Erscheint 9mal jährlich – Paraît 9 fois par an

161. Photochemical Reactions

Part 64 [1]

The Photochemistry of 3-Alkyl-cyclopent-2-en-ones

by **R. Reinfried**[1a)], **D. Belluš**[1b)], and **K. Schaffner**[1c)]

Organisch-chemisches Laboratorium der Eidg. Technischen Hochschule, 8006 Zürich

(24. V. 71)

Summary. On ultraviolet irradiation in toluene, cyclopent-2-en-one (**1a**) and 3-methyl-cyclopent-2-en-one (**1b**) undergo dimerisation (→ **3a**, **b**, **4b**), whereas 3-*t*-butyl-cyclopent-2-en-one (**1e**) and the bicyclo[3.2.1]octenone **2a** only react with the solvent (→ **5e**–**7e**, **8**–**10**). The 3-ethyl- (**1c**) and 3-isopropyl-cyclopent-2-en-ones (**1d**) afford by dimerisation products **3c**, **d**, **4c** and by reaction with the solvent **5c**, **d**, **6c**, **d**, **7d**. The β-methoxy-enones **1f** and **2b** are unreactive under comparable irradiation conditions. The head-to-head cyclobutane dimer **3b** (*HH*) by separate irradiation at < 3400 Å in toluene, is reconverted to **1b**. By similar irradiation each of the head-to-tail dimers **3b** (*anti-* and *syn-HT*) and also the unsaturated dimer **4b** give a new isomer of unknown structure besides small amounts of monomer **1b** and relatively large amounts of insoluble material.

The photoreactions of **1b**–**e** can be quenched by naphthalene. *Stern-Volmer* plots for the quenching of the dimers of **1b**, **1c**, and **1d**, and of 3-*t*-butylcyclopentanone (**5e**) and the dihydro dimer **7e** are linear and within each experiment, the slopes satisfactorily coincide, whereas the slope for the α-benzyl ketone **6c** is distinctly greater than that for the dimers **3c**. A similar differentiation, although less pronounced, is found between the benzyl ketones **6d** and **6e** and the respective accompanying products.

We have previously shown that triplet-excited cyclohexenones, such as 10-methyl-$\Delta^{1,9}$-octal-2-one and testosterone, readily add toluene to form α-benzyl ketones [3]. In preliminary experiments, the formation of similar products and of dihydro dimers and bibenzyl was observed when 3-*t*-butyl-cyclopent-2-en-one (**1e**) and 5,8,8-trimethyl-bicyclo[3.2.1]oct-3-en-2-one (**2a**) were irradiated in toluene solution[2]. A recent paper by *Mark et al.* [4] on the photodimerisation of 3-methyl-cyclopent-2-en-one now prompts us to report our results on the photochemistry of the cyclopentenones **1a**–**f** and the bicyclo[3.2.1]octenones **2a** and **2b** in toluene solution.

Irradiation of Cyclopentenones 1a–f and of Bicyclo[3.2.1]octenones 2a and 2b in Toluene Solution. The Table summarises the approximate percentages of products obtained in representative photolyses ($n \rightarrow \pi^*$ excitation) of the six enones **1a**–**e** and **2a** in toluene solution (*cf.* also Chart 1). Cyclopent-2-en-one (**1a**) gave only the *anti-HH* and *anti-HT* cyclobutane dimers[3], as previously reported by *Eaton* [5]

---

[1] a) Taken in part from the Doctoral Dissertation of *Reinfried* [2]. b) Postdoctoral Fellow 1967–1969; present address: *CIBA-GEIGY AG*, Basel. c) Address correspondence to Département de Chimie Organique, Université de Genève, 30, quai de l'Ecole-de-Médecine, 1211 Genève 4.

[2] *Cf.* [3b], footnote 14.

[3] *HH* = head-to-head dimer (*cis-anti/syn-cis*-tricyclo[5.3.0.0^{2,6}]decane-3,10-dione); *HT* = head-to-tail dimer (*cis-anti/syn-cis*-tricyclo[5.3.0.0^{2,6}]decane-3,8-dione).

for the photodimerisation of **1a** in other solvents, and no products due to reaction with the solvent could be observed. Similarly, the 3-methyl-enone **1b** formed only dimers, whereas the 3-*t*-butyl-enone **1e** did not undergo dimerisation but afforded the dihydro (**5e**) and benzyl ketone (**6e**) derivatives, a dihydro dimer (**7e**) and bibenzyl. The photomixtures resulting from the 3-ethyl- and 3-isopropyl-enones **1c** and **1d**, respectively, contained products arising both from dimerisation and from reaction with the solvent.

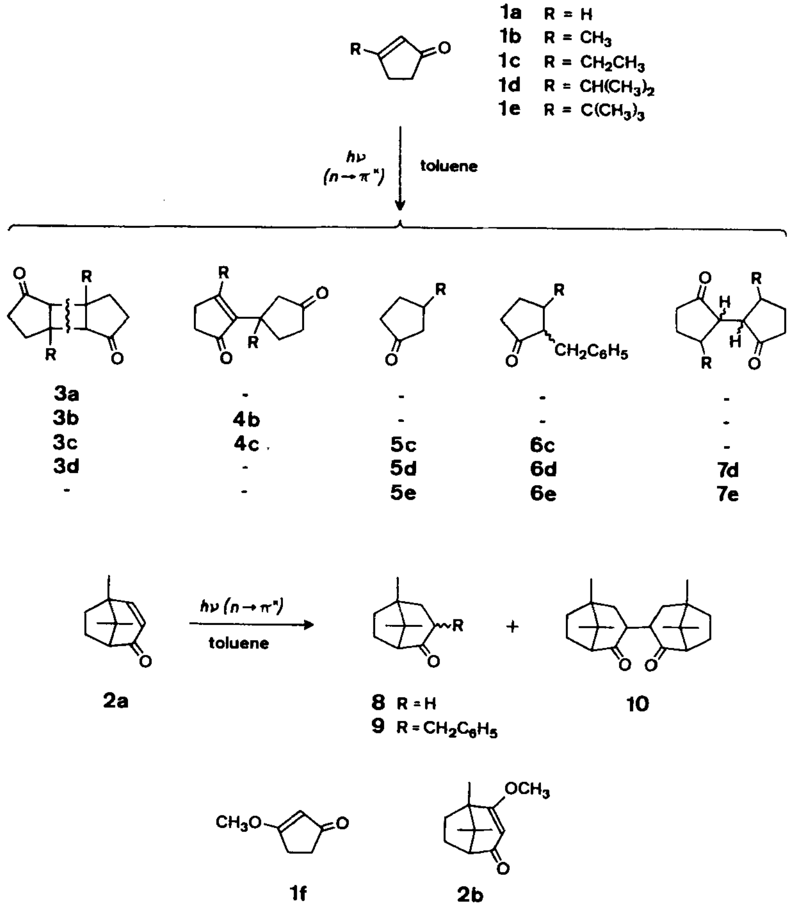


Chart 1. *Photolyses of Enones* **1a–f**, **2a**, *and* **2b** *in Toluene*

The bicyclic enone **2a** furnished its dihydro ketone (**8**), benzyl ketone (**9**), and dihydro dimer (**10**) derivatives, and bibenzyl. The β-methoxy enones **1f** and **2b** were essentially recovered unchanged after irradiation periods at > 3400 Å in toluene which sufficed to convert quantitatively the corresponding 3-methyl and 2-unsubstituted enones **1b** and **2a**, respectively, into photoproducts.

Structural Assignments. – *Baeyer-Villiger* oxidation of the three cyclobutane dimers **3b** furnished the corresponding mono- and di-lactones (Chart 2). The melting

Photolyses of Enones **1a–e** *and* **2a** *in Toluene: Composition of Product Mixtures*[a]

Enone	Concentration	Composition of Product Mixture[b]					
		3[c]	**4**	**5**	**6**	**7**	$(C_6H_5CH_2)_2$
1a	0.03 M	∼50% *anti-HH*[d] ∼50% *anti-HT*	–	–	–	–	–
1b	0.13 M	21% *HH* 47% *anti-HT* 13% *syn-HT*	17%	–	–	–	–
1c	0.14 M	23% + 27% (two isomers)	8%	2%	11%	–	22%
1d	0.08 M	15% *HH* 19% *HT*	–	3%	28%	3%	28%
1e	0.10 M	–	–	14%	46%	14%	25%
				8	**9**	**10**	$(C_6H_5CH_2)_2$
2a	0.10 M			9%	39%	25%	27%

[a] Light source: medium-pressure Hg lamp. Filters: Pyrex for **1a**; NaBr—$Pb(NO_3)_2$/Pyrex for **1b**, **1c**, and **2a** (cut-off at ∼3400 Å); acetone/Pyrex for **1d** and **1e** (cut-off at ∼3270 Å).

