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SYNTHESIS AND REARRANGEMENT OF HYDRAZONES OF ARYL BENZOATES

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Hydrazidic bromides (I, Ar = 4-$NO_2C_6H_4$-) react with an ethanolic solution of a sodium phenolate to give aryl benzoate p-nitrophenylhydrazones (II). When the reaction was carried out in ethanol buffered with sodium acetate, III (71%) was obtained in addition to a small amount (14%) of IV. If I and phenol were refluxed in ethanol only 60 % of IV was obtained.

$RC_6H_4C(Br):NNHAr$ (I) $RC_6H_4C(OAr'):NNHAr$ (II) $RC_6H_4CONHN(COCH_3)Ar$ (III)

$RC_6H_4CONHNHAr$ (IV) $RC_6H_4CON(Ar')NHAr$ (V) $RC_6H_4C(OAr'):NAr$ (VI)

$RC_6H_4C^+{=}NNHAr$ (VII)

The ester hydrazones (II) bear a structural relationship to the extensively investigated imidates (VI).[1] In contrast to imidic esters which readily undergo hydrolysis and decomposition,[1] the ester hydrazones II have been stored for up to 12 months without noticeable decomposition. Also, II are not hydrolysed in refluxing aqueous dioxan and are not attacked by potassium iodide or ammonium hydroxide. However, II undergo hydrolysis in ethanolic hydrochloric acid to give IV as the major product. This acid hydrolysis may proceed via the carbonium ion VII.[2]

Imidates (VI) rearrange on heating to give N,N-disubstituted amides (Chapman rearrangement).[3] Now we have found that ester hydrazones II rearrange on heating at 210° for 2 hrs to give the corresponding N'-aryl-N'-aroyl-p-nitrophenylhydrazines (V). Table 1 lists the ester hydrazones studied and their rearrangement products.[4]

Table 1

Ester Hydrazones					Rearrangement Products		
Compound No.	R	Ar'	Mp°C	Yield %	Compound No.	Mp°C	Yield %
IIa	H	C_6H_5	172	60	Va	180	45
IIb	4-NO_2	C_6H_5	205	80	Vb	226	52
IIc	4-CH_3	C_6H_5	218	75	Vc	176	42
IId	3-NO_2	4-$CH_3C_6H_4$	190	80	Vd	210	60

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3. A. W. Chapman, J. Chem. Soc., 1743 (1927); W. G. Dauben and R. L. Hodgson, J. AMer. Chem. Soc., 72, 3479 (1950); K. B. Wiberg and B. I. Rowland, ibid., 77, 2205 (1955).

4. The elemental analyses of the new compounds agreed well with calculations, and their infrared and ultraviolet spectra are consistent with the assigned structures.