tals.[10] The reduction of the endo,endo isomer 1 proceeds with inversion as expected, but it could also involve a prior oxygen complex. The NaBD$_4$ reduction in HMPA also proceeds with inversion with the exo,exo diiodide (3) and would not involve any complexation. These contrasting stereochemical results between NaBD$_4$ and LiAlD$_4$ thus support an oxygen–aluminum complex as an intermediate in the LiAlD$_4$ reductions.

All reported SN2 reactions of 6 proceed with retention of configuration through an episulfonium ion as an intermediate.[7] Thus a similar intermediate 13 could account for the observed retention in the hydride reduction of 6. The lack of rearrangement to the 9-thiabicyclo[4.2.1]nonane could be due to the stability of the episulfonium ion as well as the known thermodynamic stability of the bicyclo[3.3.1]nonane over the bicyclo[4.2.1]nonane.[4,11] In contrast to the oxa and thia cases, the aza analog, *endo,endo*-2,6-dichloro-*N*-methyl-9-azabicyclo[3.3.1]nonane, suffers 30% rearrangement to the [4.2.1] system.[12] The stereochemistry of this reduction is presently being investigated.

Experimental Section

Materials and Reactions. Ether was distilled from LiAlH$_4$ before use. The diiodides, 1 and 3, and the dichloride 6 were prepared from 1,5-cyclooctadiene as previously described and purified by recrystallization to the reported melting points.[4,5,7] The sulfone was prepared using acetic acid and hydrogen peroxide as reported[7] while the sulfoxide was prepared using *m*-chloroperbenzoic acid. The recrystallized products had the reported melting points.[7] The LiAlD$_4$ was purchased from Research Organic/Inorganic Corp., and the NaBD$_4$ from Ventron Corp. The analyses were done on a Varian EM-600 mass spectrometer, a Varian T-60 NMR spectrometer, and a Varian 1200 gas chromatograph. The reduction reactions were carried out on a 1-g scale with excess deuteride and worked up by standard procedures to give exclusively the products indicated. The 9-oxabicyclo[3.3.1]nonane was shown to be pure by GLC analysis at 105° on 10% CW-20M column.

Spectral Analysis. *exo,exo*-2,6-dideuterio-9-oxabicyclo-[3.3.1]nonane (2): NMR δ 4.0 (2), 1–2.0 (10); MS *m/e* 128 (P); infrared 2140, 2160, 1490, 1030 cm^{-1}. *endo,endo*-2,6-Dideuterio-9-oxabicyclo[3.3.1]nonane (5): NMR δ 4.0 (2), 1–2.0 (10); MS *m/e* 128 (P). *exo*-2-Iodo-9-oxabicyclo[3.3.1]nonane (4): NMR δ 4.4 (1) ($W_{1/2}$ = 8, endo $W_{1/2}$ = 16 Hz), 4.0 (2), 2.8–1.0 (10); infrared 1490, 1028 cm^{-1}. *endo,endo*-2,6-Dideuterio-9-thiabicyclo[3.3.1]nonane 9-dioxide (9): NMR δ 1.4–3.05; MS *m/e* 176 (P), 112 (P − SO$_2$); infrared 2920 w, 1280, 1120 (sulfone), 1090 cm^{-1}. Sulfoxide 8: NMR δ 1.4–3.2; MS *m/e* 160 (P), 144 (P − O), 112 (P − SO); infrared 2160, 2130, 1050 cm^{-1}.