[b] Integrated VPC. areas.

[c] See footnote 3 for abbreviations.

[d] *Cf.* [5].

points of the dimers **3b** and the spectral data of compounds **3b**, **4b**, and **11–13** correspond to those reported by *Mark et al.* [4] for the four major photodimers of **1b** in other solvents and also of their derived monolactones. The identification of the individual photodimers, obtained independently by these authors and by ourselves, is further strengthened by the fact that the dependence of product formation on solvent and concentration as reported in [4] is here qualitatively confirmed[4]. In partial agreement with the arguments of *Mark et al.*, the *HH*, *anti-HT*, and *syn-HT* cyclobutanedimer structures were assigned on the basis of the NMR. data of compounds **3b** and their monolactone derivatives **11–13**. Particular significance is ascribed to the cyclobutoxy proton signal of each monolactone which exhibit singlet (**12**) and doublet structure (**13**: $J \sim 1.7$ Hz, **11**: $J = 6$ Hz; spin coupling of the two cyclobutyl protons in each compound), respectively[5]. We cannot however, support, the NMR. argu-

---

[4] We have used the solvents ethanol, acetonitrile, methylene chloride, toluene, benzene, and hexane, and 0.05, 0.1, 0.2, 0.4, and 0.8 M concentrations of **1b** in toluene, as well as neat **1b**.

[5] A comparison of the IR. and *Raman* spectra of crystalline samples of the three cyclobutane dimers **3b** did not permit a distinction between the formally centrosymmetric *anti-HT* dimer and the *syn-HT* and *HH* dimers: the three compounds exhibit a similar number of corresponding absorptions within ±5 cm^{-1} in the 440–2990 cm^{-1} region of both spectra (16 correspondences in the *HH*, 24 in the *anti-HT*, and 17 in the *syn-HT* dimer). *Ziffer & Levin* [6] have succeeded in differentiating correctly the *anti-HT* structure from the *anti-HH* isomer in the cyclopentenone dimer **3a** series on the basis of the rule of mutual exclusion for IR. and *Raman* transitions in molecules with C_i symmetry. The failure of the method in the present instance is probably due to non-planarity of the four-membered ring of **3b** (*anti-HT*) and hence its lack of C_i symmetry [*cf. Margulis* [7] for the planarity of the four-membered ring in **3a** (*anti-HT*)].

ments which *Mark et al.* advanced in favour of the *syn*-conformation of the *HH*-dimer **3b**. Contrary to their view, the coupling constant of 6 Hz for the cyclobutyl protons in **11** does not seem to allow a differentiation between the *cis*- and *trans*-conformations of vicinal protons, as implicitely pointed out indeed in the references cited by *Mark et al.* (*cf.* [5] [8])[6]. It appears equally untenable to ascribe the substantial up-field shift of two methylene protons in **3b** (*HH*) (to ca. 1.5–1.9 δ *versus* ca. 2.2–2.8 δ for the remaining six methylene protons) to a positive anisotropy effect specifically exerted by the spatially opposite cyclopentanone moiety in the *syn-HH* conformer. We suggest that a definitive conformational assignment await further experimentation[7].

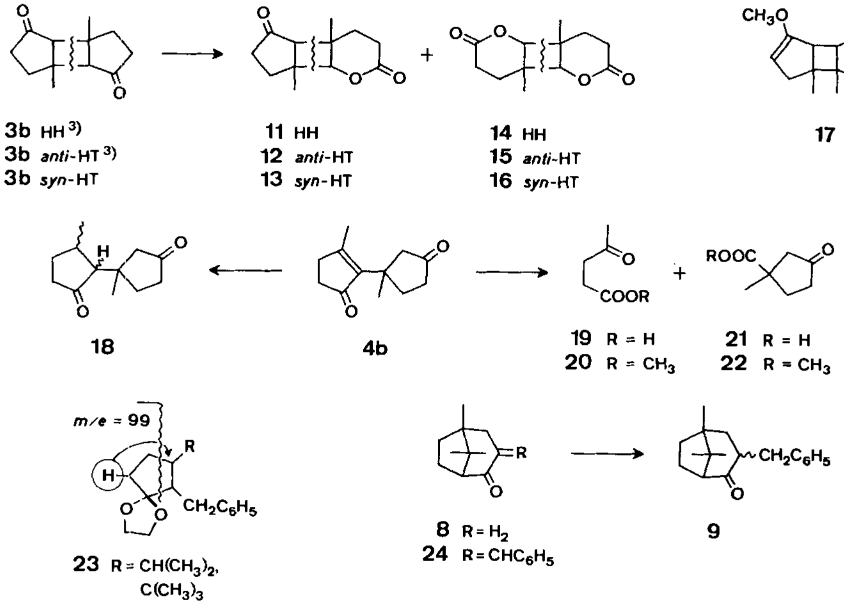


Chart 2

The catalytic hydrogenation of product **4b** [UV. (C_2H_5OH): λ_{max} = 236, ε = 14,900] gave a ca. 1:1.4 mixture of two diastereomeric dihydro derivatives **18**. The structure of **4b**, postulated by *Mark et al.* [4] on the strength of IR., NMR., and MS. data, and on mechanistic reasoning, is unequivocally confirmed by ozonolysis which afforded, after esterification of the resulting acids (**19** and **21**), methyl levulinate (**20**) and the keto methyl ester **22**. Base-catalysed hydrogen-deuterium exchange incorporated four deuterium atoms in the latter product, thus establishing the presence of two methylene groups in α,α'-positions to the keto group[8].

---

[6] See also *Ziffer et al.* [9] [10].

[7] An unsuccessful attempt to obtain complete structural evidence for the *HH*-dimer **3b** may be mentioned. The diketone was treated with hydrogen chloride in anhydrous methanol in the hope that, given the *syn*-geometry, a bridged dimethoxy diketal be formed. A monoenol ether of type **17** resulted however, possibly arising by an acid-catalysed cleavage of the product envisaged as intermediate.

[8] Syntheses of compounds **21** and **22** have been reported previously [11].

From each of the photomixtures of **1c** and **1d**, two saturated dimers were obtained. All four products exhibit the IR., NMR., and MS. spectra expected for cyclobutane dimers of type **3c** and **3d**, respectively. No attempt has been made to elucidate the structure of these products in greater detail, except for a study of the dependence of dimer formation, in the isopropyl series (**3d**), on solvent (using hexane, benzene, acetonitrile, and ethanol). The preference observed for formation of one of the two dimers in polar solvents may be taken as evidence in favour of an *HH*-alignment for the product concerned, and of an *HT*-structure for its isomer. Similarly, the spectra of a third photodimer of **1c** clearly reveal a 2-(ethyl-cyclopentanonyl)-3-ethyl-cyclopent-2-en-one constitution, but do not define the substitution pattern of the cyclopentanone moiety. For this product structure **4c** is postulated as more likely by analogy to **4b**.

For ketones **6d,e**, **7d,e**, **9**, and **10** the presence of an α-substituent is based on base-catalysed hydrogen/deuterium exchange experiments which introduced a maximum of three deuterium atoms in **6d** and **6e**, six deuterium atoms in **7d** and **7e**, one deuterium atom in **9**, and two deuterium atoms in **10**. Concomitantly, the NMR. four-line signals of the benzylic methylene protons of **6d**, **6e**, and **9** coalesced to *AB* patterns. Evidence for α and β substituents in cyclopentanones **6d** and **6e** was finally established by converting these compounds into the ethylene ketals **23**. Both ketals exhibit a base peak of *m/e* 99 in the mass spectrum, characteristic of the fragmentation indicated in formula **23**. The α-benzyl ketone **9** was synthesised from the saturated ketone **8** which was converted to the benzylidene derivative **24** and then catalytically hydrogenated. The structure of photoproduct **6c** was assigned spectroscopically (IR., NMR., MS.) and by analogy to **6d,e**, and **9**.

Photoreactions of Compounds 3b (HH, *anti*- and *syn*-HT) and 4b. Separate irradiation of the HH-cyclobutane dimer **3b** at wavelengths < 3400 Å in toluene resulted in preliminary cleavage to the monomer **1b** and then dimerisation to the four products **3b** (*HH*, *anti*- and *syn-HT*) and **4b**, accompanied by the formation of small amounts of polymeric material.

