[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND OF VITICULTURE AND ENOLOGY, UNIVERSITY OF CALIFORNIA]

Effect of Structural Changes on Adsorption of Certain Alcohol 3,5-dinitrobenzoates on Silicic Acid[1]

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The relative strengths of adsorption of a number of aromatic alcohol 3,5-dinitrobenzoates on silicic acid have been determined in terms of their rates of travel on a chromatographic column as compared to the rate of travel of ethyl-3,5-dinitrobenzoate (designated as the R_e value). The observed effects of changes in the alcohol side chains containing up to three carbon atoms and of introducing various alkyl groups onto the aromatic nucleus on the strength of adsorption of 3,5-dinitrobenzoate derivatives have been evaluated in terms of electronic and steric factors insofar as possible.

Many aspects of the effect of changes in the structure of organic molecules on the strengths of adsorption on a variety of adsorbents have been investigated.[3] In general, the strengths of adsorption on a material such as silicic acid decrease with increasing chain length and with increasing chain branching in saturated acyclic isomeric systems, with closely similar isomers being inseparable by means of paper or column chromatography. A mathematical function relating the interactions in chromatographic systems on the assumption that adsorption could be accounted for in terms of electron donor-acceptor and hydrogen-bonding theory has been proposed.[4]

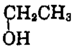
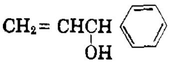
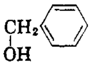
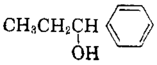
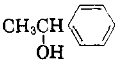
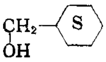
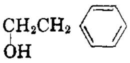
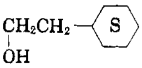
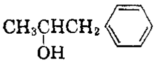
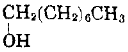
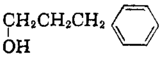
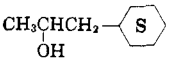
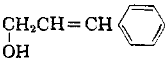
During the course of other investigations[5] in these laboratories, 2-phenylethyl 3,5-dinitrobenzoate was observed to separate as a band on silicic acid between the ethyl and methyl 3,5-dinitrobenzoate bands. It was also observed by Drumheller and Andrews[6] that the *p*-nitrobenzoates of the isomeric aromatic alcohols, 1-phenylpropanol and 3-phenylpropanol, formed separable zones on a silicic acid column. The separation of these isomeric aromatic alcohol derivatives as well as the strong adsorption of such aromatic compounds indicated the need for further study of the effect of structural variations in simple aromatic alcohols on the strengths of adsorption. In the work presented herein the effects of certain structural changes in side chains containing one to three carbon atoms, and of introducing methyl, ethyl, or isopropyl groups in various positions on the rings of aromatic alcohol 3,5-dinitrobenzoates on the strengths of adsorption on silicic acid are described.

A reasonably good estimate of the relative strengths of adsorption of substances may often be obtained by the measurement of R_f values on a chromatographic column. In the present work, due to the comparatively strong adsorption of the aromatic 3,5-dinitrobenzoates, the determination of R_f values would not permit sufficient accuracy. Instead, the relative strengths of adsorption were determined by measuring the distances which ethyl 3,5-dinitrobenzoate and any other given 3,5-dinitrobenzoate moved on a chromatographic column during a period of time and designating the ratio of these distances as the R_e value. By a careful control of the chromatographic conditions the R_e values can be determined with an accuracy of about ±0.02. The observed R_e values are listed in Tables I and II.

TABLE I

EFFECTS OF SIDE CHAIN VARIATION ON CHROMATOGRAPHIC ADSORPTION

Rates of Movement of 3,5-Dinitrobenzoate Derivatives Relative to Ethyl 3,5-dinitrobenzoate

	R_e		R_e
 $\underset{OH}{CH_2}CH_3$	1.00		1.63
	0.96[a]		1.83
	1.36		2.46
	0.76		2.49
	1.34	 $\underset{OH}{CH_2}(CH_2)_6CH_3$	3.08
	2.35		2.54
	0.65		

[a] No zone separation with the ethyl 3,5-dinitrobenzoate. Rate of movement relative to the cinnamyl derivative was determined and from this the listed value relative to the ethyl derivative calculated.

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(1) Abstracted from a thesis submitted by John J. Bost in partial fulfillment of requirements for the M.S. degree. Presented before the Organic Division of the American Chemical Society at Atlantic City in September, 1956.

