174. Photochemical α-Cleavage of β, γ-Unsaturated Aryl Ketones: Competition Between Recombination/Disproportionation and Dissociation in Geminate Singlet and Triplet Radical Pairs[1])

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(7. V. 73)

Summary. The photolysis of (*R*)-(+)-phenyl and (*R*)-(+)-*p*-anisyl 1,2,3-trimethylcyclopent-2-enyl ketone (**1**, **2**) and the corresponding *rac*-1- and 3-desmethyl analogs (**3**, **4**) led to isomerization due to formal 1,3 aroyl migration and to formation of aryl aldehydes (**7**, **8**), dienes (**9**, **10**) and dimers (**5**, **6**) of the cyclopentenyl radical. Evidence obtained from a chiroptical and mass spectrometric analysis of a crossing experiment and from photolytic CIDNP measurements including the use of CCl_4 as a free radical scavenger, supports the conclusion (*1*): that the ketones undergo photochemical α-cleavage predominantly in the triplet state; (*2*): that recombination and disproportionation reactions within the geminate singlet and triplet aroyl/allyl radical pairs (**11**) compete with the dissociation into free radicals (**12**); (*3*): that ketone isomerization by paths not involving polarizable radical intermediates is unimportant; (*4*): that no triplet oxa-di-π-methane type rearrangement products are formed.

We have previously shown that cyclopent-2-enyl methyl ketones undergo 1,3 acetyl shifts and α-cleavage to radicals in the excited singlet state faster than intersystem crossing, and oxa-di-π-methane type rearrangements to 5-acetyl bicyclopentanes (*endo* > *exo*) in the triplet state [2][2]). Recent CIDNP investigations [4] revealed, furthermore, that radical recombinations are very minor paths for these reactions.

We now report (*1*): that the corresponding aryl ketones, *e.g.* (*R*)-(+)-**1**, undergo photochemical α-cleavage predominantly in the triplet state; (*2*): that recombination and disproportionation reactions within the geminate singlet and triplet aroyl/allyl radical pairs compete with the dissociation into free radicals; (*3*): that ketone isomerization by paths not involving polarizable radical intermediates is unimportant, and (*4*): that no triplet oxa-di-π-methane type rearrangement products are formed.

Irradiation of (*R*)-(+)-**1** and (*R*)-(+)-**2**[3]) led to racemization, (+)-**1** $\rightleftarrows$ (−)-**1** and (+)-**2** $\rightleftarrows$ (−)-**2**, respectively, and to the formation of trimethylcyclopentenyl dimers (**5**) and aryl aldehydes (**7**, **8**) in each case. No aroyl bicyclopentanes could be detected

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[1]) Part of these results were presented at the IVth International IUPAC Conference on Photochemistry, Baden-Baden, July 1972 [1].

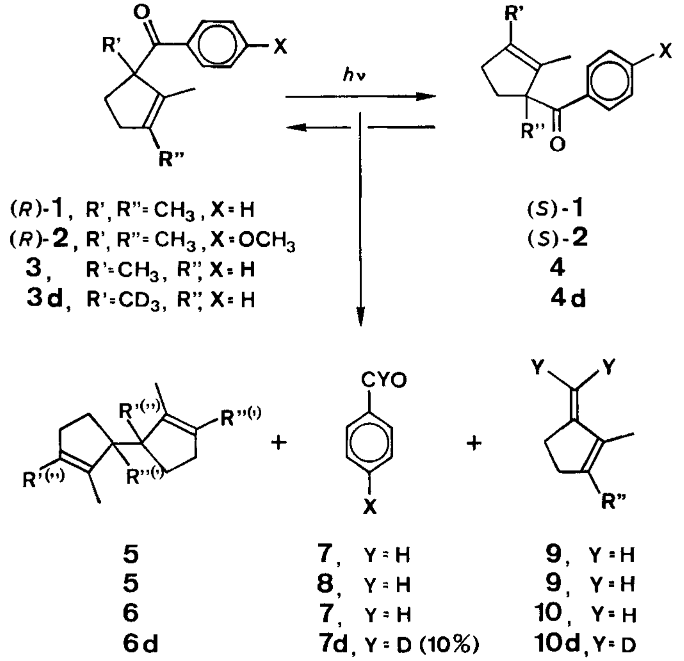
[2]) Such divergent behavior of excited singlets and triplets is often observed with β,γ-unsaturated ketones; see [3] for references.

[3]) Irradiations were carried out in *iso*-octane, benzene, or acetone at wavelengths 254 nm and > 340 nm.

by direct NMR. spectroscopy of the photolyzed solutions. Similar results were obtained with *rac*-**3**.

The two aryl ketone fractions recovered after the photolysis of a mixture of (+)-**2** and *rac*-**1d** (0.1M each) in acetone at > 340 nm, contained in part new components constitutionally corresponding to **1** and **2d**, respectively. This result indicates cross-recombinations and hence random encounters of aroyl and cyclopentenyl free radicals. A quantitative analysis (Fig. 1 and 2) revealed that the photolytically formed phenyl ketones arise *ca.* 60 ± 5% from random free-radical recombination and *ca.* 40 ± 5% from unimolecular isomerization. The corresponding data for the *p*-anisyl ketones are *ca.* 85 ± 5% from free-radical and *ca.* 15 ± 5% from unimolecular processes[4]).

Scheme 1



Complementary data came forth in the photolytic CIDNP study of some of these ketones. Irradiation of **1**–**4** in benzene (0.1–0.2M) gave strong effects attributable to products as summarized in Table 1.

