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The Photoreaction of 1-Cycloalkenyl Phenethyl Ketone

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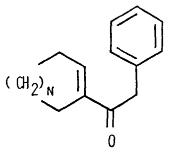
Synopsis. The UV irradiation of 1-cyclopentenyl phenethyl ketone in benzene or methanol gave a cyclobutane derivative. The irradiation of 1-cyclohexenyl phenethyl ketone in methanol or in benzene containing either BF_3–Et_2O or CF_3COOH gave a cycloheptanone derivative. The formation of the cycloheptanone derivative requires an acid catalyst.

In an earlier paper[1] we reported that 1-cycloalkenyl benzyl ketones (I and II) undergo photo-cyclization to give tricyclic ketones (III and IV). In this paper we wish to report on the difference in the photo-reactivity between 1-cyclopentenyl phenethyl ketone (V) and 1-cyclohexenyl phenethyl ketone (VI).

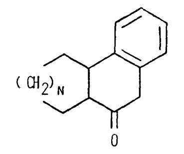
The 1-cycloalkenyl phenethyl ketones (V and VI) were synthesized by the Friedel-Crafts-type acylation[2] of cycloalkene with 3-phenylpropionyl chloride, followed by the base-catalyzed elimination of hydrogen chloride. The UV irradiation of 1-cyclopentenyl phenethyl ketone (V) in benzene containing 0.05 M BF_3–Et_2O gave the product VII in poor yield and recovered most of the starting material. The reaction did not proceed extensively due to the deterioration of the reaction mixture, which turned into a non-transparent, dark brown solution. This deterioration must be due to the interaction between the acid catalyst and the ketene formed by the photolysis of VII, as has been reported by Smith and Agosta[3] for a similar system. The photoreactions of ketone V in methanol or benzene without an acid catalyst were clean and gave the product VII in better yields (30 and 80% respectively). The structure of VII was deduced from the spectral data: an IR absorption at 1780 cm^{-1} is characteristic of cyclobutanone, the NMR signals at 3.73—3.36 ppm (δ) have an ABC pattern, and attempted decoupling by resonating the hydrogens at a higher field (cyclopentane moiety) did not change the signal pattern. This fact demonstrates that these signals are due to three hydrogens on the cyclobutanone moiety isolated from the hydrogens on the cyclopentane moiety.

The irradiation of 1-cyclohexenyl phenethyl ketone (VI) in the presence of BF_3–Et_2O under the same conditions as were used for ketone V afforded a product VIII in 67% yield. The photoreaction of VI in methanol or benzene containing 0.05 M CF_3COOH also gave ketone VIII in a 40% yield. The irradiation of ketone VI in benzene containing no acid catalyst, however, did not give any VIII, but instead a small amount of fragmentation products. The structure of VIII was deduced from the spectral data: an IR absorption at 1690 cm^{-1} is typical of a seven-membered ketone, and an absorption at 762 cm^{-1} is due to an ortho-disubstituted benzene. The NMR signals are complex but the integration showed the signal ratio of four hydrogens at 7.20—6.80 ppm, six hydrogens due to methylenes and methines adjacent to the benzene ring and the carbonyl group at 3.20—2.4 ppm.

There is no difference in the reaction pattern between 1-cyclopentenyl benzyl ketone (I) and 1-cyclohexenyl benzyl ketone (II) and irradiation in the presence of acid catalysts gives tricyclic ketones, III and IV respectively.[1] This feature of 1-cycloalkenyl benzyl ketones (I and II) is in sharp contrast with the photochemical-behavior of 1-cycloalkenyl phenethyl ketones (V and VI) described here. We previously proposed the importance of a π-aryl interaction in the excited state of the BF_3-complexes of 1-cycloalkenyl benzyl ketones for photo-cyclization.[1] The nature of this π-aryl interaction in the ketones V and VI must be a little different from that of ketones I and II due to the extension of the methylene chain. In the case of ketone VI, however, the π-aryl interaction is still effective enough to cause the photocyclization (Eq. 2) in the presence of an acid catalyst or in a protic solvent. Though the π-aryl interaction is still effective, the existence of benzylic hydrogen adequately located in relation to the enone moiety must alter the reactivity of ketone V. β-Carbon of 1-acylcyclopentenones has been reported to have a strong ability to abstract hydrogen intramolecularly.[3] The excited state of non-substituted cyclopentenone has a strong $n\pi^*$ character,[4] and the photo-reactivity of ketone V can be understood by means of the preferential hydrogen abstraction by triplet $n\pi^*$ excited state.[3]



I: N=1
II: N=2



III: N=1
IV: N=2

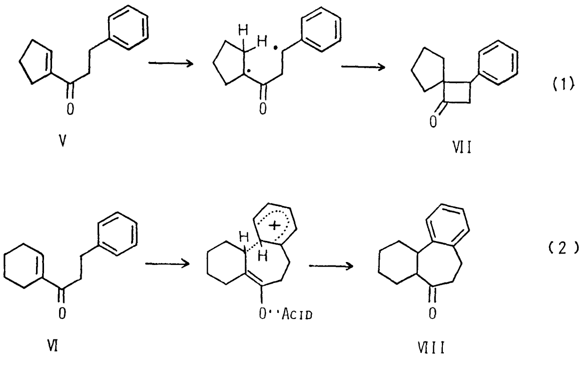


Fig. 1.

