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Aromatic Substitution. XIX.[1] Friedel–Crafts Isopropylation and *t*-Butylation of Halobenzenes

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The isopropylation and *t*-butylation of halobenzenes with alkyl halides and olefins were studied under the conditions previously described for benzene and the methylbenzenes. Relative reactivities compared with benzene and isomer distributions were determined in competitive experiments using gas chromatography.

Introduction

In previous papers of this series[1,2] the Friedel–Crafts isopropylation and *t*-butylation of benzene and methylbenzenes were investigated with alkyl bromides and olefins. This work has now been extended to the isopropylation and *t*-butylation of halobenzenes.

Results and Discussion

Competitive $AlCl_3 \cdot CH_3NO_2$, $FeCl_3 \cdot CH_3NO_2$, and $SnCl_4$ catalyzed isopropylation and *t*-butylation of benzene and halobenzenes with isopropyl bromide, *t*-butyl bromide, propylene, and isobutylene were carried out in nitromethane solution at 25°. Product compositions were analyzed by gas–liquid chromatography using Golay type capillary columns. Under the experimental conditions employed, identical with those used in previous work in connection with alkylation of benzene and methylbenzenes, no di- or higher alkylation of halobenzenes was observed. Using $AlCl_3$ as catalyst in competitive experiments with benzene sometimes substantial amounts (up to 25% of monoalkylate) of di-*t*-butylbenzene was formed, probably at least partly by disproportionation of *t*-butylbenzene. Relative rate data therefore have to be corrected, taking into account the amount of dialkylation of benzene. Using stannic chloride as catalyst the amount of dialkylation is small enough (generally less than 3%) to be neglected. From the areas of individual peaks in the gas chromatograms mole % figures were calculated for each product after first determining the individual response data.

The observed reactivities of the halobenzenes relative to that of benzene, together with the isomer distributions of the monoalkylated products, are summarized in Tables I–VI. (All data reported represent, as in previous work, the average of at least three parallel experiments.)

TABLE I

$AlCl_3 \cdot CH_3NO_2$ CATALYZED ISOPROPYLATION OF BENZENE AND HALOBENZENES WITH ISOPROPYL BROMIDE IN NITROMETHANE SOLUTION AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Isomer distribution, % ortho	meta	para
Benzene	1.00			
Fluoro-	0.23	41.8	1.9	56.3
Chloro-	.10	49.8	7.9	42.3
Bromo-	.08	51.4	11.3	37.3

TABLE II

$FeCl_3 \cdot CH_3NO_2$ CATALYZED ISOPROPYLATION OF BENZENE AND HALOBENZENES WITH ISOPROPYL BROMIDE IN NITROMETHANE SOLUTION AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Isomer distribution, % ortho	meta	para
Benzene	1.00			
Fluoro-	0.28	40.8	2.8	56.4
Chloro-	.13	51.4	8.1	40.5
Bromo-	.11	51.8	11.6	36.6

TABLE III

$AlCl_3 \cdot CH_3NO_2$ CATALYZED ISOPROPYLATION OF BENZENE AND HALOBENZENES WITH PROPYLENE IN NITROMETHANE SOLUTION AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Isomer distribution, % ortho	meta	para
Benzene	1.00			
Fluoro-	0.23	41.3	2.1	56.4
Chloro-	.11	53.9	5.1	41.0
Bromo-	.07	55.4	8.6	36.0

TABLE IV

$AlCl_3 \cdot CH_3NO_2$ CATALYZED *t*-BUTYLATION OF BENZENE AND HALOBENZENES WITH *t*-BUTYL BROMIDE IN NITROMETHANE AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Isomer distribution, % ortho	meta	para
Benzene	1.00			
Fluoro-	0.16	3.6	0.1	96.3
Chloro-	.03		5.5	94.5
Bromo-	.02		3.0	97.0

TABLE V

$SnCl_4$ CATALYZED *t*-BUTYLATION OF BENZENE AND HALOBENZENES WITH *t*-BUTYL BROMIDE IN NITROMETHANE AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Isomer distribution, % ortho	meta	para
Benzene	1.0			
Fluoro-	0.12	3.6	0.1	96.3
Chloro-	.07		5.0	95.0
Bromo-	.02			100.0

TABLE VI

$AlCl_3 \cdot CH_3NO_2$ CATALYZED *t*-BUTYLATION OF BENZENE AND HALOBENZENES WITH ISOBUTYLENE IN NITROMETHANE AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Isomer distribution, % ortho	meta	para
Benzene	1.00			
Fluoro-	0.19	1.8	0.1	98.1
Chloro-	.06		5.5	94.5
Bromo-	.03			100.0

The accuracy of the gas–liquid chromatographic method was found to be better than ±5 relative per cent, based on analyses of mixtures of known compositions. Investigation of the concentration variation of benzene and halobenzenes in competitive experiments, as described in previous work, showed that the relative ratios remained practically unchanged, if first-order dependence on the aromatic substrates is accepted. Thus the method of competitive rate determination can be applied to the present systems.

