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).

DEPARTMENT OF CHEMISTRY
EMORY UNIVERSITY
ATLANTA 22, GA.

A Synthetic Procedure for Secondary Bromides from Alcohols

GLENN L. JENKINS AND JAMES C. KELLETT, JR.[1]

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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.

(1) Present address: School of Pharmacy, University of North Carolina, Chapel Hill, N. C.

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Anal. Calcd. for $C_8H_{12}Br$: C, 44.2; H, 6.8; Br, 49.0. Found: C, 44.8; H, 6.9; Br, 48.2.

3-Ethylcyclopentyl bromide. In a similar procedure 0.62 mole (71.0 g.) of 3-ethylcyclopentanol was converted into 65.0 g. (59.3%) of 3-ethylcyclopentyl bromide boiling at 172.0–177.0° and having n_D^{24} 1.4780.

Anal. Calcd. for $C_7H_{14}Br$: C, 47.5; H, 7.4; Br, 45.1. Found: C, 48.6; H, 7.5; Br, 45.0.

2-Methylcyclopentyl bromide. 1-Methylcyclopentanol, 1.19 moles (119.0 g.), was treated with equivalent quantities of the reagents described in the preceding experiment. The displacement was allowed to proceed for 24 hours. Workup yielded 36.0 g. (18.6%) of product boiling at 45.5–49.5° at 20 mm. and having n_D^{25} 1.4757; reported[9] boiling at 150–151°.

SCHOOL OF PHARMACY
PURDUE UNIVERSITY
WEST LAFAYETTE, IND.

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Reaction of Ditolylethane with Gallium Bromide–Hydrogen Bromide in Benzene

A. STREITWIESER, JR., AND W. J. DOWNS

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On the basis of stereochemical and isotope tracer experiments a new mechanism has recently been proposed for the Lewis acid catalyzed transalkylation of ethylbenzene in benzene.[1] In this mechanism a small amount of oxidation to α-phenethyl cation initiates a carbonium ion chain process: The α-phenethyl cation alkylates benzene to form 1,1-diphenylethane, which is rapidly cleaved by acid under the experimental conditions to regenerate an α-phenethyl cation and benzene in which the two aromatic rings may have been interchanged. This mechanism has an obvious extension to related disproportionation reactions; it has the further necessary corollary that 1,1-diarylethanes react rapidly under these conditions.

To test this corollary, a solution of 1,1-di-*p*-tolylethane in benzene was treated with gallium bromide and hydrogen bromide at 50°. Aliquots of the mixture were examined at intervals by v.p.c. analysis after quenching with water. Even by the time the first aliquot was removed (15 seconds), the ditolylethane was converted completely to 1,1-diphenylethane. Toluene and a lesser amount of ethylbenzene were also identified as products. Hence, the reaction

$$Ar_2CHCH_3 + 2\ C_6H_6 \xrightleftharpoons[GaBr_3]{HBr} (C_6H_5)_2CHCH_3 + 2\ ArH$$

is orders of magnitude faster than the transalkylation studied earlier and is an allowable sequence as required in the proposed reaction mechanism. The ethylbenzene also produced in the experiment undoubtedly arises by hydride transfer to the α-phenethyl cation with concommitant formation of other by-products. Small amounts of other compounds were found by v.p.c. but could not be identified.

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EXPERIMENTAL

The experimental technique was similar to that used in the earlier report.[1] A stock solution was prepared from 8.5 g. of sublimed gallium bromide and 101 g. of sodium-dried benzene and stored in a flask carrying a side arm closed with a serum cap. Fifty milliliters of the stock solution was transferred with a syringe to a one necked flask closed with a stopcock and a serum cap. Hydrogen bromide (0.49 g.) was admitted with a syringe needle and the flask was brought to temperature in a 50° thermostat. 1,1-Di-*p*-tolylethane[2] (0.50 ml.) was syringed in and 10 ml. aliquots were removed after 15 sec., 5 min., and 1.5 hr. Each aliquot was quenched with water and the organic layer was separated, dried, and examined by v.p.c. (70°, silicone). In each aliquot, the toluene peak was 1% of the benzene peak; ethylbenzene increased from 1/4 to 1/2% during the run. A sample analyzed in the v.p.c. column at 200° showed six additional peaks, the largest of which was 1,1-diphenylethane. The remaining peaks were small and could not be identified; however, 1,1-ditolylethane was found to be absent.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIF.

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A Reappraisal Concerning the Variable Character of the Sulfone Group[1]

CAL Y. MEYERS, GIANFRANCO MORETTI, AND LILLIA MAIOLI

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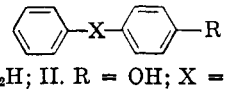
Szmant and Suld[2] reported that, in benzoic acids of type I, a 4-NO_2 group *decreased* the acidity of the parent sulfone derivative but increased that of the corresponding sulfoxide and sulfide derivative, respectively. However, similar substitution of the phenolic sulfone (II. X = SO_2) increased its acidity. In both sulfone series a 4-NH_2 group decreased the acidity, respectively.



I. R = CO_2H; II. R = OH; X = SO_2, SO, S

While it was noted that the decreased acidity of the 4-NO_2-phenylsulfonylbenzoic acid was "entirely unexpected on the basis of additive inductive effects," the combined data were utilized in suggesting that the —SO_2— group varies in character depending upon the electronic nature of the

(1) This study is part of a series dealing with the nature of the sulfone group. The authors are grateful to the Petroleum Research Fund of the American Chemical Society whose grants are making these studies possible.

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