60. Photochemical Reactions

126th Communication [1]

Photochemistry of an α,β:δ,ε-Unsaturated Ketone: 4-(2′,7′,7′-Trimethylbicyclo[3.2.0]hept-2′-en-1′-yl)-3-buten-2-one

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Summary

On $^1n,\pi^*$-excitation, the title compound **2** undergoes a photoinduced intramolecular [4+2]-cycloaddition affording the tetracyclic enol ether **3** as the only product in 79% yield. The assigned structure of **3** was confirmed by its conversion to the *p*-nitrobenzoate **6** whose structure was determined by X-ray analysis.

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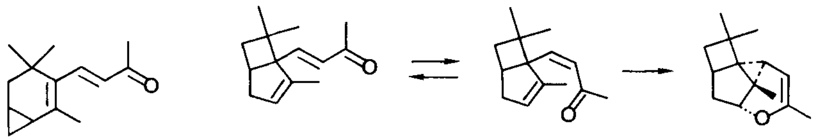
1. Introduction. - As reported previously, UV.-irradiation (λ > 347 nm) of the δ-cyclopropyl-α,γ-dienone **1** affords the bicyclo[3.2.0]heptenylbutenones (*E*/*Z*)-**2** as the main products [2]. Incorporating the chromophore of an α,β:δ,ε-unsaturated ketone, compounds (*E*/*Z*)-**2** were of interest in connection with our investigation of the photochemically induced *vinylogous β-cleavage* [3] of enones, and the results of these studies are described in the present communication.

Scheme 1



1 (*E*)-2 (*Z*)-2 3

2. Photolyses. - 2.1. *Irradiation of a mixture of* (E)- *and (Z)-2 at λ > 347 nm.* Photolysis of a 0.06 M solution of a (5:1)-mixture of (*E*)- and (*Z*)-**2** in pentane (73% conversion) gave **3** in 79% yield[3]).

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[1]) Taken in part from the Ph.D. thesis of *K. Ishii*, Diss. ETHZ No. 6858 (1981).

[2]) Group for X-ray analysis, Laboratory of Organic Chemistry.

[3]) Yields are based on converted starting material.

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Table. *Product distribution during irradiation of* (E)- *and* (Z)-**2**, *respectively, in pentane at* $\lambda > 347$ *nm*

Time [min]	*Irradiation of* (E)-**2** Relative percentage[a]) of			*Irradiation of* (Z)-**2** Relative percentage[a]) of		
	(*E*)-**2**	(*Z*)-**2**	**3**	(*Z*)-**2**	(*E*)-**2**	**3**
2	90	10	–	93	4	3
4	65	33	2	81	11	8
7	47	48	5	68	17	15
10	37	53	10	60	19	21
15	25	55	20	51	19	30
20	23	50	27	44	18	38
30	16	39	45	30	13	57
45	10	25	65	19	8	73
75	4	12	84	7	3	90

[a]) Determined by capillary GC. analysis.

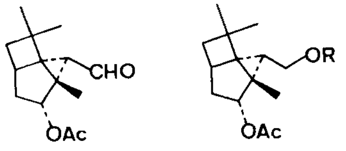
2.2. *Separate irradiation of* (E)- *and* (Z)-**2** *at* $\lambda > 347$ *nm.* Two 0.05 M solutions of (*E*)-**2** and (*Z*)-**2**, respectively, in pentane were simultaneously irradiated. The product distributions were periodically determined by capillary GC. and are shown in the *Table.*

2.3. *Irradiation of* (Z)-**2** *at* $\lambda = 254$ *nm.* Photolysis of a 1.1 M solution of (*Z*)-**2** in CH_3CN (92% conversion) gave mainly polymeric material, 3% of (*E*)-**2** and 9% of **3**.

3. Structure of compound 3. – From the spectral data, the structure of **3** could not be satisfactorily elucidated. The IR. band at 1670 cm^{-1} indicates an enol ether system which is also evidenced in the ^{13}C-NMR. spectrum by the *s* and *d* at 148.9 and 94.8 ppm, respectively. Since **3** was found to be an isomer of **2**, the ^{13}C-NMR. data suggests a tetracyclic system.