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(3) Typical examples are contained in the following: (*a*) Strain, *J. Am. Chem. Soc.*, **70**, 588 (1948); (*b*) Smith and LeRosen, *Anal. Chem.*, **23**, 732 (1951); (*c*) White and Dryden, *Anal. Chem.*, **20**, 853 (1948).

(4) LeRosen, Monaghan, Rivet, and Smith, *Anal. Chem.*, **23**, 730 (1951).

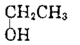
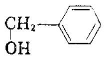
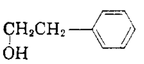
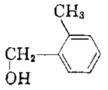
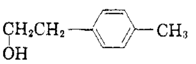
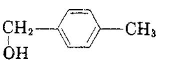
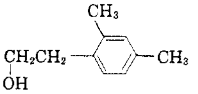
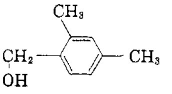
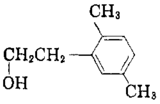
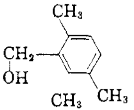
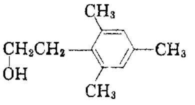
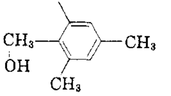
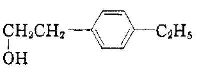
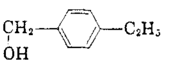
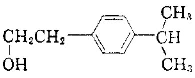
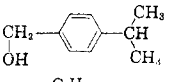
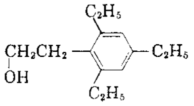
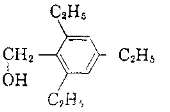
(5) Kepner and Webb, *American Journal of Enology*, **7**, 8 (1956).

(6) Drumheller and Andrews, *J. Am. Chem. Soc.*, **77**, 3290 (1955).

TABLE II

EFFECTS OF RING SUBSTITUTION ON CHROMATOGRAPHIC ADSORPTION

Rates of Movement of Aromatic 3,5-Dinitrobenzoate Derivatives Relative to Ethyl 3,5-dinitrobenzoate

	R_e		R_e
	1.00		0.96[a]
	0.76		0.88[a]
	0.85[a]		0.92[a]
	1.00[a]		1.11[a]
	1.29		1.39
	0 1		1.71
	1.31		1.46
	1.39		1.64
	2.11		2.15

[a] No zone separation with the ethyl 3,5-dinitrobenzoate. Rate of movement relative to the cinnamyl derivative was determined and from this the listed value relative to the ethyl derivative calculated.

It has been fairly well demonstrated that in general the saturated alcohol 3,5-dinitrobenzoates are adsorbed by interaction of the ester group and the dinitroaryl nucleus with the adsorbent, with the strength of adsorption steadily decreasing as the alcohol portion becomes larger and bulkier. The increased strength of adsorption of the aromatic alcohol derivatives reported here must then be primarily associated with the ability of the aromatic ring of the alcohol to participate in the donor-acceptor type of interaction with the adsorbent. Contrary to predictions based on such considerations, benzyl 3,5-dinitrobenzoate is adsorbed less strongly than 2-phenylethyl 3,5-dinitrobenzoate, as evidenced by R_e values of 0.96 and 0.76, respectively. A comparison of the various benzyl alcohol derivatives with the corresponding 2-phenylethanol derivatives in Table II shows that the R_e values for the benzyl alcohol derivatives are always somewhat greater. This is most likely due to the increased proximity of the alcohol aromatic group to the ester linkage in the case of the benzyl derivatives resulting in a certain amount of steric inhibition to the adsorption normally associated with the ester linkage and also with the aromatic ring of the alcohol portion of the molecule. The large decrease in strength of adsorption observed for the 3-phenylpropyl 3,5-dinitrobenzoate, R_e 2.35, indicates that the two-carbon side chain is sufficient to overcome any such possible inhibition. Another possible explanation of these differences in strengths of adsorption may be that, other factors being equal, the 2-phenylethyl 3,5-dinitrobenzoate is of such a molecular length and area as to fit the adsorption spaces or cavities on the silicic acid ideally, while the benzyl and 3-phenylpropyl derivatives are not of optimum size. Further study of the nature of silicic acid as an adsorbent, such as has been made on alumina,[7] might prove helpful in deciding between the above possibilities.

