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1,3-Dipolar Character of Six-membered Aromatic Rings. XIV.*[1] A Double Cycloaddition to 3-Oxido-1-phenacylpyridinium

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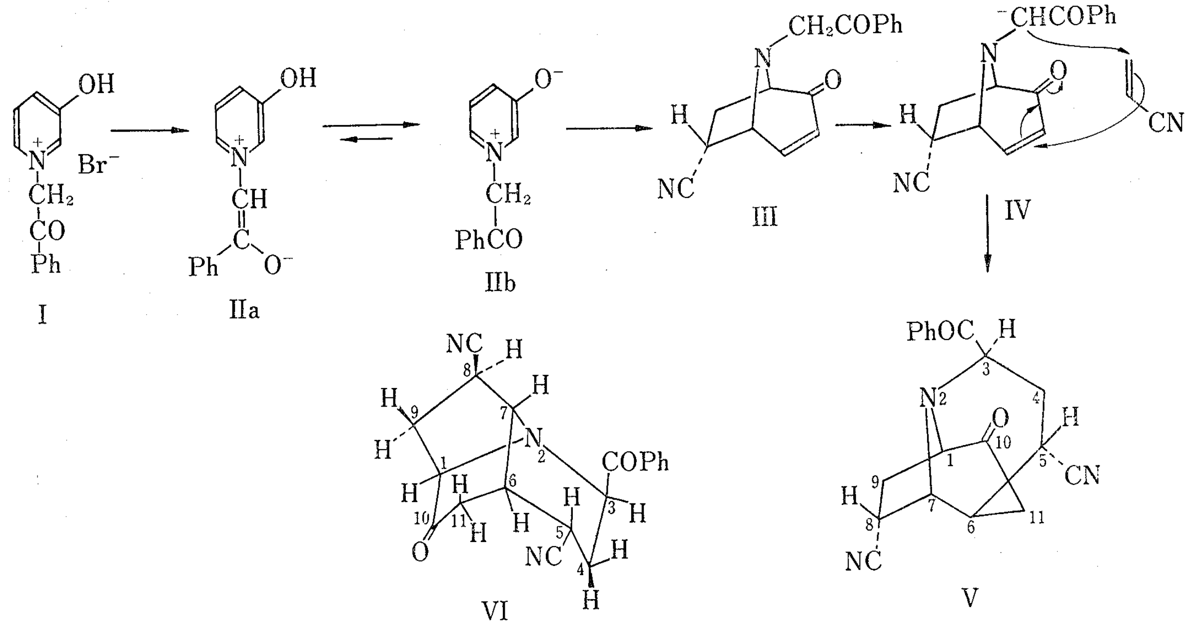
The title betaine reacts with two molecules of acrylonitrile to yield the tricyclic adduct 3-benzoyl-5,8-dicyano-2-azatricyclo[4.3.2.$0^{2,7}$]undecan-10-one (VI).

3-Hydroxypyridine and phenacyl bromide readily yield the quaternary salt I which with Na_2CO_3 gives an unstable betaine shown by spectral evidence (experimental) to be (IIb) rather than (IIa). The betaine (IIb) reacts *in situ* with acrylonitrile to form a 2-azatricyclo[4,3,2,$0^{2,7}$]-undecan-10-one (V) by proton loss from the initial adduct III and reaction with more acrylonitrile (IV). The infrared (IR) spectrum showed two cyano-groups (2240 and 2250 cm^{-1}) and saturated (1725 cm^{-1}) and unsaturated (1685 cm^{-1}) carbonyl groups. The empirical formula $C_{19}H_{17}O_2N_3$ was supported by the mass spectral parent peak at *m/e* 319.



Ph=phenyl

The nuclear magnetic resonance (NMR) spectrum (Figure and Table) discloses the double chair conformation VI (which possesses the least strain) and indicates the stereochemistry of the cyano and benzoyl substituents. The downfield 1-proton triplet H-3 is coupled equally to the methylene protons H-4, and a molecular model shows equal dihedral angles between H-3 of VI as drawn and H-4-*exo* and H-4-*endo*. The bridgehead proton H-6 appears as a quartet due to three equal couplings with both the methylene protons H-11 and with proton H-7. Proton H-1 shows as a quartet because of unequal coupling to H-9-*exo* ($J_{1,9\text{-}exo}$ 7.5 Hz)

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* Dedicated to the memory of prof. Eiji Ochiai.

