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Photoisomerisation of N-Carboethoxy-2,3-homoazepine

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In the course of our studies on tropane alkaloids, we had an occasion to photolyse N-carboethoxy-2,3-homoazepine.[2] We now wish to describe the result, which seems to be different from those reported.[3]

A dilute solution of N-carboethoxy-2,3-homoazepine (I) in chloroform or more preferably in methanol was irradiated by a medium pressure mercury lamp under nitrogen or argon atmosphere. The reaction mixture was very simple and the oily major product (II) was isolated by distillation in a yield of over 90%. An analytical sample was purified by column chromatography and redistillation. The monomeric nature of II was supported by its smaller vpc retention time than the starting I and the mass spectrum. Though the nuclear magnetic resonance (NMR) spectrum of II at room temperature has several broad and well-resolved signals, it changes to a very good resolved spectrum at 85°, which was analysed by double and triple resonances.[4] The spectrum shows the presence of three unambiguous cyclopropane hydrogens at δ 0.32, 0.84 and 1.53, and a doublet at δ 3.45 which coupled with a doublet at δ 4.55, and two hydrogens of an olefinic bond at δ 6.32 (Figure). Compound (II) absorbed one mole of hydrogen in the presence of Pd to afford a dihydro compound (III). The NMR spectrum of III, which is also temperature dependent, shows the absence of olefinic hydrogen, but instead the presence of two signals at δ 4.2 and δ 2.98 which correspond to the signals at δ 4.55 and 3.45 in the NMR of II, respectively. The change of the chemical shift indicates that these hydrogens were allylic in II. Any change of the chemical shift of cyclopropane hydrogens by the reduction, however, was not observed. The coupl-

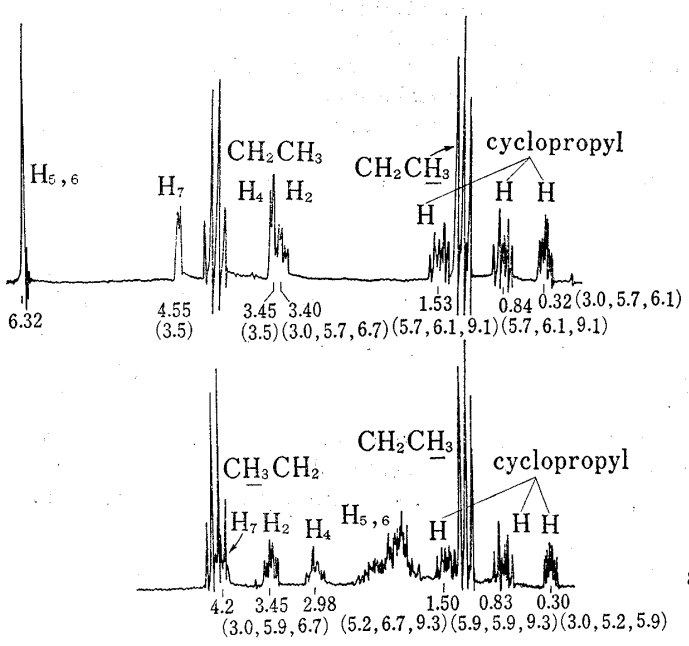
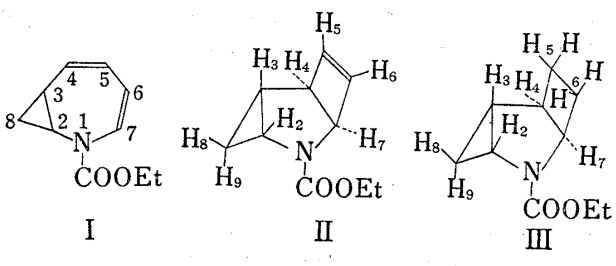


Fig. NMR Spectra of II (up) and III (down) in CCl_4 at 85° (δ in ppm, J cps in parentheses)



