Preparation and Photolysis of 1-*t*-Butyl-3-benzoylazetidine

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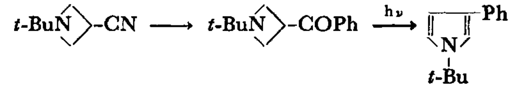
A photo-induced ring expansion of 1-*t*-butyl-2-phenyl-3-benzoylazetidine to 1-*t*-butyl-2,4-diphenylpyrrole has recently been reported by Padwa *et al.*[2] Since this is the first example of the conversion of an azetidinyl ketone into the corresponding substituted pyrrole, further study was carried out with 1-*t*-butyl-3-benzoylazetidine (II), which had been synthesized by the reaction of 1-*t*-butyl-3-cyanoazetidine (I)[3] with phenylmagnesium bromide.



I II III

The infrared spectrum of the azetidinyl ketone II shows a carbonyl band at 1680 cm^{-1} and is quite consistent with the proposed structure. The formations of 2,4-dinitrophenylhydrazone and the picrate of the azetidinyl ketone II and their analytical data all support the assigned structure.

A dilute solution of II in ethanol was irradiated through a Pyrex filter with a high-pressure mercury lamp to give the corresponding 1-*t*-butyl-3-phenylpyrrole (III). The structure of III was determined by comparing the IR and NMR spectra with those data obtained by Padwa *et al.*[2] The infrared spectrum of the distilled product exhibits some small peaks between 3080—3030 cm^{-1} and sharp peaks at 1605, 1555, 1500, 750, and 693 cm^{-1} for the characteristic absorptions of phenyl and the pyrrole ring. The strong absorptions of the tertiary butyl group appear at 1245 and 1225 cm^{-1}. The NMR spectrum of the product exhibits a sharp singlet at τ 8.54 (9H) for the *t*-butyl group, and three signals of doublet of doublet at 3.77 (1H), 3.40 (1H), and 3.12 (1H) for the three protons at the 4, 5, and 2-positions of the pyrrole ring. The phenyl group on the pyrrole ring appears between 2.6 and 3.06 (5H) as a multiplet.

Isomerization was not observed when an alcoholic solution of II was warmed in the presence of boron trifluoride etherate or when the ketone II was heated at 254°C or at 340°C.

Experimental[4]

1-*t*-Butyl-3-benzoylazetidine (II). A solution of 5.4 g (0.039 mol) of I in 7 m*l* of absolute ether was stirred into a cooled solution of phenylmagnesium bromide prepared from 2.5 g (0.12 mol) of magnesium and 21 g (0.13 mol) of bromobenzene in 80 m*l* of absolute ether. After the completion of the addition, the reaction mixture was stirred for another four hours and then set aside overnight at room temperature. The reaction mixture was decomposed with about 100 m*l* of ice water and extracted four times with a total of 200 m*l* of ether. After drying over magnesium sulfate, the ether was removed and the residue was distilled to give 3.5 g (40% yield) of a colorless liquid; bp 140—144°C/ 3 mmHg, n_D^{25} 1.5062. IR: 3060, 1600, 1580, 700 cm^{-1} (C_6H_5), 1680 cm^{-1} (CO), 1240 and 1225 cm^{-1} (*t*-Bu).

Found: C, 77.72; H, 8.75; N, 6.11%. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45%.

2,4-Dinitrophenylhydrazone of II: mp 88—89.5°C.

Found: C, 60.89; H, 5.90; N, 17.36%. Calcd for $C_{20}H_{23}N_5O_4$: C, 60.44; H, 5.83; N, 17.62%.

Picrate of II: mp 157.5—159.5°C.

Found: C, 54.11; H, 4.96; N, 12.64%. Calcd for $C_{20}H_{22}N_4O_8$: C, 53.81; H, 4.97; N, 12.55%.

Photolysis of II. A solution of 0.5 g of II in 100 m*l* of 99% ethanol was irradiated through a Pyrex filter with a 100 W high-pressure type mercury lamp under a nitrogen atmosphere for seventeen hours. After the removal of the ethanol under reduced pressure, the residue was distilled *in vacuo* to give 0.1 g of a colorless liquid; bp 120—124°C/1 mmHg. The product was positive to a pine-splinter test (red color).

Found: C, 83.93; H, 8.76; N, 6.83%. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03%.

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1) Present address: National Tsing Hua University, Taiwan, The Republic of China.

2) A Padwa, R. Gruber and L. Hamilton, *J. Am. Chem. Soc.*, **89**, 3077 (1967).

3) Part III, T. Chen, T. Sanjiki, H. Kato and M. Ohta, This Bulletin, **40**, 2401 (1967).

4) The general conditions for the measurements of the physical constants and spectra were the same as those described in Part I; T. Chen, H. Kato and M. Ohta, This Bulletin, **40**, 1964 (1967).