chloride was hydrolyzed by adding 30 ml of ice-cold 5% sodium bicarbonate solution and stirring for 10 min at 0°. The resulting mixture was then poured into 500 ml of ice-cold 1 *N* hydrochloric acid solution and the product was extracted immediately with 1 × 500 plus 2 × 200 ml of ether. The combined ether extracts were washed with 1 × 100 ml of water and 2 × 100 ml of saturated brine, dried, and freed of solvent. The residual oil (11.45 g) when crystallized from ether–hexane afforded 8.0 g (67%) of crystalline keto tosylate III, mp 49–50°.

Two more recrystallizations from ether–hexane afforded an analytical sample of III, white crystals: mp 51–52°; infrared, $\lambda_{max}^{CHCl_3}$ 5.85 (C=O) and 7.3 and 8.4 μ (tosyl ester).

Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.78; H, 6.80. Found: C, 61.05; H, 6.89.

Acknowledgment.—The author wishes to express her thanks to Professor Gilbert Stork who suggested this problem.

The Reaction of α-Substituted Toluenes with N-Bromosuccinimide[1]

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Lovins, Andrews, and Keefer in 1964 reported enhanced reactivity (relative to toluene) in N-bromosuccinimide (NBS) bromination of toluenes with electron-supplying (methoxy, phenoxy, and thiophenoxy) and with certain electron-withdrawing (chloro, nitro, and acetoxy) α substituents.[2] The results were so in discord with current beliefs with regard to polar effects in free-radical reactions,[3] including the effect of *meta* and *para* substituents on the bromination of toluenes by bromine or NBS,[4] or with regard to the effects of α substituents on reactivities of carbon–hydrogen bonds in reactions in which polar effects are not important,[5] that we decided to repeat this work employing techniques developed previously.[6] While the work was in progress Lovins, Andrews, and Keefer corrected some results reported in their 1964 paper.[7] Table I summarizes the data originally reported by Lovins, Andrews, and Keefer (column 2). Their revised reactivities[7] are given in parentheses in column 2. Our results as summarized in column 3 show discrepancies with both the original and revised data of Lovins, Andrews, and Keefer, but the agreement with the revised numbers is much better than with their original report. We find no evidence that a strong electron-withdrawing group (−I), that cannot supply electrons by a resonance interaction (+R), activates the benzylic hydrogen atoms of an α-substituted toluene to attack by the bromine atom.[8] This is in accord with the accepted theories of polar effects in free-radical processes.

TABLE I

RELATIVE REACTIVITIES OF BENZYLIC-TYPE HYDROGEN ATOMS OF $C_6H_5CH_2X$ IN BROMINATION WITH NBS

X	CCl_4, 77°[a]	CH_2Cl_2, 40°[b]
CN	0.64 (0.13)	0.56
CO_2CH_3	0.87 (0.23)	0.042 ± 0.002
NO_2	2.8	0.052 ± 0.003
	0.104[b]	
Cl	4.2 (0.31)	0.24 ± 0.02
H	1.00	1.00
$OCOCH_3$	2.4	1.08 ± 0.04
CH_3	14	21 ± 2[c]
C_6H_5	18 (10)	10 ± 1.5[c]

[a] Data from ref 2 and, in parenthesis, ref 7. [b] Present work. [c] Reference 6.

The competitive brominations were all relative to toluene and are summarized in Table II.

TABLE II

COMPETITIVE BROMINATION OF TOLUENE AND α-SUBSTITUTED TOLUENES BY NBS AT 40° IN METHYLENE CHLORIDE SOLUTION[a]

α substituent	$[A]_o$[b]	$[A]_f$[b]	$[B]_o$[c]	$[B]_f$[c]	k_A/k_B[d]
Cl	1.00	0.739	1.00	0.257	0.171
Cl	1.00	0.831	1.00	0.240	0.130
Cl	1.02	0.797	1.00	0.227	0.153
Cl	2.0	1.55	1.00	0.225	0.171
NO_2	0.989	0.910	0.990	0.084	0.034
NO_2	0.989	0.915	0.990	0.082	0.032
NO_2	1.00	0.920	1.01	0.106	0.037
CN	1.00	0.572	1.00	0.098	0.241
CN	1.00	0.460	1.00	0.085	0.505
CN[e]	1.01	0.476	3.00	0.573	0.452
CN[e]	1.01	0.440	3.00	0.535	0.480
CN	0.500	0.223	1.00	0.147	0.398
$COOCH_3$	1.00	0.953	1.01	0.189	0.029
$COOCH_3$	1.01	0.966	1.01	0.187	0.027
$OCOCH_3$	1.00	0.599	1.00	0.505	0.751
$OCOCH_3$	1.01	0.646	1.01	0.533	0.696
$OCOCH_3$	1.01	0.623	1.00	0.514	0.724
NO_2[f]	1.00	0.869	1.00	0.146	0.073
NO_2[f]	1.00	0.876	1.00	0.140	0.068
NO_2[f]	1.01	0.886	1.00	0.136	0.066

