an aliquot into aqueous potassium iodide in method 2. The sample was then analyzed immediately for the amount of iodine liberated by titrating against a standardized sodium thiosulfate solution measured from a semimicroburet. Starch was used as an indicator.

A reaction mixture which was 6.7×10^{-3} M in potassium 4-methoxy-3-nitrobenzenesulfonate and 4.3×10^{-3} M in bromine was kept at 50°; it was found that slightly less than half of the bromine disappeared after 17 hr. Sodium 3,5-dibromo-4-methoxybenzenesulfonate (XII) with bromine gave no appreciable reaction at 25°; but when a reaction mixture containing 6.7×10^{-3} M XII and 4.6×10^{-3} M bromine was heated in a sealed tube at 98°, the amount of bromine decreased to 2.4×10^{-3} M after 1.5 hr.

Bromodecarboxylation of 3,5-Dibromo-4-hydroxybenzoic Acid.—The procedure was similar to method 1 discussed above for the bromodesulfonation experiments. Solution (a) was prepared by dissolving 1.00×10^{-3} mole of the dibromohydroxybenzoic acid with 1.65×10^{-3} mole of NaOH in one l. of water. Solution (b) contained 4.84×10^{-4} mole/l. of Br_2; 25 ml. of each solution were mixed at 0°. The reaction was so rapid that with a time of 7 sec. it was over 90% complete.

Ultraviolet spectra were taken in aqueous solution on a Cary spectrophotometer, model 11.

Acknowledgment.—The author is grateful to Dr. F. H. Westheimer for his encouragement and helpful discussions through the course of this work. The author is also pleased to acknowledge financial support from the National Science Foundation.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM JOHN HARRISON LABORATORY, UNIVERSITY OF PENNSYLVANIA, AND BROOKHAVEN NATIONAL LABORATORY]

The Free Radical Phenylation of 2,4-Dinitrotritiobenzene[1]

BY CHARLES C. PRICE AND ROBERT J. CONVERY

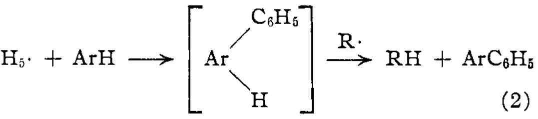
RECEIVED DECEMBER 15, 1956

The conversion of 2,4-dinitrotritiobenzene to 2,4-dinitrobiphenyl by treatment with benzoyl peroxide proceeds with the displacement of just one-half of the tritium. This proves that the product-determining step does not involve breaking the tritium- (or hydrogen-) carbon bond.

Two mechanisms have been advanced for free radical substitution in the benzene ring. One[2] involves initial hydrogen abstraction followed by coupling of two radicals.

$$C_6H_5\cdot + ArH \longrightarrow C_6H_5H + Ar\cdot \xrightarrow{C_6H_5\cdot} ArC_6H_5 \quad (1)$$

The other involves initial addition to the aromatic nucleus, followed by hydrogen abstraction.[2a,3]



(2)

In order to obtain more unequivocal evidence, we have studied the phenylation of 2,4-dinitrotritiobenzene, since mechanism 1 should show a substantial isotope effect while mechanism 2 would have little or none.

Experimental

2,4-Dinitrotritiobenzene was prepared by dissolving 2,4-dinitrobenzoic acid (5 g.) in 5 ml. of tritiated water (20 mc./10 ml.) heated at 125°, followed by decarboxylation of 5 g. of the tritiated acid by heating to 240° in 25 ml. of quinoline with 0.02 g. of copper chromite catalyst. After thorough washing of an ether solution, evaporation and recrystallization from 95% ethanol, 1.5 g. (38%) of tritiated *m*-dinitrobenzene, m.p. 108–108.8°, was obtained. This sample was mixed with 40 g. of unlabeled material and recrystallized once more from ethanol. One sample prepared in this way assayed[4] for 51.7 ± 1.6 mμc./mg. of hydrogen, a second for 22.8 ± 0.7 mμc./mg. of hydrogen.

