

A NEW METHOD FOR REARRANGEMENT OF ANILIDES

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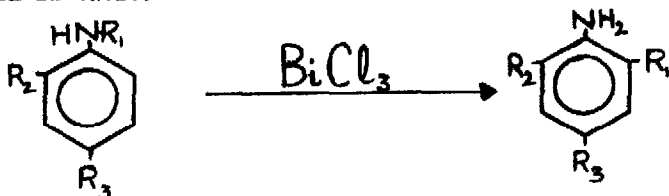
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A large number of N-substituted anilines are known to rearrange to ortho or para amino derivatives employing Lewis acids as catalyst¹. However N-acyl derivatives do not in general afford corresponding ortho or para migrated products.[†]

We now report a new high yield procedure of migration of the acyl group in various anilides to the aromatic nucleus using bismuth trichloride as catalyst. In a typical reaction an anilide as treated with BiCl_3 (5 mole excess) at $160^\circ\text{--}245^\circ$ for about 2-9 minutes. The resulting mixture is treated with water, filtered, basified with Na_2CO_3 and extracted with ethyl acetate. The products were separated by preparative tlc using silica gel as adsorbent. The substances thus obtained possessed different R_f values in various solvents from corresponding amides. The products afforded positive diazotization test and the u.v. spectra showed characteristic shifts towards longer wavelengths. The substances showed the molecular ion and fragmentation patterns in accordance with the predicted structures for the products as given in Table.



[†] A survey of the literature has shown only three cases^{2,3,4} of such rearrangement of anilides in very low yields.

Table

Substrate	Reagent/ Time	Temperature °C	Products	M ⁺ ; other major peaks	Yields
1. R ₁ , COCH ₃ R ₂ , CH ₃ R ₃ , CH ₃	5 moles 2 min.	200 - 210	R ₁ , -C=N-C ₆ H ₃ (CH ₃) ₂ (2,4) CH ₃ R ₂ , -CH ₃ R ₃ , -CH ₃	266(100%); 146(8%), 121(40%), 105(40%)	40
2. R ₁ , COCH ₃ R ₂ , H R ₃ , Br	5 moles 2.5 min.	180 - 200	R ₁ , -C=N-C ₆ H ₄ .Br(p) CH ₃ R ₂ , H R ₃ , Br	366(93%), 96/98(100%), 155(46%).	37.5
3. R ₁ , COC ₆ H ₅ R ₂ , H R ₃ , OCH ₃	5 moles 3 min.	200 - 230	R ₁ , COC ₆ H ₅ R ₂ , H R ₃ , OH	213(80%), 105(100%), 108(91%), 123(75%)	72 ^B
4. R ₁ , COCH ₃ R ₂ , H R ₃ , OCH ₃	5 moles 3 min.	180 - 200	R ₁ , C=N-C ₆ H ₄ .OCH ₃ (p) CH ₃ R ₂ , H R ₃ , OCH ₃	270(70%); 149(49%), 148(100%), 123(55%), 108(49%), 92(40%)	37.5
5. R ₁ , COCH ₃ R ₂ , H R ₃ , CH ₃	5 moles 3.5 min.	160 - 180	R ₁ , COCH ₃ R ₂ , H R ₃ , CH ₃	147(50%); 104(100%), 105(90%)	85 ^B
6. R ₁ , COC ₆ H ₄ .Cl(o) R ₂ , H R ₃ , OCH ₃	5 moles 3 min.	180 - 200	R ₁ , COC ₆ H ₄ .Cl(o) R ₂ , H R ₃ , OH	247(78%); 139(100%), 111(71%), 108(50%)	80
7. R ₁ , COC ₆ H ₄ .NO ₂ (o) R ₂ , H R ₃ , CH ₃	5 moles 3 min.	150 - 165	R ₁ , COC ₆ H ₄ .NO ₂ (o), R ₂ , H, R ₃ , CH ₃	256(100%); 121(50%), 153(95%), 106(100%)	45
8. R ₁ , COCH ₂ Cl R ₂ , H R ₃ , CH ₃	5 moles 5 min.	160 - 180	R ₁ , COCH ₂ Cl R ₂ , H R ₃ , CH ₃	183(50%); 106(100%)	55

Substrate	Reagent/ Time	Temperature °C	Products	M ⁺ ; other major peaks	Yields %
9. R ₁ , COC ₆ H ₄ Cl R ₂ , H R ₃ , Br	5 moles 9 min.	220 - 230	R ₁ , COC ₆ H ₄ Cl R ₂ , H R ₃ , Br	309(40%); 244(41%), 171(66%), 139(100%), 111(75%)	60
10. R ₁ , COCH ₂ C ₆ H ₅ R ₂ , H R ₃ , CH ₃	5 moles 8 min.	175 - 90	R ₁ , COCH ₂ C ₆ H ₅ R ₂ , H R ₃ , CH ₃	225(33%); 192(33%), 106(100%), 91(100%)	55 ^a
11. R ₁ , COCH ₂ Cl R ₂ , H R ₃ , Br	5 moles 8 min.	230 - 245	R ₁ , COCH ₂ Cl R ₂ , H R ₃ , Br	247(100%); 195(60%), 118(80%), 91(100%)	50 ^a
12. R ₁ , COC ₆ H ₅ R ₂ , CH ₃ R ₃ , CH ₃	5 moles 5 min.	170 - 180	R ₁ , COC ₆ H ₅ R ₂ , CH ₃ R ₃ , CH ₃	223(100%); 148(33%), 120(66%), 121(68%), 105(83%), 77(66%)	65 ^a
13. R ₁ , COCH ₂ Cl R ₂ , CH ₃ R ₃ , CH ₃	5 moles 8 min.	170 - 180	R ₁ , COCH ₂ Cl R ₂ , CH ₃ R ₃ , CH ₃	197(100%); 120(80%), 108(78%),	55 ^a
14. R ₁ , COC ₆ H ₅ R ₂ , H R ₃ , CH ₃	5 moles 6 min.	200 - 220	R ₁ , C=N.C ₆ H ₄ .CH ₃ (p) C ₆ H ₅ R ₂ , H R ₃ , CH ₃	300(50%); 232(32%), 195(50%), 194(100%), 135(42%), 132(50%), 122(100%), 105(100%), 91(56%), 77(87%),	46

^a yields based on recovered anilides.

It was observed that electron withdrawing groups in the aniline moiety (e.g. Cl, NO₂) tend to retard migration and deacetylated products were obtained even under vigorous conditions. On the other hand electron donating groups assists group migration which occur under mild conditions.

The above procedure offers a novel approach to prepare pharmacologically interesting and suitably substituted aniline derivatives. The rearrangement study of N-Alkylated aniline is also to be studied. A detailed study of ortho-para ratio in other anilides is under investigation.

REFERENCES

1. Molecular Rearrangements, Part I, Edited by P.D. Mayo, by John Wiley & Sons, Inc. 1967.
2. D.N. Kursonov. J. Gen. Chem. (U.S.S.R.), 13, 286 (1943); Chem. Abs. 38, 959.
3. J.F.J. Dippy and J.H. Wood, Nature, 157, 408 (1946).
4. B.I. Ardashev and V.I. Minkin, Zhur. Obschchei. Khim., 27, 1261 (1957); Chem. Abs. 52, 2856 c.