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AN INTRAMOLECULAR C-ACYLATION OF AN ENOL: PHOTOCHEMICAL REARRANGEMENT OF TRICYCLO[3.3.2.$0^{2,4}$]DECA-6,9-DIEN-8-ON-1-OL

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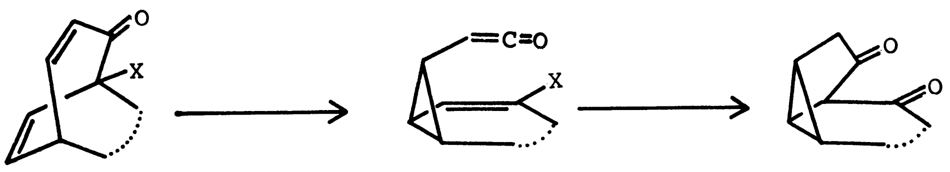
Under direct irradiation in methanol, the compound in the title (6) gave tricyclic keto-ester 7. In the presence of acetic acid, 6 in methanol gave tetracyclo[5.3.$0^{1,7}$.$0^{2,10}$.$0^{3,5}$]deca-6,8-dione (8), which underwent futher photochemical change to monocyclic keto-ester 9.

Chapman and his co-workers[1] have reported that irradiation of bicyclic ketones 1 gives reactive ketenes 2 which can only be observed by low temperature infrared and nmr spectroscopy and that the photoisomerization of 1 to 2 is apparently general. This report prompted us to study the photochemical reaction of 1-hydroxy derivatives of 1 (3) which should give corresponding labile ketenes 4, containing the other reactive function: enol. Under suitable conditions, those labile functions might react intramolecularly to give the tricyclic β-diketones, 5.



1 X=H
3 X=OH

2 X=H
4 X=OH

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As a model of 3, we chose tricyclo[3.3.2.0^{2,4}]deca-6,9-dien-8-on-1-ol (6) which is the 1,4-addition product of tropone and cyclopropene.[2] When 6 was irradiated in methanol for 1 hr,[3] tricyclic keto-ester 7 was obtained as colorless leaflets, mp 45.5-46.5°C, in 98% yield. The structure of 7 is elucidated from its spectroscopic data: ν_{max} (KBr) 3050 (w), 3020 (w), 1737 (s), 1690 (s), 1680cm^{-1} (sh); λ_{max} (MeOH) 200 (logε 3.60), 276nm (1.39); δ(CDCl$_3$) 3.64 (3H, s), 2.49-2.29 (4H, m), 1.9-1.02ppm (7H, m).[4,5] Reactions monitored by ^{1}H-nmr indicated that any other products were not formed during irradiation. After 12 min irradiation, ca. 70% of 6 was changed into 7.

On the other hand, irradiation of 6 in methanol-acetic acid (500:1) gave two products 8 and 9, which are separable by chromatography on silica gel, and did not yield even trace of 7. After 20 min irradiation, 6 disappeared completely, and 8 and 9 were formed in a ratio of 4:1. An additional 40 min irradiation gave only 9 in a yield of 80%. Irradiation of 8 under the same conditions formed 9 in 80% yield

The structure of 8 has been determined by X-ray crystallographic analysis.[6] Single crystals of 8 of suitable size for data collection were obtained from dichloromethane-hexane. The crystal belongs to the triclinic space group, P$\bar{1}$: with a=6.615, b=7.202, c=8.576Å; α=90.05, β=108.85, γ=87.29°; Z=2. A total of 1417 independent reflections were measured on a Rigaku automated diffractometer using Mo Kα radiation. The structure was solved by direct methods and refined by block-diagonal least-squares methods with anisotropic temperature factors for the non-hydrogen atoms. All hydrogen atoms were located by a difference Fourier synthesis and included with isotropic temperature factors in the refinement. The final R-value is 0.056. Figure 1 shows a perspective drawing of the molecular structure.