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An Attempt to Observe Neighboring-Group Participation in Hydrogen Abstraction from β-(Substituted Phenyl)-Ethyl Bromides[1]

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Some recent applications of the Hammett equations have been concerned with nonlinearity. Streitwieser and his co-workers, for example, have shown that the data for acetolysis of substituted benzyl tosylates define two intersecting straight lines. This has been interpreted in terms of a change in the expected SN1 mechanism to an SN2 pathway when carbonium ion destabilizing groups are present.[2] Similarly Gassman and Fentiman have determined that a nonlinear behavior for the Hammett correlation of the data for dissociations of *syn*-7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates is indicative of variable nonclassical participation by the olefinic double bond.[3]

It was felt that a similar approach might be fruitfully applied to a problem in radical chemistry. Participation by neighboring bromine atoms in the course of hydrogen abstraction was first observed by Thaler in the bromination of 1-bromobutane.[4] Although there have been several attempts at refutation, this type of participation has been observed in many related systems. A vast body of evidence may be cited in support of the original findings.[5,6] One system which has not been investigated, however, is the formation of 1-aryl-2-bromoethyl radical (1) from β-(substituted phenyl)-ethyl bromides (2) via hydrogen abstraction.
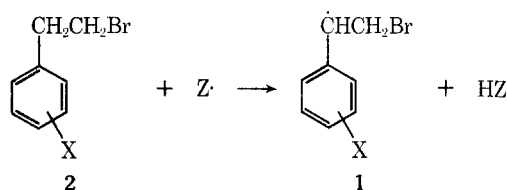
Normally a radical such as 1 would attain extensive stabilization by benzylic delocalization. Bromine participation would be unnecessary in such an event. As electron-withdrawing groups are introduced into the system, however, the destabilized radical might now make use of any additional mode of stabilization available. This should not only be true of 1, but also of the transition state leading to 1 in an endothermic reaction.[7]

As an additional point of reference, it was felt that a ρ value for hydrogen abstraction from 2 by the trichloromethyl radical could be theoretically evaluated in advance. Several series of α-substituted toluenes (3) have undergone
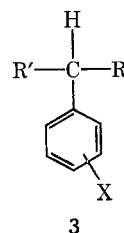
hydrogen abstraction with the radical generated from bromotrichloromethane. The corresponding ρ values are functions of the electronic and steric parameters of the groups directly attached to the reaction site. An empirical relationship has been developed which successfully correlated the available data (eq 1).[8]

$$\rho = -0.606(\textstyle\sum \sigma_p{}^+) + 0.195(\textstyle\sum E_s) - 1.063 \qquad (1)$$

Application of this equation predicts a ρ value for 2 at 70°C in the range −0.84 to −0.90 in the absence of neighboring group participation.[9]

The reaction of 2 with bromotrichloromethane is straightforward. Hydrogen abstraction occurs exclusively at the benzylic position. The products are the expected dibromides. All kinetic determinations are based on direct competition with mesitylene. They were run in replicate under nitrogen. Conversion to product varied from 10 to 85%. Analyses of reaction mixtures was by GLC. Table I summarizes the relative data obtained corrected to the parent compound.

Table I
Relative Rates of Secondary Benzylic Hydrogen Abstraction from β-(Substituted Phenyl)-Ethyl Bromides

Substituent	Registry no.	$\sigma^{+\,b}$	k_{subst}/k_H	No. of runs
p-CH$_3$O	14425-64-0	−0.778	4.23 ± 0.21	5
p-CH$_3{}^a$	6529-51-7	−0.311	1.87 ± 0.26	6
p-t-Bu	56829-61-9	−0.295	1.81 ± 0.16	7
p-F	332-42-3	−0.073	1.08 ± 0.03	6
H	103-63-9	0.000	1.00 ± 0.10	7
p-Cl	6529-53-9	0.114	0.86 ± 0.04	5
m-Cl	16799-05-6	0.399	0.49 ± 0.03	10
m-CF$_3$	1997-80-4	0.520	0.33 ± 0.04	7

^{a} Corrected for reaction at both benzylic positions. Hydrogen abstraction at the secondary site accounts for 66% of total reactivity. ^{b} Reference 10.

