

EFFECT OF BORON TRIFLUORIDE ETHERATE
ON THE PHOTOREARRANGEMENT OF N-BENZYLANILINES

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Irradiation of N-benzylanilines complexed with boron trifluoride (BF_3) results in the preferential formation of o-benzylanilines. With optically active N- α -phenethylaniline, increased retention of optical activity in the ortho migrated product was observed as compared to that found in the absence of boron trifluoride etherate ($\text{BF}_3\text{---Et}_2\text{O}$).

The thermally induced Hofmann-Martius or Reilly-Hickingbottom rearrangement of N-alkylanilines with acids is known to result in the preferential formation of para alkylated anilines.¹⁾ In contrast, the photochemical rearrangement of N-benzylanilines has recently been reported to yield o-benzylanilines as main rearranged products.²⁾ In relation to our interest in the photochemistry of complexed compounds, we have examined the photochemical behavior of N-benzylanilines complexed with boron trifluoride (BF_3) and found that predominance of the ortho migration of benzyl groups is further enhanced as compared with that in the photolysis of the free amines.

TABLE summarises the results of photolysis with a light over 2000 Å, of N-benzylaniline (I) with varied amounts of boron trifluoride etherate ($\text{BF}_3\text{---Et}_2\text{O}$) in several solvents. Products were the rearranged products, o- and p-benzylanilines (IV and V, respectively) together with 1,2-diphenylethane (II) and aniline (III). In every solvent except methanol, the yield of the ortho isomer (IV) was increased with increasing amount of $\text{BF}_3\text{---Et}_2\text{O}$, although that of the para isomer (V) was relatively insensitive to amount of the added acid. Maximal yields of IV was attained with IV/V ratios of 4 to 5, e.g., 68, 53, 32, and 48 % yields in benzene, ether, methanol, and acetonitrile, respectively. In methanol, IV was found to be

TABLE. Photolysis of N-Benzylaniline (I)
in the Presence of $\text{BF}_3\text{-Et}_2\text{O}$ with a Light Over 2000 \AA^a

Solv.	$\text{BF}_3\text{-Et}_2\text{O}$ (equiv.)	Conv. (%)	Products (%) ^{b,c}					Other products ^d	IV/V
			II	III	IV	V			
PhH	—	61	5.8	26	14	10	VI (2.7)		1.4
PhH	1.2	85	0	19	63	13	VI (8.7)		4.8
PhH	2.3	96	0	16	68	14	VI (11)		4.9
PhH ^e	6.9	100	0	15	67	14	VI (13)		4.8
Et_2O	—	70	22	45	15	8			1.9
Et_2O^f	1.2	46	12	37	29	10			2.9
Et_2O	11.5	98	0	21	53	14			3.8
MeOH	—	92	16	28	27	25	VII (tr)		1.1
MeOH	1.2	100	5.6	30	12	8.9	VII (6.9)		1.3
MeOH	11.5	96	tr	38	32	7.8	VII (19)		4.1
CH_3CN	—	96	26	43	20	19			1.1
CH_3CN	1.2	81	2.4	32	26	12			2.2
CH_3CN	2.3	74	tr	23	29	8.5			3.4
CH_3CN	4.6	92	0	23	37	10			3.7
CH_3CN	9.2	100	0	27	48	11			4.4

^a A solution of I (0.17 M) and $\text{BF}_3\text{-Et}_2\text{O}$ was irradiated from a 300 W high-pressure lamp through a quartz filter under an atmosphere of nitrogen for 20 hrs at room temperature. The photolysate was treated with aqueous ammonia and extracted with ether. The organic solution was separated, concentrated and analysed by glc.

^b Yields are based on reacted I.

^c Yields of IV and V obtained from photolysis of I without an additive in solvents other than those listed in the table, are given below (in parenthesis is given the yields (%) of IV and V, and the ratio IV/V in this order); cyclohexane (17, 10, 1.7), isopropanol (29, 27, 1.1), ethanol (26, 24, 1.1), *t*-butanol (26, 25, 1.0), cyclohexanol (20, 19, 1.1), diethylene glycol (28, 14, 2.0).

^d No indication of the formation of polybenzylated anilines was found.

^e Heating the solution at 70 — 75° in the dark gave only recovered I.

