solution gave instead a theoretical nitrogen evolution and hydrocarbon products. From *N*-nitrosodibenzylamine (I), m.p. 60–61°,[3] there was obtained a theoretical evolution of nitrogen and 77% of bibenzyl, m. p. 53-54°; a mixture melting point with an authentic sample of bibenzyl melted at 53.5–54.5°; with *cis*-1-nitroso-2,6-diphenylpiperidine (II),[4] m.p. 67–69°, 56.8% of *cis*-1,2-diphenylcyclopentane,[5] m.p. 43.5–45.5°, 21.4% of 1,5-diphenyl-1-pentene and a theoretical evolution of nitrogen was obtained. A 2,4-dinitrobenzenesulfenyl chloride derivative of the 1,5-diphenyl-1-pentene melted at 113–115°, (113.5–115°),[4] mixture melting point with the 2,4-dinitrobenzenesulfenyl chloride derivative of authentic[6] 1,5-diphenyl-1-pentene undepressed. An infrared spectrum of the mixture of products was identical with a mixture of authentic 1,5-diphenyl-1-pentene and authentic[7] *cis*-1,2-diphenylcyclopentane, m.p. 46–47°.

Treatment of *trans*-1-nitroso-2,6-diphenylpiperidine (III),[4] m.p. 87–89.5°, with sodium hydrosulfite gave a 60.4% of a mixture of *trans*-1,2-diphenylcyclopentane and *cis*-1,2-diphenylcyclopentane, 19% of 1,5-diphenyl-1-pentene and a theoretical nitrogen evolution. The infrared spectrum of the mixture of products was identical with that of a mixture of authentic *cis*- and *trans*-1,2-diphenylcyclopentane, and 1,5-diphenyl-1-pentene.

Reaction of *N*-nitrosobenzylphenylamine (IV) with sodium hydrosulfite yielded no nitrogen but gave instead a 77% yield of 1-benzyl-1-phenylhydrazine, hydrochloric acid salt, m.p. 170–172° (m.p. 167–170°).[8] With *N*-nitrosodiphenylamine (V) an 80% yield of diphenylamine, m.p. 53.2–54.4°, (m.p. 53.9°)[8] was obtained, sulfuric acid salt, m.p. 124.5–126° (123–125°).[9] The formation of diphenylamine on reduction of V has previously been reported using other reducing agents.[10] Treatment of *cis*-1-nitroso-2,6-dimethylpiperidine[3] (VI) yielded *cis*-1-amino-2,6-dimethylpiperidine, picrate salt, m.p. 167.5–169° (m.p. 168–169),[3] a mixture with the picrate of authentic *cis*-1-amino-2,6-dimethylpiperidine, m.p. 167–168°, melted at 167–169°

The products of the reaction of I, II, and III with sodium hydrosulfite are identical with those isolated in the mercuric oxide oxidation of the corresponding 1,1-disubstituted hydrazines,[4] suggesting a common intermediate for both reactions. Further work on the reaction of sodium hydrosulfite with *N*-nitrosodialkylamines is presently under investigation and will be reported at a later date.

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Free-Radical Methylation of Simple Aromatic Hydrocarbons

Sir:

The free radical methylation of anthracenes,[1] trinitrotoluene,[2] and pyridines[3] has been reported[4a]. However, there appears to be no record[5] of substitution of methyl radicals on simple aromatics not activated by electron-withdrawing substituents; in fact, it has been suggested that such a reaction is energetically disfavored.[6]

We now wish to report that heating a *ca.* 1*M* solution of acetyl peroxide in toluene at the boiling point gives (in addition to bibenzyl and other dimeric or polymeric material) *o*-, *m*-, and *p*-xylene as well as ethylbenzene and an unidentified C_9 aromatic hydrocarbon fraction, the latter in very small amount. The over-all yield of C_8 aromatics isolated by careful fractional distillation is *ca.* 10% based on acetyl peroxide. The composition of this fraction, as determined by gas chromatography and ultraviolet analysis, is *o*-xylene, 44.5%, *m*-xylene, 21%, *p*-xylene, 13.5%, and ethylbenzene, 21%. Moreover, the reaction of benzene with acetyl peroxide yields (besides higher-boiling products[4b]) toluene, identified by boiling point, infrared spec-

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(1) A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1108 (1956).

(2) L. F. Fieser, R. C. Clapp, and W. H. Daudt, *J. Am. Chem. Soc.*, **64**, 2052 (1942).