The introduction of alkyl groups into the α position of either the benzyl or 2-phenylethyl 3,5-dinitrobenzoates results in a considerable decrease in the strengths of adsorption. A consideration of molecular models suggests that there would be a definite steric inhibition to the adsorption of the ester linkage on a flat surface as a result of the introduction of an α methyl group. Any aid to adsorption associated with the electron-releasing effects of alkyl groups substituted in the α positions is apparently overshadowed by the increase in molecular size and the steric factors.

Cinnamyl 3,5-dinitrobenzoate, R_e 0.65, is, with one exception, the most strongly adsorbed of the compounds investigated. The increased electron availability associated with the double bond in conjugation with the aromatic ring and the resultant planarity of that portion of the molecule far outweigh any tendency toward decreased strength of adsorption due to increase in molecular size. The relatively small increase in strength of adsorption associated with a double bond not in conjugation with an aromatic ring is demonstrated by a comparison of the R_e values for α-vinyl and α-ethylbenzyl 3,5-dinitrobenzoates, 1.63 and 1.83, respectively.

The effects of ring substitution in the 2-phenylethyl derivatives are shown by a trend toward a general decrease in adsorption with increasing number of alkyl groups. The same trend is observed with alkyl substituted benzyl derivatives with the exception of the *o*- and *p*-methylbenzyl 3,5-dinitrobenzoates. The general sequence of decrease in strength of adsorption and increase in R_e value in the *para* substituted derivatives follows what would be expected from a consideration of the electron-releasing ability of the methyl, ethyl, and isopropyl groups. This is also, however, the same sequence which would be expected on the basis of

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[7] Russell and Cochran, *Ind. Eng. Chem.*, **42**, 1333 (1950).

the increase in molecular weight and size associated with the particular substituent.

The R_e values, 0.88 for *o*-methylbenzyl 3,5-dinitrobenzoate and 0.92 for *p*-methylbenzyl 3,5-dinitrobenzoate are just outside of experimental error from the R_e value, 0.96, of the unsubstituted benzyl 3,5-dinitrobenzoate and are believed to be real differences. The sequence of strength of adsorption, *o*-methylbenzyl greater than *p*-methylbenzyl greater than benzyl 3,5-dinitrobenzoate, is in line with the reported electronegativities of the *o*-tolyl, *p*-tolyl, and phenyl groups[8] as evidenced by the increasing dissociation constants of the corresponding carboxylic acids. The introduction of a *p*-methyl group into the 2-phenylethyl 3,5-dinitrobenzoate, on the other hand, results in a slight decrease in strength of adsorption. The 2-(2-methylphenyl)ethyl 3,5-dinitrobenzoate was not prepared in this investigation.

The 2,4,6-trialkyl substituted derivatives in general show a much weaker adsorption than the other derivatives prepared. The large decrease in adsorption in going from the 2,4-dimethylbenzyl 3,5-dinitrobenzoate (R_e 1.11) to the 2,4,6-trimethylbenzyl 3,5-dinitrobenzoate (R_e 1.71) quite clearly indicates that the effect can be attributed mainly to steric factors rather than the increased molecular weight and size accompanying the introduction of the methyl group. The R_e value (0.1) observed for the 2-(2,4,6-trimethylphenyl)ethyl 3,5-dinitrobenzoate is completely anomalous as compared to the other trialkyl substituted derivatives. No explanation of this result can be proposed at the present time.

EXPERIMENTAL[9]

Chromatographic procedure. The chromatographic column consisted of an 8 × 350 mm. tube with accessory equipment as described by Ikeda, Webb, and Kepner.[10] The adsorbent, a mixture containing two-thirds silicic acid and one-third analytical grade Celite, was prepared according to the procedure of White and Dryden.[3c] A weighed quantity (7.0 g.) of adsorbent was placed in the column using a standardized procedure designed to give a uniformly packed column approximately 24 cm. in height.

Approximately 15 mg. of ethyl 3,5-dinitrobenzoate and 15 mg. of a second 3,5-dinitrobenzoate derivative, each weighed to the nearest mg., were dissolved in the minimum volume of warm Skellysolve B and placed on the column. The column was then developed using 5% ether in Skellysolve B with a nitrogen pressure of approximately 8 lb. per sq. inch according to the techniques of White and Dryden.[3c] Development was continued until the bands were separated and in the lower half of the column. The bands at this point were usually from 1.0–1.5 cm. in length and the distance the band had traveled at any given time was determined by measuring from the top of the adsorbent column as the zero point to the mid point of the band.

