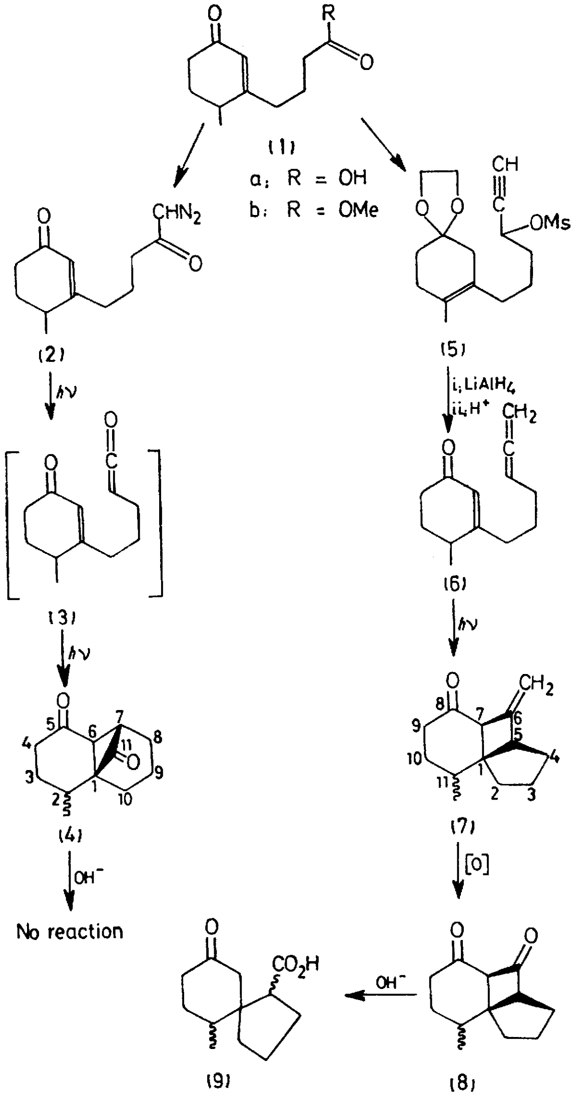
Intramolecular Photocycloadditions of Ketens and Allenes to Cyclohexenones

By Dan Becker,* Zvi Harel, and Dov Birnbaum

(*Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel*)

Summary A comparison between the intramolecular photocycloaddition of allenes and ketens to cyclohexenones is described.

Recently attention has been focused on the photocycloaddition of olefins to conjugated ketones, and work has been published showing a correlation between the structure of the starting material and the course of intramolecular photocycloaddition.[1]

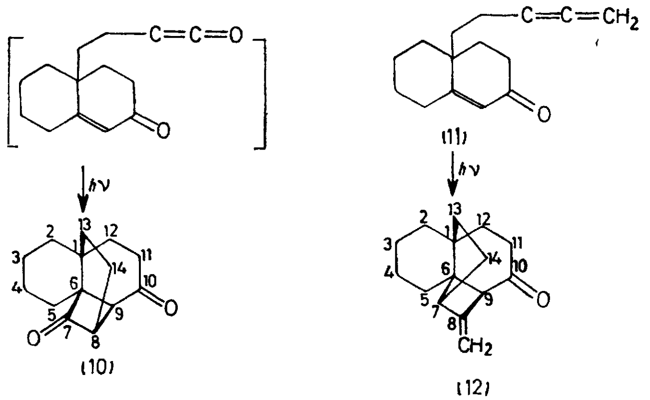


Scheme 1. Ms = MeSO$_2$

Intermolecular photocycloadditions of allenes to conjugated ketones are also well known and have been applied synthetically,[2] but only one case of an intramolecular photocycloaddition of this type has been reported.[3] We have found that the intramolecular photocycloaddition of ketens to conjugated ketones leads to 1,4-diketones,[4] and now report preliminary results on the course of the intramolecular photocycloaddition of allenes, analogous in structure to ketens, to cyclohexenones.

The keto-acid[5] (**1a**)† was converted to its acid chloride and treated with excess diazomethane. Chromatography on Florisil gave a 70% yield of the diazoketone (**2**), [ν_{max} (CHCl$_3$) 2104 (–CHN$_2$), 1660 (–C=C–C=O), 1635 (N$_2$HC–C=O) cm^{-1}; n.m.r. (CDCl$_3$), δ 5·83 (1H, s, –C=CH–C=O), 5·25 (1H, s, –CHN$_2$), 1·14 (3H, d, Me)].

The keto-allene (**6**), [ν_{max} (CHCl$_3$) 1660 (–C=C–C=O), 1960 (–CH=C=CH$_2$) cm^{-1}; n.m.r. (CDCl$_3$) δ 5·86 (1H, s, –C=CH–C=O), 5·12 (1H, m, –C–CH=C=C), 4·70 (2H, m, –C=C=CH$_2$), 1·21 (3H, d, Me); M^+ 190] was prepared from the keto ester (**1b**) *via* (**5**) [ν_{max} (CHCl$_3$) 3320 and 2130 (–C≡CH), 1370 (–OMs) cm^{-1}; n.m.r. (CDCl$_3$) δ 4·00 (4H, s, –O–CH$_2$–CH$_2$–O–), 3·14 (3H, s, MeSO$_3$–)], according to Thompson.[6]



Scheme 2.

