to a phenolphthalein end-point with 0.1 *M* nitric acid and then, by the Volhard method, for bromide ion. The initial concentration of enolate, E_0, calculated from the weight of ketone and volume of reagents was 0.092 *M*. The sum of the enolate concentration, *E*, and the halide ion concentration for each tube was 0.094 ± 0.02 *M*. The Volhard titration of an infinity sample gave the same value. Log *E* was plotted against time (Fig. 1), and a pseudo-first-order rate constant, $k_1 = 1.67 \times 10^{-6}$ sec.$^{-1}$, was determined from the slope of the curve. A second-order constant, $k_2 = 0.97 \times 10^{-6}$ liter mole^{-1} sec.$^{-1}$, was obtained by dividing k_1 by the concentration of ethyl bromide. A plot of log *E* *vs.* time (Fig. 1) is shown for three independent ethylations of butyrophenone, two of which were made with different solutions of sodium triphenylmethide. The common slope is indicative of the reproducibility of these alkylations.

Second-order rate constants for eighteen alkylations of eight ketones are listed in Tables I and II. The rapid hydrolysis of *t*-butyl bromide made necessary a modification of the analytical procedure for alkylations by this compound. Only the sealed-tube technique could be used. Sodium bromide was filtered on sintered glass, washed with anhydrous ether in an atmosphere of nitrogen and determined by the Volhard procedure.

Ebulliometric Measurements.—Relative boiling points of ethereal solutions of the sodium enolate of butyrophenone were determined with a Beckmann thermometer in a modified Cottrell ebullioscope.[28] The molal elevation of the boiling point of ethyl ether is 2.01°.[29] Several determinations of the molecular weights of naphthalene and triphenylmethane were made to a precision of ±5%. Solutions of the enolate of butyrophenone containing equimolar amounts of triphenylmethane were prepared from the ketone and sodium triphenylmethide. The average molecular weight of the two species in these solutions is 207 provided that no molecular association is present. The average molecular weight determined from boiling-point elevation was 302 ± 20 for enolate concentrations ranging from 0.0705 to 0.1263 *M*. No regular variation was observed: at enolate concentrations of 0.0705, 0.0882 and 0.1263 *M*, the average molecular weight was 294, 298 and 295, respectively. From the equation, ave. mol. wt. = $(244 + 170\ \alpha)/2$, the association number, α, for the sodium enolate at these concentrations is constant and equal to 2.0.

Acknowledgment.—The generous help afforded by a Summer Research Grant of E. I. du Pont de Nemours and Co., Inc., is gratefully acknowledged.

[28] Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1949, pp. 113, 133.

[29] C. S. Hoyt and C. K. Fink, *J. Phys. Chem.*, **41**, 453 (1937).

UNIVERSITY PARK, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Kinetics of the Reactions of Quaternary Ammonium Tribromides with Crotonic Acid in Ethylene Chloride[1]

BY ROBERT E. BUCKLES AND LELAND HARRIS[2]

RECEIVED AUGUST 20, 1956

The kinetic results obtained for the addition reaction of quaternary ammonium tribromide with crotonic acid in ethylene chloride are best explained by a combination of three reactions. The first involves both quaternary ammonium tribromide and bromine attacking the double bond. It was the predominant process when mixtures of bromine and tribromide were used with crotonic acid. The second reaction is that of quaternary ammonium tribromide or the kinetically equivalent equilibrium combination of quaternary ammonium bromide and bromine with crotonic acid. This reaction predominated in the early stages of the addition when tetrabutylammonium tribromide was used with crotonic acid. The third reaction appeared to involve a salt catalysis of the reaction of tribromide with crotonic acid. Tetrabutylammonium bromide was more effective than the nitrate, but the extent of catalysis was diminished by the presence of a large excess of the salt. The catalysis was also observed in the later stages of the reaction of tetrabutylammonium tribromide with crotonic acid. When tetramethylammonium tribromide was used without added bromine, the concentration of bromide was kept at a low, constant value by the relatively low solubility of tetramethylammonium bromide in ethylene chloride. Under these conditions, both the reaction of bromine and tribromide with crotonic acid and that of tribromide with crotonic acid took place to an appreciable extent. Rate constants for the reaction of crotonic acid with quaternary ammonium tribromide and bromine and that with quaternary ammonium tribromide alone were determined at 10, 20, 30 and 40°. They are listed in Table IV along with the heats of activation and the entropies of activation.

