Reactions of Benzylic Brominating Agents with Benzyl Methyl Ether and Its *p*-Benzhydryl Derivative

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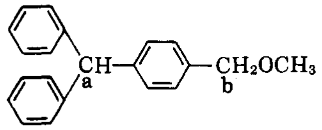
The only product isolated from the reaction of *p*-benzhydrylbenzyl methyl ether with N-bromosuccinimide is *p*-benzhydrylbenzaldehyde. In the course of an unsuccessful search for an alternate bromination procedure which would provide a substantial yield of the tertiary bromide [$(C_6H_5)_2CBrC_6H_4CH_2OCH_3$-*p*], rather than the aldehyde, a study of the competitive rates of reaction of benzyl methyl ether, toluene, ethylbenzene, and cumene with respect to attack both by N-bromosuccinimide and bromotrichloromethane in carbon tetrachloride has been made. The ether, which undergoes free radical bromination to form benzaldehyde, is substantially more reactive than any of these hydrocarbons, both with bromine atoms (from N-bromosuccinimide) and trichloromethyl radicals (from bromotrichloromethane) as the hydrogen-abstracting species. An investigation of the crude products of reaction of *p*-benzhydrylbenzyl methyl ether and N-bromosuccinimide also has been made. In addition to the aldehyde small amounts of organic bromides, probably the tertiary bromide and the α-bromo ether [$(C_6H_5)_2CHC_6H_4CH(Br)OCH_3$] are formed. Indications are that the bromo ether is not an intermediate in the formation of the aldehyde. These and related observations are discussed from a mechanistic point of view.

An attempt has been made to prepare the corresponding *p*-substituted trityl bromide through reaction of *p*-benzhydrylbenzyl methyl ether (I) with N-bromosuccinimide (NBS). Actually the crude product of this reaction contains relatively little bromine and is largely *p*-benzhydrylbenzaldehyde. The observation that carbon atom b of the ether is substantially more reactive than the tertiary carbon a has seemed, offhand, so surprising that a study of the relative reactivities of benzyl methyl ether and a group of alkylbenzenes toward benzylic brominating agents has been conducted. It has been established previously[1,2] that benzyl alkyl ethers react with N-bromosuccinimide or molecular bromine to form the corresponding aldehydes. It has been assumed that these reactions proceed *via* the abstraction of a benzylic hydrogen atom with subsequent formation of an α-bromo ether which decomposes rapidly to form an aldehyde.



I

Recently it has been shown by Russell, De Boer, and Desmond[3] that the relative reactivities of a series of aralkylbenzenes with respect to benzylic bromination are the same whether the brominating agent is N-bromosuccinimide or molecular bromine. With bromotrichloromethane as the bromine source a different reactivity series has been observed. It has been concluded, therefore, that in reactions with N-bromosuccinimide, abstraction of the benzylic hydrogen is accomplished by a bromine atom rather than by the N-succinimidyl radical, as has been suggested earlier.[4] This conclusion has been reached independently by Pearson and Martin,[5] and others have presented experimental evidence which tends to support it.[6-8] In reactions with bromotrichloromethane a trichloromethyl radical rather than a bromine atom must take part in the hydrogen abstraction process. In the present study of benzyl methyl ether reactivity it has proved interesting to employ both N-bromosuccinimide and bromotrichloromethane as bromine sources.

Experimental

The Preparation of *p*-Benzhydrylbenzyl Methyl Ether.—A sample of diphenyl-*p*-tolylmethanol was prepared from *p*-tolylmagnesium bromide and benzophenone by a procedure described previously.[9] This was converted to *p*-benzhydrylbenzoic acid by the method of Staudinger and Clark,[10] and the acid was reduced to *p*-benzhydrylbenzyl alcohol with lithium aluminum hydride.[11] A solution of 23 g. of this alcohol in 100 ml. of dry benzene was saturated with hydrogen bromide. The solvent was evaporated and the crude *p*-benzhydrylbenzyl bromide was recrystallized from petroleum ether; yield, 19 g. (67%); m.p. 66–67°.

Anal. Calcd. for $C_{20}H_{17}Br$: C, 71.22; H, 5.04; Br, 23.7. Found: C, 71.40; H, 5.17; Br, 23.6.

A solution of 2 g. of sodium and 19 g. of *p*-benzhydrylbenzyl bromide in 500 ml. of absolute methanol was refluxed for 4 hr. The reaction mixture was then diluted with a large volume of water and extracted with ether. After removing the solvent from the ether phase, the residual *p*-benzhydrylbenzyl methyl ether was distilled under reduced pressure to yield 14 g. (83%) yield of the pure product, b.p. 190–195° (1 mm.).