An enhanced absorption at *ca.* δ 4.8 (photolyses of **1**–**4**) and an emission at δ 5.3 (photolyses of **3** and **4**) were assigned to the olefinic protons of **9** and **10** (see Fig. 3). Compounds **9** and **10** have not yet been isolated but their formation together with the aldehydes **7** and **8** may be expected in the radical disproportionation reaction. Irradiation of **3d** confirmed this assignment. The CIDNP absorption at δ 4.8 did not

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[4]) The rates of the photolytic transformations of the phenyl and the *p*-anisyl ketones, (+)-**1** and (+)-**2**, are sufficiently similar to render this mixed experiment meaningful; see Fig. 6 (Exp. Part).

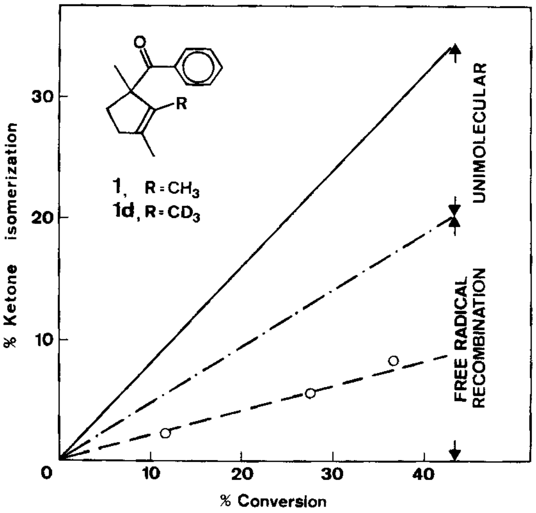


Fig. 1. *Ratio of free radical recombination to* rac-**1**+rac-**1d** vs. *unimolecular isomerization of* **1d** *on photolysis of the mixture* (R)-(+)-**2**+rac-**1d** (*0.1* M *each*) *at wavelengths* >*340 nm in acetone*

Percentage cross-recombination to **1** (- - -) was measured by mass spectrometry and extrapolated to percentage total free radical recombination (–·–) using a correction factor for **1d** (rec)/**1** equal to the mass-spectrometrically determined ratio $(M^+/2)\text{-d}_3/(M^+/2)\text{-d}_0 = 57/43$ in **5**. (——) is the percentage total racemization of (*R*)-(+)-**1**, 100 (1-[α]/[α]**2**), measured in a separate photolysis (see Fig. 6). The percentage photochemical conversion of **1** and **1d** to other products, 100 (1-[**1**+**1d**]/[(**1d**)$_0$]), was determined by gas chromatography.

Table 1. *CIDNP Effects in the Photolyses of Ketones* **1**, **2**, **3**, *and* **4**[a])

Polarization[b])	Chemical shift, δ[c])	Assignment	
A	1.30 *s*	**1, 2**	1-CH_3
A	1.40 *s*		3-CH_3
A	1.46 *m*		—CH_2—
A	2.30 *m*		—CH_2—
A	1.30 *s*	**3**	1-CH_3
E	1.46 *m*		2-CH_3
A	1.60 *m*		—CH_2—
A	2.25 *m*		—CH_2—
E	5.20 *m*		3-H
A	1.50 *s*	**4**	3-CH_3
A	1.90 *m*		two —CH_2—
E	4.10 *t*		1-H
E	1.46 *m*	**3d**	2-CH_3
A	9.41 *s*	**7, 8**	—CHO
A	4.80 *m*	**9**	=CH_2
A	4.76 *m*	**10**	=CH_2
E	5.30 *m*		=CH—

[a]) 0.1 M Solutions in benzene.

[b]) A = enhanced absorption, E = emission.

[c]) *s* = singlet, *t* = triplet, *m* = multiplet.

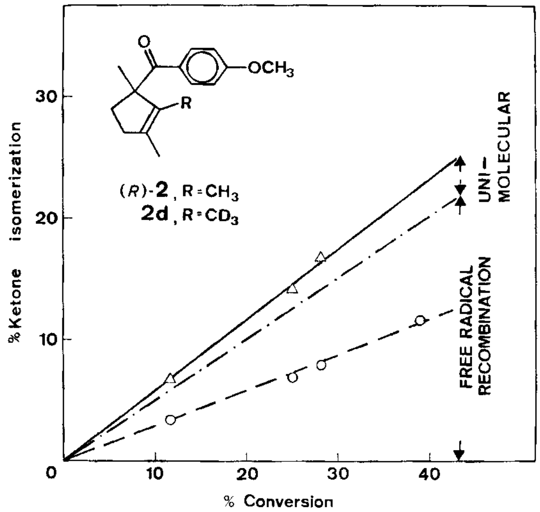


Fig. 2. *Ratio of free radical recombination to* rac-**2**+rac-**2d** vs. *unimolecular isomerization of* **2** *on photolysis of the mixture* (R)-(+)-**2**+rac-**1d** (*0.1* M *each*) *at wavelengths >340 nm in acetone.*

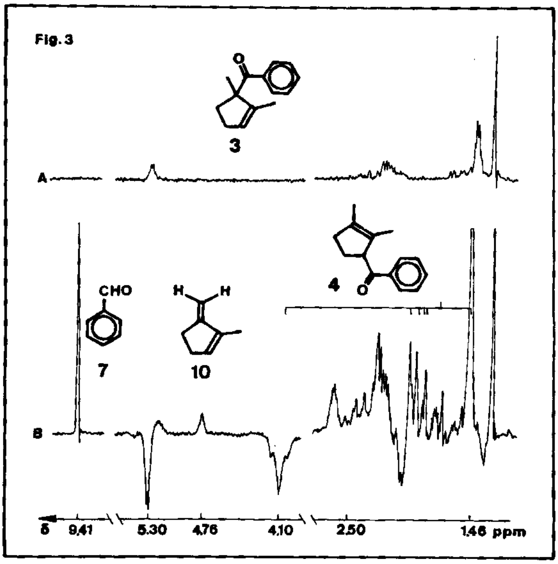
Percentage cross-recombination to **2d** (- - -) was measured by mass spectrometry and extrapolated to percentage total free radical recombination (–.–) using a correction factor for **2** (rec)/**2d** equal to the mass-spectrometrically determined ratio $(M^+/2)\text{-d}_0/(M^+/2)\text{-d}_3 = 43/57$ in **5**. The change in specific rotation of ketone **2** gave the percentage total racemization of **2**, 100 (1-[α]/[α] **2**), (——). The percentage photochemical conversion of **2** and **2d** to other products, 100 (1-[**2**+**2d**]/[$\mathbf{2}_0$]), was measured by gas chromatography.