In an earlier investigation[3] it was found that the reaction of crotonic acid with a mixture of bromine and tetramethylammonium tribromide was faster than the corresponding reaction with tribromide alone which in turn was faster than that with bromine alone. It was shown that the presence of the solid tetramethylammonium bromide, which precipitated during the reaction of tetramethylammonium tribromide with crotonic acid, had no effect on the reaction rate. It was believed desirable, however, to test the effect of bromide in solution on the reaction. To this end the present investigation is concerned with the kinetics of the reaction of tetrabutylammonium tribromide with crotonic acid since tetrabutylammonium bromide is reasonably soluble in ethylene chloride.

Experimental Part

Materials.—Ethylene chloride was purified as described for earlier investigations.[3,4] Each batch of purified solvent was tested with bromine to ensure that the solvent was not reactive. Bromine, crotonic acid, tetramethylammonium bromide and tetramethylammonium tribromide were purified as described for an earlier investigation.[3]

Tetra-*n*-butylammonium Bromide.—A solution of 185 g. (1.0 mole) of tri-*n*-butylamine and 137 g. (1.0 mole) of *n*-butyl bromide in 300 ml. of butyl acetate was boiled under reflux for 24 hr. Cooling yielded 125 g. (39%) of crude tetra-*n*-butylammonium bromide. Crystallization from benzene gave 92 g. (29%) of salt of m.p. 115.5-116° (sealed tube), 102-102.5° (open tube). Other acetate esters were found to be much less satisfactory as reaction solvents. Although the use of ethyl acetate as a solvent has been reported[5] to give rise to a product contaminated by tetrabutylammonium acetate, the product used in this investigation was reasonably pure.

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[1] Abstracted from the Ph.D. Thesis of Leland Harris. Part of this work was carried out under Contract No. At(11-1)-72, Project No. 7 with the U. S. Atomic Energy Commission. Presented before the Organic Division of the American Chemical Society, Minneapolis, Minn., September, 1955.

[2] Eastman Kodak Fellow, 1954-1955.

[3] R. E. Buckles and J. P. Yuk, THIS JOURNAL, **75**, 5048 (1953).

[4] R. E. Buckles and J. F. Mills, *ibid.*, **75**, 552 (1953).

[5] H. Sadek and R. M. Fuoss, *ibid.*, **72**, 301 (1950).

Anal. Calcd. for $C_{16}H_{36}NBr$: C, 59.61; H, 11.26; N, 4.35. Found: C, 59.50; H, 11.10; N, 4.80.

Tetra-*n*-butylammonium Tribromide.—A 50-g. (0.162 mole) sample of tetra-*n*-butylammonium bromide in a crystallizing dish was placed in a desiccator containing an excess of liquid bromine (at least 10 ml.) and left for 24 hr. The liquid or semi-solid mass was transferred from the crystallizing dish to a suction flask and mixed with 150 ml. of carbon tetrachloride. The pressure in the flask was lowered with a water-pump as air was passed through a capillary tube reaching below the surface of the solution. During the evaporation the oily liquid disappeared and orange crystals formed. The crystals were collected by filtration and washed with carbon tetrachloride. A yield of 47–55 g. (63–73%) of light orange tetra-*n*-butylammonium tribromide, m.p. 71–73°, was obtained. Further purification was usually unnecessary, but small amounts could be crystallized from carbon tetrachloride–acetic acid to give a product of m.p. 72.5–74°.[6]

Tetra-*n*-butylammonium Nitrate.—This salt was prepared by a method analogous to that used for the preparation of tetra-*n*-butylammonium chloride.[7] A solution of 50 g. (0.135 mole) of tetra-*n*-butylammonium iodide in 700 ml. of hot water was stirred with 17.5 g. (0.075 mole) of silver oxide. After the silver iodide precipitate had coagulated, it was removed by filtration. The solution was neutralized with concentrated nitric acid and allowed to evaporate. The liquid residue was cooled in ice-water to yield 37.7 g. (91%) of finely divided solid product. Crystallization from ethyl acetate gave 20 g. (49%) of tetra-*n*-butylammonium nitrate of m.p. 120–121° (open tube) which checks that reported.[8] The purity of the salt was quite satisfactory as shown by analysis.

Anal. Calcd. for $C_{16}H_{36}O_3N_2$: C, 63.1; H, 11.9; N, 9.20. Found: C, 63.1; H, 11.6; N, 9.41.