2-Phenylethanol, 1-phenylethanol, benzyl alcohol, cinnamyl alcohol, n-octanol, 3-phenylpropanol, and cyclohexylmethanol. These alcohols were obtained from Eastman Kodak Co. and used directly for the preparation of the 3,5-dinitrobenzoate derivatives. The melting points of the derivatives agreed with the literature values, except for cyclohexylmethyl 3,5-dinitrobenzoate, m.p. 95.0–95.3°, which had not been previously reported.

2-Cyclohexylethanol. Cyclohexyl chloride (0.37 mole), b.p. 138–143°, n_D^{27} 1.4621, prepared from cyclohexanol in 57% yield by the method of Whaley and Copenhaven,[11] was converted into the Grignard reagent and condensed with ethylene oxide using standard Grignard procedures. Fractionation of the dried crude product gave 2-cyclohexylethanol (10% yield), b.p. 96–97° (12 mm.), n_D^{27} 1.4656; 3,5-dinitrobenzoate, m.p. 70.0–70.5°.

1-Cyclohexyl-2-propanol. Cyclohexylmagnesium chloride (0.37 mole) was prepared and condensed with propylene oxide, by the method described above to give 1-cyclohexyl-2-propanol (8.5% yield), b.p. 92–100° (27 mm.); 3,5-dinitrobenzoate, m.p. 69.5–71.2°.

α-Vinylbenzyl alcohol. Interaction of phenylmagnesium bromide (0.62 mole) with acrolein according to the method of Duveen and Kenyon[12] gave α-vinylbenzyl alcohol as a yellow oil (46% yield), b.p. 106–110° (17 mm.), n_D^{25} 1.5435. The alcohol darkened on standing at room temperature so that a freshly prepared sample was used to prepare the 3,5-dinitrobenzoate derivative according to the method of Mills[13] for the esterification of unstable alcohols. Isolation of the derivative gave a yellow oil which could not be crystallized but chromatographed as a single sharp band characteristic of a pure 3,5-dinitrobenzoate derivative.

1-Phenyl-1-propanol. Interaction of phenylmagnesium bromide (0.20 mole) with propionaldehyde as described above gave 1-phenyl-1-propanol (73% yield), b.p. 105–109° (18 mm.), n_D^{25} 1.5200; 3,5-dinitrobenzoate,[13] m.p. 66.5–67.0°.

1-Phenyl-2-propanol. Phenylmagnesium bromide (0.32 mole) was condensed with propylene oxide according to the method of Newman[14] to give 1-phenyl-2-propanol (43% yield), b.p. 100–105° (15 mm.), n_D^{26} 1.5250; 3,5-dinitrobenzoate, m.p. 87.7–88.1°.

o-Methylbenzyl alcohol. Benzylmagnesium chloride (0.41 mole) was condensed with formaldehyde according to the method of Smith and Spillane[15] to give *o*-methylbenzyl alcohol (13% yield), b.p. 115–120° (14 mm.), n_D^{29} 1.5408, m.p. 36° out of Skellysolve A; 3,5-dinitrobenzoate, m.p. 135.0–135.5°.

p-Methylbenzyl alcohol. α-Chloro-*p*-xylene, b.p. 90–94° (20 mm.), n_D^{27} 1.5344, prepared from toluene by the method of Stephen, Short and Gladding,[16] was hydrolyzed following

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[8] Ferguson, *Electron Structures of Organic Compounds*, Prentice-Hall, Inc., New York, N. Y., 1952, p. 77.

[9] (*a*) All 3,5-dinitrobenzoate derivatives were prepared according to the procedure given by McElvain [McElvain, *The Characterization of Organic Compounds*, the MacMillan Co., rev. ed., New York, N. Y., 1953, p. 199] unless otherwise specified. The derivatives were purified by chromatography on silicic acid, by recrystallization from Skellysolve A (b.p. 35–50°) or Skellysolve B (b.p. 60–70°), or by a combination of both. (*b*) All melting points are corrected; boiling points are uncorrected. (*c*) Combustion analyses were run on the 18 3,5-dinitrobenzoate derivatives not previously reported in the literature and agreed with the calculated values within ±0.2% for both carbon and hydrogen with the exceptions of the cyclohexylmethyl and 2,4,6-triethylbenzyl 3,5-dinitrobenzoates where the carbon error was about 0.4%.

