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AMIDRAZONES V[1].
THERMOLYSIS OF N[1]-BENZYL-SUBSTITUTED AMIDRAZONE YLIDES

Richard F. Smith*, Allen S. Craig, Lorrene A. Buckley
and Richard R. Soelch

Department of Chemistry
State University College of Arts and Sciences
Geneseo, New York, 14454, USA

Thermolysis of 1,1-dimethyl-1-benzyl-2-(iminophenylmethyl)hydrazinium hydroxide inner salt gave dimethylamine, 2,4,6-triphenyl-s-triazine and 2,4,6-triphenyl-1,2-dihydro-s-triazine.

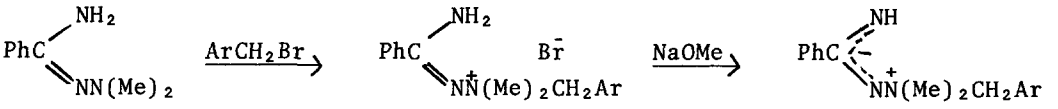
Acylaminimides (1) substituted with either a benzyl[2], allyl[3] or propargyl[4] group on the quaternary nitrogen undergo facile thermal Stevens-type rearrangements to give hydrazides (2). The mechanistic aspects of these rearrangements have been extensively studied[5].

$$\underset{1}{RCO\bar{N}\overset{+}{N}(Me)_2R'} \longrightarrow \underset{2}{RCONR'N(Me)_2}$$

R' = allyl, benzyl or propargyl.

Paper IV[1] in this series described synthetic methods for the preparation of amidrazone ylides (the imino analogs of acylaminimides). It is of interest to establish whether transformations of type 1 → 2 are feasible with these ylides. We report herein the preliminary results of our study of the thermolysis of two benzyl-substituted amidrazone ylides, 1,1-dimethyl-1-benzyl-2-(iminophenylmethyl hydrazinium hydroxide inner salt (6) and its 4-methylbenzyl analog (7). The ylides were conveniently prepared by the method outlined in the Scheme 1.

Scheme 1



3 4 Ar = Ph; 5 Ar = p-tolyl 6 Ar = Ph; 7 Ar = p-tolyl

The conjugate acid (4) of ylide 6 was obtained in 73% yield by reaction of benzamide dimethylhydrazone (3)[6] with benzyl bromide (CH_3CN, 24 hr, r.t.), mp 208-209°, nmr (polysol) δ3.53, 6H, s; 5.10, 2H, s; 7.2-7.8, 10H, m; 8.1, 2H, bd (D_2O exchangeable). Neutralization of 4 (one equivalent NaOMe, MeOH, r.t.) gave the ylide 6 as a hygroscopic solid, mp 108-109°, nmr ($CDCl_3$) δ3.39, 6H, s; 5.21, 2H, s; 5.57, 1H, bd (D_2O exchangeable), 7.0-7.6, 10H, m. Ylide 6 was reconverted to 4 by treatment with HBr in EtOH. In similar fashion, bromide (5) was obtained in 52% yield, mp 189-190°, nmr (polysol) δ2.40, 3H, s; 3.58, 6H, s; 5.00, 2H, s; 8.1, 2H, bd (D_2O exchangeable), 7.2-7.9, 9H, m. Ylide 7 was obtained as a hygroscopic solid, mp 126-129°, nmr (CCl_4) δ2.31, 3H, s; 3.25, 6H, s; 5.1, 2H, s (superimposed on bd D_2O exchangeable NH signal); 7.0-7.6, 9H, m.