It is not possible to state with certainty whether the observed isomer distributions (and relative rates) were obtained under entirely nonisomerizing conditions, from the present experimental results. The amount of *m*-isomers is higher than the benzylation[3] or nitration[4] of halobenzenes. It is, however, suggested, on the basis of our experimental data, that even if isomerization cannot entirely be excluded, it cannot be signifi-

(1) Part XVIII: *J. Am. Chem. Soc.*, **86**, 1060 (1964).

(2) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuck, part XVI, *ibid.*, **86**, 1046 (1964).

(3) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1695 (1962).

(4) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **83**, 4851 (1961).

cant. $AlCl_3 \cdot CH_3NO_2$ was replaced in a number of experiments with milder catalysts as $FeCl_3$ or $SnCl_4$, without effecting any significant changes in the isomer distributions. As example, Tables II and V show relative reactivities and isomer distributions obtained in competitive isopropylation of benzene and halobenzenes replacing $AlCl_3$ with $FeCl_3$, and *t*-butylations using $SnCl_4$ as catalyst, but keeping reaction conditions otherwise identical, in nitromethane solution. Comparison of these results with those using $AlCl_3 \cdot CH_3NO_2$ as catalyst indicate very little difference, suggesting strongly that $AlCl_3 \cdot CH_3NO_2$ probably does not cause significant isomerization. The only cases in which isomerization seems to have affected the isomer distributions is that of the bromocumenes (bromo-*t*-butylbenzenes) and to a lesser degree, the chlorocumenes. The relatively large amount of *m*-isomer formed in the $AlCl_3$ and $FeCl_3$ catalyzed isopropylations of bromobenzene with isopropyl bromide (11.3 and 11.6%, respectively) and in similar reactions of chlorobenzene (7.9 and 8.1%) are probably due to partial isomerization, as the related isopropylations with propylene show decreased amounts of *m*-isomers (5.1 and 8.6%). The aluminum chloride catalyzed isomerization of halocumenes and halo-*t*-butylbenzenes results in equilibrium mixtures containing the *m*-isomer in excess of 60%.[5]

A comparison of the relative reactivities of benzene and halobenzenes in isopropylation and *t*-butylation shows that *t*-butylation produces higher substrate selectivity than isopropylation, both giving, however, preferential *ortho–para* directions (high positional selectivity), as is the case with isopropylation and *t*-butylation of methylbenzenes.

The observed relative reactivities of halobenzenes in the case of isopropylations show good agreement with relative stabilities of complexes of halobenzenes with π-acids and also with previously established reactivities in nitration with $NO_2^+BF_4^-$[4] and benzylations with benzyl chloride.[3] Less correlation is observed in the case of *t*-butylations.

Experimental

The halobenzenes, alkyl halides, olefins, as well as the aluminum chloride, ferric chloride, and stannic chloride used were commercially available chemicals of highest purity, purified if necessary by standard methods. The isomeric halocumenes and halo-*t*-butylbenzenes, all previously reported with the exception of *o*- and *m*-fluorocumene and *m*-fluoro-*t*-butylbenzene, were available in this laboratory, prepared by known methods. They were purified and analyzed by gas–liquid chromatography and infrared spectroscopy.

***o*-Fluorocumene** was prepared from *o*-isopropylaniline (available through reduction of *o*-nitrocumene[6]) by the Schiemann reaction.[7] The intermediate *o*-isopropylphenyldiazonium tetrafluoroborate was obtained from the aniline with $NO^+BF_4^-$, according to Wannagat and Hohlstein.[8] $o\text{-}FC_6H_4CH(CH_3)_2$ had b.p. 148–150° (distillation at atmospheric pressure results in some decomposition and the compound is therefore better distilled under vacuum). *Anal.* Calcd. for $C_9H_{11}F$: C, 78.30; H, 7.94; F, 13.76. Found C, 78.48; H, 8.02; F, 13.5.

