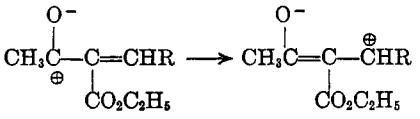
obtained by Knoevenagel condensation of crotonaldehyde and benzaldehyde with acetoacetic ester yielded only polymeric materials instead of the anticipated sorbic and cinnamic esters. It is suggested that allylic resonance may account for the failure of such esters to undergo the cleavage:



EXPERIMENTAL

General procedure. The same procedure was used for all compounds shown in Table I, except for variations in time required for completion of the reaction. Preparative details are given only for the alcoholysis of ethyl α-allylacetoacetate to *ethyl 4-pentenoate:* To a solution of 1.5 g. (0.065 g.-atom) of oxide-free sodium in 81 g. (1.76 moles) of absolute ethanol in a 500-ml. round bottomed flask was added 122 g. (0.72 mole) of freshly distilled ethyl α-allylacetoacetate. The resulting light yellow solution was refluxed under a 5-ft. distilling column packed with glass helices and fitted with an automatic liquid-divider head. When the vapor temperature at the column head had dropped from 78° to 72° (the boiling point of the ethanol–ethyl acetate azeotrope), slow distillation was begun and the take-off ratio was adjusted to maintain the vapor temperature at 72–73°. After the calculated amount of azeotrope had been collected (22 hr.), the distillation was stopped and the excess ethanol was removed on the water bath. The flask contents were cooled, transferred to a separatory funnel, and washed with 100 ml. of cold 5% sulfuric acid. After separation of the ester layer the aqueous portion was washed twice with 25-ml. portions of ether, and the ether extracts were combined with the main portion of the ester. The resulting ether solution was washed successively with 50 ml. of water, 50 ml. of 2% sodium bicarbonate solution, and 50 ml. of water, and dried over anhydrous magnesium sulfate. The dry ethereal solution was filtered from the drying agent, the ether was removed and the product, ethyl 4-pentenoate, was distilled at ordinary pressure and collected at 142–144°; yield, 81 g. (88%). The still residue consisted mainly of unchanged ethyl α-allylacetoacetate.

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Allylic Bromination by *N*-Bromo-*t*-butylamine[1]

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Currently allylic bromination is most frequently accomplished through the use of *N*-bromosuccinimide.[2] We have discovered that *N*-bromo-*t*-butylamine also reacts with olefins to give bromination at the allylic position. The yields in the *N*-bromo-*t*-butylamine reaction under certain conditions are comparable to those of the *N*-bromosuccinimide reaction.[2]

In the study of the allylic brominating ability of *N*-bromo-*t*-butylamine, cyclohexene was used as the olefin, the concentrations of the reagents and the type of solvent were varied, and the effect of azobisisobutyronitrile (AIBN) was studied. Light seemed to be inferior to AIBN as an initiator, and therefore was not investigated further. Our results appear in Table I.

TABLE I

THE EFFECTS OF VARIABLES ON THE REACTION OF *N*-BROMO-*t*-BUTYLAMINE AS AN ALLYLIC BROMINATING AGENT

Solvent	Ratio of Moles *N*-Bromo-*t*-butylamine/ Moles Olefin/ Ml. Solvent	Catalyst or Initiator	Time (Hr.)	Yield of 3-Bromocyclohexene %[a]
Carbon tetrachloride	1/1.5/750	None	6	none[b]
Isohexane	1/1.5/750	Light[c]	6.5	18[d]
Isohexane	1/1.5/750	0.2 g. AIBN	3	23
Isohexane	1/2/750	1 g. AIBN	5.5	38
Isohexane	1/3/750	1 g. AIBN	5	37
Isohexane	1/3/375	1 g. AIBN	3	59
Isohexane	1/3/187.5	1 g. AIBN	1.5	31
Isohexane	1/1.5/375	1 g. AIBN	5	40
Benzene	1/3/750	1 g. AIBN	5	30
Benzene	1/3/375	1 g. AIBN	5	42
Benzene	3/1/750	1 g. AIBN	5	17[e]

[a] Yield of 3-bromocyclohexene based on *N*-bromo-*t*-butylamine. [b] There appeared to be a competing reaction involving the carbon tetrachloride. [c] Light was supplied by sun lamp. Light seemed to favor the formation of *t*-butylamine hydrobromide. [d] All yields of 3-bromocyclohexene were corrected for the amount of product lost in working up the sample, using a technique similar to that of H. J. Dauben, Jr., and L. L. McCoy.[2] [e] 22% 3,6-Dibromocyclohexene was produced; collected 95–100° (10 mm.).

EXPERIMENTAL

Preparation of N-bromo-t-butylamine.[3] *t*-Butylamine, 0.2 mole, (freshly distilled) was mixed with 20 ml. of 10*N* sodium hydroxide and 100 ml. of water. Bromine, 0.2 mole, was added dropwise over a period of 50–70 min. The reaction was kept at 0–5° and was stirred constantly. After the bromine was added, the sample was extracted with ether, and the ether layer dried over magnesium sulfate. The ether then was removed by means of an aspirator. The *N*-bromo-*t*-butylamine remained in almost quantitative yield, about 30 g. It is a deep red-orange liquid with a strong unpleasant odor. It should be prepared immediately before use since it decomposes on standing with the formation of *t*-butylamine hydrobromide, a white crystalline solid.

(1) This work was supported by an undergraduate research grant (G-15672) from the National Science Foundation.

