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PHOTOCHEMICAL ADDITION OF N-ACYLDIPHENYLMETHYLENEIMINE TO CYCLIC AND ACYCLIC OLEFINS

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Recently, it has been reported that a 2-aza-enone compound, aza-analog of α,β-unsaturated ketone, is easily reduced on irradiation with ultraviolet light (1-4). However, there is no record on the photochemical addition reaction of the 2-aza-enone to olefin. We wish to report the photochemical addition reaction of N-acetyldiphenylmethyleneimine (I) to several olefins.

A solution of I (5.7 mmol) in cyclohexene (54 mmol) was irradiated for 100 hr with a 500W high pressure mercury lamp under a nitrogen atmosphere, which resulted in a conversion of I by 20%. Chromatography on silica-gel of the evaporated reaction mixture gave one photoproduct in 75% yield based on the consumed imine. The elemental analysis and the molecular weight measurement of the isolated product, mp 181.0°C, were consistent with those of the 1:1 adduct of I with cyclohexene (Found: C, 82.37; H, 7.32; N, 4.61; mol wt, 285 (5). Calcd for $C_{21}H_{23}ON$: C, 82.58; H, 7.59; N, 4.59; mol wt, 305). The UV spectrum (5) showed the existence of the separated phenyl group [λ_{max}^{EtOH} 253.6(logε=2.71), 259.4(2.75), 265.0(2.67), and 270.5 nm(2.47)] and the IR spectrum (5) had the same kind of bands(3290, 1660, and 1540 cm^{-1}), i.e., amide type absorption bands, as N-diphenylmethylacetamide, a photoreduction product of I (1,2). The olefin test ($KMnO_4$ test and Br_2 test) indicated the existence of C=C bond. The NMR spectrum (5) had bands at δ 7.00-7.95 (10H, singlet, phenyl protons), 6.32 (1H, broad singlet, NH proton), 5.47 (2H, broad singlet, olefin protons), 3.65-4.00 (1H, broad multiplet, methine proton), and 0.85-2.08 (9H, complex multiplet, aliphatic protons). On the basis of these informations, the product was identified with N-(diphenylcyclohex-2'-enylmethyl)acetamide (II).

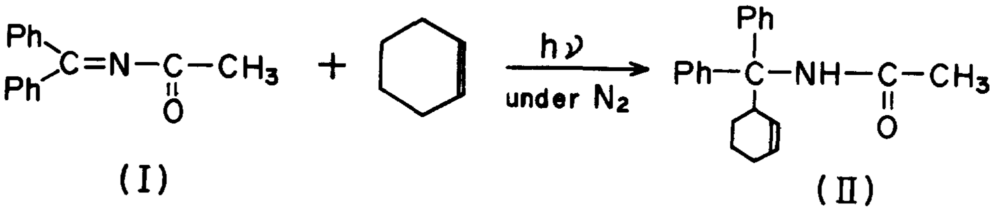
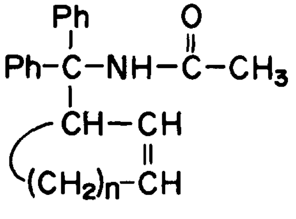


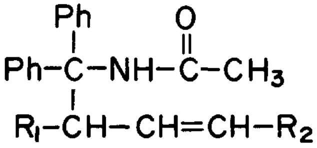
Table I. Photochemical Addition of N-Acetyldiphenylmethyleneimine to Several Olefins.

Reactant Olefin	Product		
	Yield (%)	mp (°C)	Structure
Cyclopentene	31	147.0-147.8	IIIa
Cyclohexene	15	181.0	II
Cyclooctene	2	liq.	IIIb
2-Hexene	1.0	liq.	IVa+IVb
2-Pentene	0.9	liq.	IVc

Irradiation time; 100 hr. Temp.; 15°C.