***m*-Fluorocumene** was prepared from *m*-isopropylaniline according to the preparation of the *o*-isomer, b.p. 151–152°. *Anal.* Found for $C_9H_{11}F$: C, 78.45; H, 7.95; F, 13.6.

***m*-Fluoro-*t*-butylbenzene** was prepared from *m*-*t*-butylaniline (obtained through reduction of *m*-nitro-*t*-butylbenzene[5]) by the Schiemann reaction, b.p. 170–172°. *Anal.* Calcd. for $C_{10}H_{13}F$: C, 78.95; H, 8.55; F, 12.5. Found: C, 79.18; H, 8.42; F, 12.4.

***p*-Fluoro-*t*-butylbenzene** was prepared from *p*-*t*-butylaniline according to the preparation of the *m*-isomer, b.p. 173–175°. *Anal.* Found for $C_{10}H_{13}F$: C, 78.91; H, 8.49; F, 12.6.

Competitive isopropylation and *t*-butylation of halobenzenes and benzene were carried out in the following way: Aluminum chloride (ferric chloride, stannic chloride), 0.05 mole, was dissolved in 50 g. of nitromethane. To this solution was added 0.25 mole each of benzene and halobenzene. The stirred reaction mixture, protected from atmospheric moisture, was then placed in a reaction flask (equipped with thermometer, reflux condenser, and dropping funnel or gas inlet tube) in a constant temperature bath (25 ± 0.1°) and a solution of 0.05 mole of alkyl bromide (isopropyl or *t*-butyl) dissolved in 30 g. of nitromethane was added dropwise. The addition generally was completed in 10 min. and the reaction mixture was thereafter stirred for another 10 min. In the alkylation with olefins (propylene and isobutylene) 0.05 mole of the gaseous olefin was introduced into the stirred nitromethane solution of the substrates and catalyst at the same temperature. At the end of the reactions the mixtures were washed once with water, then three times with 5% sodium hydroxide solution to remove not only the by-product acid, but also nitromethane, followed by another water washing. The organic layer was separated, dried with calcium chloride, and analyzed by gas–liquid chromatography. As the separation of *t*-butylbenzene from *o*-*t*-butylfluorobenzene by gas–liquid chromatography was not complete, the benzene:fluorobenzene reactivity ratio could not directly be determined from *t*-butylation of benzene and fluorobenzene. In this case competitive butylations of chlorobenzene and fluorobenzene, as well as bromobenzene and fluorobenzene, were carried out and the fluorobenzene–benzene reactivity rate determined from these data, taking in account the chlorobenzene–benzene reactivities, determined in direct competitive butylations.

Analyses.—All analyses of isopropylations and *t*-butylations were carried out by gas–liquid chromatography on a Perkin–Elmer Model 154-D vapor fractometer equipped with Golay type capillary column (150 ft.) coated with polypropylene glycol and using a hydrogen flame ionization detector. Peak areas were obtained by the use of an electronic printing integrator. The generally used column conditions were: He carrier gas pressure 40 p.s.i.g., with characteristic retention times and temperatures given in Table VII.

TABLE VII

CHARACTERISTIC RETENTION TIMES OF HALOALKYLBENZENES ON CAPILLARY COLUMN

Compound	*T*, °C.	Retention times, min.	Compound	*T*, °C.	Retention times, min.
Fluorobenzene	40	9	*t*-Butylbenzene	60	26
Cumene	40	35.5		100	10.6
	110	9	*o*-Fluoro-	60	26.2
o-Fluoro-	40	37		100	10.6
m-Fluoro-	40	41.2	*m*-Fluoro-	60	29
p-Fluoro-	40	42.2	*p*-Fluoro-	60	30
o-Chloro-	110	14	*o*-Chloro-	100	23.2
m-Chloro-	110	15	*m*-Chloro-	100	22.2
p-Chloro-	110	16	*p*-Chloro-	100	24.4
o-Bromo-	110	20	*m*-Bromo-	100	35
m-Bromo-	110	22	*p*-Bromo-	100	40
p-Bromo-	110	24			

Relative response data were determined by running solutions of the respective pure haloalkylbenzene isomers and the alkylbenzene (cumene and *t*-butylbenzene, respectively) in benzene in the approximate ratios in which they occurred in the reaction mixtures, according to the method of Messner, Rosie, and Argabright.[9]

(5) G. A. Olah and M. W. Meyer, unpublished results, to be reported elsewhere.

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