show in this experiment, whereas the emission at δ 5.3 appeared again (see Fig. 4). Moreover, the benzaldehyde contained *ca.* 10% aldehydic deuterium by mass spectrometry. Additional CIDNP effects were provisionally attributable to the cyclopentenyl dimers **5** and **6** and cyclopentadiene analogs of **9** and **10**.

Carbon tetrachloride was used to study its radical scavenging effect in the photolyses of **1** and **2**. After an initial increase in ketone decay rates and decrease in CIDNP intensities with increasing CCl_4 concentrations, stationary values were approached at >1 M CCl_4, with a *ca.* twofold decay rate and 48 ± 10% and 68 ± 10% decrease in CIDNP of **1** and **2**, respectively.

The observed CIDNP effects are consistent, *a priori*, with free radical reencounters (*cf.* **12**, Scheme 2) affording reconstituted aryl ketones (**1**–**4**) and cyclopentenyl dimers (**5**, **6**) by recombination, and aldehydes (**7**, **8**) and dienes (*e.g.*, **9**, **10**) by disproportionation, and/or with reactions within a geminate pair of aroyl and cyclopentenyl radicals (**11**) of predominantly triplet origin yielding **1**–**4**, **7**/**8** and **9**/**10**. The partial persistence of the CIDNP intensities in the photolyses of **1** and **2** at >1 M CCl_4 shows that in fact both modes are operating.

The observed enhancement factors for **3** (270 ± 50), **4** (250 ± 50), and **9**/**10** (225 ± 75), are similar and of the same magnitude as those observed for typical photolytic free radical reactions of aliphatic ketones [5]. This shows that any contribution to the ketone isomerization by paths not involving polarizable radical



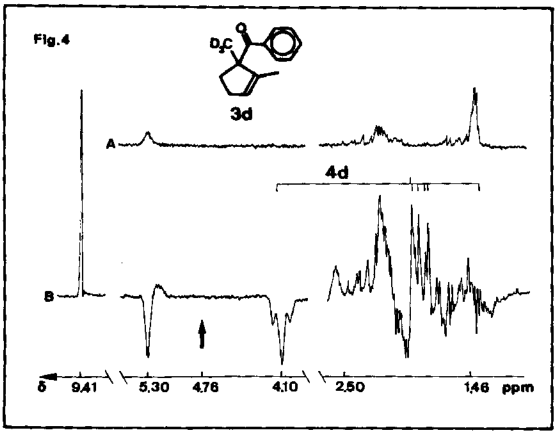


Fig. 3 and 4. *CIDNP study of the photolyses of* **3** *and* **3d**, *respectively, in benzene*
NMR. spectra prior to (A) and during (B) the photolyses.

intermediates (**11**, **12**)[5]) is of minor importance. If neglected, the percentage fractions of CIDNP intensity which are scavenged and unaffected by CCl_4, respectively, are thus correlated to the percentage fractions of free radical and unimolecular ketone isomerizations emanating from the crossing experiments (Fig. 1 and 2).

Assuming diffusion control for radical scavenging by CCl_4, no influence of CCl_4 on the primary pair-formation steps, and applying formulas for CIDNP derived by *Kaptein* [6] (p = $^1/_2$), the combination of the data gives the following percentages of

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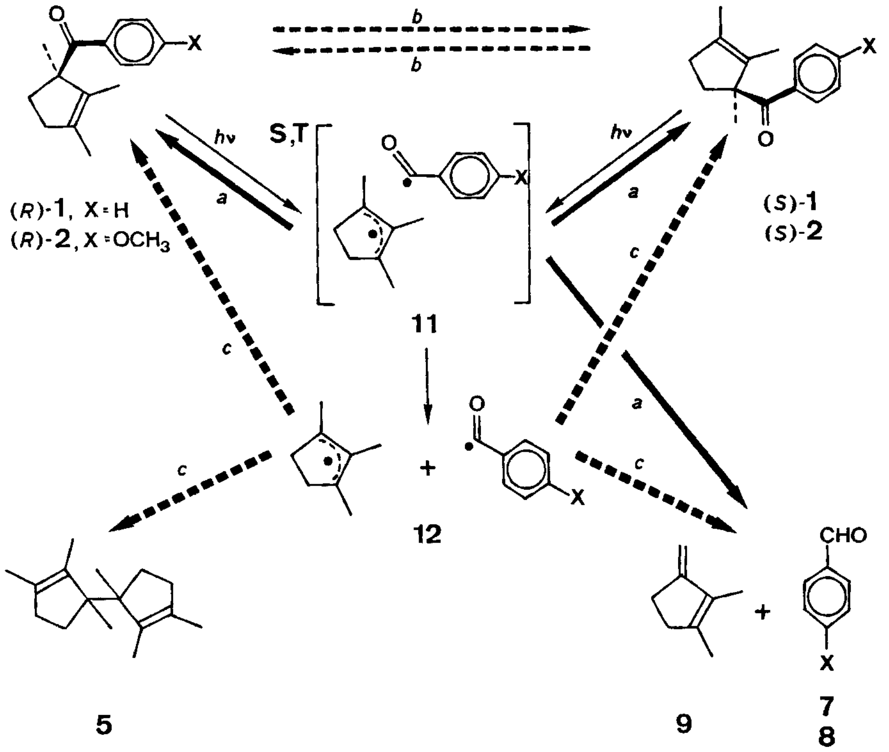
[5]) *E.g.*, a sigmatropic 1,3 aroyl shift or rearrangement *via* a bridged diradical intermediate, originating from the excited singlet state.