Experimental

Preparation of 1-Cyclopentenyl Phenethyl Ketone (V) and 1-Cyclohexenyl Phenethyl Ketone (VI). Stannic chloride (10.4 g, 0.04 mol) in dry dichloromethane (25 ml) was cooled below −70 °C and was then treated, drop by drop, with a mixture of freshly distilled 3-phenylpropionyl chloride (6.6 g, 0.04 mol) and one of the cycloalkenes (0.04 mol) over the period of 3 h. During the reaction the system was maintained below −70 °C and kept in a nitrogen atmosphere. After the completion of the treatment, the reaction mixture was slowly warmed up to 0 °C and poured onto a mixture of ice and concd hydrochloric acid. The dichloromethane layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was washed with water and dried over anhydrous sodium sulfate. The subsequent evaporation of the solvent *in vacuo* gave the crude 2-chloro-1-cycloalkenyl phenethyl ketone. The chloro ketone thus obtained was dissolved in benzene (25 ml) and heated to refluxed in the presence of triethylamine (7 g) for 20 h. After cooling, the reaction mixture was washed with 1M-hydrochloric acid, a saturated sodium hydrogencarbonate solution, and water. The evaporation of the solvent after drying over anhydrous sodium sulfate gave the oily 1-cycloalkenyl phenethyl ketone in a high yield. The ketone V was essentially pure after distillation under reduced pressure, while ketone VI was further purified by chromatography on silica gel eluted by hexane-benzene. V, 129—130 °C/0.7 mmHg. IR(neat): 1655, 1615, 1503, 750, and 695 cm^{-1}. NMR(CCl_4): 7.36(5H), 6.76 (1H, diff. s), 2.94 (4H, s), 2.75—2.33 (4H, m), and 2.12—1.15 ppm (δ) (2H, m). Semicarbazone, mp 124—124.5 °C. Found: C, 69.72: H, 7.25; N, 16.15%. Calcd for $C_{15}H_{19}N_3O$: C, 70.00; H, 7.44; N, 16.33%. VI, 100 °C/0.1 mmHg. IR(neat): 1662, 1613, 1505, 754, and 693 cm^{-1}. NMR(CCl_4): 7.36 (5H, s), 6.97 (1H, diff. s), 2.90 (4H, s), 2.50—2.12 (4H, m), and 1.88—1.60 ppm (δ) (4H, m). Semicarbazone, mp 146—147 °C. Found: C, 70.55; H, 7.81; N, 15.38%. Calcd for $C_{16}H_{21}N_3O$: C, 70.82; H, 7.80; N, 15.49%.

General Procedure for the Photoreaction. Irradiations were carried out externally with a 500-W high-pressure mercury lamp through a Pyrex filter in (a) benzene containing 0.05 M BF_3–Et_2O, (b) benzene containing 0.05 M CF_3COOH, (c) benzene, and (d) methanol under argon or nitrogen. In each run, a 0.1 M solution of the ketone V or VI was irradiated and the progress of the reaction was monitored by means of the IR spectra and by GLC analyses. The reaction mixture was passed through a column of alumina, using benzene as the eluent, to remove the acid catalyst and other polar by-products. The eluates were condensed and further purified by chromatography on silica gel, using hexane-chloroform as the eluent, to give an essentially pure product, VII or VIII. These products, VII and VIII, were further purified by a preparative GLC for spectral measurements. VII, colorless oil. MS: m/e=200 (M^+). IR(neat): 1780, 1505, 765, and 699 cm^{-1} NMR(CCl_4): 7.60 (5H, m), 3.73—3.36 (3H, ABC pattern), and 2.45—1.20 ppm (δ) (8H, m). Semicarbazone, mp 175—176 °C. Found: C, 69.69; H, 7.29; N, 16.09%. Calcd for $C_{15}H_{19}N_3O$: C, 70.00; H, 7.44; N, 16.33%. VIII, colorless oil. Found: C, 84.13; H, 8.53%. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47%. MS: m/e=214 (M^+). IR (neat): 1695, 1502, 762, and 698 cm^{-1}. NMR (CCl_4): 7.20—6.80 (4H, m), 3.20—2.4 (4H, m), and 2.4—0.90 ppm (δ) (8H, m).

References

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