[10] Ikeda, Webb, and Kepner, *Anal. Chem.*, **26**, 1228 (1954).

[11] Whaley and Copenhaven, *J. Am. Chem. Soc.*, **60**, 2497 (1938).

[12] Duveen and Kenyon, *J. Chem. Soc.*, 1697 (1939).

[13] Mills, *J. Chem. Soc.*, 2332 (1951).

[14] Newman, *J. Am. Chem. Soc.*, **62**, 2295 (1940).

[15] Smith and Spillane, *J. Am. Chem. Soc.*, **62**, 2639 (1940).

[16] Stephen, Short and Gladding, *J. Chem. Soc.*, **117**, 510 (1920).

the procedure of Bennett and Jones[17] to give *p*-methylbenzyl alcohol, b.p. 121–124° (18 mm.), n_D^{26} 1.5268, m.p. 58° after freezing and recrystallization from Skellysolve A; 3,5-dinitrobenzoate, m.p. 117–118°.

2-(p-Methylphenyl)-ethanol. Toluene (1.2 mole) and ethylene oxide (0.29 mole) were condensed using the modified Friedel-Crafts procedure of Matui[18] to give 2-(*p*-methylphenyl)-ethanol (9% yield), b.p. 120–125° (19 mm.), n_D^{26} 1.5225; 3,5-dinitrobenzoate, m.p. 103.5–104.0°.

2,4-Dimethylbenzyl alcohol. 2,4-Dimethylbenzyl chloride (0.10 mole), b.p. 100–105° (14 mm.), n_D^{25} 1.5371, prepared in 27% yield from *m*-xylene by the chloromethylation procedure of Akin, Stamatoff, and Bogert,[19] was hydrolyzed[17] to give 2,4-dimethylbenzyl alcohol (62% yield), b.p. 150–152° (44 mm.), n_D^{26} 1.5349, m.p. 20–21°; 3,5-dinitrobenzoate, m.p. 133.5–135.0°; phenylurethane, m.p. 76–78.5°.

2-(2,4-Dimethylphenyl)ethanol. By reaction with sodium cyanide in aqueous ethanol 2,4-dimethylbenzyl chloride (0.14 mole) was converted into the nitrile which was isolated as a dark brown liquid. The crude nitrile was not further purified but was hydrolyzed directly by the method of Goldberg, Ordas, and Carsch[20] to give 2,4-dimethylphenylacetic acid (79% yield), m.p. 100–101°. The 2,4-dimethylphenylacetic acid (0.068 mole) was reduced with lithium aluminum hydride in absolute ether following the method of Hunter and Hogg[21] except that the reduction was allowed to run 20 hr. After removal of the ether, distillation gave 2-(2,4-dimethylphenyl)ethanol, b.p. 125° (10 mm.), n_D^{26} 1.5289; 3,5-dinitrobenzoate, m.p. 103.5°.

2,5-Dimethylbenzyl alcohol. 2,5-Dimethylbenzyl chloride, b.p. 100–103° (12 mm.), n_D^{26} 1.5366, was prepared in 65% yield by chloromethylation of *p*-xylene (1.0 mole) as described in "Organic Reactions"[22] with the following exception. The crude reaction product was distilled at 2–3 mm. pressure from a distillation flask connected with a short adapter to a receiver cooled in a Dry-Ice–carbon tetrachloride bath in order to separate the desired product from any dichloromethylated products which otherwise tended to cause polymerization in the final distillation. The 2,5-dimethylbenzyl chloride (0.15 mole) was hydrolyzed[17] to give 2,5-dimethylbenzyl alcohol (43% yield), b.p. 140–144° (37 mm.), n_D^{26} 1.5328; 3,5-dinitrobenzoate, m.p. 100.5°.

2-(2,5-Dimethylphenyl)ethanol. 2,5-Dimethylbenzyl chloride (0.45 mole) was converted to the nitrile and hydrolyzed by the method previously described to give 2,5-dimethylphenylacetic acid (94% yield), m.p. 128°. Reduction of 2,5-dimethylphenylacetic acid (0.30 mole) with lithium aluminum hydride[21] gave 2-(2,5-dimethylphenyl)ethanol (38% yield), b.p. 110–113° (5 mm.), n_D^{26} 1.5289; 3,5-dinitrobenzoate, m.p. 119.0–119.5°.