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.50; H, 6.95; Found: C, 87.42; H, 7.04.

Bromination of *p*-Benzhydrylbenzyl Methyl Ether with N-Bromosuccinimide.—A mixture of 10 g. (0.035 mole) of *p*-benzhydrylbenzyl methyl ether, 6.3 g. (0.035 mole) of N-bromosuccinimide, and 0.1 g. of benzoyl peroxide in 50 ml. of dry carbon tetrachloride was refluxed for 1 hr. The reaction mixture was cooled in ice and then filtered. The solvent was evaporated from the filtrate and the 11 g. of oily residue was distilled at reduced pressure. Before decomposition of the pot residue became a serious problem, 4 g. of a viscous distillate, b.p. 200–210° (2 mm.), was collected. Repeated attempts to obtain an analytically acceptable sample of this material were unsuccessful. The infrared spectrum of this product was found to contain a peak (5.85 μ), characteristic of a carbonyl compound. Several unsuccessful attempts to convert this carbonyl compound to a solid nitrogen-containing derivative, *e.g.*, a 2,4-dinitrophenylhydrazone, were made. The material was found to reduce ammoniacal silver nitrate.

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(1) D. G. Markees, *J. Org. Chem.*, **23**, 1490 (1958).

(2) M. Okawara, H. Sato, and E. Imoto, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, **58**, 924 (1955).

(3) G. A. Russell, C. De Boer, and K. M. Desmond, *J. Am. Chem. Soc.*, **85**, 365 (1963).

(4) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

(5) R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354 (1963).

(6) K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958).

(7) F. L. J. Sixma and R. H. Reim, *Koninkl. Ned. Akad. Wetenschap Proc.*, **61B**, 183 (1958).

(8) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961).

(9) S. F. Acree, *Ber.*, **37**, 990 (1904).

(10) H. Staudinger and K. Clark, *ibid.*, **44**, 1623 (1911).

(11) D. F. Thompson, P. L. Bayless, and C. R. Hauser, *J. Org. Chem.*, **19**, 1490 (1954).

This carbonyl compound was identifed as *p*-benzhydrylbenzaldehyde by oxidation, in high yield, to *p*-benzhydrylbenzoic acid. A solution of 2.1 g. of the aldehyde, 8 g. of silver nitrate, 50 ml. of water, and 10 ml. of ethanol was heated on a steam bath for 2 hr. with 5 g. of potassium hydroxide in 50 ml. of ethanol. The organic acid was isolated from the filtered alkaline product mixture by standard procedures. It was recrystallized from acetic acid to provide a 2.0 g. yield (92%) of material of m.p. (and m.m.p. with an authentic sample[10]) 160°–163°. The infrared spectra of the aldehyde oxidation product and the authentic sample of the acid were found to be identical.

Relative Rates of Reaction of Benzyl Methyl Ether and Various Alkylbenzenes with N-Bromosuccinimide.—A typical experiment is outlined. To a solution of benzyl methyl ether (0.041 mole) and the alkylbenzene (0.041 mole) in 50 ml. of carbon tetrachloride was added less than an equivalent amount (0.03 mole) of N-bromosuccinimide. Benzoyl peroxide (0.1 g.) was added, and the mixture was refluxed for 1 hr., after which no unchanged N-bromosuccinimide remained. A 30-μl. sample of the cooled reaction mixture was subjected to chromatographic analysis using a 15-ft. chromatograph column with Carbowax as the liquid support. The column temperature was 150°, and the flow rate of helium carrier gas was 150 ml./min. In each case the analysis was made for unchanged hydrocarbon and unchanged benzyl methyl ether by comparing emission peak areas to those for solutions of known concentration of these substances. The relative rates (r) of reaction of benzyl methyl ether and the alkylbenzene were calculated[12] using equation 1 where k_E and k_H are the rate

$$r = \frac{k_H}{k_E} = \frac{\log H_0/H}{\log E_0/E} \qquad (1)$$

constants for the bromination of the ether and the hydrocarbon, respectively (see Table I). The terms E_0 and H_0 and E and H represent, respectively, the initial concentrations and the concentrations at completion of reaction of the ether and hydrocarbon. Within the limits of error no significant change in r values with changes in the ratio E_0/H_0 were observed. Benzaldehyde could readily be identified as a reaction product by the chromatographic procedures which were employed. A *quantitative* procedure for its determination could not be devised. Under the conditions used the benzylic bromides did not emerge from the column in recognizable form.

