Anal. Calcd. for $C_6H_{12}Br$: 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

Received July 17, 1961

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

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

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.

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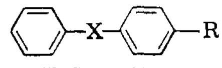
A Reappraisal Concerning the Variable Character of the Sulfone Group[1]

Cal Y. Meyers, Gianfranco Moretti, and Lillia Maioli

Received August 2, 1961

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

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(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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