2,4,6-Trimethylbenzyl alcohol. 2,4,6-Trimethylbenzyl chloride (0.65 mole), b.p. 129–131° (22 mm.), n_D^{26} 1.5362, prepared in 22% yield by chloromethylation of mesitylene as described in "Organic Synthesis,"[23] was hydrolyzed[17] to give 2,4,6-trimethylbenzyl alcohol (85% yield), b.p. 138–142° (15 mm.), m.p. 87–88°; 3,5-dinitrobenzoate, m.p. 153.5–154.0°.

2-(2,4,6-Trimethylphenyl)ethanol. 2,4,6-Trimethylbenzyl chloride (0.12 mole) was converted to the nitrile[23] (96% yield), b.p. 160–165° (22 mm.), m.p. 79–80°, which was then hydrolyzed[23] to give 2,4,6-trimethylphenylacetic acid (85% yield), m.p. 168°. Reduction of the acid (0.095 mole) with lithium aluminum hydride[21] gave the crude alcohol which, after recrystallization from Skellysolve B, gave pure 2-(2,4,6-trimethylphenyl)ethanol (12% yield), m.p. 76–78°; 3,5-dinitrobenzoate, m.p. 183–184°.

p-Isopropylbenzyl alcohol. Chloromethylation[23] of cumene (0.83 mole) gave *p*-isopropylbenzyl chloride (10% yield), b.p. 100–105° (14 mm.), n_D^{25} 1.5198, which was then hydrolyzed[17] to give *p*-isopropylbenzyl alcohol (51% yield), b.p. 120–122.5° (13 mm.), n_D^{26} 1.5151; 3,5-dinitrobenzoate, m.p. 91–92°.

2-(p-Isopropylphenyl)ethanol. *p*-Isopropylbenzyl chloride (0.19 mole) was converted to the nitrile and then hydrolyzed by the methods previously described to give the acid as a yellow oil from which a few crystals were obtained by freezing on Dry-Ice. These crystals out of Skellysolve B had a m.p. 49–51°. The crude *p*-isopropylphenylacetic acid was reduced with lithium aluminum hydride[21] to give 2-(*p*-isopropylphenyl)ethanol (43% yield), b.p. 132–133° (11 mm.), n_D^{26} 1.5160; 3,5-dinitrobenzoate, m.p. 108.5–109.0°.

p-Ethylbenzyl alcohol. *p*-Ethylbenzyl chloride (0.065 mole), b.p. 95–100° (11 mm.), n_D^{25} 1.5286, prepared in 18% yield by chloromethylation[23] of ethylbenzene, was hydrolyzed[17] to give *p*-ethylbenzyl alcohol (92% yield), b.p. 110–116° (9 mm.); 3,5-dinitrobenzoate, m.p. 85.0–86.5°.

2-(p-Ethylphenyl)ethanol. *p*-Ethylbenzyl chloride (0.09 mole) was converted to the nitrile by the procedure of Baker, Dippy, and Page.[24] An attempt was made to hydrolyze the crude nitrile without further purification by heating it under reflux with stirring for 18 hr. in a mixture of 40 ml. of concentrated sulfuric acid, 40 ml. of glacial acetic acid and 20 ml. of water following the procedure of Hill and Short.[25] The solution became dark brown soon after the heating period was started. After cooling, the reaction mixture was poured into 100 ml. of water and 300 g. of chipped ice. A brown solid, which separated from the resulting solution, was isolated by filtration and found to be insoluble in 10% sodium hydroxide. The filtrate did not yield any acidic compound on ether extration. The brown residue, which was presumably the amide, was added to a mixture of 25 g. of ethylene glycol and 100 g. of sodium hydroxide in 100 ml. of water, and refluxed for 9 hr. The reaction mixture immediately gave off ammonia. The cooled mixture was filtered and acidified with 20% hydrochloric acid to give a tan precipitate. The tan solid was filtered, washed with water, and redissolved in 100 ml. of 5% sodium bicarbonate. The solution was boiled with 4 g. of Norit, filtered, and acidified with 5% hydrochloric acid to give 4.7 g. (25%) of *p*-ethylphenylacetic acid as colorless crystals, m.p. 88–90°, after crystallization from Skellysolve B.

p-Ethylphenylacetic acid (0.021 mole) was reduced using lithium aluminum hydride in anhydrous ether[21] as previously described with the exception that at the end of 10 hr., additional portions of lithium aluminum hydride and anhydrous ether were added and the mixture stirred for 24 hr. longer. The reaction mixture was worked up as usual and removal of the ether extraction solvent under reduced pressure left 2.5 ml. of a yellow oil. The crude 2-(*p*-ethylphenyl)ethanol was not purified further but was used directly for preparation of the 3,5-dinitrobenzoate, m.p. 112.0–112.5°.

