122. Intramolecular *de Mayo* Reactions of 3-Acetoxy-2-alkenyl-2-cyclohexenones[1])

Preliminary communication

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Summary

The photoaddition, hydrolysis, retro-aldol sequences **1**→**2**→**3** and **4**→**5**+**6**→**7** proceeded in high yield and in a regiospecific manner. However, the enol acetate **8** on irradiation furnished the tricyclic ketoacetate **9** as the major product, presumably by a hydrogen shift in the intermediate diradical **11**. Hydrolysis of the minor photoadduct **10** gave the dione **13**.

In order to determine the scope and limits of intramolecular *de Mayo* reactions[2]), firstly used for the synthesis of longifolene [4] and subsequently for β-bulnesene [5], we have investigated such reactions with some readily available 3-acetoxy-2-alkenyl-2-cyclohexenones[3]).

Photolysis of the enol acetate **1**[4])[5]) *(Scheme 1)* in cyclohexane[6]) gave the isomerically pure tricyclic acetoxyketone **2**[4])[5]) (m.p. 74-75°; 89% yield), which on alkaline hydrolysis furnished the retro-aldol product **3**[4])[5]) (m.p. 65-66° (lit. [3b]: m.p. 64.5°); 45% yield)[1]). Structural evidence for **2** was obtained by the intermolecular photoaddition of cyclopentene to 3-acetoxycyclohexenone and subsequent alkaline hydrolysis of the photoadduct to give the dione **3** identical with that described above. The sequence **1**→**2**→**3** (reported recently by us)[1]) has been published independently by *Pattenden et al.* who furthermore established a *trans*-fusion for dione **3** by X-ray measurements [3b].

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[1]) Reported in part by one of us *(W.O.)* at the Swiss Chemical Society meeting, Bern on Oct. 20, 1978.

[2]) a) For recent reviews on the intermolecular *de Mayo* reaction see [1]; b) For related photoaddition-hydrolysis sequences of 2-alkenylamino- and 2-alkenyloxy-2-cyclohexenones see [2]; c) For contemporary studies of intramolecular *de Mayo* reactions see [3].

[3]) For the preparation of the starting 3-acetoxy-2-alkenyl-2-cyclohexenones see [4] [6].

[4]) The IR., ^{1}H-NMR. (100 MHz) and MS. of this compound are in agreement with the assigned structure.

[5]) The ^{13}C-NMR. spectrum of this compound agrees with the assigned structure.

[6]) Solutions (5%) in cyclohexane were irradiated with a mercury high-pressure lamp through a Pyrex filter at 15-30°.

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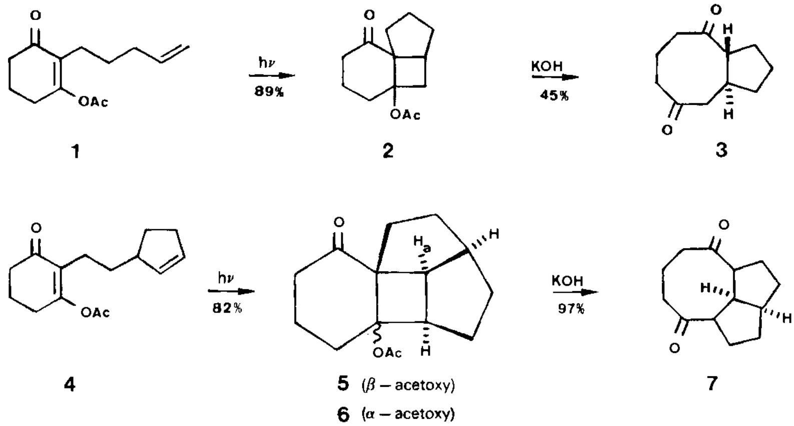
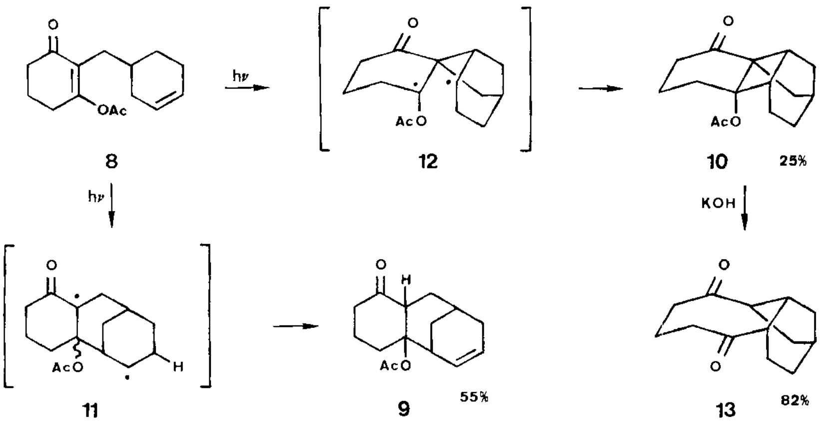
Scheme 1



Similarly, irradiation[6] of the enol acetate **4**[4][5] led regiospecifically in 82% yield to two isomers **5**[4][5] and **6**[4][5] which were separated by chromatography. The major isomer (m.p. 112-114°; 70% yield) exhibits two carbonyl peaks in the IR. spectrum (CCl_4) at 1735 (ester) and 1700 cm^{-1} (ketone) while only one signal appears in that of the minor isomer (m.p. 113-114°; 12% yield) at 1730 cm^{-1} (both ester and ketone). Reference to work by *Corey* [7] and *Cantrell* [8], who have observed that the IR. absorption in *cis*-fused [4.2.0]bicyclic compounds, such as **14** *(Scheme 3)*, occurs between 1700 and 1710 cm^{-1}, suggests that the major isomer contains a *cis*-fused ring junction[7]. Further stereochemical evidence is obtained from the ^{1}H-NMR. spectrum of the minor isomer which exhibits a low field triplet ($J = 7$) at $\delta = 3.67$ ppm,

