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Synthesis and Rearrangement of Oxanilic Esters Arylhydrazones

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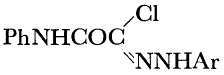
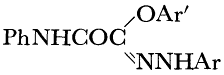
The reactivity of phenylcarbamoylarylhydrazidic chlorides (I) with various nucleophiles involving carbon and nitrogen atoms has recently been reported.[1] This communication describes the reaction of I with phenols to get the title compounds (II), which do not seem to have been reported, and the thermal rearrangement of II into III, a new Chapman-like rearrangement[2] in the hydrazone series.


$\mathrm{PhNHCOC(Cl){=}NNHAr}$

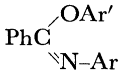
I


$\mathrm{PhNHCOC(OAr'){=}NNHAr}$

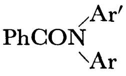
II


$\mathrm{PhNHCOCONHN(Ar')Ar}$

III


$\mathrm{PhC(OAr'){=}N{-}Ar}$

IV


$\mathrm{PhCON(Ar')Ar}$

V


$\mathrm{PhNHCOCON(Ar')NHAr}$

VI

Synthesis of II was most conveniently performed as follows. An equivalent amount of I was added to a suspension of sodium phenolate in benzene. After refluxing the mixture for 30 min, the solvent was distilled off and the residue was crystallized from methanol (Method A). Alternatively, to an ethanolic sodium phenolate solution (prepared by the addition of the appropriate phenol to sodium ethoxide in ethanol) was added an equivalent amount of I with stirring at room temperature. After standing for 24 hr, the mixture was diluted with water and the resulting product was filtered and crystallized from methanol (Method B). By the use of either method it was possible to prepare a series of aryl oxanilate arylhydrazones (IIa—j). The properties of these compounds are given in Table 1. The spectral and elemental analyses support structure II for the products listed.

Aryl imidates (IV) underwent rearrangement on heating to give *N*-aroyldiarylamines (V) (Chapman-rearrangement).[2] Aryl oxanilate arylhydrazones (II) were found to undergo a similar rearrangement to give oxanilic arylhydrazides (III) when refluxed in inert solvents. Thus, when IIa (Ar=C_6H_5; Ar′=4-CH_3-C_6H_4) was refluxed in nitrobenzene for 4 hr, giving a product which was analyzed as $C_{21}H_{19}N_3O_2$. Its IR spectrum revealed the absence of the C–O–Ar band present in the IR spectra of all compounds in the series II. Furthermore, the UV spectrum of the compound obtained in ethanol differed from that of the starting ester IIa, no band characteristic of the hydrazone chlomophore being present. Two possible structures IIIa and VIa (Ar=C_6H_5; Ar′=4-$CH_3C_6H_4$) were formulated. For the sake of confirmation we studied the rearrangement of the isomeric ester IIb (Ar=4-$CH_3C_6H_4$; Ar′=C_6H_5). It was found to give only one product identical with that obtained from IIa. This suggests strongly that the actual structure of the product is IIIa and not VIa. The correctness of such an assignment was further proved by the identity of the product IIIe (Ar=Ar′=C_6H_5) obtained by thermolysis of IIe (Ar=Ar′=C_6H_5) with an authentic sample of *N*-oxanilyl-*N′*,*N′*-diphenylhydrazine prepared by the reaction of oxanilyl chloride with asymmetric diphenylhydrazine.

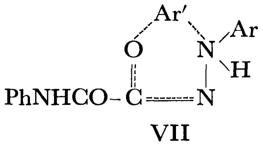
TABLE 1. ARYL OXANILATE ARYLHYDRAZONES (II) AND THEIR REARRANGEMENT PRODUCTS (III)

Compound No.	Ar	Ar′	Ester II		Hydrazide III	
			Yield[a] %	Mp °C	Yield %	Mp C°
a	C_6H_5	4-$CH_3C_4H_6$	82	187	80	242
b	4-$CH_3C_6H_4$	C_6H_5	70	188	95	242
c	C_6H_5	4-ClC_6H_4	60	185	87	263
d	4-ClC_6H_4	C_6H_5	45	183	85	263
e	C_6H_5	C_6H_5	63	197	80	271
f	C_6H_5	2-$CH_3C_6H_4$	87	186	83	211
g	C_6H_5	2-ClC_6H_4	56	175	83	194
h	4-BrC_6H_4	C_6H_5	60	197	70	259
i	3-$CH_3C_6H_4$	C_6H_5	70	169	81	215
j	C_6H_5	1-$C_{15}H_7$	72	166	86	246

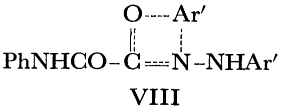
a) from Method A.

When a mixture of the iosmeric esters IIa and IIb was heated, it gave only hydrazide IIIa (Ar=C_6H_5; Ar′=4-$CH_3C_6H_4$) in an almost quantitative yield. This indicates that the II—III conversion is an intramolecular rearrangement. The results of thermolysis of the isomeric esters IIc (Ar=C_6H_5; Ar′=4-ClC_6H_4) and IId (Ar=4-ClC_6H_4; Ar′=C_6H_5) either separately or in mixture confirm such a conlcusion.

The foregoing results indicate that the thermal rearrangement of II to III involves a 1,4-shift of an aryl group from oxygen to nitrogen probably *via* a five-membered cyclic transition state of type VII. No formation of VI might be attributed to the lower stability of the four-membered cyclic transition state (VII) required for the formation.



VII



VIII

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[1] A. S. Shawali and A. Osman, *Tetrahedron*, **27**, 2517 (1971).

[2] A. W. Chapman, *J. Chem. Soc.*, **1972**, 1743; W. J. Dauben and R. L. Hodgson, *J. Amer. Chem. Soc.*, **72**, 3479 (1950); K. B. Wiberg, *ibid.*, **77**, 2205 (1955).