Further evidence for the structure was obtained by ozonization of the enol ether **3** affording the formyl acetate **4**. From comparison of the ^{13}C-NMR. data of **3** and **4** (see *Exper. Part*) it seems unlikely that the transformation of **3** to **4** gave rise to molecular rearrangements[4]). Reduction of **4** to **5** with $NaBH_4$ followed by treatment of **5** with *p*-nitrobenzoyl chloride in pyridine gave the crystalline *p*-nitrobenzoate **6** whose structure was confirmed by X-ray analysis[5]).

Scheme 2



4

5 R = H

6 R = p-$O_2NC_6H_4CO$

X-ray analysis of **6**. Monoclinic space group *P2₁/a*, $a = 13.787$, $b = 7.204$, $c = 20.638$ Å, $\beta = 101.83°$, $Z = 4$, *d*(calc) = 1.28 g/cm^3. Intensity measurements were made at room temperature with an *Enraf-*

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[4]) Treatment of **3** with aqueous acid gave a mixture of products resulting from skeletal rearrangement. The expected enol ether hydrolysis product could not be detected.

[5]) The support of these measurements by Prof. *J. D. Dunitz* is gratefully acknowledged.

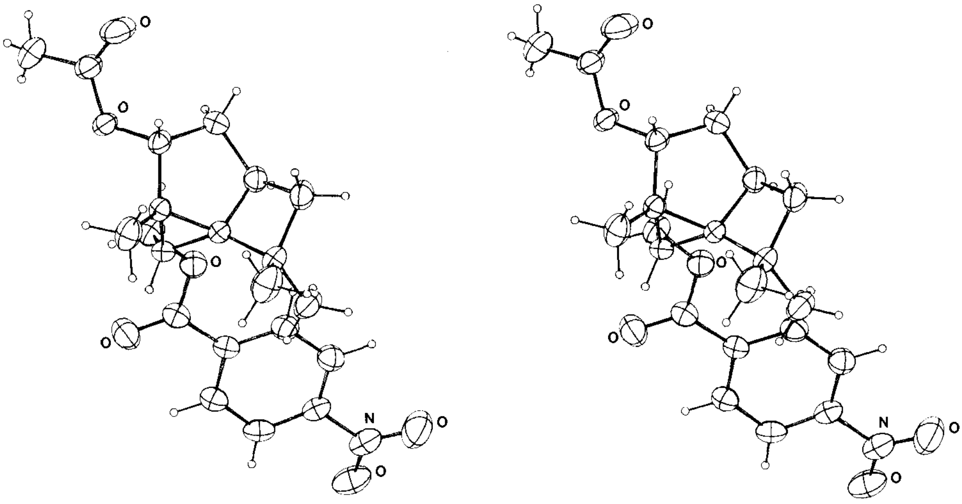

Figure. *Stereoscopic view of molecule* **6** *drawn by ORTEP* [7]. The thermal vibration ellipsoids are at the 30% probability level.

Nonius CAD-4 diffractometer (graphite monochromator, Mo*Ka* radiation, $\lambda = 0.7107$ Å, 2750 independent reflexions with $\theta \leqslant 25°$; part of the shell $22° < \theta < 25°$ was not measured because of a computer breakdown). The structure was solved by direct methods with MULTAN 80 [4] and refined by full-matrix-least-squares analysis using 1854 reflexions ($I > 3\sigma(I)$) with experimental weights (SHELX [5], XRAY-72 [6]). H-Atoms were located at an intermediate stage and included in the refinement with isotropic vibrational parameters (other atoms anisotropic)[6], final R was 0.039 ($R_W = 0.043$).