The structure of 9, colorless oil, is inferred by its spectroscopic properties: ν_{max} (neat) 1742 (s), 1710 (s), 1668 (m), 970 (m), 784cm^{-1} (m); λ_{max} (MeOH) 216 (logε 4.02), 278nm (2.92); δ (CDCl$_3$) 7.41 (1H, dd, J=5.7 and 2.7Hz), 6.06 (1H, dd, J=5.7 and 2.0), 5.52 (1H, dt, J=15.0 and 5.8), 5.41 (1H, dd, J=15.0 and 6.5), 3.61 (3H, s), 3.49 (1H, m), 2.49 (1H, dd, J=18.3 and 6.8), 2.43-2.38 (4H, m), 2.00ppm (1H, dd, J=18.3 and 2.8).

Although we can not offer conclusion as to the detailed mechanism of those reaction processes, we note that the ketene, 10, is the reasonable common intermediate. Simple paths for conversion of 10 to 7 in methanol are tautomerization

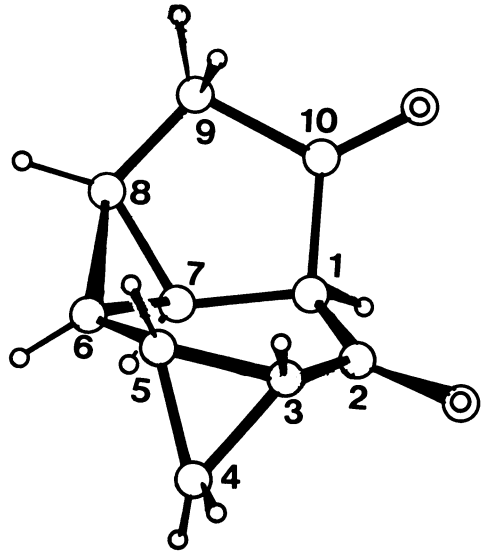
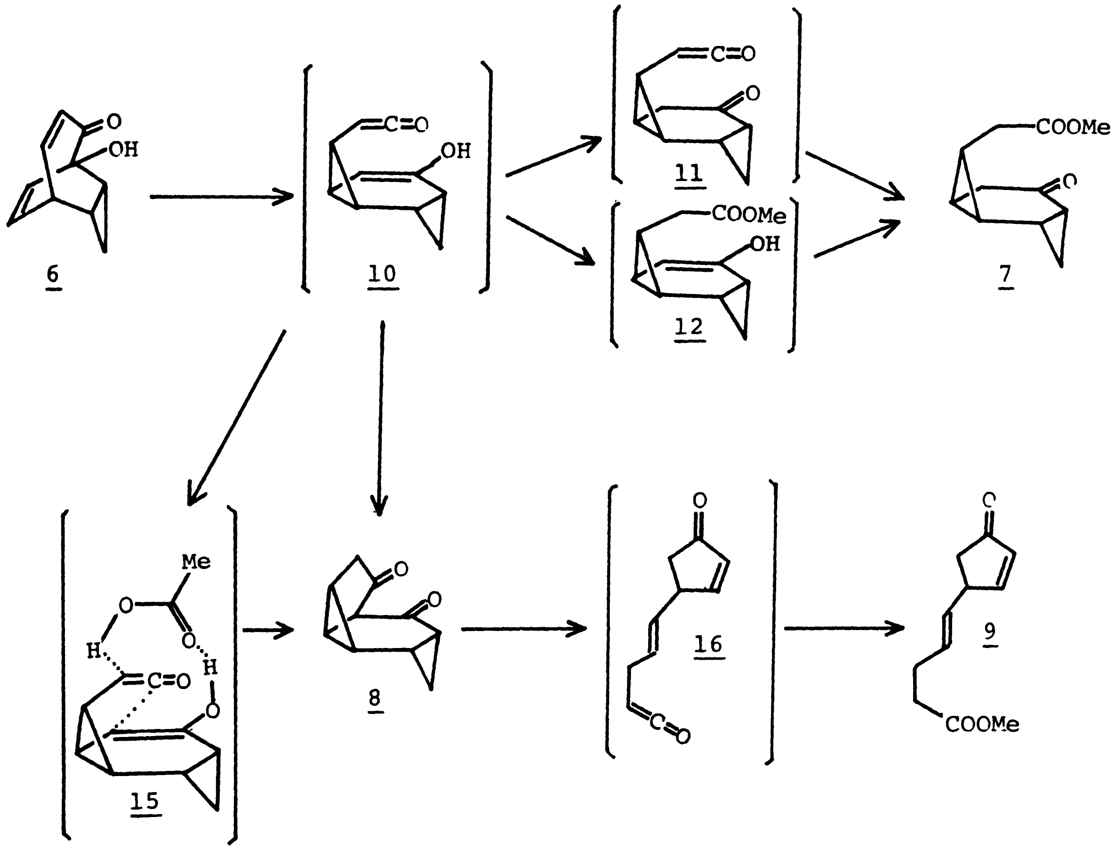
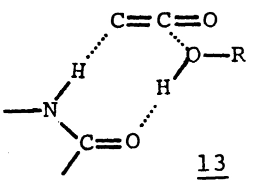