Scheme 2



a = Geminate radical pair reactions, b = reaction paths bypassing polarizable radical intermediates, c = free radical reactions.

pair formation from singlet and triplet ketones[6]: 29% and 71% for **1**, and 33% and 67% for **2**, respectively. Addition of naphthalene in photolyses of **1–3** showed relatively small triplet quenching effects. *E.g.*, at up to 2M naphthalene linear *Stern-Volmer* plots were obtained for **3**/**4**, **6** and **7**, with slopes no greater than 0.3–0.7 l · mol^{-1} (Fig. 5). These results do not suffice to rule out or support the above estimate of singlet pair reactions.

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[6] The lowest-lying triplet states of the aryl ketones **1–3** are characterized by the phosphorescence data summarized below:

Ketone[a]	E_T [kcal/mol][b]	τ [ms]
1	74	5.5
2	70	105
3	72	6

[a] Phosphorescence measured in ether/isopentane/ethanol 5:5:2 glass at 77 K; excitation at 340 nm.

[b] Approximate 0–0 transition.

In conclusion, we suggest that the photochemistry of ketones such as **1** and **2** involves the reaction paths summarized in Scheme 2. Paths a (major) and b (minor) together amount to 40 ± 5% (**1**) and 15 ± 5% (**2**) of the total reaction.

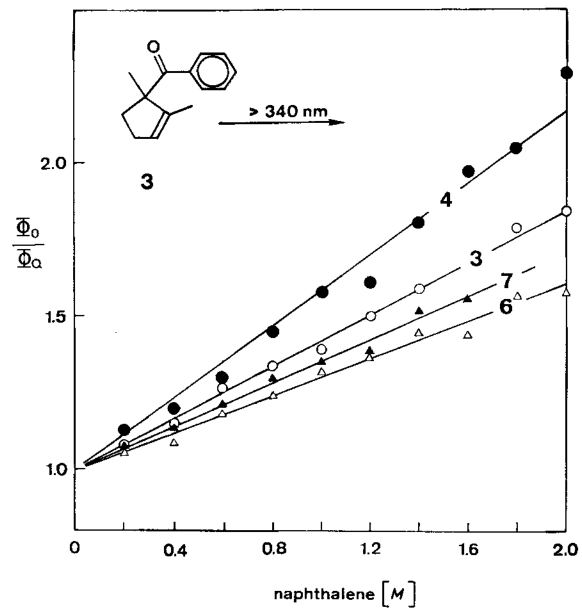


Fig. 5. *Photolysis of 0.2*M rac-**3** *in acetone at* >*340 nm*: *Stern-Volmer* plot of the quenching by naphthalene of the conversion of **3** and of the formation of **4**, **6**, and **7**.

We are grateful to the *Schweiz. Nationalfonds zur Förderung der wissenschaftlichen Forschung, Ciba-Geigy AG.*, Basel, and *Firmenich & Cie.*, Genève, for support of this research.

Experimental Part

General Remarks. Unless specified otherwise, the crude reaction mixtures were *worked up* in CH_2Cl_2 solutions which were washed neutral with satd. aqueous NaCl solution and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* in a rotatory evaporator. – *Vapor phase chromatography* (VPC.): 70–150 ml/min Helium was used as a carrier gas in packed stainless steel or glass columns: 300 × 0.6 cm or 300 × 0.9 cm; packings: 10–15% SE-30 on untreated Chromosorb W (SE-30), 15% Carbowax 20M on Chromosorb P AW-DMCS (CW) [7]; mesh: 60/80, 80/100, 100/120; flame ionization or hot wire detectors. The peaks were electronically integrated with automatic base line correction. – *UV.-Spectra*: wavelenghts of absorption maxima in nm, ε values in parentheses. – *IR-Spectra*: band positions in cm^{-1}; s = strong, m = medium, w = weak. – *NMR.-Spectra*: in CCl_4 unless specified otherwise; chemical shifts in δ, with internal $(CH_3)_4Si$ as a reference, and coupling constants (J) in Hz; s = singlet, d = doublet, t = triplet, q = quadruplet, m = other than first-order multiplet. *Mass Spectra*: base peak in italics.

