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Further Data on the Free Radical Phenylation of 2,4-Dinitrotoluenes

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Experimental support for an earlier conclusion that in the free radical phenylation of benzene there is no selective replacement of hydrogen as compared to tritium has been obtained by finding no change in isotope concentration in recovered dinitrotoluenes after over 75% of the starting material has been consumed in reaction with phenyl free radicals from decomposing benzoyl peroxide.

We have earlier¹ reported on the conversion of 2,4-dinitrotoluenes to 2,4-dinitrophenyl through reaction with phenyl free radicals from decomposing benzoyl peroxide. In view of the requirement for either high conversion or high isotope concentration,² the conclusion reached earlier that there was no isotope effect in this replacement was not justified by the experimental data then reported.

We now wish to report on experiments designed to give more definitive information. Since we could not obtain high isotope concentration using tritium, it was considered more desirable to push the reaction to high conversion. Unfortunately, high conversion leads to much polysubstitution, so isolation of dinitrophenyl from high conversion reactions was not practical. We have, however, been able to recover unreacted dinitrotoluenes from reactions after over 75% conversion.

The close agreement in tritium content of the initial and recovered dinitrotoluenes samples indicates that there is indeed no isotope effect for this reaction.³ Therefore, the earlier conclusions¹ on mechanism are substantiated.

(1) C. C. Price and R. J. Convery, *THIS JOURNAL*, **79**, 2941 (1957).

(2) L. Melander, *Arkiv für Kemi*, **2**, 248 (1950).

(3) Using the equations developed by K. Halvorsen and L. Melander (*ibid.*, **11**, 83 (1957)), and assuming that we have proceeded to 75% conversion, that we could have missed an increase of 10% in the tritium content of the recovered *m*-dinitrotoluenes and that all four

Experimental

2,4-Dinitrotoluenes were prepared as before and diluted with unlabeled *m*-dinitrotoluenes. All counting was done by liquid scintillation in dioxane.

Experiment 1.—A mixture of 15 g. of tritiated *m*-dinitrotoluenes (12,980 d.p.m./mg.) and 4.2 g. of benzoyl peroxide was gradually heated from 70 to 95° (six hours). It was cooled to 80° and 13.5 g. more of the peroxide was added in 0.3-g. portions, with stirring, at 20-minute intervals. After heating for 15 minutes at 95°, the reaction mixture was dissolved in 200 ml. of ether, washed four times with 50 ml. of 10% sodium bicarbonate and three times each with 25 ml. of 15% hydrochloric acid and of water. After drying, the neutral residue was distilled through a 7-cm. Vigreux column to yield 6.8 g. (45%) of crude, recovered *m*-dinitrotoluenes, b.p. 108–128° (0.7 mm.). Recrystallization from 95% ethanol gave 4.4 g., which was treated again with benzoyl peroxide (4.0 g.), and starting material again recovered. Recrystallization of the crude distillate (1.4 g., 30%, 13.5% over-all) gave 1.0 g. of *m*-dinitrotoluenes, m.p. 90.0–90.8°, 12,890 d.p.m./mg.

Anal. Calcd. for C₈H₄N₂O₄: C, 42.9; H, 2.4. Found: C, 43.2, 43.0; H, 2.3, 2.5.

Experiment 2.—In this case, 7.5 g. of tritiated *m*-dinitrotoluenes (11,040 d.p.m./mg.) was similarly treated with a total of 14.3 g. of benzoyl peroxide without intermediate isolation of crude starting material. The crude recovered dinitrotoluenes (1.3 g., 17%) was recrystallized from ethanol to yield 0.3 g., m.p. 90.8–91.3°, 10,250 c.p.m./mg.

Anal. Found: C, 43.2, 43.1; H, 2.7, 2.6.

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positions in *m*-dinitrotoluenes are equally reactive, we get a *maximum* k_H/k_T of 1.3. We believe our data indicate a value very much closer to unity.