TABLE I

RELATIVE REACTIVITIES, r,[a] OF ALKYLBENZENES AND BENZYL METHYL ETHER IN FREE RADICAL BROMINATIONS (CCl_4, 77°)

	Brominating agent	
Compound	NBS/Bz_2O_2	$BrCCl_3/h\nu$
t-Butylbenzene	0	0
Toluene	0.031 ± 0.001	≤0.01[b]
Ethylbenzene	.27 ± .01	.058 ± 0.003
Cumene	.31 ± .01	.101 ± .005
Benzyl methyl ether	1.00	1.00

[a] Defined by eq. 1. [b] So little toluene was consumed in the competition experiment that the r value which is reported is only semiquantitatively reliable.

Relative Rates of Reaction of Benzyl Methyl Ether and Various Alkylbenzenes with Bromotrichloromethane.—A solution of benzyl methyl ether (0.041 mole), the alkylbenzene (0.41 mole) and bromotrichloromethane (0.03 mole) in 50 cc. of carbon tetrachloride was irradiated for 2 hr. with a tungsten lamp. The heat of the lamp was sufficient to boil the reaction mixture. The analysis of the solution for unreacted ether and hydrocarbon (see Table I) was conducted as described in the preceding paragraph. Again it was found that when the ratios E_0/H_0 were varied, there were no significant changes in the r values calculated using eq. 1.

Relative Rates of Attack at Positions a and b in the Reaction of *p*-Benzhydrylbenzyl Methyl Ether (I) with N-Bromosuccinimide.—To determine the amount of bromination occurring at the tertiary carbon a, the reaction of 5.0 g. (0.017 mole) of *p*-benzhydrylbenzyl methyl ether with 3.15 g. (0.017 mole) of N-bromosuccinimide in carbon tetrachloride was conducted by the procedure described in connection with the preparation of *p*-benzhydrylbenzaldehyde. After removing the solvent and succinimide, the crude product was dissolved to a known volume in 90% aqueous acetone. An aliquot of this solution was removed and distributed between ether and water. The bromide ion content of the water phase was determined by the Volhard procedure. A sample of bromodiphenyl-*p*-tolylmethane was treated in an analogous manner and was found to be completely hydrolyzed in 90% aqueous acetone in less than 50 sec.

To analyze for its total bromine content a second sample of the crude product of bromination (obtained as described in the preceding paragraph) was dissolved to known volume in 80% aqueous ethanol. This solution was heated in a water bath at 70° for 18 hr., sufficient time (as established by separate experiment) to provide for complete solvolysis of *p*-benzhydrylbenzyl bromide. An aliquot of the cooled solution was removed and analyzed for inorganic bromide as before. See Table II for a summary of results.

TABLE II

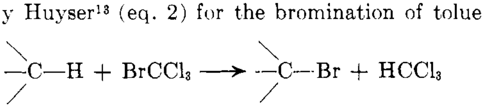
PRODUCTS OF BROMINATION OF *p*-BENZHYDRYLBENZYL METHYL ETHER (CCl_4, 77°)

	Brominating agent	
	NBS	$CBrCl_3$
Tertiary bromide, %[a]	6.9 ± 0.1	16.5 ± 0.6
Total bromide, %[a]	30.0 ± 0.2	...
Relative reactivity[b] (position a/position b)	0.07 ± 0.03	0.19 ± 0.6

[a] Based on moles of N-bromosuccinimide or bromotrichloromethane consumed (in the latter case as measured by chloroform formed). [b] This was calculated from the ratio of the moles of product formed by attack at position a (moles of II) to the moles of product formed by attack at position b (moles of brominating agent consumed less moles of II).

A third sample of the crude bromination product, as prepared from 5.0 g. of the ether, was analyzed for aldehyde by infrared spectrophotometry. The intensities of the bands at 3.65 and 5.85 μ in the infrared spectrum of a weighed sample of the product were compared with those for a solution of known concentration of *p*-benzhydrylbenzaldehyde.