Each of the two *HT*-dimers **3b** and the unsaturated isomer **4b** exhibited a more complex behaviour under the above irradiation conditions. The tendency to form polymers was distinctly greater than for **3b** (*HH*). Periodical gas-chromatographic (VPC.) analyses during the photolyse showed that in addition to a minor amount of **1b** a major new product appeared with identical retention time in each case, which proved unstable on further irradiation. According to mass spectrometric evidence, this new product is isomeric with **3b** and **4b** [M^+ at *m/e* 192 ($C_{12}H_{16}O_2$)]. Owing to its instability attempts to isolate a sufficient amount in pure form for further structural studies have failed as yet.

Triplet Quenching Experiments. – Discussion. Photolyses of **1b–e** were also effected in toluene in the presence of naphthalene at > 3400 Å. Linear *Stern-Volmer* plots were obtained for all ketonic products which were amenable to quantitative VPC. analysis (see Fig. 1–4; there was qualitative evidence of quenching for all products arising from **1b–e** listed in Chart 1), thus confirming the triplet nature of the photoreactions concerned. This result was anticipated in view of those recorded for the dimerisation of cyclopentenone [12], for toluene addition to cyclohexenones, and for reduction of enone double bonds [3].

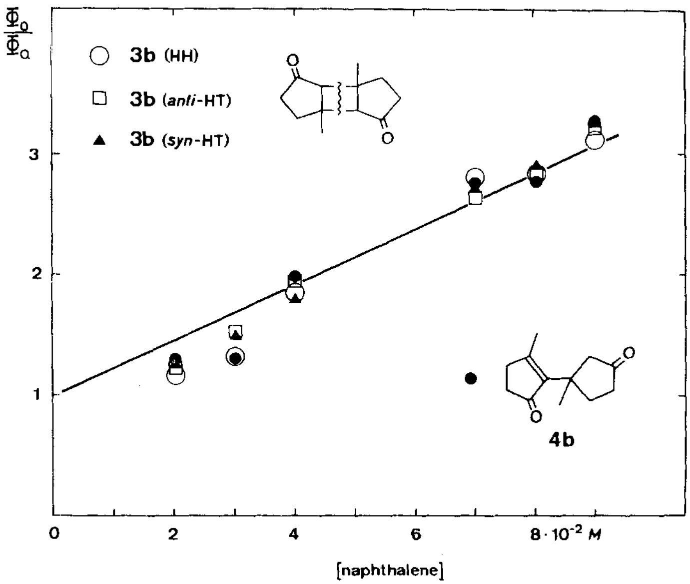


Fig. 1. Stern-Volmer *Plots for Quenching of Photoproducts*: **1b** + *Naphthalene*
0.10 M Degassed solution of **1b** in toluene at > 3400 Å; maximum conversion ca. 10%

The four dimers of methyl-cyclopentenone **1b** exhibit the same slope for quenching (Fig. 1), and hence are likely to originate from the same excited enone triplet state. Corroborative evidence has been presented by *Mark et al.* [4] who found a linear correlation of the logarithms of the dimer ratios **3b**(*anti-HT*)/**3b**(*HH*), **3b**(*syn-HT*)/**3b**(*HH*), and **4b**/**3b**(*HH*) with the *Kirkwood-Onsager* solvent parameters.

A preliminary study of the dependence of product formation from **1b** on concentration indicates that the ratio **3b**(*HH* + *anti-HT* + *syn-HT*)/**4b** increases with increasing enone concentration in the range 0.05 M–0.8 M; only negligible amounts of **4b** were formed in neat **1b**. This result may indicate that the dependence of **4b** formation on pre-oriented pairs of monomers is smaller (see *deMayo* [12f] for a recent discussion) and throws doubt on the conclusion of *Mark et al.* [4] that both *HT*-dimers **3b** and **4b** result from similar transition states. These authors envisaged the addition of two methyl-cyclopentenones with concomitant hydrogen transfer to yield **25** as intermediate and precursor of **4b**. The subsequent double-bond shift from the β,γ-position **25** into the conjugated α,β-position in **4b** would presumably require a second photochemical step which, however, appears unlikely in view of our experiments at wavelengths > 3400 Å and the observed preference for **4b** formation in dilute solution. Addition to the diradical intermediate **26**, which may also serve as the precursor of *HT*-dimers [12a], and a subsequent 1,3-hydrogen shift can be seen as a

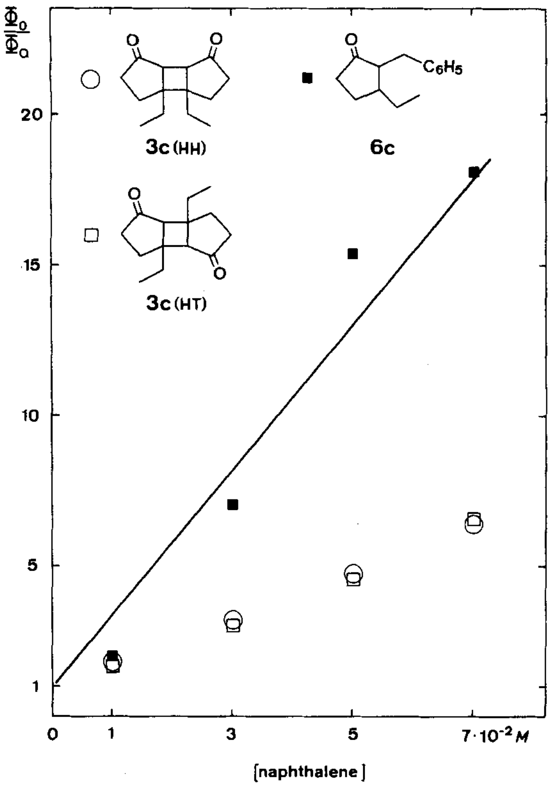
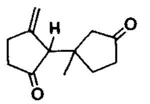
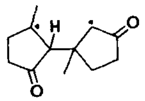


Fig. 2. Stern-Volmer *Plots for Quenching of Photoproducts*: **1c** + *Naphthalene*

0.09 M Degassed solution of **1c** in toluene at > 3400 Å; maximum conversion ca. 10%. Tentative structural assignment to **3c** (*HH*) and **3c** (*HT*) by analogy with relative VPC retention times of **3b** (*HH* and *anti-HT*) and **3d** (*HH* and *HT*)



25



26

plausible and more economic alternative, but additional experiments are clearly needed to gain insight into the formation of unsaturated dimers of type **4**[9]).

The respective slopes of each pair of the cyclobutane dimers **3c** and **3d** again show satisfactory coincidence, whereas the slope for benzyl ketone **6c** is greater beyond the limits of experimental error (Fig. 2). It seems likely that the analogous compounds **6d** and **6e** are also quenched more rapidly than the other products in each of the two systems (Figs. 3 and 4), although the differences in the respective slopes are much less pronounced. The results using **1c** can nevertheless be considered to constitute evidence in favor of *two* triplet-excited states which lead to the benzyl ketone **6c** and to

---

[9]) The formation of an analogous unsaturated photodimer of 3-ethyl-cyclohex-2-enone has been previously reported by *Dauben* [13].

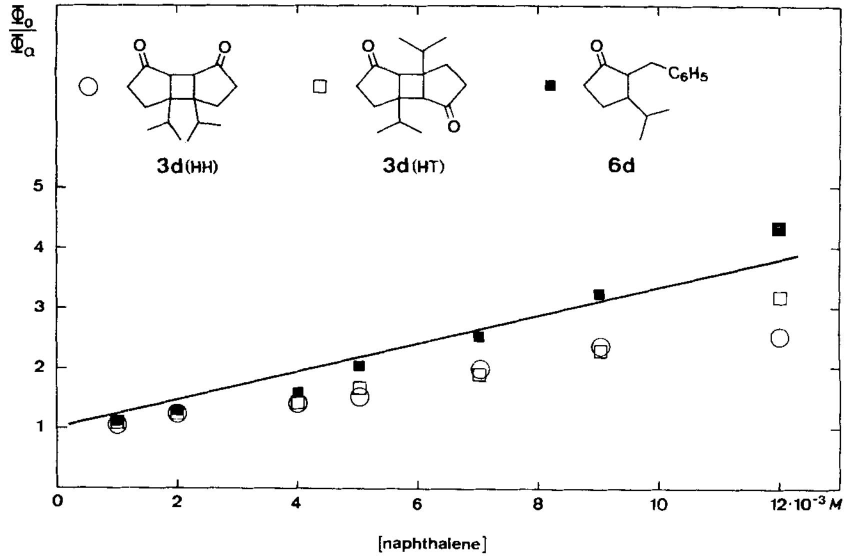


Fig. 3. Stern-Volmer *Plots for Quenching of Photoproducts*: **1d** + *Naphthalene*
0.12 M Degassed solution of **1d** in toluene at > 3400 Å; maximum conversion ca. 10%

