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THE REARRANGEMENTS OF A NEW GROUP OF AZIDES - HYDRAZIDIC AZIDES

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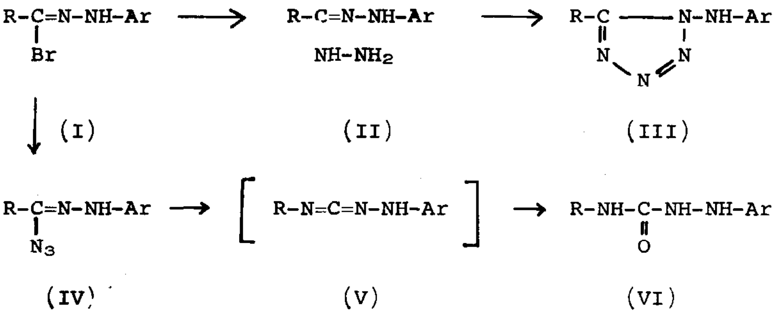
The reaction of nitrous acid with a number of hydrazidines (II) has been reported (1) to give the tetrazoles (III). We have now found that the isomeric azides (IV) are formed in high yield on treatment of the hydrazidic bromides (I) with azide ion. Thus the reaction of a variety of the hydrazidic bromides (I; R = XC_6H_4, Ar = 2-Br,4-$NO_2C_6H_3$ or 4-$NO_2C_6H_4$), prepared as previously described (2), with equimolar quantities of sodium azide in 80 : 20 dioxan - water at 25° gave exclusively the corresponding azides (IV), characterized (3) by the strong azide absorption at 2130 cm^{-1} in the infrared.



Attempts to cyclize these azides (IV) to the isomeric tetrazoles (III) e.g. by warming in an inert solvent (4), or in the presence of excess sodium azide or by dissolution in 10% sodium hydroxide followed by reprecipitation with acid, were not successful, the azide being recovered quantitatively. The stability and ease of formation of these hydrazidic azides contrasts with the properties of the imidic azides in which almost generally the tetrazole is obtained exclusively on treatment of the imidic chloride with azide ion (5). Moreover, isomerization to tetrazole of those imidic azides (6), or more generally azidoazomethines (7) isolated is generally effected under mild conditions.

In an attempt to establish an equilibrium between the two forms, (III) and (IV), the azide (IV; R = C_6H_5, Ar = 2-Br,4-$NO_2C_6H_3$) was suspended in trifluoroacetic acid (8) for one hour. Instead of isomerization, rearrangement took place and two compounds were isolated. These were shown, from spectral data and by alternative synthesis to be the semicarbazide (VI; R = C_6H_5, Ar = 2-Br,4-$NO_2C_6H_3$), m.p. 236° isolated in 5% yield, and its trifluoroacetyl derivative, 1-(2′-bromo-4′-nitrophenyl)-1-trifluoroacetyl-4-phenylsemicarbazide m.p. 163° (81%). A possible mechanism for the formation of these involves an acid-catalysed Schmidt-type rearrangement of the azide to give the (protonated) N-aminocarbodiimide (V). This reacts either with water to give the semicarbazide (VI) or with trifluoroacetate ion (9), the intermediate acetate thus obtained rearranging to the more stable N-acetyl compound (a reaction analogous to the ready rearrangement of azoacetates to N-acetyl hydrazides (10)). The intermediacy of the species (V) is supported by the fact that the semicarbazide (VI) does not react with trifluoroacetic acid (to give the N-trifluoroacetyl derivative) under the conditions used for the rearrangement.

The rearrangement of the azide to the semicarbazide was readily achieved without product complications and in almost quantitative yield by suspending the azide in 2.2M sulphuric acid - acetic acid at room temperature until the evolution of nitrogen had ceased (usually 15 min.; compounds with electron-withdrawing substituents required a longer time). Addition of water then precipitated the semicarbazides (VI). Seven compounds with R and Ar variously substituted phenyl were thus prepared. The analogous tetrazoles (III) failed to react under these moderately strong acidic conditions and were recovered quantitatively.