Product Isolation.—In an earlier investigation[3] it was found that the reaction of tetramethylammonium tribromide with crotonic acid yielded the dibromide of m.p. 87–88°. With tetrabutylammonium tribromide (4.82 g., 0.010 mole) in the presence of the tetrabutylammonium bromide (3.22 g., 0.010 mole), crotonic acid (0.86 g., 0.010 mole) gave 1.73 g. (70%) of the same product.

Analytical Procedures.—Two-phase mixtures of tetra-*n*-butylammonium triiodide in ethylene chloride–water could not be titrated with thiosulfate solution, because so much of the triiodide was distributed into the ethylene chloride layer that the mixture failed to give any color with starch.[3] This difficulty was not encountered with tetramethylammonium triiodide so that the samples could be titrated to the starch end-point.

When tetrabutylammonium ion was present in the ethylene chloride, enough methanol was added with the potassium iodide so that the solution remained homogeneous throughout the titration.[7] The end-point was the disappearance of the color characteristic of the triiodide ion. On the addition of enough water to cause the separation of two layers any remaining triiodide ion caused a coloring of the ethylene chloride layer. The end-point could then be reached only by a very slow titration with rapid stirring. This method of titrating a homogeneous solution to the disappearance of the triiodide color gave the same results with solutions of bromine in ethylene chloride as the method of titrating a two-phase mixture to the starch end-point. The accuracy of neither of the two methods was affected by the presence of 2,3-dibromobutyric acid unless the solution was allowed to stand more than half an hour after the addition of potassium iodide.

Kinetic Measurements.—The reactions were carried out in complete darkness in baths controlled to within 0.05°. Known volumes of standard solutions of the reagents were mixed as rapidly as possible at the temperature of the bath. At appropriate intervals 10-ml. samples were withdrawn under illumination by a small ruby safelight. Each sample was immediately mixed with 50 ml. of methanol containing 0.2 g. of potassium iodide and titrated with standard thiosulfate solution. Calculations of the rate constants were carried out as described for the earlier investigation.[3]

Solubility of Tetramethylammonium Bromide.—Ethylene chloride was saturated with tetramethylammonium bromide at a temperature somewhat above 30°. The solution was then allowed to come to equilibrium with the solid salt at 30°. Samples of the solution in equilibrium with solid bromide were measured and mixed with measured volumes of solutions of bromine so that the bromine had approximately ten times the molarity of the bromide. The spectra of the solutions were measured at 25° in silica cells of path length 1.00 ± 0.01 cm. with a Cary model 11 recording spectrophotometer. The concentration of tetramethylammonium bromide was calculated from the spectrum[3] of the undissociated tribromide ion which was observed because the excess bromine had suppressed the dissociation. The average value for the solubility at 30° was 3.6×10^{-5} *M*.

Results and Discussion

The best explanation of the results obtained for the reactions of tribromide with crotonic acid under various conditions involved the four reactions represented in equations 1–4 in which E is crotonic acid.

$$R_4NBr_3 \rightleftarrows Br_2 + R_4NBr \qquad (1)$$

$$E + R_4NBr_3 + Br_2 \longrightarrow EBr_2 + R_4NBr_3 \qquad (2)$$

$$E + R_4NBr_3 \longrightarrow EBr_2 + R_4NBr \qquad (3)$$

$$E + R_4NBr_3 + R_4NBr \longrightarrow EBr_2 + 2R_4NBr \qquad (4)$$

The over-all rate law for the reaction of tribromide with crotonic acid is given in equation 5 in which the subscript on each rate constant refers to the equation of the reaction involved.

$$-\frac{d(E)}{dt} = k_2(E)(R_4NBr_3)(Br_2) + k_3(E)(R_4NBr_3) + k_4(E)(R_4NBr_3)(R_4NBr) \qquad (5)$$

When bromine was present initially with the tribromide only the first term contributed appreciably to the rate of reaction. Values of k_2 calculated for this reaction when tetrabutylammonium tribromide, bromine and crotonic acid were used are given in Table I. The values obtained at 30° compare favorably with the average value of 9.7×10^{-2} l.^{2} mole^{-2} sec.$^{-1}$ which was reported[3] for the analogous reaction of tetramethylammonium tribromide. For all of the runs with both tribromides (from the previous investigation[3] and from Table I) the average value of k_2 at 30° is $(9.9 \pm 0.5) \times 10^{-2}$ l.^{2} mole^{-2} sec.$^{-1}$ where the measure of the precision sets the 95% confidence limits of the average.