1) Location: *7-3-1, Hongo, Bunkyo-ku, Tokyo.*
2) W.H. Okamura, W.H. Snider, and T.J. Katz, *Tetrahedron Letters*, **1968**, 1370; L.A. Paquette and R.J. Haluska, *Chem. Comm.*, **1968**, 1370.
3) L.A. Paquette and R.J. Haluska, *J. Org. Chem.*, **35**, 132 (1970).
4) We are indebted to Prof. Hara, Tokyo Pharmaceutical College, for NMR measurement.

ing constants and assignment of the signals are shown in the Figure. These NMR data are compatible with the tricyclic structure, II, for the photoproduct. The stereochemistry of cyclopropane and cyclobutane is now thought to be *anti* (both rings are in relation of *trans*), because the fact that NMR signal of H_3 does not couple with H_4 shows the dihedral angle of these two hydrogens are nearly 90°.[5] If *syn*, the angle is about 10°, and in the *anti* structure, the angle is about 90° according to the Büchi model, in which case a very small coupling constant is expected. The conclusion is consistent with the absence of anisotropic effect of the double bond on the cyclopropyl hydrogen. The *endo* hydrogen of cyclopropane *gem* hydrogens should be shielded by the olefinic bond in the *syn* structure, and the saturation of the olefinic bond should cause an appreciable deshielding.[6]

The stereochemical result is incompatible with the reported work on N-carbomethoxy-2,3-homoazepine by Paquette, *et al.*[3] which has appeared at the same time as the present work was completed. They have drawn a conclusion that the photoproduct from the carbomethoxy compound was the *syn* isomer without any concrete evidence but analogy to the case of 2,3-homotropone[7] and 2,3-homotropilidene.[8]

The temperature dependent NMR may be due to the restricted rotation or inversion of N-COOEt group. We have not enough data for the discussion on the problem.[9]

Experimental

Irradiation of N-Carboethoxy-2,3-homoazepine——A solution of 4.0 g of N-carboethoxy-2,3-homoazepine[2] in methanol (90 ml) was irradiated in a cylindrical vessel with a medium pressure mercury lamp under nitrogen or argon. After the starting material disappeared (usually 5—20 hr according to the ammount of the material), methanol was evaporated under a reduced pressure. The oily redidue was distilled at 0.02 mmHg to give a pale yellow oil (II), bp 63°. Small contaminates were removed by a silica gel column chromatography (pet. ether–methylene chloride), and the main fraction was distilled, bp $_{0.02}$ 63°. IR ν_{max}^{cap} cm^{-1}: 1700, 3065, 1420, 1327, 1115, 895, 855, 763, 707. UV $\lambda_{max}^{95\%\ ethanol}$: end absorption above 205 nm. ε 3800 at 210 nm. *Anal.* Calcd. for $C_{10}H_{13}O_2N$: 67.02; H, 7.31; N, 7.82. Found: C, 67.26; H, 7.48, N, 7.95. Mass Spectrum *m/e*, 179 (M^+).

Catalytic Reduction of the Photoproduct——A solution of 184 mg of II in 5 ml of methanol was hydrogenated in the presence of 10% Pd-C at room temperature. After removal of the solvent, the residue was distilled at 0.02 mmHg in a bath (75°), and a colorless liquid was obtained quantitatively. UV $\lambda^{95\%\ ethanol}$: end absorption above 210 nm, ε 2800 at 210 nm. *Anal.* Calcd. for $C_{10}H_{15}O_2N$: C, 66.27; H, 8.34; N, 7.95. Found: C, 65.88; H, 8.46; N, 7.69. Mass Spectrum *m/e*, 181 (M^+).

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6) L.M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Spectroscopy in Organic Chemistry," 2nd ed., Pergamon Press, New York, 1969, p. 230.
7) L.A. Paquette and O. Cox, *J. Am. Chem. Soc.*, **89**, 5633 (1967).
8) W.R. Roth and B. Peltzer, *Ann.*, **685**, 56 (1965).
9) for N-carboethoxyazocine, see K. Hojo and S. Masamune, *J. Am. Chem. Soc.*, **92**, 6690 (1970).