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Reactions of Enamino Ketones. VII. The Photochemical Reaction of 4-Methylamino-3-penten-2-one and 2,4-Pentanedione with Benzophenone

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Synopsis. The photochemical reaction of 4-methylamino-3-penten-2-one with benzophenone gave *N*-(2,2-dipenyl-2-hydroxyethyl)-4-amino-3-penten-2-one. The reaction of 2,4-pentanedione gave oxetane, resulting from the cycloaddition of benzophenone to the double bond of the enol form.

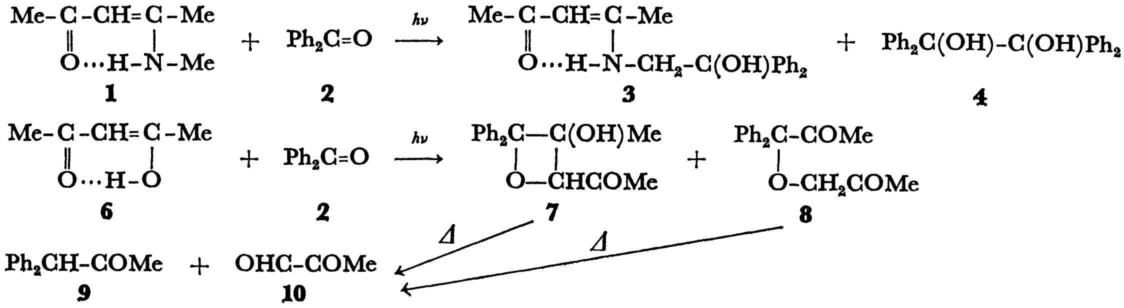
The photochemical reactions of enamines,[1] ketenimines,[2] and *N*-acyl enamines[3] with benzophenone (**2**) have been widely investigated. In general, the reactions of their compounds with **2** give diphenylmethylation products and/or oxetanes by the photocycloaddition of **2** to the carbon-carbon double bond. We have now investigated the photochemical reaction of **2** with secondary enamino ketones and *β*-diketones containing an analogous chelated structure.

The irradiation of a benzene solution containing an equimolar mixture of 4-methylamino-3-penten-2-one (**1**) and **2** for 48 h afforded *N*-(2,2-diphenyl-2-hydroxyethyl)-4-amino-3-penten-2-one (**3**) in a 17% yield, accompanied by benzopinacol (**4**). The structure of **3** was confirmed by the spectral data, and the regeneration, by the condensation of 2,4-pentanedione (**6**) with 2-amino-1,1-diphenylethanol (**5**),[4] which had been obtained by the acid hydrolysis of **3**. In this reaction, the light energy was absorbed exclusively by **2**. However, no oxetane, benzhydrol, and dimer of **1** was obtained. The reaction was also completely inhibited in the presence of 1,3-pentadiene, an efficient triplet quencher of **2**.[5] The hydrogen-source for the formation of **4** is presumed to be the amine part of **1** and the resinous by-products, which are produced in quantity in the reaction.[1]

The photochemical reaction of **2** with 4-anilino-3-penten-2-one (**11**) and 3-methylamino-1-phenyl-2-buten-1-one (**12**) containing the intramolecular hydrogen bonding did not give any photoadduct, the starting materials being recovered. This may be attributed to the circumstance that 95%< of the light energy was absorbed by **11** (at 365 nm ε *ca.* 2000) or **12** (at 365 nm ε *ca.* 8600) under the present reaction conditions. In contrast, 4-dimethylamino-3-penten-2-one (**13**), which can not form a chelate ring, gave, under similar conditions and in addition to **4**, *N*-(2,2-diphenyl-2-hydroxyethyl)-*N*-methylacetamide (**14**) in a 6% yield. The structure of **14** was also assigned on the basis of the spectral data and by elemental analysis. The formation of the amide **14** can be explained by assuming the formation of diphenylhydroxymethylation of **13**, which is oxidative-decomposed to yield the amide during the chromatographic treatment.

In the photochemical reaction of **2** with enamino ketones with a hydrogen atom at the *α*-position to the nitrogen, the diphenylhydroxymethylation exclusively occurs at this position, since its proton is easily abstracted by excited **2**.[1,3,6,7] Consequently, it appears that the intramolecular hydrogen bonding contributes only to the stability of the substrates and the products.