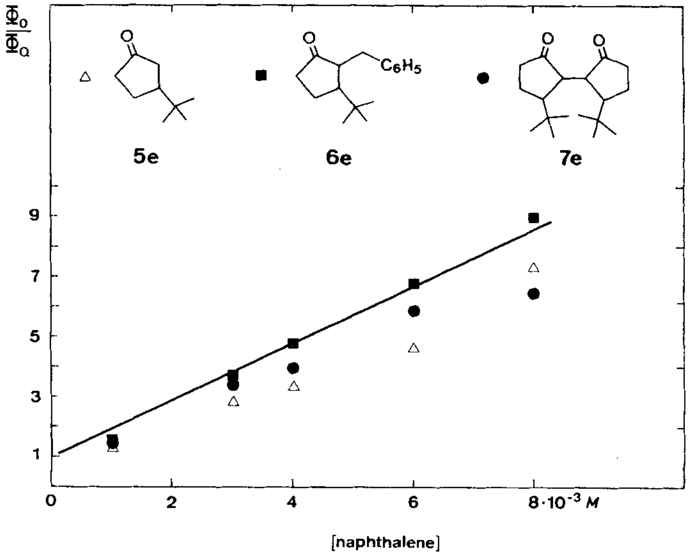


Fig. 4. Stern-Volmer *Plots for Quenching of Photoproducts*: **1e** + *Naphthalene*
0.12 M Degassed solution of **1e** in toluene at > 3400 Å; maximum conversion ca. 10%

the two dimers **3c**, respectively. We have previously demonstrated that two triplet-excited cyclohexenone states are capable of competitively and selectively participating in product formation, using similar differential quenching techniques [3]. Assignments of electron configuration to these reactive triplets have been proposed on the strength of arguments relating to the nature of the primary photochemical processes involved and to their dependence on solvent. Specifically, formation of an α-benzyl substituted ketone from, *e.g.*, 10-methyl-$\Delta^{1,9}$-octal-2-one in toluene, which apparently arises through hydrogen abstraction by the β-carbon, as well as photoreduction to saturated ketone (in isopropyl alcohol) and the rearrangement to a bicyclo[3.1.0]-hexanone were ascribed to the $^3\pi,\pi^*$-state. The $\alpha,\beta \rightarrow \beta,\gamma$ double bond shift in benzene, shown to involve intermolecular hydrogen abstraction by the excited ketone oxygen, was attributed to the n,π^*-state[10]. However, attribution of the α-benzyl-cyclopentanones **6** to $^3\pi,\pi^*$-states implicitly contests the conclusion by *Wagner* [12c] that cyclopentenone dimerisation also occurs from the $^3\pi,\pi^*$-state. Furthermore, the structural relationship between the α-benzyl ketones **6** and the α,α-linked dihydro-dimers **7** suggests that both products result from the same primary photochemical processes (and hence from the same reactive excited species), *i.e.* hydrogen abstraction by the β-carbon, followed by cross-coupling of the α-keto and benzyl radicals to **6** and combinations to **7** and bibenzyl, respectively. However, the *Stern-Volmer* slopes for, *e.g.*, reactions **1e** → **6e** and **1e** → **7e** (Fig. 4), albeit close-lying, do not coincide as satisfactorily as desired in support of the above mechanistic relationship between the two reactions. It would seem premature to elaborate on these (possible) ambiguities concerning assignments to excited-state configurations and reaction mechanisms[11] prior to additional experiments which are in progress.

We gratefull acknowledge financial support for this research afforded by the *Schweiz. Nationalfonds zur Förderung der wissenschaftlichen Forschung* and by *CIBA-GEIGY AG*, Basel.

Experimental Part

General Remarks. – Unless otherwise stated, the *working up* of crude reaction mixtures involved extraction with ether or ethyl acetate, washing of the organic layer with water to the neutral point, drying over anhydrous $MgSO_4$, and evaporation of solvent *in vacuo* in a rotatory evaporator.

Preparative UV.-irradiations were carried out at room temperature with 70 W (Q81, *Quarzlampen GmbH*, Hanau) and 125 W (QM125, *Meda Licht AG*, Basel) medium-pressure Hg lamps placed in a central double Pyrex immersion well. The inner jacket was water-cooled, and the outer jacket contained a filter solution (cut-off at ~3270 Å: acetone; ~3400 Å: aqueous solution of 750 g NaBr + 8 g $Pb(NO_3)_2$ per liter). The solution was agitated by a stream of N_2.

Melting points (taken in open capillaries in an oil bath) and *boiling points* are not corrected.

For *preparative column chromatography* silica gel *Merck* (0.05–0.20 mm) and, unless specified otherwise, benzene-ethyl acetate 4:1 were used.

Gas chromatograms (VPC.) were run on *Varian-Aerograph* A-90P3 models with helium as carrier.

UV. spectra: λ_{max} are given in nm (ε values in parantheses). – *IR. spectra*: ν_{max} in cm^{-1}. – *NMR. spectra*: at 60 or 100 MHz. Chemical shifts are given in δ values, with $(CH_3)_4Si$ as internal standard. Abbreviations: *s* (singlet), *d* (doublet), *t* (triplet), and *q* (quartet) for first-order mul-

---

[10] According to emission spectroscopic evidence [14] the $^3\pi,\pi^*$-states of such cyclohexenones adopt a non-planar equilibrium conformation which can best be accomodated by a rotation about the C=C bond of the enone group. This conformational change is likely to approximate to that required for initiating the rearrangement to the bicyclohexanone isomer, thus lending further circumstantial support for the $^3\pi,\pi^*$-assignment to the state involved in both the rearrangement and the formation of α-benzyl substituted ketones.

[11] See, *e.g.*, *Wagner & Leavitt* [15] for the possibility of photoreduction of triplet-excited ketones involving electron transfer from alkylbenzenes.

tiplets, *m* for multiplets not described by other symbols, *b* (broad), and *J* for coupling constants in Hz. Proton integration of each signal is in agreement with the assignments given.

Syntheses and Preparative Irradiations of Ketones. – *Cyclopent-2-en-one* (**1a**). Irradiation of 0.03 M solutions of **1a** (purchased from *Aldrich*) in toluene and in benzene [5] gave, in each case, a ~1:1 ratio of cis, anti, cis-*tricyclo[5.3.0.0^{2,6}]decane-3,10-dione* (**3a**, anti-HH) [5] and cis, anti, cis-*tricyclo[5.3.0.0^{2,6}]decane-3,8-dione* (**3a**, anti-HT3)) [5] (analysis by VPC. (20% SE-30) and mass spectra of the isolated products).

3-Methyl-cyclopent-2-en-one (**1b**). **1b** [UV. (toluene): 321 (59). NMR. (C_6D_6): 1.5/*d*, $J = 1$, 3–CH_3; 5.75/*q*, $J = 1$, CH–2] was prepared according to *Acheson & Robinson* [16]. A 0.13 M solution of **1b** in toluene was irradiated for 17 h with a 125 W lamp at > 3400 Å (50% conversion of **1b**). After removal of the toluene (by azeotropic distillation with CH_3OH in a rotatory evaporator) and unchanged **1b** (by distillation *in vacuo*), the crude mixture was separated by column chromatography into *2-(1-methyl-3-oxo-cyclopentan-1-yl)-3-methyl-cyclopent-2-en-one* (**4b**) [4] [UV. (C_2H_5OH): 236 (14,900), 303 (77); (toluene): 299 (74), 310 (74), ca. 320 (shoulder), ca. 351 (shoulder). IR. (CCl_4): 1628, 1698, 1743. NMR. (C_6D_6): 1.05/*s*, 1′–CH_3; 1.50/*s*, 3–CH_3. MS.: 192 (M^+, $C_{12}H_{16}O_2$; 51%), 177 (100%), 97 (17%), 96 (13%)] and a ternary mixture from which the following products were isolated by VPC. (20% SE-30):

1. *1,6-Dimethyl*-cis, anti, cis-*tricyclo[5.3.0.0^{2,6}]decane-3,8-dione* (**3b**, anti-HT3)), m.p. 128–129° ([4]: m.p. 126–133°). UV. (toluene): 307 (42). IR. (CCl_4): 1743. NMR. ($CDCl_3$): 1.21/*s*, 1- and 6-CH_3. MS.: 192 (M^+, $C_{12}H_{16}O_2$; 8%), 177 (4%), 97 (81%), 96 (100%).