[a] Solutions of 20-ml volume at 25° were employed. [b] Substituted toluene. [c] Toluene. [d] Per molecule, calculated by the equation $k_A/k_B = \log([A]_f/[A]_o)/\log([B]_f/[B]_o)$. [e] Solutions of 10-ml. volume. [f] Carbon tetrachloride at 77°.

Our results with phenylacetonitrile were not reproducible and suggest that possibly the nitrile was in part consumed by some other reaction, perhaps the addition of an acidic material to the nitrile group. With benzyl acetate and dibenzyl ether we found by gas–liquid partition chromatography (glpc) the presence of two substances indicative of molecular cleavage, since they were eluted prior to benzyl acetate. These substances were not formed with any of the other substrates. The most important of these substances was identified as benzaldehyde, presumably found by the following reaction.[9] If R· is not trapped by

$$C_6H_5\dot{C}HOR \longrightarrow C_6H_5CHO + R\cdot$$
$$R = CH_3CO,\ C_6H_5CH_2$$

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(1) Directive Effects in Aliphatic Substitutions. XXVIII. For part XXVII, see D. G. Hendry and G. A. Russell, *J. Am. Chem. Soc.*, **86**, 2371 (1964).

(2) R. E. Lovins, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **29**, 1616 (1964).

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(4) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 354 (1963); **86**, 3142 (1964); C. Walling, D. Tanner, and A. Riegers, *ibid.*, **85**, 3129 (1963).

(5) R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963); G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963).

(6) G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3139 (1963).

(7) R. Lovins, L. S. Andrews, and R. M. Keefer, *J. Org. Chem.*, **30**, 1577 (1965).

(8) Evidence that bromination by NBS involves attack by a bromine atom has been presented in ref 4 and 6.

(9) For additional examples of this process, see R. L. Huang, H. H. Lee, and S. H. Ong, *J. Chem. Soc.*, 3336 (1962).

molecular bromine or by NBS, the possibility exists that further consumption of the ether or acetate may occur by benzylic attack of R·.

Experimental Section

Procedure.—Weighed amounts of the α-substituted toluene and toluene were diluted to a 50-ml volume with methylene chloride, and a 20-ml aliquot was placed in an erlenmeyer flask containing a known weight of NBS. There was a sufficient amount of NBS added to react with about 50% of the total amount of α-substituted toluene and toluene present. The flask was attached to a water condenser under a positive nitrogen pressure. The reaction mixture was stirred using a Teflon-covered magnetic stirring bar and illuminated with a 150-w tungsten filament bulb about 4 in. from the flask. This served to keep the reaction mixture at the reflux temperature of 40°. Reaction was considered complete when the solution gave a negative test for bromine with starch–iodide paper.

After reaction was complete, the mixture was analyzed for unreacted α-substituted toluene and toluene by glpc. Ethylbenzene was used as the internal standard in all the analyses.

Competitive brominations of toluene and α-chlorotoluene were analyzed at 150° with a 2-m polypropylene glycol column utilizing a F and M Scientific Corp. Model 500 chromatograph. The other analyses employed linear temperature programming (50–180°) with a 2-m GE XF-1150 cyanosilicone oil column. The chromatograph peaks were measured with a planimeter. The peak areas were converted to moles by using the known number of moles of the internal standard and the correction factors calculated from the analysis of the standard solutions. The mixture of α-nitrotoluene and toluene was analyzed only for the unreacted reference compound, toluene. In this case the final concentrations of α-nitrotoluene was calculated from the starting quantity of NBS and the amount of toluene reacted.