2,4-Dinitrobiphenyl.—A mixture of 4.3 g. of benzoyl peroxide (0.02 mole) and 29.6 g. of tritiated *m*-dinitrobenzene (0.2 mole) was heated, gradually increasing the temperature from 75 to 100° over a period of 5 hr. After dissolving in 400 ml. of ether, the product was washed with five 50-ml. portions of 10% sodium bicarbonate, with three 50-ml. portions of 15% hydrochloric acid and three 50-ml. portions of water. Drying and evaporation left a solid residue which was distilled at 0.4 mm. to remove most of the excess *m*-dinitrobenzene (b.p. 98° (0.4 mm.)). The still residue was extracted with 150 ml. of boiling methanol. After cooling to room temperature and evaporation to 10 ml., the precipitate was collected and recrystallized four times from methanol to yield 0.7 g. (16%) of 2,4-dinitrobiphenyl. Before assay, 0.1 g. of this material in 5 ml. of benzene was put through a column of magnesium oxide.[5] After development with additional benzene, elution of the purple band with benzene, followed by evaporation of the benzene and recrystallization from methanol gave material melting at 109.3–110°. The results of tritium assay are summarized in Table I.

TABLE I

TRITIUM CONTENT OF *m*-DINITROBENZENE AND 2,4-DINITROBIPHENYL (MμC./MG. OF HYDROGEN)

Sample	$C_6H_4(NO_2)_2$ (exptl.)	$C_6H_5C_6H_3(NO_2)_2$ (exptl.)	$C_6H_5C_6H_3$-$(NO_2)_2$ (calcd.)[a]
1	51.7 ± 1.6	13.2 ± 0.4	12.9 ± 0.4
2	22.8 ± 0.7	5.54 ± 0.17	5.7 ± 0.2

[a] Calculated assuming starting material is exclusively 2,4-isomer and that replacement of hydrogen and tritium occur at identical rates.

An authentic sample of 2,4-dinitrobiphenyl was prepared by mixed Ullmann coupling of 2,4-dinitrochlorobenzene and iodobenzene in 3.5% yield,[6] m.p. 109.3–110°.[7] This showed no depression of melting point when admixed with the preceding sample.

Anal. Calcd. for $C_{12}H_8N_2O_4$: C, 59.01; H, 3.26; N, 11.47. Found: C, 58.96; H, 3.25; N, 11.39.

Discussion

The agreement of the tritium content of the

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[1] Research carried out in part under the auspices of the U. S. Atomic Energy Commission.

[2] (a) W. A. Waters, *J. Chem. Soc.*, 727 (1948); (b) H. Lobel, G. Stein and J. Weiss, *ibid.*, 2704 (1950).

[3] C. C. Price, "Reactions at the Carbon–Carbon Double Bond," Interscience Publishers, Inc., New York, N. Y., 1946; D. H. Hey, A. Nechvatal and T. S. Robinson, *J. Chem. Soc.*, 2892 (1951).

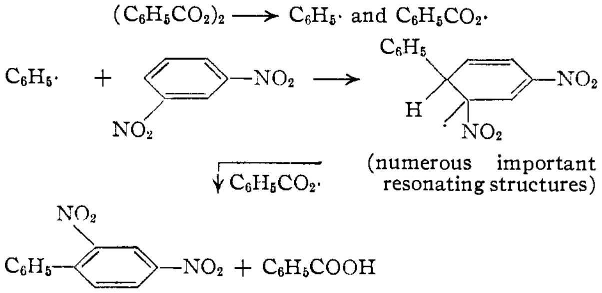
[4] Tritium assay was performed at Brookhaven by Dr. D. R. Christman.

[5] K. Cruse and R. Mittag, *Z. anal. Chem.*, **131**, 273 (1950).

[6] By the procedure of N. Kornblum and D. L. Kendall, THIS JOURNAL, **74**, 5182 (1952).

[7] H. C. Gull and E. E. Turner, *J. Chem. Soc.*, 496 (1929).

2,4-dinitrobiphenyl formed by benzoyl peroxide phenylation of 2,4-dinitrotritiobenzene with that calculated assuming no isotope effect is in accord with expectation if the phenylation occurred by mechanism 2. Mechanism 1 would have predicted a substantial isotope effect. We therefore conclude that, at least for the free radical phenylation of *m*-dinitrobenzene, the mechanism is clearly established as involving intermediate addition of the phenyl radical to the dinitrobenzene, followed by a non-rate controlling loss of hydrogen.