2. *1,6-Dimethyl*-cis, syn, cis-*tricyclo[5.3.0.0^{2,6}]decane-3,8-dione* (**3b**, syn-HT3)), m.p. 72–75° ([4]: m.p. 80–82°). UV. (toluene): 304 (86). IR. (CCl_4): 1732. NMR. ($CDCl_3$): 1.48/*s*, 1- and 6-CH_3. MS.: 192 (M^+, $C_{12}H_{16}O_2$; 5%), 177 (4%), 97 (77%), 96 (100%).

3. *6,7-Dimethyl*-cis, ξ, cis-*tricyclo[5.3.0.0^{2,6}]decane-3,10-dione* (**3b**, HH3)), m.p. 133.5–134° ([4]: m.p. 129–136° for *HH* dimer assigned *syn*-conformation). UV. (toluene): 310 (97). IR. (CCl_4): 1748. NMR. ($CDCl_3$): 1.25/*s*, 6- and 7-CH_3. MS.: 192 (M^+, $C_{12}H_{16}O_2$; 2%), 177 (10%), 97 (93%), 96 (100%).

For the composition of the product mixture see Table.

Comparison of the IR. and Raman *spectra*5)12). The IR. spectra were measured in KBr on a *Perkin-Elmer* model 125 spectrophotometer. An argon laser (wavelength 4880 Å) of *Coherent Radiation Laboratories* and a double monochromator *Spex* 1400 with two *Bausch and Lomb* 124 × 124 mm gratings (12,000 grooves/cm) served for the *Raman* spectroscopy, using ca. 2 mg samples of crystalline material and the photon counting method (band positions ± 4 cm^{-1}). Results (correspondences in *italics*):

3b (*anti-HT*3)) – IR.: *2955*, *2928*, 2883, *2865*, *1722*, *1468*, *1451*, *1403*, 1379, 1310, 1297, 1270, *1220*, 1208, *1195*, *1165*, *1120*, 1102, *1089*, *1060*, 1050, *991*, 918, *896*, 849, *822*, *785*, *765*, *670*, *628*, 598, *577*, 547, *519*, *491*, *441*. *Raman*: *2952*, *2931*, 2900, *2863*, *1722*, *1467*, *1448*, *1404*, *1224*, *1195*, 1172, *1164*, *1125*, *1088*, *1061*, *992*, 935, 910, *897*, *822*, *784*, *765*, 738, *669*, *627*, *575*, *524*, *494*, *443*.

3b (*syn-HT*3)) – IR.: *2957*, 2952, *2863*, 1722, 1447, *1418*, 1401, 1380, 1330, 1311, 1269, 1242, 1220, *1189*, *1159*, 1137, *1104*, *1061*, *1050*, 1025, *997*, *940*, *922*, 870, 793, *760*, *648*, *623*, *570*, *540*, 512, 469, *450*. *Raman*: *2956*, 2932, *2862*, 1711, 1455, *1422*, 1227, *1192*, *1157*, *1105*, *1061*, *1053*, *998*, 983, *940*, *921*, 898, *757*, 727, *646*, *624*, *570*, 564, *540*, 522, *448*.

3b (*HH*3)) – IR.: *2980*, *2959*, *2940*, *2875*, 1738, *1722*, *1449*, *1412*, 1373, 1318, *1279*, 1218, *1169*, 1130, *1097*, *1072*, 1058, *990*, *920*, 908, 794, *770*, 648, *560*, 543, 504, *461*. *Raman*: *2982*, *2959*, *2937*, 2900, *2871*, *1722*, 1718, *1455*, *1410*, *1282*, 1233, 1199, *1167*, 1149, 1142, *1097*, *1077*, *987*, *919*, 885, 846, *771*, 735, *562*, 528, *461*.

3-Ethyl-cyclopent-2-en-one (**1c**). *Grignard* reaction of 3-isobutoxy-cyclopent-2-en-one, prepared from cyclopentane-1,3-dione [17] according to [18], with ethyl magnesium bromide gave **1c**, b.p. 86–88°/20 Torr. IR. (CCl_4): 1623, 1676, 1718. UV. (toluene): 320 (96). NMR. (CCl_4): 2.15/*t*, $J = 8$, CH_3; 5.86/*s* with fine splitting, CH-2. MS.: 110 (M^+, $C_7H_{10}O$; base peak), 81, 67, 53.

---

12) We thank Miss *E. Bechtel* and Mr. *P. Groner*, Laboratorium für physikalische Chemie, ETH Zürich, for measuring the *Raman* spectra.

A second synthesis of **1c** started from commercially available cyclopent-2-en-one (**1a**) which was subjected to sensitised irradiation with benzophenone (through Pyrex filter) in C_2H_5OH[13]. *3-(1-Hydroxyethyl)-cyclopentanone* was isolated in almost quantitative yield by preparative VPC. (20% SE-30 column, 170°). IR. (CCl_4): 1740, 3610. NMR. (CCl_4): 1.2/*d*, $J = 7$, CH_3-2′; 3.6/*b*, CH-1′. MS.: 128 (M^+, $C_7H_{12}O_2$), 83 (base peak), 55, 45, 43. When this hydroxyketone was treated for 15 h with catalytic amounts of *p*-toluenesulfonic acid in toluene in a water separator, a mixture of **1c** and another product, presumably the isomeric 3-vinyl-cyclopentanone, was formed.

A 0.14 M solution of **1c** in toluene was irradiated for 60 h with a 70 W lamp at > 3400 Å (60% conversion of **1c**). The toluene was removed by azeotropic distillation with CH_3OH in a rotatory evaporator and the residue was separated by VPC. (20% SE-30 glass column) into **1c**, *bibenzyl*, and the following products:

1. Two cyclobutane dimers, presumably a *1,6-diethyl-tricyclo[5.3.0.0^{2,6}]decane-3,8-dione* (**3c**, HT[3][14]) and a *6,7-diethyl-tricyclo[5.3.0.0^{2,6}]decane-3,10-dione* (**3c**, HH[3][14]). IR. (CCl_4): 1732; 1733. NMR. (CCl_4): 1.0/*t*, $J = 7$, two CH_3; 0.95/*t*, $J = 7$, two CH_3. MS.: 220 (M^+, $C_{14}H_{20}O_2$; 9%), 191 (8%), 111 (100%), 110 (97%), 91 (31%), 81 (41%); 220 (M^+, 23%), 191 (29%), 111 (100%), 110 (70%), 91 (27%), 81 (31%).

2. One dimer, presumably *2-(1-ethyl-3-oxo-cyclopentan-1-yl)-3-ethyl-cyclopent-2-en-one* (**4c**). IR. (CCl_4): 1619, 1704, 1748. NMR. (CCl_4): 0.6–2.9/*m*. MS.: 220 (M^+, $C_{14}H_{20}O_2$), 191 (base peak), 91.

3. *3-Ethyl-cyclopentanone* (**5c**). IR. (CCl_4): 1741. MS.: 112 (M^+, $C_7H_{12}O$), 83 (base peak). Identification by comparison (IR., VPC.) with the product of catalytic hydrogenation of **1c**.

4. *2-Benzyl-3-ethyl-cyclopentanone* (**6c**). IR. (CCl_4): 707, 1500, 1608, 1745. NMR. (CCl_4): 2.90/*d*, $J = 5.5$, benzylic CH_2; 7.2/*bs*, arom. H. MS.: 202 (M^+, $C_{14}H_{18}O$), 173, 146, 91 (base peak).

For the composition of the product mixture see Table.[15]

3-Isopropyl-cyclopent-2-en-one (**1d**). **1d** [UV. (toluene): 304 (54). NMR. (CCl_4): 1.20/*d*, $J = 7$, $CH(CH_3)_2$; 5.95/*s* with fine splitting, CH-2] was prepared according to *Pfau & al.* [19]. A 0.04 M solution of **1d** in toluene was irradiated for 7 h with a 70 W lamp at > 3270 Å (50% conversion of **1d**). After removal of the toluene by azeotropic distillation with CH_3OH in a rotatory evaporator, the following products were isolated by repeated preparative VPC. on 20% SE-30 and 20% Apiezon-L columns:

1. *Bibenzyl.*

2. Two cyclobutane dimers, presumably a *1,6-diisopropyl-tricyclo[5.3.0.0^{2,6}]decane-3,8-dione* (**3d**, HT[3][16]) and a *6,7-diisopropyl-tricyclo[5.3.0.0^{2,6}]decane-3,10-dione* (**3d**, HH[3][16]). IR. ($CHCl_3$): 1726 (broad); 1728. MS.: 248 (M^+, $C_{16}H_{24}O_2$; 10%), 205 (20%), 125 (33%), 124 (19%), 91 (41%), 43 (89%), 41 (100%); 248 (M^+; 3%), 205 (9%), 125 (32%), 124 (18%), 91 (30%), 43 (68%), 41 (100%).