4. Discussion. - Instead of products arising from *vinylogous β-cleavage* and subsequent 1,3- or di-π-methane-rearrangements, ^{1}n,π^*-excitation of (*E*)- and (*Z*)-**2** causes rapid *cis/trans*-isomerization. This process is accompanied by formation of **3** in a photoinduced intramolecular [4+2]-cycloaddition[7][8]) (see *Scheme 1*). It is evident from the periodic analysis of the simultaneous irradiations (see *Table*) that **3** is formed more rapidly from (*Z*)-**2** than from (*E*)-**2**. Also, in the irradiation of (*E*)-**2**, *trans/cis*-isomerization preceeds formation of **3**. Therefore, it seems most likely that **3** arises directly from (*Z*)-**2**.

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Experimental Part

General. See [9] except as noted below. Melting points were determined in capillary tubes using a *Büchi* melting point apparatus and are uncorrected. Analytical gas chromatography (GC.) was performed using a 20 m × 0.32 mm *SE-52* capillary column. *Filter solution A* see [10].

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[6]) Atomic parameters have been deposited with the *Cambridge Crystallographic Data Centre*, Lensfield Road, Cambridge CB2 1EW, England.

[7]) Thermolysis of either (*E*)- or (*Z*)-**2** (170° in toluene) gives rise to rearrangement products, but the formation of **3** could not be detected [2].

[8]) For a recent review of photocycloaddition reactions of conjugated enones see [8].

1. Photolyses. - 1.1. *Irradiation of* (E)- *and* (Z)-**2** *in pentane at* $\lambda > 347$ *nm.* a) A solution of 478 mg (2.34 mmol) of a (5:1)-mixture of (*E*)- and (*Z*)-**2** [2] in 40 ml of pentane was irradiated (lamp *B*, filter *A*, under Ar; 73% conversion). Chromatography (Al_2O_3, *Woelm B*, activity III; hexane/ether 9:1 to 4:1) afforded 275 mg (79%) of **3**.

b) The solutions of 5 mg (0.025 mmol) of (*E*)-**2** and (*Z*)-**2** [2], respectively, in 5 ml of pentane were irradiated (lamp *B*, filter *A*). Aliquots were periodically removed and analyzed by capillary GC. The results are shown in the *Table.* (1R*,4R*,6R*,10S*,11S*)-*2,2,8,11-Tetramethyl-7-oxatetracyclo*$[4.4.1.0^{1,4}0^{10,11}]$*undec-8-ene* (**3**), b.p. 40°/0.05 Torr. - IR.: 3055*w*, 3025*w*, 2950*s*, 2920*s*, 2865*m*, 2840*w*, 1670*m*, 1460*w*, 1446*m*, 1430*w*, 1423*w* S, 1418*w* S, 1378*m*, 1363*m*, 1308*w*, 1300*w*, 1277*w*, 1265*w*, 1239*w*, 1219*w*, 1191*m*, 1162*w*, 1135*w*, 1109*w*, 1098*w* S, 1082*w*, 1026*m*, 984*w*, 977*w*, 964*w*, 948*w*, 941*w*, 929*w*, 901*w*, 886*w*. - ^{1}H-NMR. (300 MHz, $CDCl_3$): 1.00, 1.14 and 1.45 (3 *s*, 2 $H_3C-C(2)$ and $H_3C-C(11)$); 1.21 (*m* with *d* character, $J=4$, H-C(10)); 1.39 ($d \times d$, $J_1=11$, $J_2=7$, H-C(3)); 1.69 (*m*, $w_{1/2}=3$, $H_3C-C(8)$); 1.78 ($d \times d$, $J_1=14.3$, $J_2=7.5$, broadened to *m*, $w_{1/2}=3$, H-C(5)); 1.98 ($d \times d$, $J_1=11$, $J_2=8$, H-C(3)); 2.02 ($d \times d \times d$, $J_1=14.3$, $J_2=6.8$, $J_3=6.2$, overlapping with $d \times d$ at 1.98, H-C(5)); 2.32 (*qi*, broadened to *m*, $J=7$, $w_{1/2}=3$, H-C(4)); 4.64 (*d*, $J=6.8$, broadened, $w_{1/2}=2$, H-C(6)); 4.71 (*m* with *d* character, $J=4$, H-C(9)). - ^{13}C-NMR.: 18.3, 20.7, 26.3 and 27.6 (4 *qa*, 4 CH_3); 42.3, 48.4 (2 *t*, C(5), C(3)); 23.8 (*d*, C(10)); 34.1 (*d*, C(4)); 88.5 (*d*, C(6)); 94.8 (*d*, C(9)); 27.2, 35.5 (2 *s*, C(2), C(11)); 57.7 (*s*, C(1)); 148.9 (*s*, C(8)). - MS.: 204 (7, M^+, $C_{14}H_{20}O$), 189 (8), 161 (16), *148* (100), 147 (21), 146 (18), 133 (83), 131 (14), 119 (16), 106 (14), 105 (91), 103 (10), 91 (21), 79 (16), 77 (20), 43 (44), 41 (12).