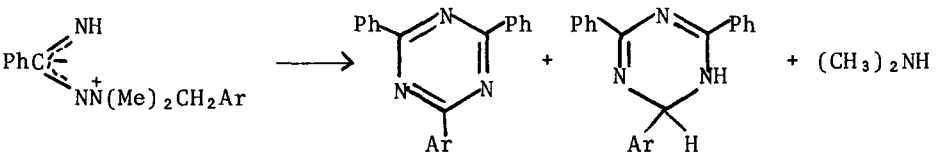
Thermolysis of ylide 6 in either refluxing toluene (2 hr) or without solvent (120°, 30 min) afforded dimethylamine (isolated in 51% yield as its benzoyl derivative from a neat thermolysis experiment) and mixtures of 2,4,6-triphenyl-s-triazine (8) and 2,4,6-triphenyl-1,2-dihydro-s-triazine (9). In a typical experiment, a solution containing 3.0 g 6 in 15 ml of dry toluene was heated under reflux for 2 hr, after which further evolution of $(Me)_2NH$ could not be detected. On cooling, a mixture of crystals was deposited which was manually separated to give 0.41 g 8, mp 226-238° (lit[7] 238-240°) and 0.56 g 9, mp 167-173° (lit[7] 175-177°). Recrystallized samples of both 8 and 9 were identical in all respects with authentic samples. The toluene soluble material proved to be a complex mixture which has not been successfully separated although glc analysis indicated the absence of benzonitrile. Extending the reaction time (2 g, 7 hr) gave 8 (0.6 g) as the only isolable solid product. Lower yields of 8 and 9 were obtained from thermolysis experiments conducted on neat samples.

The oxidative conversion of 9 to 8 has been observed under a variety of con ditions by others[7,8,9]. In considering the mechanistic aspects of the thermal decomposition of 6, we have assumed that 8 is formed by oxidation of the initially formed dihydrotriazine 9.

Thermolysis of the methyl-labelled ylide 7 (refluxing toluene, 2 hr) gave a solid mixture which was judged (by nmr) to consist of 2,4-diphenyl-6-p-tolyl-s-triazine (10) and its dihydroderivative (11). Thermolysis of the mixture (190°)

resulted in aromatization of the dihydrotriazine component and after recrystallization from acetic acid, pure 10 was obtained, mp 198-199° (lit[10] 199-200°), nmr ($CDCl_3$), δ2.40, 3H, s; 7.2-7.7, 8H, m; 8.6-8.8, 6H, m. This latter experiment establishes that one of the aryl groups in the triazine products originates from the benzyl substituent.

Scheme 2



6 Ar = Ph
7 Ar = p-tolyl

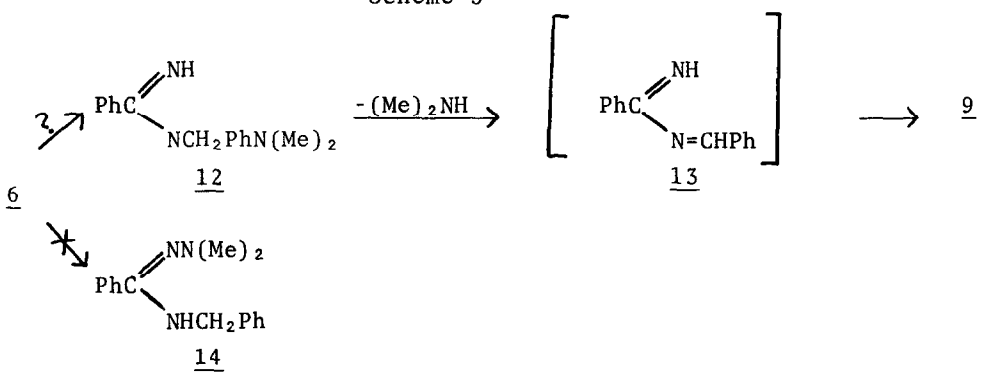
8 Ar = Ph
10 Ar = p-tolyl

9 Ar = Ph
11 Ar = p-tolyl

The formation of the dihydrotriazine 9 and dimethylamine may arise from the initial formation of 12 which is anticipated from Stevens rearrangement of 6. Elimination of dimethylamine from 12 would give benzylidenebenzamidine (13). Pinner[11] has reported the preparation of 13 by condensation of benzaldehyde with benzamidine but Cherkasov, Kapran and Zavatskii[9] have shown this earlier work to be in error and that the product actually obtained from the latter reaction is the dihydrotriazine (9). The Russian workers have prepared a series of 2-aryl-4,6-diphenyl-1,2-dihydro-s-triazines by condensation of aryl aldehydes with benzamidine and have proposed that the dihydrotriazines are formed from 13 via a 2 + 4 cycloaddition accompanied by elimination of an arylideneimine.

We have been unsuccessful in several diverse attempts to synthesize 12 and, therefore, are unable to test the sequence proposed in Scheme 3. We have synthesized 14, [12] the product which would result from a [1,4] benzyl migration, and have found it to be thermally stable, thus an unlikely intermediate in the thermal decomposition of 6.

Scheme 3



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