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Photochemical Reactions of Diphenylacetylene with Enaminoesters[1)]

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As a consequence of our continuing interest in the behavior of enamines in photochemistry[2,3)] we have investigated the photochemical reaction of diphenylacetylene (I) with 3-alkylaminocrotonate (II) or 3-dialkylaminocrotonate (III), and found that the reaction resulted in the formation of heterocyclic compounds. This unprecedented result is the subject of this note.

When a benzene solution of I and IIa was irradiated by means of a high pressure Hg lamp and the reaction mixture was chromatographed on an alumina column, the following compounds were obtained: 4,5-diphenyl-1,6-dimethyl-2-pyridone (IVa) (19%), ethyl 4,5-diphenyl-1,2-dimethylpyrrole-3-carboxylate (Va) (4%), a mixture of photodimers of I[4)] along with some unidentified materials (trace).

The structure of IVa was assigned by spectroscopic methods and the conclusive evidence for the structure was obtained by the following chemical transformations. Hauser reported that the reaction of benzyl methyl ketone with benzoylacetonitrile in the presence of PPA gave a pyridone whose structure was estimated as VII

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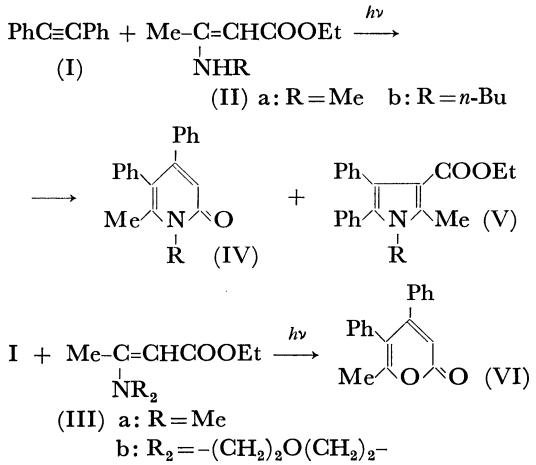
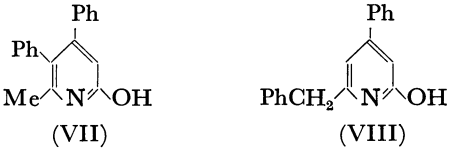


or VIII.[5] We have reinvestigated this reaction, and the pyridone obtained was scrutinized by means of NMR for the benzylic protons, but there was none. Thus the structure VII was established for the reaction product.



Methylation of VII with dimethyl sulfate in alkaline medium[6] proceeded in a selective manner giving an *N*-methylated pyridone which was identical in all respects with the photochemical product IVa.

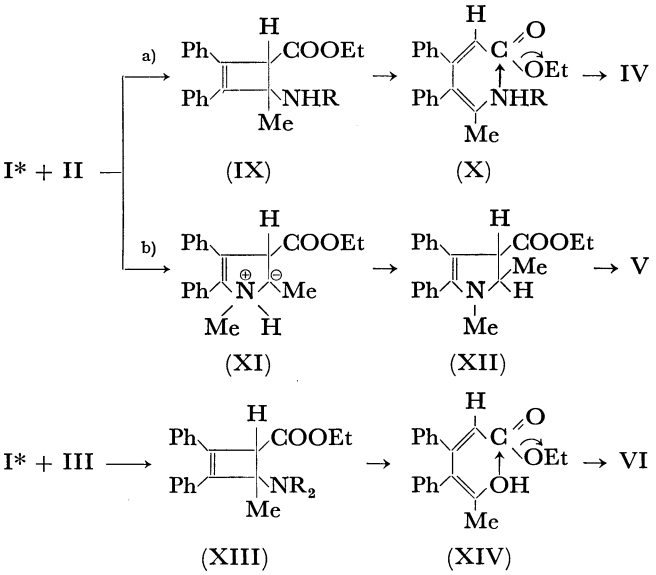
The structure of Va was established by spectroscopic methods as well as the independent synthesis described by Huisgen from *N*-acetyl-*N*-methylphenylglycine and ethyl phenylpropiolate.[7]

The reaction of IIb proceeded similarly and IVb was obtained in 28% yield. The spectroscopic data for IVb were essentially identical with those of IVa. In this case no Vb was isolated probably due to the difficulty in separation.