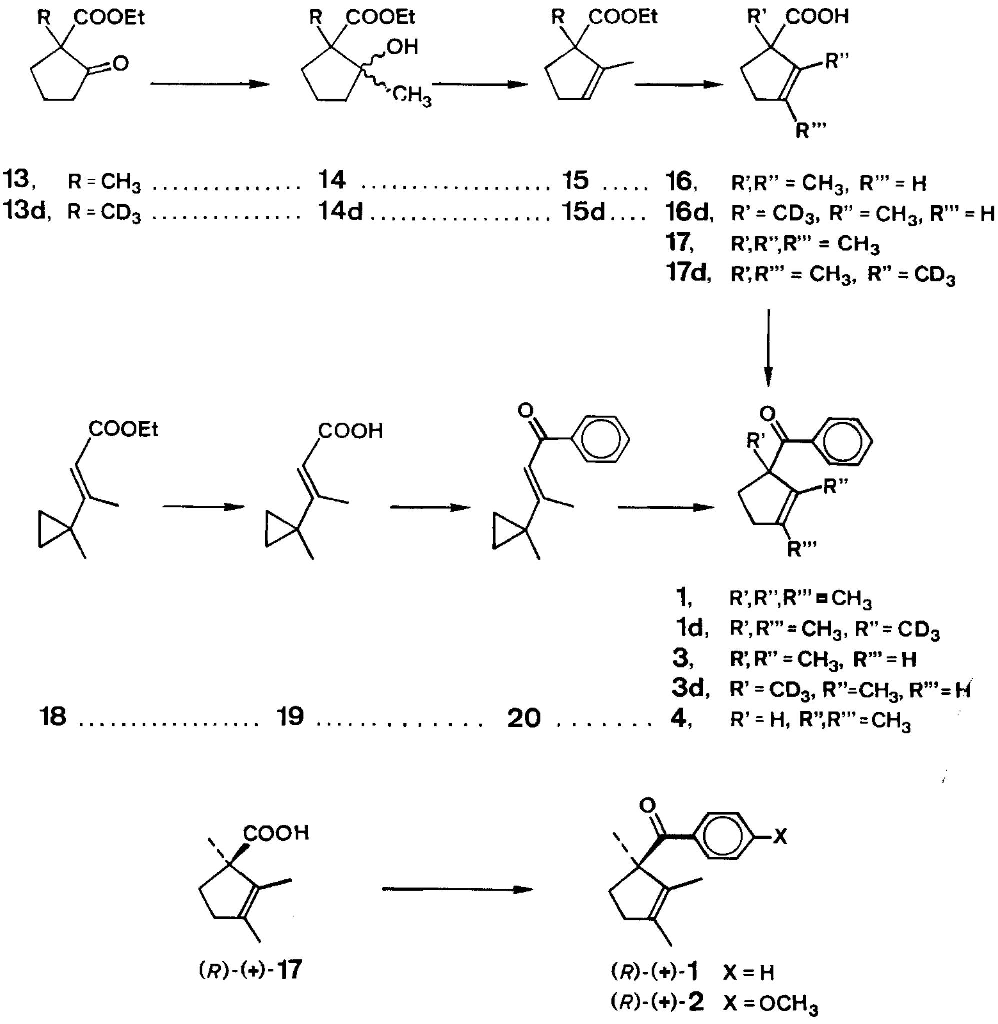
Syntheses of the Aroyl Ketones 1–4. – *Ethyl* rac-*1,2-dimethylcyclopentan-2-ol-1-carboxylate* (**14**). 1,1 equivalents of *ca.* 2M ethereal solutions of either CH_3Li or CH_3MgJ (filtered and titrated) were rapidly dropped to a solution of **13** [8] in ether. The initially boiling reaction mixture was stirred overnight at room temperature. The work-up gave mixtures containing up to 90% of predominantly one diastereomeric form of **14** besides starting material (VPC.: SE-30/180°).

A sample of **14** was isolated by VPC. IR. (film): 1720^{s}, 3500^{m} (broad). NMR.: 1.18/*s*, H_3—C(2); 1.22/*s*, H_3—C(1); 1.26/*t*+4.10/*q*, *J* = 7, H_5—C_2(O); 1.5–2.3/*m*, H_2—C(3,4,5).

Ethyl rac-*1-trideuteriomethyl-2-methylcyclopentan-2-ol-1-carboxylate* (**14d**). The above procedure was also applied to **13d** [8]. IR. (CCl_4): 1720^{s}, 2220^{m}, $2500–3620^{m}$. NMR.: 1.18/*s*, H_3—C(2); 1.26/*t*+4.10/*q*, *J* = 7, H_5—C_2(O); 1.5–2.3/*m*, H_2—C(3,4,5).

The *dehydrations of* **14** *and* **14d** were carried out with J_2 [9], using the crude products containing *ca.* 10% of the corresponding starting keto esters. Samples of the olefinic products were isolated by VPC. (SE-30/160°):

Scheme 3



Ethyl rac-*1,2-dimethylcyclopent-2-ene-1-carboxylate* (**15**). IR. (film): 1730^{s}. NMR.: 1.23/*s*, H_3—C(1); 1.23/*t*+4.25/*q*, *J* = 7, H_5—C_2(O); 1.65/*m*, H_3—C(2); 2.4/*m*, H_2—C(4,5); 5.42/*m*, H—C(3).

Ethyl rac-*1-trideuteriomethyl-2-methylcyclopent-2-ene-1-carboxylate* (**15d**). IR. (film): 1720^{s}, 2220^{w}. NMR.: 1.23/*t*+4.25/*q*, *J* = 7, H_5—C_2(O); 1.65/*m*, H_3—C(2); 2.4/*m*, H_2—C(4,5); 5.42/*m*, H—C(3). MS.: 98 ± 1% d_3.

The *hydrolyses of* **15**, **15d**, *and* **18** [10] were carried out in boiling CH_3OH/H_2O 1:1 solutions of 20% KOH under N_2. Extraction of the alkaline reaction mixture with CH_2Cl_2 removed the cyclopentanones formed from the β-keto esters which accompanied the ethyl cyclopentenecarboxylate samples. After the acidification of the aqueous layer with 10% H_2SO_4 and the work-up the resulting acids were either distilled or recrystallized:

rac-*1,2-Dimethylcyclopent-2-ene-1-carboxylic acid* (**16**), yield 60% (from **13**). B.p. 70°/0.07 Torr. IR. ($CHCl_3$): 1690^{s} (broad), $2400–3400^{s}$ (broad), 3500^{w}. NMR.: 1.31/*s*, H_3—C(1); 1.65/broad *s*, H_3—C(2), 1.4–2.8/*m*, H_2—C(4,5); 5.5/broad *s*, H—C(3). MS.: 140 (M^+, $C_8H_{12}O_2$), *95*.

rac-*1-Trideuteriomethyl-2-methylcyclopent-2-ene-1-carboxylic acid* (**16d**), yield 59% (from **13d**). IR. ($CHCl_3$): 1690^{s} (broad), 2230^{m}, $2400–3400^{s}$ (broad), 3500^{w}. NMR.: 1.65/broad *s*, H_3—C(2); 1.4–2.8/*m*, H_2—C(4,5); 5.5/broad *s*, H—C(3).