(2) See H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, 81, 4863 (1959).

(3) See N. Kijner, *J. prakt. Chem.*, 172, 64 (1901).

Bromination of cyclohexene. Cyclohexene, solvent, AIBN (when used), and *N*-bromo-*t*-butylamine were mixed in that order and in the ratios given in Table I. (About 0.16 mole of *N*-bromo-*t*-butylamine was used in most runs.) The mixture was distilled at a reflux ratio of about 1:5 until a negative starch–iodide paper test for *N*-bromoamine was obtained. This was done to remove the *t*-butylamine as it was formed. Additional solvent was added at intervals to keep the volume of the reaction mixture approximately the same. Varying amounts of *t*-butylamine hydrobromide were formed in the reaction, but no quantitative measurements were made of it. After refluxing, the solid *t*-butylamine hydrobromide was filtered off, and the liquid was washed first with 10*N* sodium hydroxide and then with 6*N* hydrochloric acid. The nonaqueous layer then was dried and distilled, the 3-bromocyclohexene being collected at 48–51° at 10 mm. Further confirmation of the structure of the product was obtained through NMR and infrared analysis. The NMR spectrum had peaks at 4.25 τ (2 vinyl protons), 5.32 τ (allylic proton on brominated carbon), and a broad unresolved peak around 7.9 τ (other protons).

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A Synthetic Procedure for Secondary Bromides from Alcohols

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In connection with other researches in these laboratories we desired to prepare certain substituted cyclopentyl bromides from the corresponding alcohols. Several workers have reported that halogenation of secondary alcohols with "conventional" reagents (PX_3, HX) results in rearrangement of the product.[2,3] As the rearranging species is evidently a carbonium ion, an effort was made by Pines, Rudin, and Ipatieff to employ a bimolecular displacement of the *p*-toluenesulfonate ester of the alcohol with bromide ion.[4] The reaction conditions employed in their research resulted in nonrearranged bromides but were, by the admission of the authors, not synthetically feasible.

By the use of a homogeneous system consisting of the *p*-toluenesulfonate ester of the requisite alcohol, aqueous dimethylformamide, and calcium bromide at room temperature, we have been able to prepare secondary bromides in 50–65% yields. Such conditions are expected to result in non-rearranged bromides.

The course of the reaction with this system may be easily followed by quenching a 1-ml. aliquot of the reaction mixture in 50 ml. of water, extracting the water with three 50-ml. portions of ether, removing the last traces of ether on a steam bath, and titrating the residual bromide ion with standard silver nitrate in the presence of fifteen drops of Dichlorofluorescein test solution and 1 ml. of 2% dextrin solution.

Precautions must be taken to prevent the interaction of the alkyl bromide produced in the reaction and the dimethylformamide solvent. This interaction has been previously studied.[5] The reaction between the alkyl bromide and dimethylformamide is sufficiently slow at room temperature not to interfere with the synthesis of the halide; however, attempted distillation of a mixture of dimethylformamide with an alkyl bromide results in extensive decomposition. The work-up procedure results in a solution of the alkyl bromide with traces of dimethylformamide in petroleum ether; the dimethylformamide may be readily removed by passing this solution through alumina.

As would be expected, the procedure is not applicable to alcohols sterically hindered to nucleophilic attack. Thus 2-methylcyclopentyl bromide was obtained only in poor yields while 3-methyl- or 3-ethylcyclopentyl bromide was obtained in good yields.

EXPERIMENTAL[6]

Cyclopentyl bromide. Although rearrangement of this compound is undetectable, it was prepared in a study of solvents and reaction conditions before the application of these conditions to various substituted cyclopentyl bromides. One-fourth mole (21.5 g.) of cyclopentanol was esterified with *p*-toluenesulfonyl chloride according to the procedure of Streitweiser[7] except that the product was extracted with ether, the combined extracts were dried, and the solvent was removed under reduced pressure. The crude ester was then stirred at room temperature for 12 hr. with a solution of 120 g. of calcium bromide (N.F.) in 600 ml. of dimethylformamide containing 1.5% water. The reaction mixture was then poured into ice water, the product which separated was removed, and the aqueous layer was extracted with 125 ml. of petroleum ether. The combined extract and product, after drying over potassium carbonate, was then passed through a 50 × 2 cm. column containing *ca.* 100 g. of alumina which had been wetted with petroleum ether. The column was then eluted with 100 ml. of petroleum ether. The combined eluates were distilled to yield 19.0 g. (51.0%) of cyclopentyl bromide boiling at 134.0–136.0° and having n_D^{23} 1.4863; reported[8] boiling at 135–136° and having n_D^{20} 1.4882.

3-Methylcyclopentyl bromide. In a similar procedure 0.7 mole (70.0 g.) of 3-methylcyclopentanol was converted into 73.0 g. (64.0%) of 3-methylcyclopentyl bromide boiling at 146.0–151.0° and having n_D^{20} 1.4762.

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(3) F. C. Whitmore and F. A. Kornatz, *J. Am. Chem. Soc.*, 60, 2536 (1938).

(4) H. Pines, A. Rudin, and V. N Ipatieff, *J. Am. Chem. Soc.*, 74, 4063 (1952).

(5) N. Kornblum and R. K. Blackwood, *J. Am. Chem. Soc.*, 78, 4037 (1956).

(6) All boiling points are uncorrected. Microanalyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium in Max-Planck Institut, Mülheim (Ruhr), Germany.

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