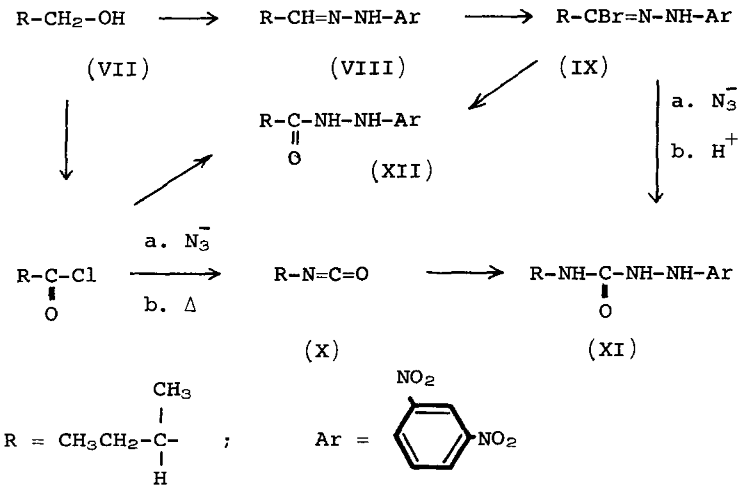
Evidence that in the rearrangement migration occurs with the retention of optical and geometric configuration and thus that the migrating group is never free, was shown by the following sequence. D-(-)-2-methyl-1-butanol (VII) was oxidized to the corresponding

TABLE I

Melting Point Data for Semicarbazides and Hydrazidic Azides

R	Ar	Azide (IV)	Semicarbazide (VI)
C_6H_5	2-Br, 4-$NO_2C_6H_3$	111°	236°
4-ClC_6H_4	2-Br, 4-$NO_2C_6H_3$	125°	250°
4-$(CH_3)_2CHC_6H_4$	2-Br, 4-$NO_2C_6H_3$	118°	221°
C_6H_5	4-$NO_2C_6H_4$	130°	224°
4-$CH_3C_6H_4$	4-$NO_2C_6H_4$	131°	232°
4-BrC_6H_4	4-$NO_2C_6H_4$	142°	239°
C_6H_5	2,4-$Br_2C_6H_3$	96°	213°

aldehyde and coupled with 2,4-dinitrophenylhydrazine to give the hydrazone (VIII) whose maximum specific rotation is known (11). Bromination gave compound (IX) with retention of configuration (12). This bromo compound was reacted with azide ion and the azide rearranged to form 1-(2',4'-dinitrophenyl)-4-(1'-methylbutyl)semicarbazide (XI; Ar = 2,4-$(NO_2)_2C_6H_3$, R = EtMeCH) by contact with the sulphuric acid - acetic acid solution for 4 min. The substituted semicarbazide had a specific rotation $\alpha]^{25}_{578} = +36.5^\circ$ (c = 1.0, acetic acid).



This semicarbazide was also prepared by the reaction of the isocyanate (X), formed from the same alcohol by the reaction sequence shown, with 2,4-dinitrophenylhydrazine in anhydrous ether. Since the formation of the isocyanate by this reaction sequence is known (13) to occur with almost complete retention of configuration at the asymmetric carbon and racemization is unlikely to occur at the last step to form compound (XI), the semicarbazide obtained by this route is formed with the retention of optical activity. Its specific rotation, measured under the same conditions was almost identical (actually = +37.0°) with that for the semicarbazide prepared by the other route. That racemization had not occured in the bromination step (VIII ⟶ IX) was indicated by the hydrolysis of the bromo compound (IX) to the hydrazide (XII), which compound had the same rotation as a sample of the material prepared by reaction of D-(+)-2-methylbutyryl chloride and 2,4-dinitrophenyl hydrazine.

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