2,4,6-Triethylbenzyl alcohol. 1,3,5-Triethylbenzene was obtained by the method of Smith and Guss[26] from triethylbenzene (Matheson Co.) which was a mixture of isomers. 2,4,6-Triethylbenzyl chloride (0.17 mole), b.p. 115–125° (4 mm.), n_D^{27} 1.5263, prepared in 50% yield by chloromethylation[23] of 1,3,5-triethylbenzene, was hydrolyzed[17] to give 2,4,6-triethylbenzyl alcohol (90% yield) as colorless needles, m.p. 52.5–54.0°; 3,5-dinitrobenzoate, m.p. 117–118°.

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2 - (2,4,6 - Triethylphenyl)ethanol. 2,4,6 - Triethylbenzyl chloride (0.063 mole) was converted to the nitrile and the crude nitrile hydrolyzed as described under the preparation of 2-(*p*-ethylphenyl)ethanol to give 2,4,6-triethylphenylacetic acid (16% yield), m.p. 95–96°. The 2,4,6-triethylphenylacetic acid (0.01 mole) was reduced using lithium aluminum hydride[21] to give 2-(2,4,6-triethylphenyl)ethanol (80% yield), m.p. 39–40°; 3,5-dinitrobenzoate, m.p. 97.5–98.0°.

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Comparison of *N*-Bromoacetamide and *N*-Bromosuccinimide as Brominating Agents[1]

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A comparison of *N*-bromoacetamide and *N*-bromosuccinimide as brominating agents in reactions which were presumably free radical in type has been carried out especially with reference to their tendencies to give allylic bromination or addition to the double bond. It was found qualitatively that *N*-bromoacetamide showed more tendency toward addition and was the more reactive reagent. *N*-Bromodiacetimide, which closely resembles *N*-bromosuccinimide from the standpoint of electronic configuration but which is more like *N*-bromoacetamide from the standpoint of steric strain, was so reactive it could not be prepared pure. Crude solutions of it reacted with olefins to give bromine addition products as the only ones isolated, but these could have arisen from the reaction with bromine formed by decomposition. An investigation of the fate of the acetamidyl radical during the reaction of *N*-bromoacetamide with styrene to give styrene dibromide showed that when the reactants were carefully mixed so that the reaction proceeded rapidly and smoothly nearly all of the acetamidyl radical could be identified as acetamide. The source of the hydrogen necessary for acetamide formation, at least in some of the cases, must have been either styrene or a brominated product, but no products formed by such hydrogen abstraction could be isolated.

N-Bromoacetamide has been used[2] as a source of bromine atoms for substitution on the allylic position, and N-bromosuccinimide has been developed[3–7] extensively as a brominating agent for allylic positions and aromatic side chains. For each of these *N*-bromo compounds, however, addition of bromine to the double bond has at times been observed under conditions expected to favor free radical reactions. *N*-Bromoacetamide appears to give this type of reaction quite readily.[8,9] In the case of its reaction with styrene the free radical nature of the reaction was especially apparent.[8] Addition with *N*-bromosuccinimide has been observed[10–16] as the main reaction in several cases while in other cases some addition has been observed when substitution was the main reaction.[6,15–19] In several instances there was extensive addition under conditions favorable to free radical reactions.[10–13] In other cases the beneficial effects of antioxidants such as *p-tert*-butylcatechol[15,16] and of halide ion[14,16] in promoting addition reactions have been interpreted in terms of polar mechanisms.

The results of the present investigation are summarized in Table I. In the cases studied *N*-bromoacetamide tended to give addition preferentially and *N*-bromosuccinimide gave the expected allylic bromination where possible. In detail the results of Table I do not always agree with results reported elsewhere. For example, no cyclohexene dibromide was isolated from the reaction with *N*-bromosuccinimide but small amounts have been reported[15–18] under conditions favorable to free radical reactions. No dibromide could be isolated from extended interaction of styrene with *N*-bromosuccinimide in the

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