The irradiation of 2,4-pentanedione (**6**) with **2** for 72 h afforded 1:1 adducts, 2-acetyl-3-hydroxy-3-methyl-2,2-diphenyloxetane (**7**) in a 43.5% yield and acetonyl *α*,*α*-diphenylacetonyl ether (**8**) in a 44% yield. The structure of an adduct, **7**, was assigned to the oxetane on the basis of the spectral data and the elemental analysis. The IR absorptions at 3400 and 1704 cm^{-1} of **7** show the presence of an intramolecular hydrogen-bonded hydroxyl and carbonyl group. Furthermore, **7** reacts with 2,4-dinitrophenylhydrazine to give a single 2,4-dinitrophenylhydrazone. These results suggest that the methyl and acetyl groups on the oxetane ring have a *trans*-configuration. The oxetane, **7**, was cleaved to an ether, **8**, by boiling it with a solvent, such as benzene or ethanol, or by column chromatography. These conditions define the stability of the *β*-hydroxy ketone, since the dealdolization may involve a thermal process.[8] Consequently, it is considered that the ether, **8**, was produced by the cleavage of the oxetane, **7**, during the separation, by analogy with the photoadducts of cycloalkene and *β*-diketones.[8,9] **7** and **8** also afforded 1,1-diphenyl-2-propanone (**9**)[10] and methylglyoxal (**10**)[11] respectively by thermal cleavage under a nitrogen atmosphere. In this photoreaction, the light energy was absorbed exclusively by **2**; the reaction was also inhibited com-



pletely in the presence of 1,3-pentadiene.⁵⁾ The photodimerization of enones is sensitized by **2**,¹²⁾ but no cross-coupling reaction of these compounds has been known. The formation of the oxetane, **7**, can easily be interpreted by assuming the attack of **2** in the triplet state on the double bond of the enolated **6**. An electron-deficient oxygen of the excited **2** can attack the more negative center at the 3-position of **6** to give the more stable intermediate diradical, followed by cyclization to form an oxetane. This consideration clearly explains the orientation mode in the formation of the oxetane, **7**.

The photochemical reaction of **2** with ethyl acetoacetate (**15**) and benzoylacetone (**16**) did not give a photoadduct such as oxetane. This may be attributed to the facts that the former has a low enol content and that the latter absorbs most of the light energy under the present reaction conditions.

The difference in the photochemical reactivity of **1** and enolated **6** with **2** may be attributed to the presence or absence of an α-hydrogen atom, which is easily abstracted by excited **2**.

Experimental

The enamino ketones were prepared from the corresponding β-diketones and amines. The **2**, benzene, and the other materials were purified in the usual way. The IR, NMR, and UV spectra were recorded with JASCO IRG, Hitachi R24B, and Hitachi 124 spectrometers respectively. The MS spectra were determined with a CEC21-110B mass spectrometer.

The irradiations were performed under a nitrogen atmosphere with a 100-W high pressure mercury lamp which had been lowered into a water-cooled Pyrex immersion well. The yields are based on the consumed **2**. All the melting points are uncorrected.

*Photochemical Reaction of **1** with **2***: A solution containing 7.9 g (70 mmol) of **1** and 12.7 g (70 mmol) of **2** in 400 ml of benzene was irradiated for 48 h. The reaction mixture was then concentrated *in vacuo* to *ca.* 30 ml, the residual solid was removed by filtration, and the filtrate was chromatographed on silica gel. Elution with benzene gave **4** (5.9 g, 75%) and **2** (4.9 g, 39% recovery). Elution with benzene–acetone (10:1) gave **1** (1.3 g, 17% recovery). Further elution with acetone gave a resinous substance. The collected solid was recrystallized with chloroform to give 2.1 g (17%) of **3** as colorless prisms; mp 223—224 °C. MS *m/e*: 295 (M^+). IR($CHCl_3$): 3570, 1610, and 1570 cm^{-1}. NMR (DMSO-d_6) δ=1.85 (3H, s), 1.89 (3H, s), 4.23 (2H, d, J=6 Hz), 5.02 (1H, s), 6.26 (1H, s), 7.5—7.9 (10H, m), and 11.12 (1H, s). UVmax (EtOH): 312.5 (ε 18000) and 318^{sh} nm (17000). Found: C, 76.98; H, 6.99; N, 4.72%. Calcd for $C_{19}H_{21}NO_2$: C, 77.25: H, 7.13; N, 4.74%. Hydrolysis of **3** by dil-HCl yielded **5** and **6**.

