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AMIDRAZONES III.[1] THE SYNTHESIS AND PROPERTIES OF 1,1,1-TRIMETHYL-2-(N-PHENLBENZIMIDOYL)HYDRAZINIUM HYDROXIDE INNER SALT - A NOVEL YLID

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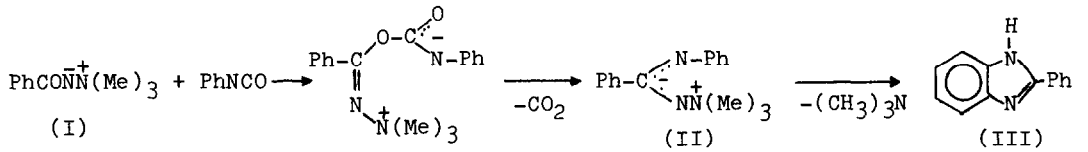
The major products obtained from the thermolysis of 1,1,1-trimethyl-2-benzoylhydrazinium hydroxide inner salt (I)[2] are triphenyl isocyanurate and trimethylamine which result from a Curtius-type rearrangement.[3] Small amounts of CO_2, 2-phenylbenzimidazole (III), benzanilide and 1,3-diphenylurea are formed as by-products in this reaction.[4]

We have proposed[4] that the formation of CO_2 and III in the above reaction may be accounted for by a secondary reaction of phenyl isocyanate with I as outlined in Scheme I.

Scheme I



(I) (II) (III)

This communication reports the synthesis of II (the first example of an amidrazone ylid), the thermal conversion of II to III and the reaction of II with methyl iodide.

Ylid II[5] [mp 174-175° (dec)], together with its hydrochloride [mp 209-210° (dec)], were obtained in yields of 32% and 14% respectively by the reaction of N-phenybenzimidoyl chloride with a THF solution of the di-t-butanol complex of 1,1,1- trimethylhydrazinium hydroxide inner salt (IV), which was generated *in situ* by the reaction of KO-t-Bu (containing t-BuOH) with 1,1,1-trimethylhydra-

zinium chloride.[6]

$$(CH_3)_3\overset{+}{N}\overset{-}{N}H\cdot 2t\text{-}BuOH + PhCCl{=}NPh \xrightarrow[0°]{THF} (CH_3)_3\overset{+}{N}NH_2\ Cl^- + II + II\cdot HCl$$

(IV)

The structures of II and its hydrochloride were established by analytical[7] and spectral data. Compound II gave the following data: M/e (20e.v.): 253($M^{+\cdot}$,15%), 194(100%, 2-phenylbenzimidazole$^{+\cdot}$). NMR ($CDCl_3$), δ3.50 (9H,s), 6.3-7.3 (10H,m). The hydrochloride of II gave the following data: NMR ($CDCl_3$): δ3.90 (9H,s), 6.8-7.3 (11H,m). M/e (20e.v.): 253 (10%), 194 (100%). Neutralization of the hydrochloride gave II.

When heated at its decomposition temperature (172°), II rapidly gave trimethylamine (identified as its picrate) and an 85% yield of pure 2-phenylbenzimidazole.

Reaction of II with methyl iodide gave V (mp 135-136°) in 82% yield. NMR (DMSO-d_6): δ2.92 (3H,s), 3.82 (9H,s), and 6.6-7.2 (10H,m). The properties of V differed in all respects from those of the previously reported[6] isomer VI.

$$II + MeI \longrightarrow PhC(=NPh)\overset{+}{N}MeN(Me)_3\ I^-$$

(V)

$$PhC(=NMePh)\overset{+}{N}N(Me)_3\ I^-$$

(VI)

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2. Chemical Abstracts nomenclature is used throughout for naming hydrazinium ylids. Compound I is commonly referred to as trimethylamine-benzimide.

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7. All new compounds described herein gave satisfactory combustion data.