Optimum correlation was with σ^+ parameters. An experimental ρ value of −0.83 ± 0.02 was obtained. The correlation coefficient was −0.997. No systematic deviation from linearity was observed. This is graphically represented in Figure 1.
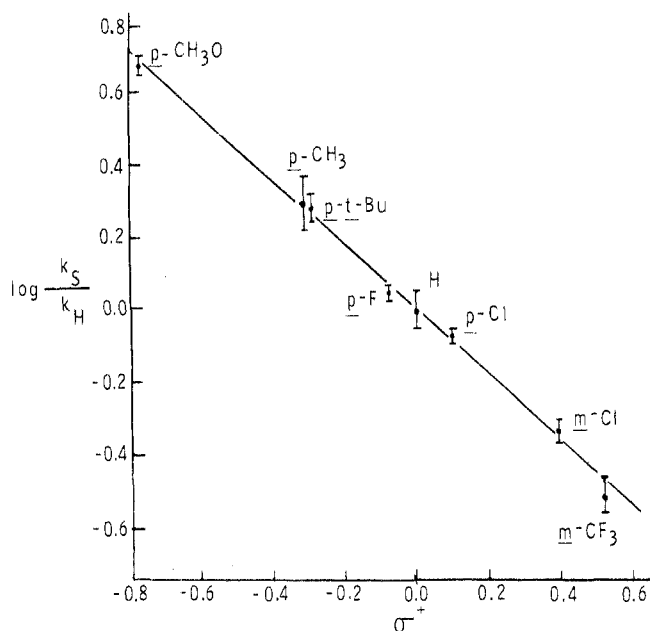

Figure 1. Logarithms of the relative rates of reaction of β-(substituted phenyl)-ethyl bromides vs. σ^+ parameters.

It is apparent that no evidence for participation is found. Unlike aliphatic radicals, radicals such as 1, even with electron-withdrawing groups present, must achieve sufficient stabilization so as to make bromine participation unnecessary under the reaction conditions employed.

Experimental Section

Materials. With the exception of the parent compound, all the β-(substituted phenyl)-ethyl bromides were prepared from the corresponding alcohols by reaction with phosphorous tribromide. All compounds showed physical properties (boiling points and indices of refraction) in agreement with literature values. The NMR spectra of all compounds were as expected and GLC indicated purities in excess of 98%. Bromotrichloromethane, mesitylene, and bromobenzene were purified by distillation prior to use. Purity was again in excess of 98%.

Kinetic Determinations. Solutions of substituted phenethyl bromides, mesitylene or (2-bromoethyl)benzene, bromobenzene, and bromotrichloromethane were prepared in the approximate molar ratios of 1:1:0.5:10. Approximately 0.75 ml of the solution was placed in each of several ampules.

The ampules were cooled to dry ice–isopropyl alcohol temperature until the solutions solidified. The ampules were evacuated at 2.0–3.0 mm and flushed several times with nitrogen with intermediate thawing. The ampules were sealed under vacuum and one was reserved for the analysis of the unreacted starting materials. The remainder were placed horizontally just below the surface of mineral oil constant-temperature bath maintained at 70.0 ± 0.5°C. The solutions were irradiated with uv light provided by a Sylvania 275-W sun lamp placed 20 cm above the surface of the oil. Reaction times varied from 1 to 3 hr, by which time up to 85% of substituted phenethyl bromides and mesitylene had reacted. The ampules were then cooled and opened. Analysis of the mixtures, both before and after the reaction, was via GLC on a 5% SE-30 on Chromosorb W column.

Conversion of raw data to relative rates involved the use of standard formulas.[11]

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Reactions Which Relate to the Environmental Mobility of Arsenic and Antimony. I. Quaternization of Trimethylarsine and Trimethylstibine

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Several papers have appeared which discuss the environmental distribution of arsenic[2-8] and antimony.[6-9] However, little attention has been given to the chemical changes which facilitate the movement of these elements from one subsystem of the biosphere to another. One of the more important processes in arsenic mobilization has been shown to be the reduction and methylation of inorganic arsenic compounds by microorganisms to produce trimethyl- and dimethylarsine.[10-12] At this time, it has not been demonstrated that methylstibines are metabolites of microorga-