E-*3-(1′-Methylcyclopropyl)-3-methylacrylic acid* (**19**), yield >95% (from **18**). M.p. 88–89° (cryst. from hexane and sublimed at *ca.* 60°). IR. ($CHCl_3$): 1620^{s}, 1640^{s}, 1685^{s}, $2400–3400^{s}$ (broad), 3520^{w}. NMR.: 0.5–0.9/*m*, H_2—C (cyclopropyl); 1.25/*s*, H_3—C(cyclopropyl); 2.08/*d*, $J = 1.5$, H_3—C(3); 5.73/*q*, $J = 1.5$, H—C(2). MS.: 140 (M^+, $C_8H_{12}O_2$), 125, *112*.

The *syntheses of* **1**, **1d**, **3**, **3d**, **4** *and* **20** *from* **16**, **16d**, (R)-(+)-**17** (*laurolenic acid*) [9] [11], rac-**17** [12], rac-**17d** [11], *and* **19** were effected with 2.2 equivalents of *ca.* 2M phenyl lithium (benzene/ether 7:3) and *p*-anisyl lithium solutions (diglyme) [13]. The reaction mixtures were stirred overnight at room temperature, then refluxed for several hours and poured onto aqueous satd. NH_4Cl solutions prior to the work-up. The crude products were chromatographed with benzene on 50–100fold weights of silica gel *Merck* (0.05–0.2 mm) and subsequently distilled:

(R)-(+)-*1,2,3-Trimethylcyclopent-2-enyl phenyl ketone* (**1**)[7], yield 79% (from (*R*)-(+)-**17**)[8]. B.p. *ca.* 100°/0.5 Torr. $n_D^{23} = 1.5383$. $[\alpha]_D^{25} = +395°$ ($c = 2.6$, $CHCl_3$). UV. (*iso*-octane): 237 (10000), 271 (835), 329 (120); (C_2H_5OH): 244 (9700), 265 (1500), 326 (166). IR. (film): 693^{s}, 715^{s}, 970^{s}, 1580^{m}, 1600^{m}, 1675^{s}. NMR.: 1.25/*s*, H_3—C(1); 1.52/broad *s*, H_3—C(2); 1.74/broad *s*, H_3—C(3); 1.6–2.6/*m*, H_2—C(4,5); 7.2–7.5/*m*, H—C(*m*-, *p*-arom.); 7.7–7.9/*m*, H—C(*o*-arom.). MS.: 214 (M^+), *109*. Phosphorescence: see footnote 6.

$C_{15}H_{18}O$ Calc. C 84.67 H 8.47% Found C 84.07 H 8.54%

2,4-Dinitrophenylhydrazone of (+)-**1**: m.p. 154°.

$C_{21}H_{22}N_4O_4$ Calc. C 63.94 H 5.62% Found C 63.86 H 5.73%

rac-*1,2,3-Trimethylcyclopent-2-enyl phenyl ketone* (**1**), yield 80% (from *rac*-**17**). B.p. 78–80°/0.05 Torr. UV., IR., NMR., MS., and phosphorescence: see (*R*)-(+)-**1**.

rac-*1,3-Dimethyl-2-trideuteriomethylcyclopent-2-enyl phenyl ketone* (**1d**), yield 95% (from **17d**). NMR.: 1.25/*s*, H_3—C(1); 1.74/broad *s*, H_3—C(3); 1.6–2.6/*m*, H_2—C(4,5); 7.2–7.5/*m* H—C(*m*-, *p*-arom.); 7.7–7.9/*m*, H—C(*o*-arom.). MS.: 98.4 ± 1% d_3.

(R)-(+)-*1,2,3-Trimethylcyclopent-2-enyl* p-*anisyl ketone* (**2**)[7], yield 66% (from (*R*)-(+)-**17**)[8]. B.p. 75–80°/0.03 Torr. $n_D^{23} = 1.5469$. $[\alpha]_D^{23.5} = +259°$ ($c = 1.6$, $CHCl_3$). UV. (*iso*-octane): 265 (16300), 329 (141); (C_2H_5OH): 275 (13000), 323 (290). IR. ($CHCl_3$): 1575^{m}, 1600^{s}, 1660^{s}, 2830^{s}. NMR.: 1.30/*s*, H_3—C(1); 1.55/broad *s*, H_3—C(2); 1.72/broad *s*, H_3—C(2); 1.9–2.8/*m*, H_2—C(4,5); 3.87/*s*, H_3—C(O); *ca.* 6.8 + 8.0/*AA′BB′* pattern, H—C(arom.). MS: 244 (M^+), *109*. Phosphorescence: see footnote 6.

$C_{16}H_{20}O_2$ Calc. C 78.65 H 8.25% Found C 78.62 H 8.30%

2,4-Dinitrophenylhydrazone of (+)-**2**: m.p. 114–116°.

rac-*1,2-Dimethylcyclopent-2-enyl phenyl ketone* (**3**), yield 62% (from **16**). B.p. 72°/0.01 Torr. UV. (*iso*-octane): 238 (10500), 330 (124). IR. (film): 1675^{s}. NMR.: 1.30/*s*, H_3—C(1); 1.65/*m*, H_3—C(2); 1.6–2.7/*m*, H_2—C(4,5); 5.55/broad *s*, H—C(3); 7.4/*m*, H—C(*m*-, *p*-arom.); 7.95/*m*, H—C (*o*-arom.). MS.: 200 (M^+, $C_{14}H_{16}O$), *95*. Phosphorescence: see footnote 6.

rac-*1-Trideuteriomethyl-2-methylcyclopent-2-enyl phenyl ketone* (**3d**), yield 65% (from **16d**). IR. (CCl_4): 1680^{s}, 2230^{m}. NMR.: 1.65/*m*, H_3—C(2); 1.6–2.7/*m*, H_2—C(4,5); 5.55/broad *s*, H—C(3); 7.4/*m*, H—C (*m*, *p*-arom.); 7.95/*m*, H—C (*o*-arom.). MS.: 99 ± 1% d_3.

