Abnormal *meta*-Rearrangement of *N*-Benzylanilines Induced by Irradiation in the Presence of Ethylaluminium Dichloride

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Summary Photolysis of *N*-benzylanilines in the presence of an excess of ethylaluminium dichloride in benzene gives *m*-benzylanilines as well as the *o*- and *p*-benzylanilines.

VARIOUS aromatic esters, ethers, amines, amides, *etc.*, are known to rearrange thermally and/or photochemically to result in migration of the leaving groups to the *ortho*- and/or *para*-positions of the ring.[1] Usually, *meta*-migration does not take place. *N*-Benzylanilines rearrange in this way thermally in the presence of acids[2,3] or photochemically[4] to the *ortho*- and *para*-benzylated anilines but not to the *meta*-isomers. We have studied the effect of addition of $EtAlCl_2$ on the photorearrangement of *N*-benzylanilines and found that the unusual *meta*-rearranged products are formed in comparable yields to the *ortho*- and *para*-benzylated products provided that an excess of $EtAlCl_2$ over the amines was used.

TABLE

Photodecomposition of (I) in the presence of aluminium compounds[a]

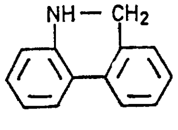
	Products (%)[b]			Benzylaniline		
Additive (equiv.)	Ph_2CH_2	$(PhCH_2)_2$	$PhNH_2$	*o*-	*m*-	*p*-
—	3	6	30	12	0	7
$AlBr_3$ (5)	29	0	15	6	9[c]	
$AlCl_3$[d] (4)	32	0	23	9	8	5
$EtAlCl_2$ (0·9)	4	5	20	28	0	8
$EtAlCl_2$ (1·1)	15	tr	17	13	22	7
$EtAlCl_2$ (2)	17	tr	14	13	25	8
Et_2AlCl[e] (2)	4	14	50	8	0	7
Et_3Al[f] (2)	tr	8	68	tr	0	tr

[a] Irradiation for 25—50 h. In most cases, >80% of (I) was consumed. [b] Yields are based on consumed (I). [c] Total yields of *m*- and *p*-benzylanilines as estimated by g.l.c. [d] A large amount of $AlCl_3$ remained undissolved. [e] Toluene and n-propylbenzene were also formed. [f] Toluene (14%) and n-propylbenzene (28%) were also formed.

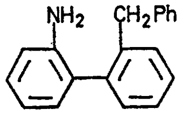
A benzene solution of *N*-benzylaniline (I) (0·17 mmol) and $EtAlCl_2$ (0·19 mmol) was irradiated from a 300 W high-pressure mercury lamp through a quartz filter under nitrogen at room temperature. After treatment with aqueous alkali, the benzene solution was evaporated to dryness, and chromatography of the residue on silica gel with benzene as eluant gave *m*-benzylaniline[5] (22%) in addition to the *ortho*- and *para*-isomers (13 and 7%, respectively). Polybenzylated anilines were apparently not formed. No reaction took place when the solution was heated at 60° in the dark. *N*-2-Phenylethylaniline and *N*-benzyl-*N*-methylaniline were similarly irradiated in the presence of excess of $EtAlCl_2$ to afford the corresponding *ortho*- (12 and 7%, respectively), *meta*- (13 and 11%, respectively), and *para*-migrated products (2 and 25%, respectively). Their structures were determined by i.r. and ^1H n.m.r. spectroscopy.

The photoreactions of (I) under various conditions are summarized in the Table. *meta*-Migration of the benzyl group was not observed with a molar ratio of $EtAlCl_2$ to (I) of less than 1. There seems to be no significant difference in the product distribution when a slight excess or a large excess of $EtAlCl_2$ is used. We assume that the presence of a catalytic amount of uncomplexed $EtAlCl_2$ is enough to cause the *meta*-rearrangement. This unusual photorearrangement of (I) was also brought about by addition of $AlCl_3$ or $AlBr_3$ in place of $EtAlCl_2$, but the reactions in these cases were rather complicated and the yields of *m*-benzylaniline were much lower. The benzylic carbon–nitrogen bond of (I) was cleaved as readily by Et_2AlCl as by triethylaluminium, but the leaving benzyl group reacted predominantly with the organoaluminium compounds to afford toluene and n-propylbenzene; *m*-benzylaniline was not formed.

The *meta*-rearranged product may not be derived from a secondary reaction of the initially formed *o*- and/or *p*-benzylanilines since they did not rearrange to the *meta*-isomer when irradiated or heated at 75° with or without $EtAlCl_2$ or $AlCl_3$.[6]



(II)



(III)

Similar irradiation of a cyclic benzylamine, 5,6-dihydrophenanthridine (II),[7] with an excess of $EtAlCl_2$ in benzene gave 2-amino-2′-benzylbiphenyl (III), m.p. 77°, almost quantitatively. The structure of (III) was established by elemental analysis and mass [m/e 259 (M^+)]; ^1H n.m.r. [τ (CCl_4) 2·79 (s, 5-H), 2·9—3·5 (m, 8-H), 6·20 (s, 2-H), and 6·77br (s, 2-H)]; i.r. [ν_{max} (CCl_4) 2475 and 3387; (CS_2) 1613, 1297, 766, 749, and 697 cm^{-1}] and u.v. spectra [λ_{max} (MeOH) 204 (ϵ 31,000) and shoulders at *ca.* 245 and 292 nm (990)].

All attempts to obtain (III) from (II) and benzene under other related conditions failed: irradiation without an additive or with excess of $BF_3{\cdot}OEt_2$, excess of $AlCl_3$, or 0·75 equiv. of $EtAlCl_2$, or heating at 150° with excess of $EtAlCl_2$ or $AlCl_3$.

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