[1] Part XIII: N. Dennis, A.R. Katritzky, and S.K. Parton, preceding paper.

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and weak ω-type long-range coupling to H-11-*exo* ($J_{1,11\text{-}exo}$ 1.5 Hz), further evidence for the double chair conformation. Proton H-7 appears as a quartet due to unequal coupling with H-8-*exo* and H-6. Proton H-8-*exo* forms a symmetrical sextet due to coupling with H-9-*exo*, H-9-*endo* and H-7. The methylene protons H-11 and H-4 appear as a broad 4-proton multiplet centred at 2.70 δ. Proton H-9-*exo* forms a symmetrical octet due to coupling with H-9-*endo*, H-8-*exo* and H-1. Proton H-9-*endo* coupled to protons H-9-*exo* and H-8-*exo* forms a quartet, whilst proton H-5-*endo* appears as a quartet due to unequal coupling with methylene protons H-4.

These assignments were confirmed by double resonance. Irradiation at the frequency of the H-11 and H-4 methylene multiplet collapsed protons H-7 and H-1 to doublets, whilst partial decoupling was observed for the protons H-3 and H-5-*endo*. Irradiation of the proton H-8-*exo* collapsed the H-7 quartet. The coupling constants of protons 7, 8 and 9 (in compound VI) are in agreement with those of the corresponding protons of previously reported[3] cycloadducts of type III and with the Karplus Equation.

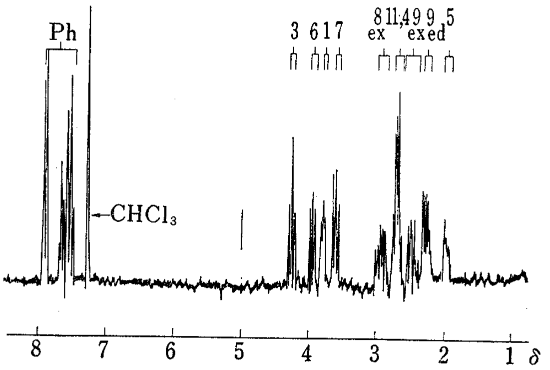

Fig. 1. H^1-NMR Spectrum of Cycloadduct duct (VI) in $CDCl_3$

The mass spectrum shows a base peak at *m/e* 214 due to loss of a benzoyl radical; further loss of carbon monoxide gives the fragment ion *m/e* 186, which then fragments further with subsequent losses of hydrogen cyanide and acrylonitrile to give peaks at *m/e* 158 and *m/e* 105, respectively. Alternatively the peak at *m/e* 186 could have arisen from the initial expulsion of carbon dioxide to give *m/e* 291 and then loss of the benzoyl radical.

TABLE I. Proton NMR Spectrum of Adduct (VI)[a,b]

Chemical shifts (δ)		Coupling constants (Hz)	
1	3.80[c]	1,11-*exo*	1.5
11-*exo*	2.70[d]	1,9-*exo*	7.5
11-*endo*	2.70[d]	11-*exo*, 11-*endo*	14.0
6	3.95[c]	11-*exo*, 6	5.0
7	3.60[c]	11-*endo*, 6	5.0
8-*exo*	2.94[e]	6,7	5.0
9-*exo*	2.49[f]	7,8-*exo*	7.5
9-*endo*	2.29[c]	8-*exo*, 9-*exo*	10.0
3	4.26[g]	8-*exo*, 9-*endo*	7.5
4-*exo*	2.70[d]	9-*endo*, 9-*exo*	13.0
4-*endo*	2.70[d]	3,4-*exo*	7.5
5-*exo*	—	3,4-*endo*	7.5
5-*endo*	1.97[c]	4-*exo*, 5-*endo*	5.5
Ph	7.96—7.22	4-*endo*, 5-*endo*	10.0
		6,5-*endo*	1.0

a) in ppm relative to Me_4Si as internal standard *b*) in $CDCl_3$
c) quartet *d*) centre of multiplet *e*) sextet *f*) octet
g) triplet

The betaine II reacts with methyl acrylate to yield a mixture of adducts.