$C_{14}H_{20}O$ (204.31) Calc. C 82.30 H 9.87% Found C 82.20 H 9.97%

1.2. *Irradiation of* (Z)-**2** *in* CH_3CN *at* $\lambda = 254$ *nm.* A solution of 117 mg (0.57 mmol) of (*Z*)-**2** [2] in 50 ml of CH_3CN was irradiated (lamp *A*, quartz; 92% conversion). Chromatography (SiO_2, ether/hexane 3:17) afforded 10 mg (9%) of **3** and 3 mg (3%) of (*E*)-**2**.

2. Additional Experiments. - 2.1. *Ozonolysis of* **3**. A solution of 31 mg (0.15 mmol) of **3** in 20 ml of CH_2Cl_2 and 10 ml of pyridine was cooled to -78° and ozone bubbled through the solution until a faint blue color persisted. The solution was purged with oxygen and allowed to warm to room temp. After pouring into cold water, the organic phase was washed with a sat. solution of copper sulfate and worked up. The residue was distilled (100°/0.01 Torr) and chromatographed (*Florisil*, ether/hexane 1:3) to give 13 mg (36%) of (1R*,2S*,3S*,4R*,6R*)-*2-formyl-3,8,8-trimethyltricyclo*$[4.2.0.0^{1,3}]$*oct-4-yl acetate* (**4**), m.p. 64-67°. - IR.: 2955*m*, 2930*m*, 2905*w* S, 2860*m*, 2850*w* S, 2750*w*, 1740*s*, 1700*s*, 1467*w*, 1452*m*, 1437*w* S, 1427*w*, 1419*w* S, 1386*w*, 1370*m*, 1353*w*, 1310*w*, 1280*w* S, 1260*m* S, 1235*s*, 1213*m* S, 1154*m*, 1147*m* S, 1117*m*, 1092*w*, 1058*m*, 1046*m* S, 1024*m*, 1000*m* S, 986*m*, 968*w*, 908*w*, 898*w* S. - ^{1}H-NMR. ($CDCl_3$): 1.02, 1.22 and 1.46 (3 *s*, $H_3C-C(3)$ and 2 $H_3C-C(8)$); 1.56-1.95 (*m*, H-C(5) and H-C(7)); 1.79 (*d*, $J=7$, overlapping with *m* at 1.56-1.95, H-C(2)); 1.95 (*s*, CH_3COO); 2.13 ($d \times d$, $J_1=10.5$, $J_2=8$, H-C(7)); 2.51 ($d \times d \times d$, $J_1=15.5$, $J_2=9.5$, $J_3=3$, H-C(5)); 3.09 ($d \times d \times d \times d$, $J_1=J_2=J_3=8$, $J_4=3$, H-C(6)); 5.69 ($d \times d$, $J_1=9.5$, $J_2=4$, H-C(4)); 9.16 (*d*, $J=7$, HCO). - ^{13}C-NMR.: 19.8, 20.8, 25.6 and 26.4 (4 *qa*, 4 CH_3); 40.9 and 43.2 (2 *t*, C(5) and C(7)); 37.9 and 43.3 (2 *d*, C(2) and C(6)); 84.8 (*d*, C(4)); 200.4 (*d*, HCO); 39.4 and 47.3 (2 *s*, C(3) and C(8)); 59.0 (*s*, C(1)); 170.6 (*s*, CH_3COO). - MS.: 236 (4, M^+, $C_{14}H_{20}O_3$), 221 (25), 194 (6), 176 (14), 161 (21), 147 (29), 137 (14), 135 (14), 133 (38), 131 (14), 123 (58), 121 (47), 120 (75), 119 (57), 117 (29), 109 (20), 107 (17), 106 (20), *105* (100), 95 (14), 93 (24), 92 (27), 91 (53), 79 (18), 77 (24), 55 (28), 43 (93), 41 (31).