3. *3-Isopropyl-cyclopentanone* (**5d**). IR. (CCl_4): 1742. MS.: 126 (M^+, $C_8H_{14}O$). Identification by comparison (IR., MS., VPC. co-injection on a SE-30 column) with the product of hydrogenation of **1d** on 5% Pd/$CaCO_3$.

4. *2-Benzyl-3-isopropyl-cyclopentanone* (**6d**). IR. ($CHCl_3$): 700, 1602, 1732. NMR. ($CDCl_3$): 0.77 + 0.90/2 *d*, $J = 6$, two $CH(CH_3)_2$; 2.83 + 2.98/2 *dd*, $J_{gem} = 16$, $J_{vic} = 1.5$, benzylic CH_2; 7.18/*m*, arom. H. MS.: 216 (M^+, $C_{15}H_{20}O$), 173, 146, 91 (base peak). *2,4-Dinitrophenylhydrazone*: m.p. 134–135°. MS.: 396 (M^+), 305, 170, 122, 91 (base peak).

$C_{21}H_{24}N_4O_4$ Calc. C 63.62 H 6.10 N 14.13% Found C 63.49 H 6.18 N 14.15%

5. *2-(5-Isopropyl-2-oxo-cyclopentan-1-yl)-3-isopropyl-cyclopentanone* (**7d**). IR. ($CHCl_3$): 1725. NMR. ($CDCl_3$): 0.9/*bt*, $J = 6$, two $CH(CH_3)_2$. MS.: 250 (M^+, $C_{16}H_{26}O_2$), 207, 125 (base peak), 83.

---

[13] Method as described by *Pfau & al.* [19] for 3-isopropyl-cyclopent-2-en-one (**1d**).

[14] Structural assignment on the basis of spectral evidence and in analogy to the major cyclobutane dimers formed from **1b**.

[15] An additional product in approximately 5% yield, which could be the dihydro dimer of **1c** (product type **7**), has not been isolated.

[16] Structural assignment based on the spectral evidence, the solvent effect on dimer formation, and analogy with the major cyclobutane dimers formed from **1b**.

For the composition of the product mixture see Table.

*3-*t*-Butyl-cyclopent-2-en-one* (**1e**). **1e** was prepared according to *Al-Jallo & Waight* [20]. A 0.09 M solution of **1e** in toluene was irradiated for 24 h with a 70 W lamp at > 3270 Å (60% conversion of **1e**). The toluene was removed by azeotropic distillation with CH_3OH in a rotatory evaporator, and the following products were isolated by VPC. on a 20% NPGS column:

1. *Bibenzyl.*

2. *3-*t*-Butyl-cyclopentanone* (**5e**). IR. (CCl_4): 1746. MS.: 140 (M^+, $C_9H_{16}O$). *2,4-Dinitrophenylhydrazone*: m.p. 138–139°. Identification by comparison (IR., mixed m.p. of the 2,4-dinitrophenylhydrazones) with the product of catalytic hydrogenation of **1e**.

3. *2-Benzyl-3-*t*-butyl-cyclopentanone* (**6e**). IR. (CCl_4): 703, 1602, 1740. NMR. ($CDCl_3$): 0.89/*s*, $C(CH_3)_3$; 2.81 + 3.05/2 *dd*, $J_{gem} = 14$, $J_{vic} = 5.6$, benzylic CH_2; 7.25/*m*, arom. H. MS.: 230 (M^+), 173, 146, 91 (base peak).

$C_{16}H_{22}O$ Calc. C 83.43 H 9.63% Found C 83.45 H 9.46%

2,4-Dinitrophenylhydrazone: m.p. 154–155°.

$C_{22}H_{26}N_4O_4$ Calc. C 64.37 H 6.39 N 13.65% Found C 64.32 H 6.34 N 13.72%

4. *2-(5-*t*-Butyl-2-oxo-cyclopentan-1-yl)-3-*t*-butyl-cyclopentanone* (**7e**). IR. (CCl_4): 1732. MS.: 279 (M^+ ($C_{18}H_{30}O_2$) + 1), 263, 221, 139 (base peak), 57, 41.

For the composition of the product mixture see Table.

(±)-5,8,8-Trimethyl-bicyclo[3.2.1]oct-3-en-2-one (**2a**). A 0.10 M solution of **2a** ([21]; UV. (toluene): 330 (31), 344 (34), 357 (26), ca. 375 (shoulder, 9). NMR. ($CDCl_3$): 0.93 (6 H) + 1.15 (3 H)/2 *s*, 1-CH_3 and 8,8-$(CH_3)_2$; 5.92/*dd*, $J_{2,3} = 9.5$, $J_{3,5} = 1.5$, CH-3; 6.79/*d*, $J_{2,3} = 9.5$, CH-2) in toluene was irradiated for 24 h with a 125 W lamp at > 3400 Å (80% conversion of **2a**). After evaporation of the solvent *in vacuo*, the following products were isolated by VPC (SF-96, 215°):

1. *Bibenzyl.*

2. *(±)-5,8,8-Trimethyl-bicyclo[3.2.1]octan-2-one* (**8**) [21] [22]. NMR. ($CDCl_3$): 0.87 + 0.97/3 *s*, 1-CH_3 and 8,8-$(CH_3)_2$. MS.: 166 (M^+, $C_{11}H_{18}O$). Identified by comparison with a sample obtained on hydrogenation of **2a** on Pd/charcoal in C_2H_5OH (mixed m.p., IR., NMR., MS.) and by mixed m.p. of their 2,4-dinitrophenylhydrazones.

3. *(±)-5,8,8-Trimethyl-3ξ-benzyl-bicyclo[3.2.1]octan-2-one* (**9**). IR. (CCl_4): 700, 1495, 1603, 1710. NMR. (CCl_4): 0.77 (3 H) + 0.93 (6 H)/2 *s*, 5-CH_3 and 8,8-$(CH_3)_2$; 1.3–2.7/*m* (9 H); 3.21/*dd*, $J = 13$ and 3.5, one benzylic H; ca. 7.1/*s* with fine splitting, arom. H. MS.: 256 (M^+, $C_{18}H_{24}O$), 91 (base peak). *2,4-Dinitrophenylhydrazone*: m.p. 172–173°.

$C_{24}H_{28}N_4O_4$ Calc. C 66.03 H 6.47 N 12.84% Found C 65.97 H 6.50 N 12.90%

4. *(±)-Bi-(5,8,8-trimethyl-bicyclo[3.2.1]octan-2-on-3-yl)* (**10**). IR. (CCl_4): 1702. MS.: 330 (M^+), 165 (base peak).

$C_{22}H_{34}O_2$ Calc. C 79.95 H 10.37% Found C 80.00 H 10.39%

For the composition of the product mixture see Table.

3-Methoxy-cyclopent-2-en-one (**1f**) *and (±)-5,8,8-Trimethyl-4-methoxy-bicyclo[3.2.1]oct-3-en-2-one* (**2b**) [21] [23]. 0.1 M solutions of **1b** and **1f**, and of **2a** and **2b**, respectively, were irradiated in toluene at > 3400 Å for periods twice as long as necessary to complete conversion of **1b** and **2a** to their photoproducts. Compounds **1f** and **2b** remained mostly unchanged under these conditions.

Structure of Products 3b, 4b, 6d,e, 7d,e, 9, and 10. – Baeyer-Villiger *Oxidation of Products* **3b**. 60 mg (0.3 mmol) of each dimer (**3b**, *HH*, *anti-HT*, and *syn-HT*[3])) were oxidised for 45 min. with 0.24 mmol of monoperphthalic acid in boiling anhydrous ether; after concentrating the solution *in vacuo*, the precipitate (phthalic anhydride) was filtered off. The filtrates contained, besides some of the respective starting material, the lactones **11** + **14**, **12** + **15**, and **13** + **16** (approximate ratio 5:1 in each case), respectively, which were isolated by preparative VPC. (SE-52 column at 240–280°):

*7,8-Dimethyl-*cis*,ξ,*cis*-tricyclo[6.3.0.0^{2,7}]-3-oxa-undecane-4,11-dione* (**11**), m.p. 164–167° ([4]: m.p. 114–162° for product assigned *syn-HH* conformation). IR. (nujol): 1730 (broad). NMR.

(C_5D_5N): 1.06 + 1.09/2 *s*, 7- and 8-CH_3; 1.83/*d*, $J_{1,2}$ = 6, CH-1[16]; 4.58/*d*, $J_{1,2}$ = 6, CH-2[16]. MS.: 208 (M^+, $C_{12}H_{16}O_3$), 112 (base peak), 97, 41.