^f Insoluble material was deposited on the surface of a reaction tube, which retarded the reaction.

rather unstable when irradiated in the presence of $\text{BF}_3\text{-Et}_2\text{O}$. When the photochemical rearrangement of free I (i.e., in the absence of $\text{BF}_3\text{-Et}_2\text{O}$) was carried out in several solvents having various viscosities and polarities, the yields of IV were found to be varied in the range of 14 to 29 % with IV/V ratios of 1 to 2, although Ogata and Takagi²⁾ report that photolysis of I in benzene and t-butanol gives IV and V with high IV/V ratios but in low yields.

Amount of a complex between I and BF_3 may increase with increasing amount of $\text{BF}_3\text{-Et}_2\text{O}$ with liberation of ether. Excessive addition of $\text{BF}_3\text{-Et}_2\text{O}$ in benzene did not much affect the product distribution, and this fact may indicate that most of I can be complexed in benzene by adding a little more than one equivalent amount of $\text{BF}_3\text{-Et}_2\text{O}$ to I. In ether, methanol or acetonitrile, addition of large excess of $\text{BF}_3\text{-Et}_2\text{O}$ was necessary to get IV in as high yields as possible, presumably because complexation of BF_3 to the solvent was competing (see below).

Free I was similarly rearranged by irradiation with a light over 2800 Å. However, as expected from the ultraviolet spectrum of I- BF_3 complex prepared in situ [$\lambda_{\text{max}}^{\text{MeOH}}$ 207 (ϵ 14,600) and 250 nm (ca. 300)], the complex was found to be hardly decomposed when irradiated with the light over 2800 Å in place of that over 2000 Å. The decomposition of I in benzene was thus much retarded and virtually prohibited by adding a slight excess and two equivalent amounts of $\text{BF}_3\text{-Et}_2\text{O}$, respectively. Owing to the competitive complexation of BF_3 to solvents, addition of a large excess of $\text{BF}_3\text{-Et}_2\text{O}$ was required for the complete complexation of I, and correspondingly for the inhibition of the photodecomposition of I in ether, acetonitrile or methanol.

It was unexpected that the yield of 1,2-diphenylethane (II) was reduced with increasing amount of $\text{BF}_3\text{-Et}_2\text{O}$. Instead, diphenylmethane (VI) and methyl benzyl ether (VII) appeared increasingly in benzene and in methanol, respectively.

Irradiation of I was similarly carried out in the presence of various acids (aluminum chloride, sulfuric acid, hydrochloric acid, acetic acid or trifluoroacetic acid) in acetonitrile, methanol, water or benzene. The yields of IV were, however, lower than those found in the irradiation with $\text{BF}_3\text{-Et}_2\text{O}$. It was observed that IV is more or less unstable under these photochemical conditions.

The enhancement of the ortho rearrangement by complexing I with BF_3 may be related to increased intramolecularity of the rearrangement as indicated by increased retention of optical activity in the ortho isomer from optically active N- α -phenethylaniline (VIII). The rearranged products from the thermal isomerization

of VIII with acids have been reported to be essentially racemic.³⁾ Irradiation of VIII, $[\alpha]_D^{25}$ (EtOH) $-26.1^\circ \pm 0.9^\circ$, in methanol/t-butanol (1:1) gives the ortho isomer (25 %) with $[\alpha]_D^{25}$ (EtOH) of $+3.9^\circ \pm 1.5^\circ$ at 60 % conversion of VIII.²⁾ Under similar conditions the irradiation in benzene with excess $\text{BF}_3\text{-Et}_2\text{O}$ yielded the ortho isomer (56 %) with $[\alpha]_D^{25}$ (EtOH) of $+9.7^\circ \pm 0.4^\circ$ at 62 % conversion of VIII, $[\alpha]_D^{25}$ (EtOH) $-25.4^\circ \pm 0.3^\circ$.

The reaction may anyway be useful for synthesis of o-benzylanilines. Irradiation of other N-benzylanilines, N- α -phenethylaniline, N-methyl-N-benzylaniline, N-(p-methylbenzyl)aniline, and N-(p-tolyl)benzylamine, in benzene in the presence of excess $\text{BF}_3\text{-Et}_2\text{O}$ gave the corresponding ortho isomers in yields of 56 (6.3), 65 (8.7), 69 (9.3), and 69 % (-), respectively (ratio of the yield of the ortho to the para isomer is given in parenthesis).

Thermal rearrangement of I with $\text{BF}_3\text{-Et}_2\text{O}$ (1.2 equivalent amount to I) at 200° gave IV (12 %) and V (14 %) together with substantial amounts of aniline and polybenzylated anilines. Diphenylamine and N-ethylaniline were virtually stable toward irradiation in the presence of excess $\text{BF}_3\text{-Et}_2\text{O}$ in benzene.

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