(3) St. Goldschmidt and M. Minsinger, *Ber.*, **87**, 956 (1954); St. Goldschmidt, *Angew. Chem.*, **69**, 132 (1957).

(4) *ADDED MAY 27, 1957:* (*a*) After this communication was submitted, we learned of the publication of A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1665 (1957) in which they describe the decomposition of di-*t*-butyl peroxide in chlorobenzene to give chlorotoluenes and 3,3′-dichloro-4,4′-dimethylbiphenyl. (*b*) We have identified 4,4′-dimethylbiphenyl as one of the products of the decomposition of acetyl peroxide in benzene.

(5) M. S. Kharasch, A. Fono, and W. Nudenberg [*J. Org. Chem.*, **16**, 111 (1951)] have stated that the decomposition of acetyl peroxide in benzene yields toluene and xylenes, but no experimental data are available.

(6) M. Szwarc, *Nature*, **161**, 890 (1948); see also F. R. Mayo, *Discussions Faraday Soc.*, 372 (1947); P. F. Nelson, *J. Chem. Ed.*, **32**, 606 (1955), and C. S. Rondestvedt and H. S. Blanchard, *J. Org. Chem.*, **21**, 229 (1956).

trum, and preparation of the dinitro substitution product.

We were encouraged to look for xylenes from the decomposition of acetyl peroxide in toluene after discovering[7] that the decomposition of a *ca.* 1*M* solution in ring-deuterated toluene gave rise to some methane-*d* (6–7% of the total methane evolved), the stoichiometric equation being[8]

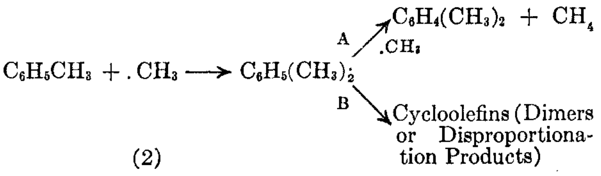
$$(CH_3CO_2)_2 + C_6D_5CH_3 \longrightarrow C_6D_4(CH_3)_2 + CH_3D + 2CO_2 \quad (1)$$

This finding, incidentally, invalidates previous determinations[9] of isotope-effects from the CH_3D/CH_4 ratio in the reaction of acetyl peroxide (1*M* solution) with $C_6H_5CH_2D$, since evidently part of the CH_4 originates by abstraction of ring hydrogens.

Szwarc has shown[10,11] that in the reaction of acetyl peroxide with toluene, the ratio

$$\frac{CH_4 + 2C_2H_6}{CO_2}$$

is less than unity (0.71–0.87) indicating that some methyl radicals fail to be converted to either methane or ethane. He ascribed this "methyl loss" to addition of methyl radicals to the aromatic ring with the formation of cycloolefins.[10] The results summarized above suggest that "methyl loss" may also occur through substitution (Equation 1). Apparently such loss through substitution (*cf.* Equation 2, path A) occurs only at high acetyl peroxide concentrations, for we have been able to show that at the much lower concentrations (*ca.* 0.1*M*) used by Szwarc, ring-deuterated toluene gives little methane-*d*, in agreement with Equation 2, path B, which is similar to the reaction path postulated by Szwarc.[10]



$$C_6H_5CH_3 + .CH_3 \longrightarrow C_6H_5(CH_3)_2^{\cdot} \begin{cases} \xrightarrow[.CH_3]{A} C_6H_4(CH_3)_2 + CH_4 \\ \xrightarrow{B} \text{Cycloolefins (Dimers or Disproportionation Products)} \end{cases}$$

(2)

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[7] Reported at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956. See E. L. Eliel, F. T. Fang, and S. H. Wilen, Division of Petroleum Chemistry Preprints, Vol. 1, No. 3, p. 135.

[8] In fact only partially deuterated substrate was used, but this does not affect the argument.

[9] F. B. Colton, Ph.D. dissertation, University of Chicago, 1950, p. 71; W. H. Urry. Abstracts of the Twelfth National Organic Chemistry Symposium, American Chemical Society, Denver, Colo., June, 1951, p. 30; data cited by K. B. Wiberg. *Chem. Revs.*, **55**, 713 (1955) and by F. D. Greene, W. A. Remers, and J. W. Wilson, *J. Am. Chem. Soc.*, **79**, 1416 (1957).

[10] M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 5981 (1954); *J. Am. Chem. Soc.*, **77**, 1949 (1955).

[11] R. P. Buckley, F. Leavitt, and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 5557 (1956).