Scheme 2



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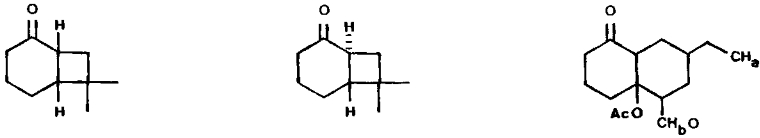
[7] The *trans*-fused bicyclic ketone **15**, prepared by *Corey*, shows an IR. absorption at 1721 cm^{-1} [7] which implies that the minor product **6** contains a *trans*-fused ring junction.

whereas in the spectrum of the major product no signal appears below $\delta = 3.0$ ppm. The low-field position of this triplet probably arises from the proximity of the acetate group to H_a in the *trans*-isomer **6** [9].

Hydrolysis of each tetracyclic ketoacetate, **5** and **6**, gave an identical (7:3:1)-mixture of the three possible tricyclodiones **7**[4] in 97% yield[8].

In contrast, the enol acetate **8**[4][5] (*Scheme 2*) afforded on irradiation[6] the tricyclic ketoacetate **9**[4][5] (m.p. 107–108°; 55% yield) as the major product, besides the expected tetracyclic photoadduct **10**[4][5] (m.p. 87–88°; 25% yield). The structural assignment of the major product **9** was supported by NMR.-evidence[9] and by *bis*-hydroxylation (OsO_4/*N*-methylmorpholine-*N*-oxide) and periodate cleavage of the resulting diol to afford the dialdehyde **16**, $\delta = 9.76$ (*t*, $J = 1.5$, 1 H_a) and $\delta = 9.85$ (*d*, $J = 0.8$, 1 H_b) ppm.

Scheme 3



14 **15** **16**

The major product **9** probably arises from a hydrogen shift in the diradical intermediate **11**[10]. A pathway to the minor adduct **10** could involve the diradical intermediate **12**. The minor product **10**, which was tentatively assigned the *cis*-fused ring junction by comparison with the spectra of the products from photocyclization of the enol acetate **4**, was converted to the single crystalline dione **13**[4][11] (m.p. 136–137°; 82% yield) by hydrolysis.

Accordingly, intramolecular *de Mayo* reactions of 3-acetoxy-2-alkenyl-2-cyclohexenones may efficiently provide complex ring systems whereas the photochemical behaviour of **8** demonstrates a limit to the scope of this synthetic method.

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[8] Each of the three possible diones **7** were interconverted to the same mixture by treatment with KOH.

[9] ^{1}H-NMR. (100 MHz, $CDCl_3$): 1.20–3.00 (*m*, 17 H); 2.04 (*s*, 3 H); 3.36 (*m*, 1 H); 5.94 (*m*, 2 H) ppm. – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 21.4 (*t*); 21.7 (*qa*); 25.7 (*d*); 26.2 (*t*); 28.5 (*t*); 30.7 (*t*); 32.6 (*t*); 34.7 (*d*); 40.7 (*t*); 50.2 (*d*); 89.7 (*s*); 128.5 (*d*); 132.2 (*d*); 169.6 (*s*); 209.2 (*s*) ppm. – TMS was used as internal standard and splitting patterns are designated as singlet (*s*), doublet (*d*), triplet (*t*)... multiplet (*m*). Chemical shifts are given in δ values.

[10] For a related hydrogen shift in the intramolecular photochemistry of vinylogous imides see [10].

[11] IR. (CCl_4): 1712, 1703 cm^{-1}. – ^{1}H-NMR. (400 MHz, $CDCl_3$): 1.40–1.70 (*m*, 5 H); 1.86–2.04 (*m*, 4 H); 2.09 (*d*×*d*×*d*, $J = 14$, 6, 1.5, 1H); 2.26–2.39 (*m*, 4 H); 2.70–2.89 (*m*, 2 H); 3.11 (*d*×*t*, $J = 11$, 6, 6, 1H); 3.39 (br.*s*, 1 H) ppm. Coupling constants are given in Hz.

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123. Azimine. III^1). Kristallstruktur von (1*E*,2*Z*)- und (1*Z*,2*E*)-2,3-Dimethyl-1-phthalimido-azimin^2)

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Azimines. III^1). Crystal structure of (1*E*,2*Z*)- and (1*Z*,2*E*)-2,3-dimethyl-1-phthalimido-azimine^2)

Summary

The structures of two diastereoisomeric 2,3-dimethyl-1-phthalimido-azimines, obtained by addition of phthalimido-nitrene to (*E*)-azomethane, have been determined by X-ray analysis. The major adduct **2a** forms rhombic (space group $Cmc2_1$), the minor one **2b** triclinic crystals (space group $P\bar{1}$). The molecular structures of **2a** and **2b** in the crystal exhibit several interesting features: (1) The azimines **2a** and **2b** are true dipolar systems with a coplanar skeleton and with bond angles of about 120°. Thus both azimine N,N bonds are potentially stereogenic centers; (2) **2a** and **2b** differ in configuration at both of these centers: **2a** has

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^{1}) Teil II s. [1].

^{2}) Teilweise vorgetragen in Bern an der Jahresversammlung der Schweizerischen Gesellschaft für Kristallographie, 7. Oktober 1977, und als Autoreferat veröffentlicht [2].

^{3}) Teilweise aus der Diplomarbeit von *R.M.*, ETH Zürich 1977.

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