1,7-Dimethyl-cis, anti, cis-*tricyclo[6.3.0.0^{2,7}]-3-oxa-undecane-4,9-dione* (**12**), m.p. 152–154° ([4]: m.p. 100–154°). IR. (nujol): 1730 (broad). NMR. (C_5D_5N): 1.02 + 1.17/2 *s*, 1- and 7-CH_3; 4.45/*s*, CH-2. MS.: 208 (M^+, $C_{12}H_{16}O_3$), 112, 97 (base peak), 41.

1,7-Dimethyl-cis, syn, cis-*tricyclo[6.3.0.0^{2,7}]-3-oxa-undecane-4,9-dione* (**13**), m.p. 85–88° ([4]: m.p. 65–92°). IR. (nujol): 1730 (broad). NMR. (C_6D_6): 0.87 + 0.95/2 *s*, 1- and 7-CH_3; 3.62/*d*, $J \sim 1.7$, CH-2[16]. MS.: 208 (M^+, $C_{12}H_{16}O_3$), 112, 97, 41 (base peak).

7,8-Dimethyl-cis, ξ, cis-*tricyclo[6.4.0.0^{2,7}]-3,12-dioxa-dodecane-4,11-dione* (**14**). MS.: 225 (M^+ ($C_{12}H_{16}O_4$) + 1), 113, 112 (base peak).

1,7-Dimethyl-cis-anti, cis-*tricyclo[6.4.0.0^{2,7}]-3,9-dioxa-dodecane-4,10-dione* (**15**). MS.: 225 (M^+ ($C_{12}H_{16}O_4$) + 1), 113 (base peak), 112.

1,7-Dimethyl-cis, syn, cis-*tricyclo[6.4.0.0^{2,7}]-3,9-dioxa-dodecane-4,10-dione* (**16**). MS.: (M^+ ($C_{12}H_{16}O_4$) + 1), 113 (base peak), 112.

6,7-Dimethyl-10-methoxy-cis, ξ, cis-*tricyclo[5.3.0.0^{2,6}]dec-9-en-3-one* (**17**). Gaseous HCl was passed through a solution of **3b** (*HH*[3]) in anhydrous ether for 5 min. The reaction proceeded exothermally to give **17** after the usual procedure for isolation. IR. (CCl_4): 1645, 1735. NMR. ($CDCl_3$): 1.24/*bs*, 6- and 7-CH_3; 3.62/*s*, 10-OCH_3; 4.44/*b*, CH-9. MS.: 206 (M^+, $C_{13}H_{18}O_2$).

Diastereomeric 2-(1-Methyl-3-oxo-cyclopentan-1-yl)-3-methyl-cyclopentanones **18**. 145 mg of **4b** were hydrogenated over 100 mg of 5% Pd/charcoal in 20 ml of C_2H_5OH. 16.0 ml of H_2 were absorbed (calc. 16.9 ml). After filtration through celite and concentration of the filtrate *in vacuo*, 71 mg of a ca. 1:1.4 mixture of *diastereomeric diketones* **18** were isolated by VPC. (SE-30 column, 220°). IR. (CCl_4): 1743. NMR. ($CDCl_3$): 1.00 + 1.18/2 *s*, CH_3; 1.10 + 1.20/2 *d*, *J* = 6, CH_3. MS.: 194 (M^+, $C_{12}H_{18}O_2$), 97, 41 (base peak).

Ozonisation of **4b**. 420 mg of **4b** were exhaustively ozonised at –70° in 10 ml of ethyl acetate. The further oxidative treatment involved addition of 2 ml of H_2O, 2 ml of CH_3COOH, and 10 drops of 30% H_2O_2 solution, and stirring overnight at room temperature. From an ether extract of the resultant mixture the *carboxylic acids* (**19** + **21**) were isolated with treatment with ice-cold 2% NaOH solution followed by acidification with conc. HCl. The crude mixture was esterified in ether with CH_2N_2 at 0° (215 mg esters). *Methyllevulinate* (**20**) (identified by comparison with an authentic sample using IR., MS., and VPC. co-injection on SE-30 and Apiezon-L columns) and *3-methyl-3-carbomethoxy-cyclopentanone* (**22**) [IR. (CCl_4): 1740, 1750. NMR. ($CDCl_3$): 1.40/*s*, 3-CH_3; 3.75/*s*, 3-$COOCH_3$. MS.: 156 (M^+, $C_8H_{12}O_3$)] were isolated by VPC. (SE-30, 130°)[8].

70 mg of **22** were deuteriated with 6 ml D_2O containing 250 mg NaOH for 2.5 h under N_2 in 4 ml boiling dioxan. The cooled solution was acidified with 0.7 ml conc. HCl and extracted with ether. After washing with aqueous satd. NaCl solution and drying over $MgSO_4$, the ether solution was treated with CH_2N_2. Isolation by VPC. (SE-30, 130°) gave 39 mg of *deuteriated* **22**. NMR. ($CDCl_3$): 1.40/*s*, 3-CH_3; 1.88 + 2.42/*AB* pattern, CH_2-4; 3.75/*s*, 3-$COOCH_3$. MS.: 93% d_4, 7% d_3.

Base-catalysed Hydrogen/Deuterium Exchange of **3d**, **6d**, **6e**, **7d**, **7e**, **9**, *and* **10**. 19 mg of **6d** were deuteriated with 1 ml D_2O containing 50 mg NaOH for 2 h under N_2 in 1.5 ml boiling dioxane. After isolation using D_2O, pure *deuteriated* **6d** was obtained by VPC. (NPGS column). NMR. ($CDCl_3$): 0.82 + 0.94/2 *d*, *J* = 6.5, $CH(CH_3)_2$; 2.93/*bs*, benzylic CH_2; 7.25/*m*, arom. H. MS.: 65% d_3, 26% d_2, 7% d_1, 2% d_0.

Compounds **6e**, **7d**, **e**, **9**, **10**, and the mixture of the two dimers **3d** were deuteriated as described above for **6d**. *Mixture of the two deuteriated dimers* **3d**: 35% d_6, 31.5% d_5, 24.5% d_4, 9% d_3. *Deuteriated* **6e**: 78% d_3, 20% d_2, 2% d_1. NMR. ($CDCl_3$): 0.89/*s*, $C(CH_3)_3$; 2.81 + 3.05/*AB* pattern, *J* = 14, benzylic CH_2; 7.22/*m*, arom. H. *Deuteriated* **7d**: $M^+/2$ = 60.5% d_3, 31% d_2, 8.5% d_1. *Deuteriated* **7e**: $M^+/2$ = 51% d_3, 38.5% d_2, 10.5% d_1. *Deuteriated* **9**: 88% d_1, 12% d_0. *Deuteriated* **10**: 74% d_2, 23% d_1, 3% d_0.

Ethylene Ketals of **6d** *and* **6e**. 12 mg of **6d**, 25 mg of ethylene glycol, and a catalytic amount of *p*-toluene sulfonic acid were dissolved in 20 ml of benzene and kept at boiling temperature in a water separator for 3 days. After working up, a pure sample of *2-benzyl-3-isopropyl-cyclopentanone*

---

[16] Spin coupling confirmed by double-resonance experiments.

ethylene ketal (**23**, *R* = *CH*$(CH_3)_2$) was isolated by VPC. (SE-30, 140°). IR. (CCl_4): 700, 1602. MS.: 260 (M^+, $C_{17}H_{24}O_2$), 99 (base peak).

*2-Benzyl-3-*t*-butyl-cyclopentanone ethylene ketal* (**23**, *R* = *C*$(CH_3)_3$) was prepared from **6e** as described above. IR. (CCl_4): 703, 1602. MS.: 274 (M^+, $C_{18}H_{26}O_2$), 99 (base peak).

Synthesis of **9** *from* **8**. 400 mg of **8** and 8 ml of freshly distilled benzaldehyde were dissolved in 80 ml of ethanolic 1 N KOH solution and stirred for 3 days at room temperature. After working up, the excess benzaldehyde was distilled off at 12 Torr and the residue was chromatographed with benzene-ethyl acetate 15:1. 510 mg of *3-benzylidene-5,8,8-trimethyl-bicyclo[3.2.1]octan-2-one* (**24**) were obtained; m.p. 122° after sublimation at 0.03 Torr. UV. (C_2H_5OH): 294 (17,800). IR. (CCl_4): 695, 1600, 1692. NMR. ($CDCl_3$): 1.02+1.07+1.11/3 *s*, 3 CH_3; ca. 7.4/*b*, 6 H. MS.: 254 (M^+), 116 (base peak). $C_{18}H_{22}O$ Calc. C 84.99 H 8.72% Found C 84.96 H 8.55%

Hydrogenation of **24** over Pd-charcoal catalyst in C_2H_5OH solution gave quantitatively **9** (identification by comparison with the photoproduct using VPC.) which was converted into the 2,4-dinitrophenylhydrazone, m.p. 172–173° (no m.p. depression upon admixture of the corresponding derivative of the photoproduct).