It should be pointed out that the mechanism demonstrated for the case of phenylation of *m* dinitrobenzene may not necessarily hold for attack on less activated aromatic rings. For example, where resonance stabilization for the intermediate radical adduct with two groups as favorable for radical stability as the two nitro groups in *m*-dinitrobenzene is absent, radical abstraction could become more important. Such a mechanism would be particularly favored for a radical like the hydroxyl radical[2b] because of the contribution of the very strong hydrogen–oxygen bond that would be formed in the process.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Mechanism of the Sandmeyer and Meerwein Reactions

BY JAY K. KOCHI*

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The Sandmeyer and Meerwein reactions are postulated to proceed *via* a common aryl radical. Reaction of the aryl radical with metal halide or its addition to olefin followed by reaction with metal halide gives Sandmeyer or Meerwein products, respectively. Evidence is given for the existence of aryl and aralkyl radicals and for the radical chain termination properties of metal halides. By utilizing these reactions, Sandmeyer and Meerwein products are obtained from sources other than arenediazonium salts.

Previous kinetic studies of the Sandmeyer[1] and related Meerwein[2] reactions have shown that these reactions are first order in both diazonium ion and cuprous salt, but they have not given complete information on the mechanisms of these reactions. We wish to give evidence for a common mechanistic path involving free radical intermediates. The essential feature of this mechanism is the role of the metal ion (copper) in acting as an effective radical chain terminator.[3] In the case of the two metal ions we studied (copper and iron), the process can be formulated as

$$R\cdot + MCl^{q}_{n} \longrightarrow RCl + MCl^{q}_{n-1} \quad (1)$$

$$R\cdot + MCl^{p}_{m} \longrightarrow R^{+} + MCl^{p-1}_{m} \quad (2)$$

These processes represent alternate routes by which radicals can react with metal and complex-metal ions; that is, (1) directly through a ligand bridge or (2) *via* an electron transfer process.[4,5] In the Sandmeyer reaction aryl radicals react predominantly by equation 1, whereas with alkyl radicals produced in the Meerwein reaction, processes 1 and 2 sometimes appear to be competitive.

Sandmeyer Reaction.—The free radical nature of the Sandmeyer reaction has been most consistently advocated by Waters[6a] and more recently by Pfeil,[6b] who postulate a quasi-intramolecular reaction involving one-electron transfers as

$$ArN_2{}^{+} + Cu^{I}\,Cl_n \rightleftarrows ArN_2CuCl_n{}^{7}$$

$$ArN_2CuCl_n \longrightarrow N_2 + Ar..Cl..Cu^{II}Cl_{n-1} \longrightarrow Ar\text{–}Cl + N_2 + Cu^{I}Cl_{n-}$$

The important characteristic of this mechanism is the unique role played by cuprous ion in an oxidation–reduction capacity. We believe that it is *not*

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(1) W. Cowdrey and D. Davies, *J. Chem. Soc.*, S48 (1949).

(2) J. K. Kochi, THIS JOURNAL, **78**, 1228 (1956).

(3) C. Bamford, A. Jenkins and R. Johnston, *Nature*, **177**, 992 (1956); F. Dainton and E. Collinson, *ibid.*, **177**, 1224 (1956); J. K. Kochi, THIS JOURNAL, **78**, 4815 (1956).

(4) The various aspects of these transfers have been elegantly presented by Taube and co-workers (H. Taube, *et al.*, THIS JOURNAL, **75**, 4119 (1953); **76**, 2103 (1954); **76**, 4053 (1954); **77**, 4481 (1955).

(5) The cupric ion alone is not wholly sufficient for its ability to act as a chain terminator. It appears that the most efficacious species is a higher chloro-complex, probably $CuCl_3$. Thus, our experiments (*vide infra*) indicate that in the presence of limited chloride ions, an appreciable number of aryl radicals react by dimerization, while high chloride ion concentrations enhance the yields of Sandmeyer product (*cf.* references 1, 9b and 35).

(6) (a) W. Waters, "Chemistry of Free Radicals," 2nd Ed., Oxford Univ. Press, London, 1948, p. 163. (b) E. Pfeil and O. Velten, *Ann.*, **562**, 163 (1949); **565**, 183 (1949).

(7) Most mechanisms of the Sandmeyer reaction involve the intermediate formation of a diazonium–cuprous complex. This postulate is based partially on the observed formation of a colored complex when gross amounts of diazonium and cuprous salts are mixed. Whether these represent true intermediates has not been rigorously shown. For a discussion regarding the nature of these complexes see references 6b and 19a. It is not important for the purposes of what follows whether the reaction proceeds (a) through the rapid reversible formation of a complex intermediate followed by its slow decomposition or (b) by a slow bimolecular reaction of the diazonium ion and cuprous salt (see footnote 38). The contrary notwithstanding we shall treat the reaction as proceeding by the former path.