Reagents.—N-Bromosuccinimide, obtained from Matheson Coleman and Bell, was purified by recrystallization from ten times its weight of hot water, followed by filtration. It was allowed to dry in air for 2 days. Reagent grade phenylacetonitrile and toluene were used without further purification. α-Nitrotoluene obtained from K and K Laboratories was distilled under 0.06-mm pressure and had a boiling point of 61–62°. Methyl phenylacetate, which had a boiling point of 54–55° at 1-mm pressure, was prepared by the sulfuric acid catalyzed reaction of phenylacetic acid and methanol. Benzyl acetate, which had a boiling point of 46–47° at 0.06-mm pressure, was prepared by the sulfuric acid catalyzed reaction of benzyl alcohol and acetic acid. Methylene chloride, obtained from Mallinckrodt, was washed with water and sodium carbonate, dried over calcium chloride, and distilled at 39.5–40°.

The Oxidation of Substituted Aziridines with Peracids[1]

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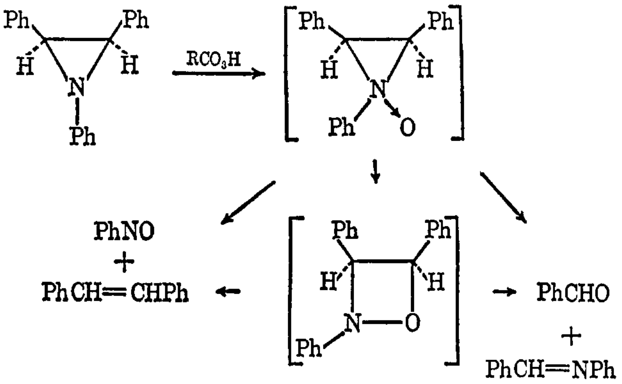
The formation of a four-membered 1,2-oxazetidine ring by the cycloaddition of nitrosobenzene with diethyl methylenemalonate and 1,1-diphenylethylene had been reported by Ingold and Weaver in 1924.[4] A reinvestigation of the structural assignments by Lapworth[5] and more recently by Griffin[6] has shown that the products obtained are in fact N-phenyl-N-(β,β′-dicarboethoxyvinyl)hydroxylamine and α,α-N-triphenylnitrone. With the refutation of the oxazetidine formulation for these products, the only authentic examples of this ring system are the fluorinated[7] and tetramethoxy 1,2-oxazetidines.[8] In an attempt to find a more convenient route to the 1,2-oxazetidine ring, we investigated the reaction of phenyl-substituted aziridines with organic peracids. It was anticipated that the reaction would produce 1,2-oxazetidines through the intermediate formation of aziridine N-oxides. This latter method would be advantageous in that low temperatures could be employed.

It was observed that *cis*-1,2,3-triphenylaziridine[9] reacted smoothly with 1 equiv of *m*-chloroperbenzoic acid in methylene chloride. The reaction was followed by gas–liquid partition chromatography of aliquots withdrawn during the reaction, and product assignments were made by comparison of spectra and glpc retention times with those of known compounds, and were checked by product isolation using preparative glpc. Analysis by gas–liquid partition chromatography of the crude reaction mixture showed that it contained 16% benzaldehyde, 14% nitrosobenzene, 8% benzalaniline, 7% *cis*-stilbene, and 7% *trans*-stilbene. A substantial amount (19%) of a mixture of *cis*- and *trans*-stilbene oxide was obtained as a by-product in the reaction. It appears as though low temperature and equivalent amount of peracid gave the best yield of stilbenes (see Experimental Section). The peracid oxidation was extended also to *cis*-1,2-diphenylaziridine, to give benzaldehyde (44%), and *cis*- and *trans*-stilbene (8%).

The reaction bears a formal resemblance to the peracid oxidation of imines to nitrosoalkane dimers in which a three-membered N-oxide was postulated as an intermediate.[10] Rearrangement of the initially formed aziridine N-oxide to a 1,2-oxazetidine, followed by fragmentation of the four-membered ring readily accounts for the products observed. There still remains the possibility of fragmentation of the initially produced aziridine oxide prior to ring expansion.



Although we are unaware of any close analogy for the expansion of the N-oxide to the 1,2-oxazetidine, the

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[1] Epoxidation Studies. IV. For part III, see A. Padwa, *J. Am. Chem. Soc.*, **87**, 4365 (1965).

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[3] National Institutes of Health Predoctoral Fellow, 1964–present.

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