

REACTIONS OF DIARYLBROMONIUM SALTS WITH SODIUM ALKOXIDES

Jacek J. Lubinkowski and William E. McEwen

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

(Received in USA 21 September 1972; received in UK for publication 23 October 1972)

Very high yields of alkyl aryl ethers have been obtained by reactions of diphenylbromonium and phenyl-*p*-tolylbromonium fluoroborates with sodium alkoxides in solutions in the corresponding alcohols at moderate temperatures. For example, the reaction of 2.5×10^{-4} mole of diphenylbromonium fluoroborate¹ with 3.5×10^{-4} mole of sodium ethoxide in 2 ml. of ethanol at 71° for 90 min. in the atmosphere gives phenetole in $98 \pm 2\%$ yield and benzene in only about 2.6% yield; bromobenzene is produced in 100% yield, and a trace amount of biphenyl is formed. These and data for additional experiments are presented in the Table of Results. By way of contrast, the reaction of diphenyliodonium fluoroborate with sodium ethoxide under the same reaction conditions gives phenetole (14%), benzene (68%) and iodobenzene (92%).² Thus, the diphenylbromonium salt is vastly superior to the diphenyliodonium salt as a phenylating reagent in the aromatic S_N process leading to ether.

In our previous studies of the reactions of sodium alkoxides with diphenyliodonium salts² (and also triarylsulfonium salts³) we demonstrated that benzene arises by a free radical chain reaction, while phenetole arises by an aromatic S_N reaction. The radical process can be suppressed to a considerable extent by the addition of an inhibitor to the reaction mixture, and 1,1-diphenylethylene has been found to be the most suitable additive of many that were tested. The data presented in the Table of Results indicate that the same holds true for the reactions of diarylbromonium salts with sodium alkoxides. Even though relatively little benzene is produced in the reaction of diphenylbromonium fluoroborate with sodium ethoxide, this amount is reduced markedly by the addition of one equivalent of 1,1-diphenylethylene to the reaction mixture. It is also evident that oxygen of the air serves to inhibit the radical reaction leading to benzene. The effect of the addition of 1,1-diphenylethylene is even more apparent in the reaction of diphenylbromonium fluoroborate with sodium isopropoxide in isopropyl alcohol, where phenyl isopropyl ether is produced in 83% yield

when the reaction is carried out in an argon atmosphere with no additive present, but in 92% yield when one equivalent of 1,1-diphenylethylene is present; the corresponding yields of benzene (and acetone) are 20% and 6.2%, respectively.⁴

Two major reasons can be given for the superiority of the diarylbromonium salts over the diaryliodonium salts in the aromatic S_N reactions with sodium alkoxides. In the first place, the undesirable radical chain reaction is presumed to be initiated by the attack of alkoxide ion on the positive halogen to give a tricovalent halogen intermediate, which subsequently dissociates into radicals.² The known⁵ greater ease of iodine over bromine in forming tricovalent compounds thus explains the greater propensity of the iodonium salts to undergo the radical chain reaction. Secondly, the more electronegative bromine gives rise to a larger bond dipole in the C-X bond than the less electronegative iodine. Thus, nucleophilic attack at the 1-carbon is favored in the diarylbromonium cation as against the diaryliodonium cation.

The fact that three times as much phenetole as *p*-methylphenetole is produced in the reaction of phenyl-*p*-tolylbromonium fluoroborate with sodium ethoxide constitutes valid additional evidence for the aromatic nucleophilic substitution process.⁶ In the case of the diarylbromonium salts, however, it does not seem to be reasonable to suspect that the displacement reaction takes place on a trivalent bromine intermediate, as proposed by Reutov and his co-workers for certain aromatic S_N reactions of diaryliodonium salts.⁷ It is also significant that the ratio of benzene to toluene produced in the phenyl-*p*-tolyliodonium case is nearly unity. This lack of discrimination in the formation of aryl radicals has been observed in various other radical reactions of diaryliodonium salts.^{2,8}

Although it is clear that diarylbromonium salts are superior to diaryliodonium salts as arylating agents in at least the one type of aromatic nucleophilic displacement reaction considered in this communication,⁹ the bromonium salts will not achieve a preeminent status in synthesis until a better method of preparation of the salts than the one presently available¹ is discovered. However, the results reported herein indicate that efforts to devise a better method of synthesis of the bromonium salts should be undertaken.