When a mixture of I and IIIa or IIIb was treated similarly, 4,5-diphenyl-6-methyl-2-pyrone (VI) (8% and 2%, respectively) was obtained. The structure of VI was established by spectroscopic methods as well as by the independent synthesis.[8]

Although the intermediate products are not identified yet, the mechanism for the formation of IV, V, and VI is tentatively considered as follows. The reactions of some electrophilic acetylenes with enamines or enaminoesters have been well documented,[9] whereas the electrophilic nature of excited simple acetylenes such as I have been demonstrated in the cycloaddition of I with dihydropyran.[10] Consequently it may be safely stated that the photoexcited I might react with II in two ways giving a) a cyclobutene IX and b) an ionic intermediate XI. Ring opening of IX to X followed by reclosure may give IV, while proton shift in XI followed by aromatization will afford V.

On the other hand the cycloaddition of the photoexcited I with III might give XIII, ring opening and hydrolysis followed by reclosure will lead to VI. The reason why hydrolysis takes place in the case of XIII and does not in the case of X is still obscure. However, we feel that NH-hydrogen seems to be responsible to some extent for the reaction.



Experimental

All boiling and melting points are uncorrected. Microanalyses were performed at the Elemental Analyses Center of Kyoto University. The IR spectra were recorded in neat liquid film or as KBr pellets on a Shimadzu IR-27G spectrometer. The NMR spectra were taken on a JOEL C-60-H spectrometer in CCl_4 solutions and TMS as an internal standard. The UV spectra were obtained in ethanol solutions on Shimadzu MPS-50L spectrophotometer.

Reagents. The starting materials I, IIa, and IIIa were prepared according to the published methods and have following properties; I, mp 64—66°C (lit.[11,12] mp 60—61°C), IR: 1600, 1490, 1070, 910, 760, 690 cm^{-1}, NMR: δ 7.1—7.5 (10H), UV: λ_{max} 265 nm (ε=21800), 275 (24100), 280 (31900), 289 (23000), 297 (28000). IIa, bp 107—108°C/17 mmHg (lit.[13] bp 105—106°C/15 mmHg), IR: 3310, 2990, 1950, 1650, 1610, 1265, 1160, 780 cm^{-1}, NMR: δ 1.2 (t, 3H), 1.9 (s, 3H), 2.9 (d, 3H), 4.0 (q, 2H), 8.4 (1H), UV: λ_{max} 282 nm (ε=16600). IIIa, bp 87—89°C/3 mmHg (lit.[14] bp 131.2—132.2°C/15 mmHg), IR: 1695, 1585, 1140 cm^{-1}, NMR: δ 1.2 (t, 3H), 2.4 (s, 3H), 2.9 (s, 6H), 3.95 (q, 2H), 4.4 (s, 1H), UV: λ_{max} 284 nm (ε=28200).

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3-Butylaminocrotonate (IIb): A mixture of ethyl acetoacetate (13 g, 0.1 mol) and *n*-butylamine (7.3 g, 0.1 mol) in benzene was refluxed for several hr and the water formed was removed continuously in a Dean-Stark apparatus. The reaction mixture was concentrated *in vacuo* and repeatedly distilled throuth Vigreaux column to give IIb quantitatively as a colorless liquid, bp 86.5—87°C/3.5 mmHg (lit.[15] bp 129.5—131°C/14 mmHg), IR: 3290, 2960, 2860, 1650, 1610, 1265, 1170, 1140, 780 cm^{-1}, NMR: δ 1.0—1.5 (10H), 1.9 (s, 3H), 3.2 (q, 2H), 4.0 (q, 2H), 4.3 (s, 1H), 8.5 (1H), UV: λ_{max} 300 nm (ε=23000).