The diazo-ketone (**2**) and keto-allene (**6**) were irradiated in cyclohexane under nitrogen for 1 h at room temp. through Pyrex with a 450 W Hanovia lamp. The reaction mixture gave, after chromatography on Florisil, the diketone (**4**), m.p. 58·5—59·5° C, [ν_{max} (CHCl$_3$) 1780 (CH$_2$CH$_2$CH$_2$C=O), 1715 (–C=O) cm^{-1}; n.m.r. (CDCl$_3$) δ 3·37 [1H, m, –C(6)–H], 1·07 (3H, d, Me); M^+ 192], and the cyclization product (**7**) {ν_{max} (CDCl$_3$) 1690 (C=O), 895 (>C=CH$_2$) cm^{-1}; n.m.r. (CDCl$_3$) δ 4·95 (2H, m, C=CH$_2$), 3·12 [2H, m, –C(5)–H and –C(7)–H], 0·95 (3H, d, Me); M^+ 190}, in 34% and 95% yields respectively (Scheme 1).

To determine the structure of (**4**) and (**7**) the following reactions were carried out. Compound (**7**) was ozonized at −78 °C in methylene chloride and treated with excess dimethyl sulphide to give the diketone (**8**) (96%), [ν_{max} (CHCl$_3$) 1695 (C=O), 1785 (CH$_2$CH$_2$CH$_2$C=O) cm^{-1}; n.m.r. (CDCl$_3$) δ 3·60 [1H, m, –C(:O)CHC(:O)–], 1·10 (3H, d, Me)]; there was no indication of the presence of compound (**4**). It was found that compound (**8**) was unstable and cleaved under mild conditions to give the keto-acid (**9**) [ν_{max} (CHCl$_3$) 3200—3700 (–CO$_2$H), 1720 (C=O) cm^{-1}; n.m.r. δ

---

† All new compounds gave spectral data (including high resolution m.s.) in accord with assigned structures.

8·40 (1H, s, $-CO_2H$), indicating that (**8**) is a 1,3-diketone. Adduct (**8**) was sufficiently stable under t.l.c. conditions to enable us to exclude its presence in the crude photoreaction mixture of the diazo-ketone (**2**). On the other hand, (**4**) was recovered unchanged after reflux in 1 : 1 aqueous methanolic 10% potassium hydroxide solution, eliminating the possibility of a 1,3-relationship between the keto groups.

Corresponding results were obtained in the bicyclic system (Scheme 2). Compound (**10**) was isolated as reported earlier.[4] Cyclization product (**12**) {ν_{max} ($CHCl_3$) 1690 (C=O), 890 ($>C=CH_2$) cm^{-1}; n.m.r. ($CDCl_3$) δ 4·95 (2H, m, $>C=CH_2$), 2·90 [2H, m, –C(7)-H and –C(9)-H]; M^+ 216}, was obtained from compound (**11**), [ν_{max} ($CHCl_3$) 1970 ($-C=C=CH_2$), 1680 (–C=C–C=O) cm^{-1}; n.m.r. ($CDCl_3$) δ 5·77 (1H, s, –C=CH–C=O), 5·10 (1H, s, –CH=C=C), 4·70 (2H, s, $-C=C=CH_2$) in 88% yield. Assuming these additions occur *via* Corey's mechanism,[7] one possible explanation of these results is to assume that opposite charge distribution of allenes and ketens in the ground state is responsible for the different orientations of addition.

We thank The Israel National Commission for Basic Research for financial support.

(*Received, 18th February* 1975; *Com.* 205.)

---

[1] R. Ramage and A. Sattar, *Tetrahedron Letters*, 1971, 649; Y. Tamura, H. Ishibashi, Y. Kita, and M. Ikeda, *J.C.S. Chem. Comm.*, 1973, 101; V. Georgian and M. Saltzman, *Tetrahedron Letters*, 1972, 4315.

[2] R. B. Kelly, J. Zamecnic, and B. A. Beckett, *Canad. J. Chem.*, 1972, **50**, 3455; R. W. Guthrie, Z. Valenta, and K. Weisner, *Tetrahedron Letters*, 1966, 4645; K. Weisner, L. Poon, I. Jirkovsky, and M. Fishman, *Canad. J. Chem.*, 1969, **47**, 433.

[3] K. Weisner, V. Mussil, and K. J. Wiesner, *Tetrahedron Letters*, 1968, 5643.

[4] D. Becker, M. Nagler, and D. Birnbaum, *J. Amer. Chem. Soc.*, 1972, **94**, 4771.

[5] S. Swaminathan and M. S. Newman, *Tetrahedron*, 1958, **2**, 88.

[6] H. W. Thompson, *J. Org. Chem.*, 1967, **32**, 3712.

[7] E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, 1964, **86**, 5570.