2.2. *Reduction of* **4**. A solution of 13 mg (0.055 mmol) of **4** in 10 ml of methanol was cooled to 0°, and 20 mg (0.5 mmol) of sodium borohydride was added to the stirred solution. After stirring for 1 h, the reaction was quenched with water and worked up with ether to give 13 mg (100%) of **5**.

2.3. *Esterification of* **5**. A stirred solution of 9 mg (0.038 mmol) of **5** and 110 mg (0.64 mmol) of *p*-nitrobenzoyl chloride in 2 ml of pyridine was heated at 55° for 60 h, cooled, and poured into a cold solution of HCl (5%). Workup with ether and chromatography (SiO_2, ethyl acetate/hexane 1:19) afforded 6 mg (41%) of (1R*,2S*,3S*,4R*,6R*)-*(4-acetoxy-3,8,8-trimethyltricyclo*$[4.2.0.0^{1,3}]$*oct-2-yl)-methyl* p-*nitrobenzoate* (**6**), m.p. 133-134 (ethanol). - IR.: 2980*s*, 2960*m* S, 2930*m*, 2900*m*, 2865*m*, 1740*s*, 1725*s*, 1610*w*, 1530*m*, 1520*m* S, 1460*w* br., 1455*w*, 1440*w*, 1410*w*, 1380*m*, 1370*m*, 1350*m*, 1320*w*, 1310*w*, 1300*w*, 1270*s*, 1240*s*, 1215*w* S, 1180*w*, 1160*m* S, 1155*m*, 1120*s*, 1100*m*, 1075*w* br., 1030*w*, 1015*m*, 1005*w* S, 975*w*, 935*w*, 920*w*, 900*w*, 875*w*, 855*w*, 845*w*, 720*m*. - ^{1}H-NMR.: 1.01, 1.14 and 1.42 (3 *s*, 2 $H_3C-C(8)$ and $H_3C-C(3)$); 1.20-1.82 (*m*, H-C(2), H-C(5), H-C(7)); 1.88 (*s*, CH_3COO); 1.93-2.93 (*m*, H-C(5), H−C(6) and H−C(7)); 4.18 (*d*×*d*, *A* part of *ABX* system, $J_1 = 10$, $J_2 = 12$, *H*CH−C(2)); 4.59 (*d*×*d*, *B* part of *ABX* system, $J_1 = 6$, $J_2 = 12$, HC*H*−C(2)); 5.48 (*d*×*d*, $J_1 = 9$, $J_2 = 4$, H−C(4)); 8.09-8.36 (*m*, 4 arom. H). - MS.: 387 (< 1, M^+, $C_{21}H_{25}NO_6$), 289 (11), 178 (11), 161 (30), 160 (89), 151 (16), 150 (89), 147 (28), 146 (14), *145* (100), 135 (13), 123 (16), 122 (60), 121 (19), 120 (16), 119 (24), 117 (13), 107 (18), 106 (12), 105 (87), 104 (57), 94 (10), 93 (22), 92 (19), 91 (27), 79 (22), 77 (18), 76 (23), 55 (18), 43 (93), 41 (17).

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