E-*2-(1′-Methylcyclopropyl)-prop-1-enyl phenyl ketone* (**20**). The work-up afforded in 88% yield (from **19**) a crude product which according to NMR. [0.5–1.0/*m*, H_2—C(cyclopropyl); 1.30/*s*,

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[7] Prepared by *P. Gianola*, Diploma Thesis, ETH Zürich (1970).

[8] The enantiomeric purity of the laurolenic acid (**17**) used was 96% (*cf.* [9]).

H_3—C (cyclopropyl); 2.1/weakly split *s*, H_3—C(3); 6.80/weakly split *s*, H—C(1); 7.1–7.6/*m*, H—C (*m*-, *p*-arom. of **20**+diphenyl); 7.8–8.1/*m*, H—C (*o*-arom.)] contained *ca.* 20% diphenyl and which was used without further purification.

rac-*2,3-Dimethylcyclopent-2-enyl phenyl ketone* (**4**). A 1% solution of **20** in benzene was dropped in a stream of N_2 onto a column filled with glass beads and heated to 350–380°. The vapors were condensed and recycled until full conversion of **20** was achieved (NMR. control). The crude product was chromatographed on the 50fold weight of silica gel *Merck* (0.05–0.2 mm) in benzene, affording **4** in 65% yield. UV. (*iso*-octane): 237 (12000), $n \rightarrow \pi^*$ band visible as shoulder only. IR. (CCl_4): 1685^s. NMR.: 1.60/broad *s*, H_3—C(2); 1.75/broad *s*, H_3—C(3); 1.5–2.6/*m*, H_2—C(4,5); 4.30/*m*, H—C(1); 7.5–7.7/*m*, H—C(*m*-, *p*-arom.); 7.9–8.2/*m*, H—C(*o*-arom.). MS.: 200 (M^+, $C_{14}H_{16}O$), *95*.

UV. Irradiations. – Light sources, at 254 nm: low-pressure Hg lamp Minerallight PCQXl (*Ultraviolet Products Inc.*); at > 340 nm: 250 W high-pressure Hg lamp (*Philips*) placed in a water-cooled Pyrex jacket equipped with a mantel for the filter solution (aqueous solution of 750 g NaBr and 8 g $Pb(NO_3)_2$/l). The sample solutions were irradiated in quartz and Pyrex tubes (1–2 ml) which were sealed with serum caps and placed in the centre of the circular low-pressure lamp assembly and close to the jacket with the high-pressure lamp, respectively.

Qualitative Photolyses. a) (*R*)-(+)-**1** was irradiated in 0.1–0.2 M solutions of *iso*-octane, acetone (both 254 and > 340 nm), and benzene (254 nm). In all cases VPC. (SE-30/200°, CW/230°) showed the formation of two products which were isolated by VPC.: (*1*) *Benzaldehyde* (**7**), identified by VPC., NMR., and MS. (*2*) *Bis-(1,2,3-trimethylcyclopent-2-enyl)* (**5**). NMR.: 1.00+1.03/two *s*, H_3—C(1); 1.6/broad *s*, H_3—C(2,3); 1.0–2.2/*m*, H_2—C(4,5). MS.: no M^+, 110, *109*, 108.

$C_{16}H_{26}$ Calc. C 88.00 H 12.00% Found C 87.96 H 11.97%

The optical activity of recovered starting material (**1**) was reduced to 60–80%. – VPC. retention times: **7** < **5** < **1**.

b) (*R*)-(+)-**2** gave the analogous results under the same irradiation conditions. p-*Methoxybenzaldehyde* (**8**) was identified by VPC. and NMR.-VPC. (SE-30/230°) retention times: **8** < **5** < **2**.

c) rac-**3** was irradiated in 0.1–0.2 M acetone solutions at 254 and > 340 nm. Product analysis and isolation by VPC. (SE-30/230°; retention times: **7** < **6** < **3** < **4**): (*1*) **7**. (*2*) Unseparable *mixture of bis-dimethylcyclopent-2-enyl isomers* (**6**). NMR.: 1.0–1.2/several *s*, H_3—C(1); 1.6/broad *s*, H_3—C(2,3); 1.0–3.0/*m*, H_2—C(4,5), H—C(1); 5.2/*m*, H—C(3). MS.: 190 (M^+, $C_{14}H_{22}$), 96, *95*, 94 (*3*) **4**, identified by VPC., IR., NMR., MS.

c) rac-**3d** was irradiated at > 340 nm in 0.2 M benzene and hexadeuteriobenzene solutions Isolation of the benzaldehyde by VPC. (SE-30/160°) and MS. comparison with **7** and **7d** showed that the product contained 10 ± 1% aldehydic deuterium in both runs.

Crossing Experiment. – a) *Photoracemization of* (R)-(+)-**1**. Eight samples of 0.2 M solutions of (*R*)-(+)-**1** in acetone were irradiated at > 340 nm in a turn-table reactor for varying time periods. The percentage product composition of each sample was determined by VPC. (SE-30/220°) and, after evaporation of the solvent and isolation by VPC., the optical rotation of the starting material (**1**) was measured at 436, 546, 578, and 589 nm. The data are plotted in Fig. 6 as a function of time.

b) *Determination of Unimolecular Isomerization and Free Radical Recombination.* Solutions of 0.1 M *rac*-**1d**+0.1 M (*R*)-(+)-**2** were photolyzed and analyzed as described above (a). For further details and results see captions of Fig. 1 and 2. The deuterium analyses by MS. were carried out with samples isolated by VPC. As the base peaks at *m/e* = 109 and 112 of the phenyl ketones and the cyclopentenyl dimers were accompanied by peaks of similar intensity at *m/e* = 108/110 and 111/113, respectively, owing to radical disproportionation, the signal intensities at *m/e* = 108–110 and 111–113 were integrated after correction for ^{13}C.