The Relative Rates of Attack at Positions a and b in the Reaction of *p*-Benzhydrylbenzyl Methyl Ether with Bromotrichloromethane.—A solution of 2.0 g. (0.007 mole) of *p*-benzhydrylbenzyl methyl ether and 1.0 g. (0.005 mole) of bromotrichloromethane in 50 ml. of dry carbon tetrachloride was irradiated with a tungsten lamp for 2 hr. The heat of the lamp was sufficient to cause refluxing of the solvent. A sample of the cooled product mixture was subjected to vapor phase chromatography to determine its chloroform content. The column described in a previous section was used in this analysis and operated at a temperature of 150° with a helium flow rate of 120 ml./min. Only about one-third of the bromotrichloromethane which was used was consumed during the 2-hr. reaction period. This conclusion is based on the assumption that the stoichiometry of the reaction is like that reported by Huyser[13] (eq. 2) for the bromination of toluene. In



$$\geq C{-}H + BrCCl_3 \longrightarrow \geq C{-}Br + HCCl_3 \qquad (2)$$

other words it has been assumed that the moles of bromotrichloromethane consumed are equivalent to the moles of chloroform produced.

Essentially the same analytical procedure which was used in estimating the tertiary bromide content of the product of reaction of the ether I with N-bromosuccinimide was used in estimating the tertiary bromide content of the products obtained from the ether and bromotrichloromethane. The difference in the molar quantities of chloroform and of tertiary bromide formed in the reaction is considered to represent the amount of ether consumed by reaction at site b.

Preparation of Bromodiphenyl-*p*-tolylmethane.—A solution of 10 g. (0.036 mole) of diphenyl-*p*-tolylmethanol in 100 ml. of dry benzene was saturated with hydrogen bromide gas. The solvent was removed, and the crude bromide was recrystallized from petroleum ether to yield 8 g. (65%) of white crystals, m.p. 105–106°.

Anal. Calcd. for $C_{20}H_{17}Br$: C, 71.22; H, 5.04; Br, 23.7. Found: C, 71.02; H, 4.93; Br, 23.6.

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[12] A. Weissberger, "Technique of Organic Chemistry," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1953, pp. 108–113.

[13] E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960).

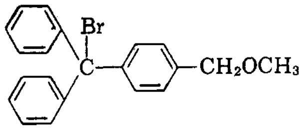
Another sample of this bromide was prepared from N-bromosuccinimide and diphenyl-*p*-tolylmethane. The latter was obtained by reduction of diphenyl-*p*-tolylmethanol.[10] From the reaction of 8 g. (0.031 mole) of the hydrocarbon and 5.5 g. (0.031 mole) of N-bromosuccinimide under much the same conditions employed in brominating *p*-benzhydrylbenzyl methyl ether, a crude sample of product was obtained which, after recrystallization from petroleum ether weighed 7.1 g. (68% yield); mixtures of samples prepared by this method and the preceding method melted without depression.

Other Materials.—Samples of commercially available toluene, ethylbenzene, cumene, *t*-butylbenzene, and bromotrichloromethane (Eastman Organic Chemicals) and N-bromosuccinimide (Arapahoe Chemical Co.) were used without further purification. Benzyl methyl ether was prepared from benzyl bromide and sodium methoxide in the same manner as described for the preparation of *p*-benzhydrylbenzyl methyl ether; b.p. 170–171° (lit.[14] b.p. 170°).

Results

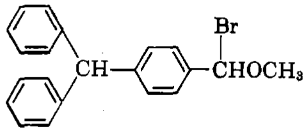
The only product which actually has been isolated from the reaction of equimolar quantities of *p*-benzhydrylbenzyl methyl ether and N-bromosuccinimide is *p*-benzhydrylbenzaldehyde. It has a considerably higher boiling point than is reported for the product of a Friedel–Crafts type reaction of terephthaldehyde and benzene, which has previously[15] been assumed to be this same aldehyde. As has been described in detail in the Experimental section, the product of the reaction with N-bromosuccinimide also contains some bromine.

It was hoped originally that the study of the relative reactivities of benzyl methyl ether and various alkylbenzenes in brominations with N-bromosuccinimide and also with bromotrichloromethane might provide a lead to a method suitable for preparing the tertiary bromide II in good yield. Actually as indicated in Table I the results of this competitive rate study are disappointing in this regard. With both brominating agents benzyl methyl ether is considerably more reactive than toluene, ethylbenzene, or cumene. It is interesting to note that, as has been mentioned earlier in the Experimental section, the *r* values calculated using equation 1 do not change with changes in the initial mole ratios (E_0/H_0) of benzyl methyl ether and alkylbenzene. This can only be the case if the reactions are first-order with respect to the ether and alkylbenzene. It is comforting to observe that, as is indicated by the inert character of *t*-butylbenzene in these experiments, there is no complication from reaction at nonbenzylic positions in these experiments.



