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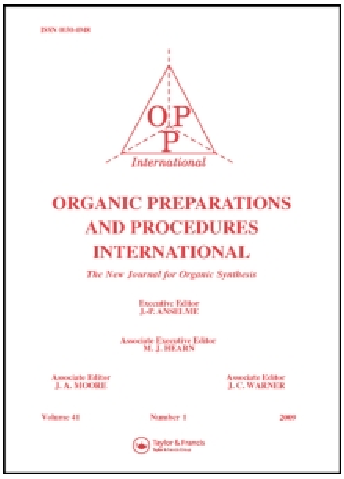

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THE PREPARATION OF 1,4-DIBROMOMETHYL-1,4-DIPHENYL-AZINEMETHYLENE AND ITS REACTION WITH BENZYLAMINE

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ORGANIC PREPARATIONS AND PROCEDURES, INT. 3(6), 289-293 (1971)

THE PREPARATION OF 1,4-DIBROMOMETHYL-1,4-DIPHENYLAZINEMETHYLENE AND ITS REACTION WITH BENZYLAMINE[1]

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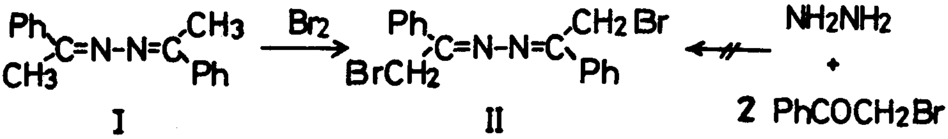
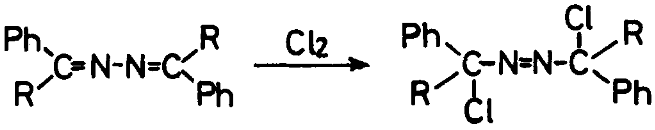
Although many azines have been prepared[3-5] since their original synthesis by Curtius,[6] very little of their chemical transformations is known, save for numerous pyrolytic studies.[6-17] We now report the novel bromination of acetophenone ketazine (I) to 1,4-dibromomethyl-1,4-diphenylazinemethylene (phenacyl bromide ketazine) and the cyclization of the dibromo compound to a triazepine derivative.



I

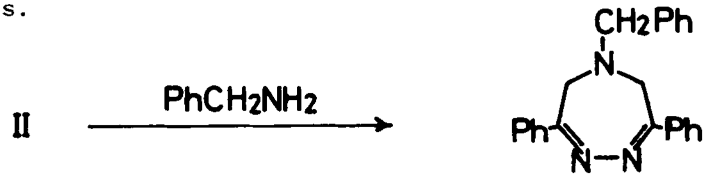
II

The bromination of I in methanol[18] gave II as an orange crystalline compound, mp 151-152°C, in 60% yield. Its structure was confirmed by the results of the elemental analysis and its mass and nmr spectra. The formation of II by direct bromination of I[19] is particularly important since the reaction of phenacyl bromide with hydrazine did not give II but resulted in the formation of resinous material exclusively. It is also of interest to note that the chlorination of I[20] and of benzaldazine[21,22] yielded the corresponding α,α'-dichloroazo compound (III).



(R=H, CH_3)

The dibromide II having two active bromine atoms would expected to react with primary amines, affording the corresponding triazepine derivatives. We found that in the presence of triethylamine, II reacts with benzylamine to give the expected product, 5-benzyl-4,6-dihydro-3,7-diphenyl-1,2,5-triazepine (IV), mp. 121-122°C, in a good yield. The structure of IV was established by its spectral data as well as by the elemental analysis.



IV

Further studies of the related reactions are in progress in our laboratory.

EXPERIMENTAL

All the melting points are uncorrected. The nmr spectra were determined at 60 MHz with a Hitachi R-20 nmr spectrometer using TMS as an internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer using a direct inlet and an ionization energy at 70 eV. The elemental analyses were performed by Miss M. Akita at our laboratory.

1,4-Dibromomethyl-1,4-diphenylazinemethylene (II). To a stirred suspension of 50 g. of acetophenone ketazine (I) in 30 ml. of methanol kept at 0-5°C, was added dropwise a solution of 75 g. of bromine in 15 ml. of methanol. After the reaction mixture was stirred at room temperature for 30 minutes, filtration gave 40.5 g. of orange crystals. The filtrate was concentrated under reduced pressure, giving 9.5 g. of crystals. The total yield: 50 g. (60%). Recrystallization from chloroform afforded the dibromide II, mp. 151-152°C, as orange prisms.

Anal. Calcd. for $C_{16}H_{14}N_2Br_2$: C, 48.76; H, 3.57; N, 7.11.
Found: C, 48.74; H, 3.36; N, 6.83.

Mass spectrum: m/e 392, 394 (M.).

Nmr spectrum ($CDCl_3$): τ 5.47 (4H, two methylenes, singlet) and τ 1.8-2.7 (10H, aromatic protons, multiplet).

Reaction of II with Benzylamine. A solution of 0.68 g. of benzylamine and 1.28 g. of triethylamine in 25 ml. of benzene was added dropwise to a refluxing solution of 2.5 g. of II in 50 ml. of benzene. After the reaction mixture was refluxed for 30 minutes, it was cooled to room temperature. The precipitated triethylamine hydrobromide (1.98 g.) was filtered and the filtrate was evaporated under reduced pressure, leaving a semicrystalline residue which was extracted with 500 ml. of boiling petroleum ether (bp. 42-60°C). The extract was concentrated to about 50 ml. and then allowed to stand overnight. Filtration gave 1.33 g. of colorless crystals, which on recrystallization from petroleum ether gave the triazepine IV, mp. 121-122°C, as colorless prisms.

Anal. Calcd. for $C_{23}H_{22}N_2$: C, 81.39; H, 6.24; N, 12.38.
Found: C, 81.71; H, 6.21; N, 12.29.

Mass spectrum: m/e 339 (M).

Nmr spectrum (CDCl$_3$): τ 6.44 (2H, PhC$\underline{H}_2$-, singlet), 6.19 (4H, -C$\underline{H}_2$-, singlet) and 2.7-1.9 (15H, aromatic protons, multiplet).

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