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3) N. Dennis, A.R. Katritzky, T. Matsuo, S.K. Parton, and Y. Takeuchi, *J. Chem. Soc. Perk. Trans.* 1, **1974**, 746.

Experimental

3-Hydroxy-1-phenacylpyridinium Bromide (I)——3-Hydroxypyridine (5.0 g, 0.05 mol.) and phenacyl bromide (10.0 g, 0.05 mol.) were stirred in refluxing tetrahydrofuran (25 ml) for 8 hr. The product (13.0 g, 87%) deposited; it crystallized from 95% ethanol as needles, mp 228—229°. *Anal.* $C_{13}H_{12}O_2NBr$ requires C, 53.1; H, 4.1; N, 4.8. Found: C, 52.8; H, 4.2; N, 4.7. IR Nujol ν_{max} cm^{-1}: 3300 (OH), 1700 (C=O), 1590 (arom.)

3-Oxido-1-phenacylpyridinium (IIb)——Aqueous sodium carbonate (10 g, 30 ml H_2O) added to the bromide (3.8 g, 0.013 mol.) in water (5 ml) at 0° gave the betaine (IIb) as a deep-yellow precipitate (2.5 g, 90%); IR Nujol ν_{max} cm^{-1}: 1690 (C=O), 1600 (arom.) UV (H_2O) λ_{max} 332 nm (log ε 3.64), 248 (3.97), 215 (4.23). The betaine IIb rapidly deteriorated on isolation, and no analysis or mp could be obtained.

Reaction of 3-Hydroxy-1-phenacylpyridinium Bromide with Acrylonitrile——3-Hydroxy-1-phenacylpyridinium bromide (I) (5 g, 0.023 mol.) and acrylonitrile (5.3 g, 0.10 mol.) in dry acetonitrile (30 ml) were heated under reflux, triethylamine (5 ml) was added dropwise during 0.5 hr and the refluxing was continued for a further 18 hr. The cooled reaction mixture was chloroform-extracted (3 × 50 ml) and the solvent removed *in vacuo*. The solid residue was purified by thick-layer chromatography [Kieselgel PF 254, toluene–ethyl acetate, (50: 50)] to give the 3-benzoyl-5,8-dicyano-2-azatricyclo[4.3.2.0^{2,7}]undecan-10-one VI (1.5 g, 20%) which separated from *n*-propanol as prisms mp 180—181°. *Anal.* $C_{19}H_{17}O_2N_3$ requires C, 71.5; H, 5.4; N, 13.2. Found: C, 71.1; H, 5.5; N, 13.0. IR $CHBr_3$ ν_{max} cm^{-1}: 2250, 2240 (CN), 1725 (sat. C=O), 1685 (α,β-unsat. C=O), 1600, 1500 (arom.). UV (EtOH) λ_{max} 208 nm (log ε 4.11), 247 (4.11). Mass Spectrum *m/e*: 319.

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Professor Eiji Ochiai: A European's Appreciation The passing of Professor Ochiai has saddened his many friends and admirers in Europe. His outstanding work in N-oxide chemistry rapidly became widely known throughout the Western World after the publication in 1953 of a review article in *Journal of Organic Chemistry*, and since then his methods have been utilised world-wide by many research groups who have found inspiration in his work.

I myself read Professor Ochiai's 1953 review while a research student of Sir Robert Robinson, and it made such a strong impression on me that I decided that my first independent research should be in this field. Professor Ochiai's classic work has remained for me ever since as an inspiration. It is a source of joy to all Organic Chemists the world over that his School of Chemistry has been so well founded in Japan that we have a steady stream of papers from several centres established by his pupils and associates.

I am proud to have had the honour of meeting Professor Ochiai in person, and to have perceived his kindness and courtesy to a younger and junior colleague and his knowledge of Japanese history and culture. Professor Ochiai's name is enshrined in the minds of Chemists the world over as one of the outstanding figures of this century. (A.R. Katritzky).