TABLE I

SUMMARY OF KINETIC DATA FOR THE REACTION OF CROTONIC ACID WITH MIXTURES OF TETRABUTYLAMMONIUM TRIBROMIDE AND BROMINE IN ETHYLENE CHLORIDE AT 30°

Concentrations, $M \times 10^2$			$k_2 \times 10^2$
Acid	Br_2	Bu_4NBr_3	l.^{2} mole^{-2} sec.$^{-1}$
2.04	1.17	0.81	10.5
2.04	1.17	.81	10.8
2.04	1.17	.81	10.5
2.04	0.59	1.22	10.5
2.04	1.75	0.41	11.5

When tetrabutylammonium tribromide reacted alone with crotonic acid, it was found that during the early stages of the reaction the second term of equation 5 contributed most predominantly to the rate law so that k_3 could be calculated satisfactorily using this term alone. The results of these calculations are given in Table II. The values ob-

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[6] R. E. Buckles, A. I. Popov, W. F. Zelezny and R. J. Smith, THIS JOURNAL, **73**, 4525 (1951).

[7] R. E. Buckles and J. F. Mills, *ibid.*, **76**, 4845 (1954).

[8] C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

tained were considerably lower than the average value of (2.29 ± 0.22) $\times 10^{-4}$ l. mole^{-1} sec.$^{-1}$ reported[3] for the analogous reaction of tetramethylammonium tribromide at 30°. Besides this discrepancy the plots used for the calculation of the rate constants when tetrabutylammonium tribromide was used curved upward as the reaction progressed while the analogous plots for tetramethylammonium tribromide curved downward somewhat. In fact the reaction of tetramethylammonium tribromide appeared[3] to be somewhere between first and second order with respect to tribromide ion. The most consistent values for the rate constant were obtained when the reaction was assumed to be three-halves order with respect to tribromide ion. In the present investigation these results for tetramethylammonium tribromide were verified.

TABLE II

SUMMARY OF KINETIC DATA FOR THE REACTION OF CROTONIC ACID WITH TETRABUTYLAMMONIUM TRIBROMIDE IN ETHYLENE CHLORIDE AT 30°

Acid	Concn. $M \times 10^{-2}$ Bu_4NBr_3	$k_3 \times 10^5$, l. mole^{-1} sec.$^{-1}$	Acid	Concn., $M \times 10^{-2}$ Bu_4NBr_3	$k_3 \times 10^5$, l. mole^{-1} sec.$^{-1}$
0.50	5.00	7.6	2.50	5.00	6.7
0.50	5.00	6.9	5.00	2.40	6.2
1.00	1.00	6.5	10.00	2.40	6.0
1.00	1.00	7.7	10.00	4.89	6.5
1.00	2.50	6.8	20.00	2.40	5.7
1.00	5.00	7.0	20.00	4.84	7.3
2.50	2.40	6.5		Average[a]	6.7 ± 0.4

[a] The measure of the precision sets the 95% confidence limits of the average.

On the basis of equation 5 the behavior of tetramethylammonium tribromide can be explained. Since tetramethylammonium bromide precipitated when the reaction started, the concentration of bromide was kept at such a low, constant value that the first term of equation 5 contributed appreciably to the rate law as shown in equation 6 where K_1 is the equilibrium constant of the reaction given in equation 1. The approximate form given in equation 7 was used over relatively small changes in concentration of tribromide to calculate k' for the data available from the present investigation as well as the earlier investigation.[3] The values of k' obtained at various concentrations of tribromide are shown in Fig. 1 where they are compared with the parabola calculated from equation 8.

$$-\frac{dE}{dt} = \frac{k_2K_1}{(R_4NBr)}(E)(R_4NBr_3)^2 + k_3(E)(R_4NBr_3) \quad (6)$$

$$-dE/dt = k'(E) \quad (7)$$

$$k' = \frac{k_2K_1}{(R_4NBr)}(R_4NBr_3)^2 + k_3(R_4NBr_3) \quad (8)$$

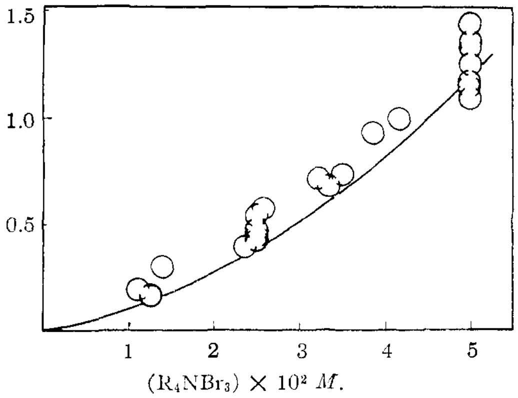

Fig. 1.—The variation of k' of equation 7 with the concentration of tetramethylammonium tribromide in ethylene chloride at 30°. The curve is that calculated from equation 8 with numerical values: $K_1 = 1.25 \times 10^{-6}$ mole (footnote 3); $k_2 = 9.9 \times 10^{-2}$ l.^{2} mole^{-2} sec.$^{-1}$; $k_3 = 6.7 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$; and $(R_4NBr) = 3.6 \times 10^{-5}$ mole l.$^{-1}$.