II

Analyses of the products of reaction of *p*-benzhydrylbenzyl methyl ether with both brominating agents are reported in Table II. The procedure which has been used to determine tertiary bromide II is based on the fact that trityl bromides hydrolyze very rapidly in 90% aqueous acetone.[16] The total organic bromide content of the product of the reaction with N-bromosuccinimide also has been determined by solvolysis under considerably more stringent conditions. A less reactive bromide than II, presumably the bromoether III, which must form competitively with *p*-benzhydrylbenzaldehyde by reaction at site b in the ether I, has been found in some abundance in the product.



III

The aldehyde content of the product of the N-bromosuccinimide reaction, as estimated by infrared spectrophotometry, was found to be about 60 weight % or, assuming that the product was a mixture of organic bromide and aldehyde, about 70 mole % of the total product. It is gratifying to observe that the sum of the quantities of aldehyde and organic bromide produced are approximately equal on a molar basis to the N-bromosuccinimide consumed. A small amount of a succinimidyl derivative of I may also have been produced since some hydrogen bromide was evolved during the course of the bromination reaction. The relative reactivities at positions a and b of ether I which are reported in Table II may, with some reservation, be used to approximate *r* values (Table I) for triphenylmethane. Actually the reactivity at position a of the ether is probably not greatly affected by the *p*-CH_2OCH_3 group. Conversely, the reactivity at position b is probably not much affected by the *p*-benzhydryl group. On this basis the *r* values of triphenylmethane, as compared to those of the other alkylbenzenes in Table I, fall between those for toluene and ethylbenzene in the reaction with N-bromosuccinimide and above that for cumene in the reaction with bromotrichloromethane. The same relative placement has been reported previously for triphenylmethane in reactions with the two brominating agents at 40° in methylene chloride.[3] The relative rates of reaction at positions a and b (Table II) are subject to some error, probably relatively minor in nature, resulting from the fact that they are calculated on the assumption that no bromoaldehyde, $(C_6H_5)_2C(Br)(C_6H_5)CHO$, or dibromide, $(C_6H_5)_2C(Br)C_6H_4CH(Br)OCH_3$-*p*, is formed in the bromination reactions.

The fact that in its reaction with N-bromosuccinimide, triphenylmethane is attacked by a bromine atom more slowly than is cumene[3] might be explained on the assumption that the center of reaction of the former hydrocarbon is more hindered than that in the latter. It should be expected, however, that, if the steric problem is serious, replacement of the bromine atom by the bulky trichloromethyl radical as the hydrogen-abstracting species should lead to diminished reactivity of triphenylmethane relative to cumene. As mentioned before, this is contrary to experimental findings.[3] It is somewhat more apparent in the results of Russell, *et al.*,[3] than in those of the present investigation, that the relative reactivities of the series of hydrocarbons, toluene, ethylbenzene, cumene, and triphenylmethane vary more with N-bromosuccinimide

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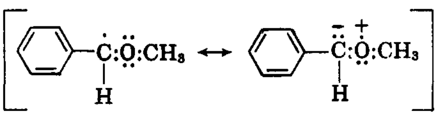
(14) W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, and L. C. Gibbons, *J. Am. Chem. Soc.*, **69**, 2451 (1947).

(15) H. Oppenheimer, *Ber.*, **19**, 2028 (1886).

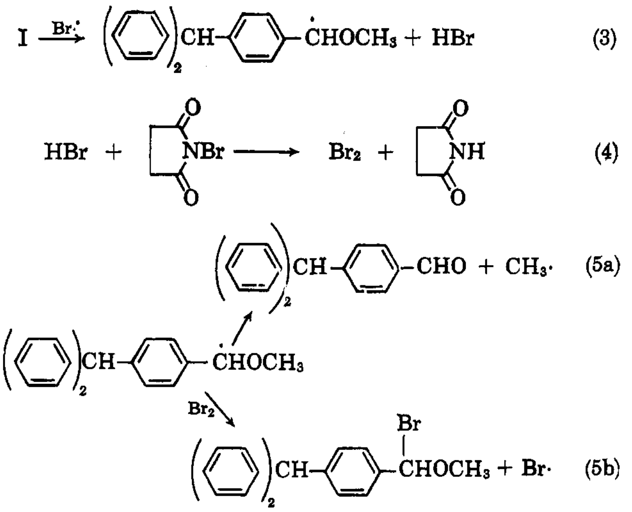
(16) A. Singh, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 1179 (1962).