Dimer Formation from 1b and 1d Dependence on Solvent and Concentration. – 0.5 ml solutions of 10 mg of **1b** in toluene, hexane, benzene, ethanol, methylene chloride, and acetonitrile, respectively, were flushed with N_2 and simultaneously irradiated through Pyrex. Dimer analysis was effected by VPC. on a SE-30 glass column at 220°. The ratio **3b** (*anti-HT*): **3b** (*syn-HT*)[3]) = ca. 3:1 was approximately the same in all solvents. The formation of **3b** (*HH*) was favoured in ethanol, methylene chloride, and acetonitrile relative to the hydrocarbon solvents, whereas relatively much **4b** was formed in the hydrocarbon solvents, little in ethanol and methylene chloride, and only a negligible amount in acetonitrile.

VPC. analysis of 0.5 ml solutions of 2.5, 5, 10, 20, and 40 mg of **1b**, respectively, in toluene, and of neat **1b**, which had been irradiated as above, showed that the formation of dimers **3b** (*HH*, *anti-HT*, and *syn-HT*[3])) increased at the expense of **4b** with increasing enone concentration. The formation of **4b** in neat **1b** was negligible.

VPC. analysis (Apiezon-L column, 285°) of 0.5 ml solutions of 10 mg of **1d** in hexane, benzene, ethanol, and acetonitrile, respectively, which had been irradiated as above, showed that the ratio of the two dimers **3d** changed with change in solvent polarity.

Irradiation of Dimers 3b and 4b. – 2 ml solutions of 30 mg each of **3b** (*HH*), **3b** (*anti-HT*), **3b** (*syn-HT*)[3]), and **4b** in toluene were flushed with N_2 and irradiated through Pyrex. Periodical VPC. analysis (SE-30 column, 190°) showed that **3b** (*HH*) fragmented almost exclusively to the monomer **1b** (accompanied by formation of all four dimers and small amounts of polymers at increasing conversion). **3b** (*anti-HT*), **3b** (*syn-HT*), and **4b** gave small amounts of **1b**, a dimer [MS.: 192 (M^+, $C_{12}H_{16}O_2$)] which was highly unstable and not further investigated, and polymers.

Triplet Quenching Experiments. – Four series of Pyrex tubes (14 mm inner diameter) with toluene solutions of tetradecane (internal reference for VPC.), enones **1b**, **1c**, **1d**, and **1e**, and various concentrations of naphthalene (for enone and naphthalene concentrations, further experimental details, and results see Figs. 1–4) were degassed in two freeze-thaw cycles at 10^{-5} Torr and irradiated in a turn-table reactor equipped with magnetic stirring. SE-30 glass columns at 205° (**b**-series), 220° (**c**-series), and 230° (**d**- and **e**-series) served for the quantitative analysis of the products by VPC.

The elemental analyses were carried out by Mr. *W. Manser* of the Microanalytical Laboratory of ETH Zürich. We should like to thank PD Dr. *J. Seibl* for measuring the mass spectra and for helpful comments.

BIBLIOGRAPHY

[1] Part 63: *H. Küntzel, H. Wolf & K. Schaffner*, Helv. *54*, 868 (1971).

[2] *R. Reinfried*, Doctoral Dissertation, ETH Zürich 1971.

[3] a) *D. Belluš & K. Schaffner*, Chimia *23*, 182 (1969); b) *D. Belluš, D. R. Kearns & K. Schaffner*, Helv. *52*, 971 (1969).

[4] *G. Mark, H. Matthäus, F. Mark, J. Leitich, D. Henneberg, G. Schomburg, I. v. Wilucki & O. E. Polansky*, Monatsh. Chem. *102*, 37 (1971).

[5] *P.E.Eaton*, J. Amer. chem. Soc. *84*, 2344 (1962).

[6] *H.Ziffer & I.W.Levin*, J. org. Chemistry *34*, 4056 (1969).

[7] *T.N.Margulis*, Acta crystall. *18*, 742 (1965).

[8] *J.Křepinsky, Z.Samek, F.Šorm, D.Lamparsky, P.Ochsner & Y.-R.Naves*, Tetrahedron, Suppl. 8, *1966*, 53.

[9] ***H.**Ziffer, N.E.Sharpless & R.O.Kan*, Tetrahedron *22*, 3011 (1966).

[10] ***H.**Ziffer & B. W. Matthews*, Chem. Commun. *1970*, 294.

[11] *L.Ruzicka*, Ber. deutsch. chem. Ges. *50*, 1362 (1917); *J.D.Roberts, A.K.Jeydel & R.Armstrong*, J. Amer. chem. Soc. *71*, 3249 (1949).

[12] a) *P.E.Eaton*, Accounts chem. Res. *1*, 50 (1968), and references cited; b) *R.L.Cargill, A.C.Miller, D.M.Pond, P.deMayo, M.F.Tchir, K.R.Neuberger & J.Saltiel*, Mol. Photochemistry *1*, 301 (1969); c) *P.J.Wagner & D.J.Bucheck*, J. Amer. chem. Soc. *91*, 5090 (1969); d) *P.deMayo, A.A.Nicholson & M.F.Tchir*, Canad. J. Chemistry *48*, 225 (1970); e) *R.O.Loutfy & P.deMayo*, Chem. Commun. *1970*, 1040; f) *P.deMayo*, Accounts chem. Res. *4*, 41 (1971).

[13] *W.G.Dauben, G.W.Shaffer & N.D.Vietmeyer*, J. organ. Chemistry *33*, 4060 (1968).

[14] *G.Marsh, D.R.Kearns & K.Schaffner*, Helv. *51*, 1890 (1968); J. Amer. chem. Soc. *93*, 3129 (1971).

[15] *P.J.Wagner & R.A.Leavitt*, J. Amer. chem. Soc. *92*, 5806 (1970).

[16] *R.M.Acheson & R.Robinson*, J. chem. Soc. *1952*, 1127.

[17] *M.Korach, D.R.Nielson & W.H.Rideout*, Organ. Synth. *42*, 50 (1962); *C.H.DePuy & E.F. Zaweski*, J. Amer. chem. Soc. *81*, 4920 (1959); *J.H.Boothe, R.G.Wilkinson, S.Kushner & J.B.Williams, ibid. 75*, 1732 (1953).

[18] *M.F.Ansell & J.W.Ducker*, J. chem. Soc. *1959*, 329.

[19] *M.Pfau, R.Dulou & M.Vilkas*, C. r. hebd. Séances Acad. Sci. *254*, 1817 (1962).

[20] *H.N.A.Al-Jallo & E.S.Waight*, J. chem. Soc. (B) *1966*, 73.

[21] *H.Favre, B.Marinier & J.-C.Richer*, Canad. J. Chemistry *34*, 1329 (1956).

[22] *F.Salmon-Legagneur*, Bull. Soc. chim. France *51*, 807 (1932).

[23] *H.Rupe & C.Frey*, Helv. *27*, 627 (1944).

---

162. Réactions d'élimination présentées par des acides polyhydroxyadipiques

par **A. Gabbai** et **Th. Posternak**

Laboratoire de Chimie Biologique et Organique Spéciale de l'Université, Genève

(25 V 71)

Summary. The tetrahydroxyadipic acids and one trihydroxyadipic acid have been methylated, using methyl iodide and silver oxide in the presence of dimethylformamide.

In addition to Δ^2-di- or tri-methoxyadipic esters and the products expected for a double $E2$ elimination, *cis-trans* α,α'-dimethoxymuconic ester was frequently the principal product. The proposed theoretical interpretations involve as intermediates either a silver complex or a lactonic compound. A few preferential conformations, based on NMR. data, are proposed.

Dans un mémoire antérieur [1], nous avions établi par RMN. les configurations respectives des trois acides α,α'-diméthoxymuconiques Va, VIa et VIIa prévus par la théorie. Nous nous étions intéressés à ces substances en raison de la formation inattendue de l'une d'entre elles (l'isomère *cis-trans* VIb) à partir du D-glucosaccharate d'argent1) par méthylation d'après la méthode de *Purdie-Kuhn*, c'est-à-dire par

---

1) Plus récemment, nous avons constaté, dans les mêmes conditions, l'obtention exclusive de cet isomère *cis-trans* à partir des deux D-glucosaccharonalactones-1,4 et -6,3 (II et III).