The curve upward which was observed in the plots used for calculating the rate constant when tetrabutylammonium tribromide was used with crotonic acid is consistent with equation 5 also. Because of the low bromine concentrations present the first term would be negligible. With tetrabutylammonium bromide initially present, values for k_3' were calculated according to equation 9. As more and more bromide was added initially a concentration (*ca.* 0.05 *M*) was reached above which the plots used to calculate k_3' were essentially linear, and the values obtained were somewhat more precise. These results would be expected if the upward curve in the plots obtained in the absence of added bromide was caused by the development of bromide catalysis as the reaction progressed. The apparent second-order constant, k_3', obtained when excess tetrabutylammonium bromide was present are given in Table III. The catalytic effect passed through a maximum at about 0.08 *M* bromide. An inhibition brought about by increasing salt concentration appeared to be competing with the catalysis. A similar but less effective catalysis by tetrabutylammonium nitrate also was observed.

TABLE III

SUMMARY OF KINETIC DATA FOR THE REACTION OF CROTONIC ACID WITH TETRABUTYLAMMONIUM TRIBROMIDE IN THE PRESENCE OF TETRABUTYLAMMONIUM BROMIDE IN ETHYLENE CHLORIDE AT 30°

Acid	Concentrations, $M \times 10^2$ Bu_4NBr_3	Bu_4NBr	$k_3 \times 10^4$, l. mole^{-1} sec.$^{-1}$
2.50	2.50	2.50	1.17
5.00	2.48	2.50	1.48
2.50	5.00	2.50	1.70
5.00	5.00	5.00	1.58
2.50	2.50	6.00	1.60
2.50	2.50	8.00	2.08
2.50	2.50	10.0	1.85
1.00	2.50	17.9	1.60[a]
2.50	2.50	20.0	1.41
2.50	2.50	31.8	1.20
2.50	2.50	5.02[b]	1.18
2.50	2.50	13.3[b]	1.19
2.50	2.50	10.0[b]	1.03
2.50	2.50	10.0[c]	1.40

[a] An independent run gave exactly the same result. [b] Tetrabutylammonium nitrate was used in place of the bromide. [c] A mixture of half tetrabutylammonium nitrate and tetrabutylammonium bromide was used.

$$-d(E)/dt = k_3'(E)(R_4NBr_3) \quad (9)$$

$$k_3' = k_3 + k_4(R_4NBr) \quad (10)$$

The values of k_3' were plotted against the initial concentrations of bromide. The slope at zero concentration was estimated on the basis of equation 10, to give an approximate value of 2×10^{-3} l.^{2} mole^{-2} sec.$^{-1}$ for k_4 at 30°.

Values for the rate constants k_2 and k_3 were obtained at 10, 20, 30 and 40°. These results are summarized in Table IV along with the energies of activation and entropies of activation calculated from them. The relatively high negative values obtained for the entropies of activation are consistent with a highly ordered transition state for each reaction.

TABLE IV

SUMMARY OF THE RATE CONSTANTS AT VARIOUS TEMPERATURES AND OF THE ENTHALPIES AND ENTROPIES OF ACTIVATION

	Temp., °C.	Equation 2[a]	Equation 3[b]
k^c	10	$(2.6 \pm 0.2)10^{-2}$	$(0.86 \pm 0.01)10^{-5}$
k^c	20	$(4.3 \pm .4)10^{-2}$	$(2.2 \pm .1)10^{-5}$
k^c	30	$(9.9 \pm .3)10^{-2}$	$(6.7 \pm .2)10^{-5}$
k^c	40	$(13.8 \pm 1.2)10^{-2}$	$(14.3 \pm .4)10^{-5}$
$\Delta H^{\pm}$, kcal.	..	10.6	16.1
$\Delta S^{\pm}$, e.u.	30	−28.2	−24.6

[a] The units of k_2 are l.^{2} mole^{-2} sec.^{1}. [b] The units of k_3 are l. mole^{-1} sec.$^{-1}$. [c] The measure of the precision is the standard deviation of the average values used.