than with bromotrichloromethane as the brominating agent. The greater selectivity of the trichloromethyl radical may result because it is more stable than a bromine atom and, therefore, more discriminating in its attack on alternate reaction centers. With both brominating agents benzyl methyl ether is, however, substantially more reactive than the several alkylbenzenes which have been investigated. Presumably the methoxyl substituent like the phenyl group makes a significant contribution (IV) to stabilization of the radical formed by extraction of one of the benzylic hydrogen atoms of the ether.[17]



IV

It has been inferred that the initial product of radical bromination of benzyl methyl ether is α-bromobenzyl methyl ether, which decomposes rapidly to form benzaldehyde and methyl bromide.[1] It is questionable, however, whether the bromo ether necessarily must be an intermediate in the formation of the aldehyde. In the reaction of *p*-benzhydrylbenzyl methyl ether three high boiling products are formed in significant quantity. These are *p*-benzhydrylbenzaldehyde, tertiary bromide, and the α-bromo ether III. It has been found that the composition of products is not noticeably affected by varying the period of reflux of the reaction mixture from one to four hours; α-bromo ether in this mixture is not decomposing during the course of the reaction to form the aldehyde. This does not preclude the possibility that on distillation of the product the bromo ether may decompose to the aldehyde. It is, therefore, probable that two alternate paths (equations 3–5), in addition to that leading to the formation of tertiary bromide, are available to the ether I, when it reacts with N-bromosuccinimide.



It is interesting to note that aldehydes are not the dominant products in the reactions of N-bromosuccinimide with either *p*-nitrobenzyl methyl ether[1] or *p*-bromophenyl benzyl ether.[18] It is improbable from an energetic standpoint that the radical intermediates in these two reactions should decompose by processes of the type depicted in equation 5a.

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

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[17] As was noted by a referee, the reactivities of substances of the type $\rangle C{=}\underset{|}{C}{-}R$ with respect to radical initiated polymerization vary with R in the order H ~ OCH_3 < OAc ~ CH_3 < Cl < COOR, etc. (C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 120). Apparently resonance stabilization of the radical intermediate $\left[\rangle C{-}\underset{|}{\dot{C}}{-}\underset{\cdot\cdot}{\ddot{O}}{:}CH_3 \longleftrightarrow \rangle C{-}\underset{|}{\overset{-}{\ddot{C}}}{-}\overset{+}{\dot{O}}{:}CH_3\right]$ is not a dominant rate-influencing factor in the reaction of a vinyl ether. There is other evidence that substituent effects on the rates of hydrogen abstraction processes in benzylic or allylic halogenations cannot be predicted on the basis of the effects of those same substituents on vinyl polymerization. For example, although –COOR is an activating group in the latter process, methyl vinylacetate yields $BrCH_2CHBrCH_2COOCH_3$ rather than $CH_2{=}CHCH(Br)COOCH_3$ as the primary product of reaction with N-bromosuccinimide [E. J. Corey, *J. Am. Chem. Soc.*, **75**, 2251 (1963)].

[18] L. L. Braun and J. H. Looker, *J. Org. Chem.*, **26**, 574 (1961).

Small Charged Rings. IV. Expansion of the Aziridinium Ring by Reaction with Aldehydes[1-3]

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Aromatic aldehydes have been shown to react with an aziridinium salt (III) to produce oxazolidinium compounds (V) by inclusion of the carbonyl group. The ring structure present in the products was established by n.m.r. spectral studies and by chemical degradation. The generality of the new ring-expansion reaction has been demonstrated by varying the aziridinium compound (VIII, X, XII) as well as the aldehyde reactant.

The introduction of a general method for the synthesis of aziridinium salts II (X = ClO_4 or BF_4) by nucleophilic attack of diazomethane on ternary iminium compounds I[1,4,5] has permitted a detailed study of the chemistry of the aziridinium ring system. The reactions of ethylene oxide with carbonyl compounds to form di-

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[1] For the preceding article in this series, see N. J. Leonard, K. Jann, J. V. Paukstelis, and C. K. Steinhardt, *J. Org. Chem.*, **28**, 1499 (1963).

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[3] Introduced at the 17th National Organic Chemistry Symposium of the American Chemical Society, June, 1961, Bloomington, Ind. (see Abstracts, pp. 1-10), and presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963 (see Abstracts, p. 30M).

[4] N. J. Leonard and K. Jann, *J. Am. Chem. Soc.*, **84**, 4806 (1962).

[5] N. J. Leonard and K. Jann, *ibid.*, **82**, 6418 (1960).