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.

GREENVILLE, SOUTH CAROLINA

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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.

colorless needles, m. p. 190–191°. The crude tetrabromide mixed with warm alcoholic potassium acetate reacted promptly; yield, 6.1 g. Slender yellow needles separated from a nitromethane–alcohol solution, m. p. 169–170°.

Anal. Calcd. for $C_{10}H_6Br_2N_2O_4$: Br, 42.3. Found: Br, 42.5.

2-Nitro-1,4-bis-(β-nitrovinyl)-benzene.—I, following nitration with fuming acid, crystallized from nitromethane in clusters of tiny yellow needles, m. p. 173–174°.

Anal. Calcd. for $C_{10}H_7N_3O_6$: C, 45.3; H, 2.6. Found: C, 45.0; H, 2.9.

1,4-Bis-(α-methoxy-β-dibromo-β-nitroethyl)-benzene.—To 1 g. of II suspended in cold methyl alcohol was introduced two equivalents of alcoholic potash. The clear solution following dilution with ice water became cloudy as bromine water precipitated an oil that rapidly became crystalline, separating from nitromethane as lustrous white plates. It gradually decomposed above 210°, melting with foaming at 215–216°.

Anal. Calcd. for $C_{12}H_{12}Br_4N_2O_6$: Br, 53.3. Found: Br, 53.2.

1,4-Bis-(α-oxo-β-nitroethyl)-benzene.—A mixture prepared by boiling 4 g. of II for two hours with potassium hydroxide dissolved in methyl alcohol was diluted with water and slowly mixed with cold dilute hydrochloric acid. The resulting gum dissolved in glacial acetic acid containing a few drops of concd. sulfuric acid deposited 0.8 g. of crystalline material on short standing. It appeared as tiny colorless needles on crystallization from nitromethane, melting indefinitely above 190° with decompn.

Anal. Calcd. for $C_{10}H_8N_2O_6$: C, 47.6; H, 3.2. Found: C, 47.2; H, 3.4.

1,4-Bis-(α-anilino-β-nitroethyl)-benzene.—A solution prepared by heating I on a water-bath with an excess of aniline immediately clouded up if seeded. The resulting magma, following dilution with alcohol and crystallization from nitromethane, yielded a good quantity of sparkling straw colored needles, m. p. 157–158° with decompn.

Anal. Calcd. for $C_{22}H_{22}N_4O_4$: C, 65.0; H, 5.4. Found: C, 65.4; H, 5.4.

It formed salts with hydrochloric acid as well as with potassium hydroxide.

I probably formed an addition compound with ammonia, as on long standing with this reagent in benzene, a few colorless crystals appeared. The principal product was an amorphous discolored substance, the analysis of which indicated a polymer of I. It slowly decomposed when heated above 300°.

1,4-Bis-(β-methyl-β-nitrovinyl)-benzene.—Although attempts to condense nitroethane and terephthalaldehyde failed with a primary amine, a poor yield of the expected product did result on using triethylamine. It separated from alcohol as yellow needles, m. p. 119–120°.

Anal. Calcd. for $C_{12}H_{12}N_2O_4$: C, 58.1; H, 4.8. Found: C, 58.4; H, 4.5°.

1,4-Bis-(β-nitro-β-phenylvinyl)-benzene (III).—Phenylnitromethane heated on a water-bath with 10 g. of terephthalaldehyde and amylamine yielded 12 g. of crude product, after thorough washing with warm alcohol. On recrystallization from nitrobenzene yellow prismatic plates separated, m. p. 228–229° with decompn.

Anal. Calcd. for $C_{22}H_{16}N_2O_4$: C, 71.0; H, 4.3. Found: C, 70.9; H, 4.4.

1,4-Bis-(2-oxo-3,5-diphenylisoxazolinyl)-benzene.—Alcoholic ammonia, containing 3 g. of III and of phenylnitromethane heated gently for an hour, formed a product that was thoroughly washed with hot alcohol, yield 1.2 g. It was sparingly soluble in nitromethane, separating in tiny hair-like crystals, m. p. 253–254° with decompn.

Anal. Calcd. for $C_{36}H_{28}N_2O_4$: C, 78.3; H, 5.1. Found: C, 78.0; H, 5.1.

1,4-Bis-(3,5-diphenylisoxazolyl)-benzene.—It soon became apparent that while hot nitrobenzene was an excellent solvent for the isoxazoline oxide, the substance separating out was the corresponding isoxazole, tiny slender needles, m. p. 316–317°.

Anal. Calcd. for $C_{36}H_{24}N_2O_2$: C, 83.7; H, 4.7. Found: C, 83.3; H, 4.7.

The filtrate from the original preparation probably contained a small amount of the bis-dibenzoylmethane monoxime derivative of benzene, as it quickly changed into the isoxazole on heating with acid.

1,4-Bis-[2-oxo-3-phenyl-5-(4-bromophenyl)-isoxazolinyl]-benzene.—A suspension of 2 g. of III in 50 cc. of alcoholic ammonia containing two equivalents of *p*-bromophenylnitromethane was heated gently for an hour. The flocculent product, filtered by decantation from unchanged III and washed with a large volume of hot alcohol, yielded 0.5 g. of white crystalline material, m. p. 229–230° with decompn.

Anal. Calcd. for $C_{36}H_{26}Br_2N_2O_4$: Br, 22.5. Found: Br, 22.5.

1,4-Bis-[3-phenyl-5-(4-bromophenyl)-isoxazolyl]-benzene.—Obtained as small needles by recrystallization of the above isoxazoline from hot nitrobenzene, m. p. 298–299°.

Anal. Calcd. for $C_{36}H_{22}Br_2N_2O_2$: Br, 23.7. Found: Br, 23.6.

1,4-Bis-[β-nitro-β-(4-bromophenyl)-vinyl]-benzene.—This stilbine, obtained from terephthalaldehyde and *p*-bromophenylnitromethane, crystallized from nitrobenzene in yellow prismatic needles, m. p. 222–223° with decompn.

Anal. Calcd. for $C_{22}H_{14}Br_2N_2O_4$: C, 49.6; H, 2.6. Found: C, 49.3; H, 2.9.

It was converted into the corresponding isoxazoline oxide, m. p. 248–249° with decompn., and the isoxazole which decomposed slowly above 290°, melting at 323–324°. Satisfactory analyses were made.

Summary

Terephthalaldehyde has been condensed with nitromethane, nitroethane, phenylnitromethane and *p*-bromophenylnitromethane. The behavior of the nitromethane derivative with bromine, nitric acid, alkali and organic bases was examined. Several isoxazoline oxides and isoxazoles were prepared from the nitrostilbenes.

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