during this investigation.

## Summary

1. Measurements have been made on the rates of side-chain bromination of twenty-six derivatives of toluene in sunlight and under 600 watts.

2. Bromine readily entered the side-chain under strong irradiation at moderate temperatures.

3. Rates of bromination varied as much as 100% in different samples of Reagent and C. P. grades of carbon disulfide.

4. A sodium acetate method of analysis showed bromination was predominantly in the side-chain.

GREENVILLE, SOUTH CAROLINA RECEIVED MAY 11, 1940