3-Morpholinocrotonate (IIIb): A mixture of ethyl acetoacetate (19.5 g; 0.15 mol) and morpholine (16 g; 0.18 mol) and *p*-toluenesulfonic acid in benzene was refluxed and the water formed was removed continuously. The reaction mixture was concentrated *in vacuo* and distilled to give IIIb, bp 120—122°C/5 mmHg, IR: 1690, 1595, 1140, 1120 cm^{-1}, NMR: δ 1.2 (t, 3H), 2.35 (s, 3H), 3.05—3.25 (4H), 3.5—3.75 (4H), 4.0 (q, 2H), 4.65 (s, 1H), UV: λ_{max} 283 nm (ε=20500). Found: C, 60.05; H, 8.53; N, 6.7%. Calcd for $C_{10}H_{17}O_3N$: C, 60.28; H, 8.60; N, 7.03%.

UV Irradiation. Solutions of I (590 mg; 3.3 mol) and IIa, IIb (a, 720 mg; b, 920 mg; each 5 mmol) or IIIa, IIIb (a, 790 mg; b, 1.0 g; each 5 mmol) in benzene (20 m*l*) were irradiated by means of a high pressure Hg lamp for 150 hr and the solvent was removed by distillation *in vacuo*. The residues were chromatographed on an alumina column to give IV, V, and VI, respectively. 4,5-Diphenyl-1,6-dimethyl-2-pyridone (IVa), mp 166.5—169°C, obtained by photolysis had following properties. IR: 3060, 2960, 1650, 1580, 1515, 1490, 860, 770, 700 cm^{-1}, NMR: δ 2.1 (s, 3H), 3.5 (s, 3H), 6.4 (s, 1H), 7.0—7.1 (10H), UV: λ_{max} 243 nm (ε= 17500), 324 (5880). Found: C, 82.66; H, 6.21; N, 4.95%. Calcd for $C_{19}H_{17}ON$: C, 82.88; H, 6.22; N, 5.09%. 1-Butyl-4,5-diphenyl-6-methyl-2-pyridone (IVb), mp 191—192.5°C, obtained by photolysis had following properties. IR: 3060, 2970, 1650, 1515, 1495, 865, 770, 705, 700 cm^{-1}, NMR: δ 1.0 (t, 3H), 1.3—2.0 (4H), 2.3 (s, 3H), 4.2 (t, 2H), 6.6 (s, 3H), 1.3—2.0 (10H), UV: λ_{max} 244 nm (ε=19000), 323 (6200). Found: C, 83.15; H, 7.11; N, 4.33. Cacld for $C_{22}H_{23}ON$: C, 83.24; H, 7.30; N, 4.41%. Ethyl 4,5-diphenyl-1,2-dimethylpyrrole-3-carboxylate (V), mp 116.5—117.5°C, obtained by photolysis had following properties. IR: 3060, 2930, 1690, 1600, 1280, 1160, 750, 690 cm^{-1}, NMR: δ 0.9 (t, 2H), 2.5 (s, 3H), 3.35 (s, 3H), 3.9 (q, 2H), 6.9—7.1 (10H), UV: λ_{max} 230 nm (ε=28900), 277 (15400), MS: *m/e* 319 (M^+), 290 (M^+-29), 274 (M^+-45). The MS supports the structure of IV. The authentic specimen prepared by the published method[7] had spectral properties quite identical with those of the photochemical product (V), and showed no depression of the mixed mp. 4,5-Diphenyl-6-methyl-2-pyrone (VI), mp 136—136.5°C (lit.[7] 135°C) obtained by photolysis had following properties. IR: 3060, 1720, 1630, 1530, 1495, 860, 770, 700 cm^{-1}, NMR: δ 2.2 (s, 3H), 6.2 (s, 1H), 6.85—7.25 (10H), UV: λ_{max} 233 nm (ε=16200), 282 (6800), 314 (5800).

Methylation of VII. A sample (1.82 g; 6.9 mmol) of V, mp 258—262°C (lit[4] mp 264—266°C), was dissolved in a warm, freshly prepared solution of sodium (0.8 g) in methanol (20 m*l*). After cooling to room temperature, dimethyl sulfate (5 g; 0.04 mol) was added with stirring in the course of 15 min. After refluxing for 12 hr, the solution was made strongly alkaline by adding aqueous sodium hydroxide (25%), and the mixture was poured into ice water. The precipitates were collected by filtration and recrystallized from ether, mp 169—171°C. The spectra of the compound was completely superimposable with the one of IVa obtained photochemically.

The authors wish to thank Professor Hitosi Nozaki for help and stimulating discussion.

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