Acknowledgement. This work was supported in part by a grant from the National Science Foundation.

References and Footnotes

1. A. N. Nesmeyanov, T. P. Tolstaya and L. S. Isaeva, *Doklady Akad. Nauk S.S.S.R.*, 117, 996 (1957).
2. W. E. McEwen, J. J. Lubinkowski and J. W. Knapczyk, *Tetrahedron Lett.*, 3301 (1972).
3. C. C. Lai and W. E. McEwen, *Tetrahedron Lett.*, 3271 (1971).
4. The reaction of diphenyliodonium fluoroborate with sodium isopropoxide in an argon atmosphere under the same conditions gave phenyl isopropyl ether in 47% yield, the remainder of the available phenyl groups being converted mainly to benzene; when one equivalent of 1,1-diphenylethylene was added to the reaction mixture, the yield of ether rose to 69% and that of benzene dropped to 32%.²
5. J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry*, W. A. Benjamin, Inc., New York, N.Y., 1964, p. 853.
6. The reaction of phenyl-*p*-tolyliodonium fluoroborate with sodium ethoxide also gave about 3 times as much phenetole as *p*-methylphenetole.² The reaction of diphenyl-*p*-tolylsulfonium iodide with sodium ethoxide gave about 36 times as much phenetole as *p*-methylphenetole, which means an 18-fold rate spread when account is taken of the statistical factor.³ 2-Nitrobromobenzene undergoes an aromatic nucleophilic displacement reaction with piperidine about 7 times faster than does 2-nitro-4-methylbromobenzene: E. Berliner and L. C. Monash, *J. Amer. Chem. Soc.*, 74, 1574 (1952).
7. O. A. Reutov, O. A. Ptitsyana and G. G. Lyatiev, *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, 1631 (1967); *Doklady Akad. Nauk S.S.S.R.*, 182, 119 (1968).
8. M. C. Caserio, D. L. Glusker and J. D. Roberts, *J. Amer. Chem. Soc.*, 81, 336 (1959). F. M. Beringer and R. A. Falk have also made use of unsymmetrical diaryliodonium salts to assess the relative importance of ionic and radical pathways in reactions with a variety of nucleophiles: *J. Chem. Soc.*, 4442 (1964).
9. Nesmeyanov and his co-workers¹ have provided somewhat sketchy data to indicate that diphenylbromonium salts are quite reactive towards many common nucleophiles; cf. also A. N. Nesmeyanov, L. G. Makarova and T. P. Tolstaya, *Tetrahedron*, 1, 145 (1957).

Table of Results

Reaction of $(C_6H_5BrAr)^+BF_4^-$ (2.5×10^{-4} mole)
 with NaOR (3.5×10^{-4} mole) in ROH (2 ml.)
 for 90 min. in Sealed Tube

Ar	Atm.	Additive	RO ⁻	% Yield Products					
				C ₆ H ₆	C ₇ H ₈	C ₆ H ₅ OR	p-C ₇ H ₇ OR	C ₆ H ₅ Br	p-C ₇ H ₇ Br
p-Tolyl ^a	Argon	None	OEt ⁻	2.6	2.9	72	24	28	71
"	"	DPE ^b	"	0.6	0.4	76	26	27	74
" ^a	Air	None	"	1.9	1.8	75	24	27	73
"	"	DPE ^b	"	0.5	0.5	75	25	28	73
Phenyl ^c	Argon	None	"	5.9	---	96	--	100	--
"	"	DPE ^b	"	1.8	---	98	--	99	--
" ^c	Air	None	"	2.6	---	98	--	100	--
"	"	DPE ^b	"	1.0	---	100	--	100	--
" ^c	Argon	None	i-PrO ⁻	20.0 ^d	---	83	--	100	--
" ^c	"	DPE ^b	"	6.2 ^e	---	92	--	98	--
" ^c	Air	None	"	11.0 ^f	---	83	--	99	--
" ^c	"	DPE ^b	"	4.1 ^e	---	92	--	100	--

- ^a -- Traces of biphenyl, di-p-tolyl and p-methylbiphenyl were detected
^b -- 2.5×10^{-4} mole of 1,1-diphenylethylene, of which 96-100% was recovered unchanged
^c -- Trace of biphenyl detected
^d -- Acetone was obtained in 22% yield
^e -- Acetone was obtained in 4.2% yield
^f -- Acetone was obtained in 11% yield