*Photochemical Reaction of **13** with **2***: A solution containing 8.9 g (70 mmol) of **13** and 12.8 g (70 mmol) of **2** in bezene (400 ml) was irradiated for 72 h. The solution was then removed, and the residue was chromatographed on silica gel. From the benzene eluents, 3.0 g (35%) of **4** were isolated; 4.2 g (33%) of **2** were also recovered. Further elution with benzene-methanol (5:1) gave a brown viscous oil, which was separated by carbon tetrachloride-hexane (1:1) to give 0.7 g of **14**; mp 138—139 °C. MS *m/e* 269 (M^+). IR ($CHCl_3$): 3280 (O–H), and 1620 cm^{-1} (C=O). NMR ($CDCl_3$) δ=2.03 (3H, s), 2.47 (3H, s), 4.22 (2H, s), 5.38 (1H, s), and 7.1—7.6 (10H, m). Found: C, 75.57; H, 7.06; N, 5.11%. Calcd for $C_{17}H_{19}NO_2$: C, 75.74; H, 7.11; N, 5.20%.

*Photochemical Reaction of **6** with **2***: A solution containing 8.0 g (80 mmol) of **6** and 14.5 g (80 mmol) of **2** in 400 ml of benzene was irradiated for 72 h. The reaction mixture was then concentrated *in vacuo* to *ca.* 30 ml, the crystals of the oxetane, **7**, were removed by filtration, and the filtrate was chromatographed on silica gel. From the benzene eluent, 0.5 g (12%) of **4** was isolated, while 10.5 g (72%) of **2** and 5 g (62%) of **6** were recovered. From the benzene-acetone (10:1) eluent we obtained 2.7 g (44%) of **8** as a viscous liquid; IR ($CHCl_3$): 1714, 1598, 1354, and 1098 cm^{-1}. NMR ($CDCl_3$) δ=2.11 (3H, s), 2.21 (3H, s), 3.35 (2H, s), and 7.3 (10H, s). Found: C, 76.40; H, 6.50%. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.45%. The product, **8**, gave a mixture of 2,4-dinitrophenylhydrazones of **9** and **10** in ethanol. The former had a mp of 141—142 °C (from EtOH), undepressed on admixture with an independently synthesized authentic specimen with the same melting point.¹⁰⁾ The latter had a mp of 299—300 °C (from DMF) (Lit,¹¹⁾ mp 299—300 °C). The oxetane, **7**, was washed with benzene; 2.7 g (43.5%); mp 141—142 °C (dec). IR ($CHCl_3$): 3550, 3400, 1721, 1704, 995, and 977 cm^{-1}. NMR ($CDCl_3$) δ=1.35 (3H, s), 2.13 (3H, s), 2.63 (1H, s), 4.90 (1H, s), and 7.3—7.7 (10H. m). UVmax (EtOH): 224 (ε 20000), 259 (3500), and 290^{sh} nm (1300). Found: C, 76.62; H, 6.48%. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.45%. 2,4-Dinitrophenylhydrazone of **7** had mp 161—162 °C (from EtOH); IR (Nujol): 3550 (O–H), 3300 (N–H), and 995 cm^{-1} (C–O–C). Found: C, 62.41; H, 4.71; N, 12.14%.

Other Photochemical Reactions: The irradiation of a benzene solution containing 1,3-pentadiene, **1** or **6**, and **2** caused the unreacted starting materials to be recovered. The reaction of **15** with **2** in benzene for 48 h gave **4** (92%) and a resinous substance, while **2** (47%) and **15** (46%) were recovered. The irradiations of **11**, **12**, and **16** with **2**, a benzene solution containing only **1** and/or **6**, and a cyclohexene solution of **1** caused the unreacted starting materials to be recovered quantitatively.

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