IIIa n=2, IIIb n=5



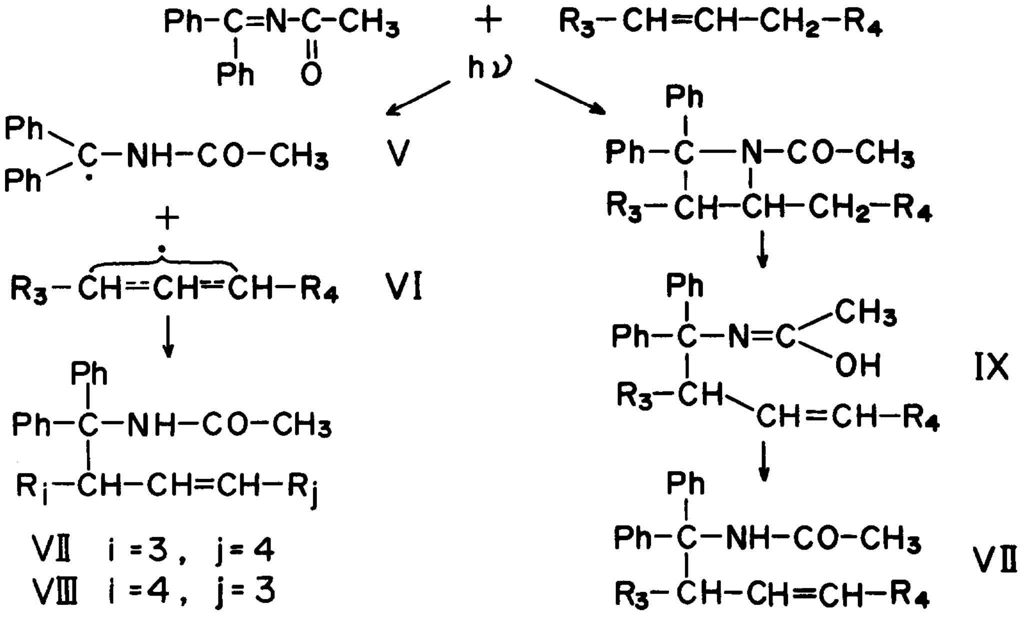
$$Ph_2C(NHCOCH_3)-CH(R_1)-CH=CH-R_2$$

IVa R_1=Me, R_2=Et

IVb R_1=Et , R_2=Me

IVc R_1=R_2=Me

No reaction took place on refluxing of the solution under the same condition without light. The photoreaction of I with several olefins yielded the corresponding reaction products (see Table I). Amide IVa and IVb could not be separated, but the presence of both compounds was confirmed by NMR spectra of the mixtures (6). The structures of the products suggest that I reacts with cyclic and acyclic olefins in a common process. In consideration of the structures of the photoproducts, two kinds of reaction mechanism can be assumed. One is a radical mechanism, in which the excited imine abstracts the hydrogen atom in allylic position of olefin to produce benzhydryl radical V and allyl radical VI. Intermolecular coupling of these two radicals gives the photoproduct. An alternative mechanism is via a cycloaddition intermediate. This mechanism involves the cycloaddition of C=N bond to C=C bond of olefin and rearrangement to alcohol



IX accompanied by decomposition of four membered ring. Compound IX isomerises to VII in the same way as a keto-enol tautomerism. In the radical mechanism, the radical position of VI is changeable. If proper olefin is used on the reaction with I, two isomers (VII and VIII) should be produced. But such isomers are impossible to be found in the other alternative mechanism. Formation of two isomers on the reaction with 2-hexene suggests the radical mechanism.

The UV spectra of I displayed weak inflections on the long wavelength side of the principal absorption band at 363 nm ($\log\varepsilon$=2.05) and 382 nm (0.72) in cyclohexane. These weak bands showed blue-shifts in polar solvents and are probably assignable to the $n \to \pi^*$ transitions. When irradiation was carried out either using a glass ampule or cutting light of shorter wavelength than 350 nm with a liquid filter (7), the same photochemical addition product was obtained. These facts suggest that the photochemical addition reactions occurred via (n, π^*).

When benzophenone or acetophenone was used as a sensitizer, the yield of the photoadduct was found to increase. On the contrary, the photoaddition reaction was completely inhibited in the presence of piperylene, an efficient triplet quencher (8) (see Table II). These results suggest that the triplet state of I is involved in this reaction.

Table II. Effect of Additives on the Photochemical Addition of N-Acetyldiphenylmethyleneimine (I) to Cyclohexene.

Cyclohexene (mmol)	I (mmol)	Additive (mmol)	Product Yield (%)
54.3	5.73	None	15
56.9	4.67	Benzophenone (0.58)	38
55.3	4.53	Acetophenone (6.71)	25
56.9	4.56	Piperylene (23.2)	0

Irradiation time; 100 hr.

In conclusion, this photochemical addition reaction seems to proceed via $^3(n, \pi^*)$ state of I. Further mechanistic studies are in progress.

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(5) Molecular weight was measured in ethyl acetate with a Mechrolab model 301A vapor pressure osmometer. IR spectra were obtained with a JASCO IR-E spectrophotometer. NMR spectra were recorded with a JEOLCO C-60 spectrometer using tetramethylsilane as an internal standard.

(6) Product IVa has a characteristic band at δ 1.9 for methylene protons of R_2 and IVb, at δ 1.6 for methyl protons of R_2.

(7) A mixed solution of $NaBr \cdot 2H_2O$ (650 g/liter) and $Pb(NO_3)_2$ (3.00 g/liter) in water; A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag New York Inc., New York, 1968, p.492.

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