Figure 1. X-Ray structure of diketone 8





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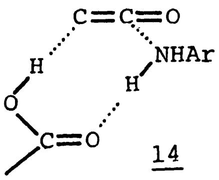

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to ketone 11 which undergoes the addition of the solvent to 7 and/or the methanol addition to give ester 12 which undergoes tautomerization to the keto-ester, 7. While no detailed mechanism has been reported, it is general that the reaction of ketenes with alcohols is accelerated with acids, even with carboxylic acids.[7] However, keto-ester 7 was not formed in the presence of acetic acid in methanol. The results seem to suggest novel catalytic roles of acetic acid in the intramolecular conversion of the ketene into diketone 8.

For the reaction of ketenes with alcohols, Tielle and Procejus have proposed the cyclic transition state.[8] Similar cyclic transition states 13[9] and 14[10] have been offered for the amide-catalyzed reaction of ketenes with alcohol and for the carboxylic acid-catalyzed reaction of ketenes with anilines, respectively. If the intamolecular reaction of ketene 10 to 8 proceeds similarly with those reactions of ketenes, 15 might be the transition state of the cyclization, in which acetic acid is a proton transferor.[11]

Diketone 8 may undergo symmetry allowed photochemical [$\pi 2s + \pi 2s + \pi 2a$] cycloreversion to ketene intermediate 16, which reacts with methanol to give the monocyclic keto-ester, 9.

References and Notes

1) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, J. Amer. Chem. Soc., 91, 6856 (1969).

2) T. Uyehara, N. Sako, and Y. Kitahara, Chem. & ind., 1973, 41.

3) 0.006-0.008M solutions of 6 were irradiated, using a Riko 100-W high-pressure mercury lamp, through Pyrex filter under an inert atmosphere at room temperature.

4) Satisfactory elemental analyses were obtained for all the compounds described in this letter.

5) ^{1}H-nmr studies using shift reagent Eu(DPM)$_3$ were effective to elucidate the structure.

6) The structure was not completely assignable on the basis of its spectra: νmax (KBr) 3070 (w), 3025 (w), 1748 (s), 1684cm^{-1} (s); λmax (MeOH) 201 (logε 3.78), 277nm (1.35); δ (CDCl$_3$) 3.18 (1H, broad d, J=5.2Hz), 2.63 (1H, dm, J=19.2), 2.44(1H, dm, J=19.2), 1.79 (2H, m), 1.65-1.10 (4H, m), 0.63 (1H, dt, J= 4.7 and 3.8). Mp 70-71°C.

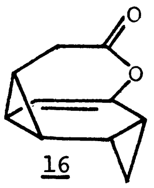
7) R. N. Lacey in " The Chemistry of Alkenes," S. Patai, Ed., Wiley-interscience, New York, N.Y., 1964, p 1174.

8) A. Tille and H. Procejus, Chem. Ber., 100, 196 (1967).

9) H. Procejus and R. Samtleben, Tetrahedron Lett., 1970, 2189.

10) P. J. Lillford and D. P. N. Satchell, J. Chem. Soc. (B), 1967, 360.

11) The intramolecular O-acylation of 10 to give tetracyclic enol-lactone 16 seems to be difficult, because of large I-strain of the product.



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