Triplet Quenching Experiments. a) Acetone solutions of 0.1–0.25 M (*R*)-(+)-**1** and (*R*)-(+)-**2** without and with 1 M naphthalene were photolyzed at > 340 nm in a 10-cm polarimeter tube. At several time intervals, the optical rotations were measured at 405, 436, 546, and 589 nm. Simultaneously, the concentrations of **1** and **2** were determined by VPC. (CW/250°; with *n*-nonadecane and *n*-heptadecane, respectively, as internal standards). The quenching effect on the conversion and photoracemization proved to be small in both series: *e.g.*, 74% optical rotation at 69% conversion of **1** *without*, and 86% optical rotation at 59% conversion *with* added naphthalene.

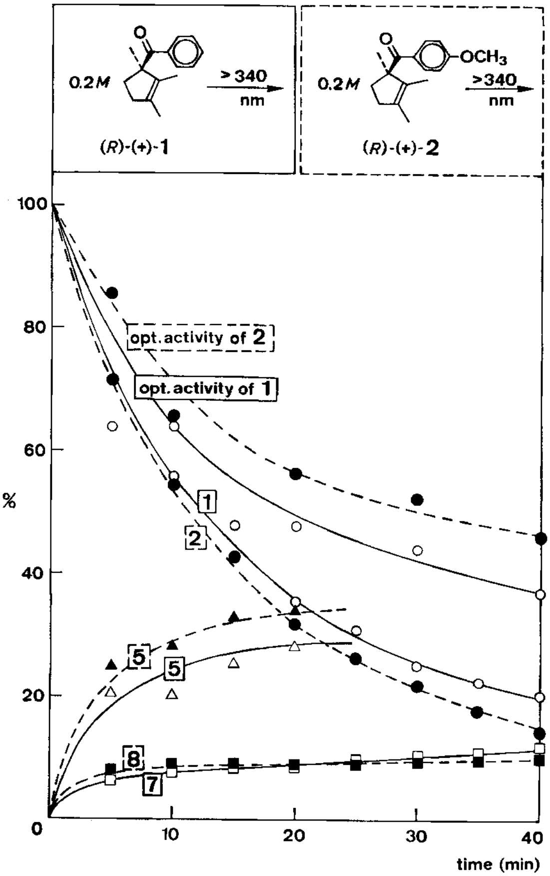

Fig. 6. *Photolysis of* (R)-(+)-**1** *and* (R)-(+)-**2**: Photoracemization and product formation

b) Stern-Volmer *Analysis of the Photolysis of* rac-**3**. Twelve samples of 0.2 M *rac*-**3** in acetone + 0–2 M naphthalene were irradiated in a turn-table reactor. The conversion of **3** and the formation of **4**, **6**, and **7** were determined by VPC. (SE-30/100–250°, programmed). For the results see Fig. 5.

CIDNP Experiments. 0.1–0.2 M samples solutions in benzene or hexadeuteriobenzene were photolyzed in quartz tubes in the probe of a *Varian* HA-100 NMR. spectrometer at 25 ± 3° with a *Philips* SP-1000 Hg-pressure lamp. Conversions of 5–35% were observed after irradiations of 60–120 s. Enhancement factors were calculated using the expression $V = (I - I_0)t/I_0 \cdot T$, with I = intensity at time t, T = estimated relaxation time (30 s for CHO, 10 s for CH_3).

For the results see the text, Fig. 3 and 4, and Table 1.

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175. Über den Einfluss nichtpolarer Lösungsmittel auf Lage und Intensität von Absorptionsbanden in den Elektronenspektren apolarer Molekeln: II. Polyacetylene

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(7. III. 73)

Summary. The dispersive interaction of nonpolar solutes with nonpolar solvents is investigated in model systems consisting of solutions of dimethyl-tetraacetylene, di-*t*-butyl-tetraacetylene, dimethyl-pentaacetylene or di-*t*-butyl-pentaacetylene in binary mixtures of cyclohexane/carbondisulfide or *n*-pentan/carbondisulfide. For this purpose the ${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ transition in the electronic spectrum of the solutions has been recorded. With increasing concentration of the more strongly interacting solvent component (*i.e.* carbondisulfide) bathochromic shifts $\delta\nu$ of the transition frequency accompanied by a decrease in oscillator strength f_M are observed, which are consistent with calculated values based on a previously proposed exciton model [1].

Einleitung. – In einer ersten Mitteilung [1] wurde anhand eines störungstheoretischen Modells gezeigt, wie man die im Elektronenspektrum gelöster Verbindungen beobachtete Bandenverschiebung und Intensitätsänderung, welche das Lösungsmittel erzeugt, berechnen kann. Die Methode beruht auf der Voraussetzung, dass die gelöste Verbindung und das Lösungsmittel unpolar sind. Das bedeutet, dass nur Dispersionskräfte für die Änderungen verantwortlich gemacht werden können. Von besonderer Bedeutung ist der von einer gelösten Molekel M im Lösungsmittel eingenommene Hohlraum, dessen Grösse und Form die Lösungsmitteleffekte in hohem Masse beeinflusst (s. [1], Tab. 4).

Das Ergebnis der Störungsrechnung lässt sich in zwei Formeln zusammenfassen, welche es erlauben, bei bekannter Absorptionsenergie E_M und integraler Bandenintensität f_M (Oszillatorstärke) die Energieverschiebung δE_M und die Intensitätsänderung δf_M zu berechnen, welche im Elektronenspektrum gelöster Molekeln gegenüber der Gasphase auftreten. In atomaren Einheiten gilt [1]:

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