Such actions of quaternary ammonium tribromide as a nucleophilic agent which have been assumed in the explanations used here have been suggested[9] as possible for carbon–carbon double bonds substituted with electron-withdrawing groups. Kinetic data for the addition of bromine to such unsaturated compounds in the presence of halide ions have been interpreted as showing that either a polyhalide ion is involved in a nucleophilic attack on the double bond[10] or a halide ion and bromine are involved, in a concerted attack.[10,11] In no case reported has this type of trihalide–olefin interaction been as well defined as it is in the present case. Of course, the reaction given in equation 3 might just as well have been interpreted as a concerted action of bromine and bromide on crotonic acid as far as the kinetic results were concerned. This type of behavior of polyhalides is to be contrasted with that observed[12] for tribromide ion which reacted much more slowly than bromine in the addition of *trans*-stilbene in methanol.

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[9] P. B. D. de la Mare, *Quart. Revs.*, **3**, 126 (1949).

[10] P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 2838 (1950), and the references which they give.

[11] K. Nozaki and R. A. Ogg, Jr., THIS JOURNAL, **64**, 697, 704, 709 (1942).

[12] P. D. Bartlett and D. S. Tarbell, *ibid.*, **58**, 466 (1936).

IOWA CITY, IOWA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF COMPAGNIE PARENTO, INC.]

Preparation of α,β-Unsaturated Aldehyde Dimethyl Acetals and their Free Aldehydes

BY PAUL Z. BEDOUKIAN

RECEIVED JULY 11, 1956

Elimination of hydrogen bromide from the α-bromoacetals of the fatty aldehydes (C-7 to C-12) gave the acetals of the corresponding α,β-unsaturated aldehydes. The free aldehydes were obtained from the acetals by acid hydrolysis. A study was made of the odor properties of these compounds. The physical properties of the enol acetates and bromoaldehyde dimethyl acetals of the saturated aldehydes are reported.

This investigation was carried out for the purpose of determining the odor characteristics of the acetals of α,β-unsaturated fatty aldehydes (C-7 to C-12) as well as those of the free aldehydes. The saturated fatty aldehydes of this series play an important role in perfume compositions and are extensively used in perfumes, cosmetics and soaps.

The preparation of α,β-unsaturated aldehydes has presented considerable difficulties and involved indirect and lengthy procedures. The present method, although it does not give high overall yields, is very convenient and is generally applicable to the conversion of any saturated aldehyde, possessing an α- and β-hydrogen, to its α,β-unsaturated analog.

The following reactions are used in preparing α,β-unsaturated aldehydes: The saturated aldehyde is converted to the enol acetate and then brominated in carbon tetrachloride. On adding methanol to the brominated mixture, the dimethyl acetal of α-bromoaldehyde is obtained in good yields. The latter on treatment with potassium hydroxide in butanol gives the unsaturated acetal which is converted to the free α,β-unsaturated aldehyde by acid hydrolysis.

The preparation of the α-bromoaldehyde dimethyl acetal of heptaldehyde has been reported.[1]

$$\begin{tikzcd}
\mathrm{RCH_2CH_2CHO + Ac_2O(KAc)} \arrow[r] & \mathrm{RCH_2CH{=}CHOCOCH_3} \arrow[d, "\mathrm{Br_2}\ (\text{in } \mathrm{CCl_4})"] \\
\mathrm{RCH_2CHBrCH(OMe)_2} \arrow[d, "\mathrm{KOH}\ (\text{in } \mathrm{BuOH})"] & \mathrm{RCH_2CHBrCHBrOCOCH_3} \arrow[l, "\mathrm{MeOH}"'] \\
\mathrm{RCH{=}CHCH(OMe)_2} \arrow[r, "\text{acid}"] & \mathrm{RCH{=}CHCHO}
\end{tikzcd}$$

Identical procedures were used in the preparation of the bromoacetals of higher aldehydes.

None of the acetals of the α,β-unsaturated aldehydes (C-7 to C-12) has been reported previously. All of the free aldehydes have been prepared by various methods but no comments have been made on their odor properties.

2-Heptenal has been prepared by the chromic

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[1] P. Z. Bedoukian, THIS JOURNAL, **66**, 1325 (1944); P. Z. Bedoukian, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 127.