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87. Photochemical Reactions

Part 63 [1]

The Photodecarbonylation of α-Aryl Aldehydes

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(16. II. 71)

Summary. Ultraviolet irradiation of the aldehydes **6**–**11** in degassed solutions results exclusively in decarbonylation to the major products **34**, **35** and **37**–**40**, and to small amounts of 2,3-diphenyl-2,3-dimethyl-butanes **36** from the phenyl aldehydes **6** and **7**. In the presence of tri-*n*-butyl-stannane, incorporation of stannane hydrogen competes, to substrate-specific limits, with the intramolecular deuterium transfer in **7** → **35** and **11** → **40**. The quantum yields for decarbonylation are $\Phi_{-CO}^{3130} \sim 0.4$–1.0 for the phenyl aldehydes **6** and **9**, and 0.02 for **8**. *Hammett* correlations of Φ_{-CO}^{3130} with resonance constants ($\bar{R}$) for **6** (X = H, *p*-CH_3, -OCH_3 and -CF_3) and with σ_m^+ values for the *meta*-substituted isomers are in agreement with the proposed α-cleavage to an associated radical pair with only moderate free radical character as the primary photochemical step.

Φ_{-CO}^{3130} for **10** (X = H) is 0.11, and for **10** (X = OCH_3) 0.065. It is noteworthy that decarbonylation of **10** (X = OCH_3) occurs also at 3340 Å ($\Phi_{-CO} = 0.11$) *i.e.*, upon excitation in an absorption band which is presumably lower in energy than the $n \rightarrow \pi^*$ transition and corresponds to the aromatic L_b transition of 2-methoxynaphthalene.

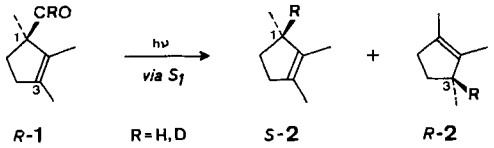
Singlet multiplicity of the reactive excited states is probable on the basis of the fact that the decarbonylation of **6** (X = H) and **10** (X = H and OCH_3) could be sensitised neither by acetone nor acetophenone, and could be quenched neither by naphthalene nor by *cis*-1,3-pentadiene and nor by 1,3-cyclohexadiene.

β,γ-Unsaturated homoconjugated aldehydes have been shown to undergo a predominantly unimolecular decarbonylation in deaerated solution [3] [4]. The preceding paper on this subject [3] dealt with the mechanistic investigation of aldehydes such as *R*-laurolenal (**1**; Chart 1). It presented evidence that the reaction occurs from the singlet-excited state and that in fact two products, in this specific case the

[1]) Taken in part from the Doctoral Dissertation of *H. Küntzel* [2].

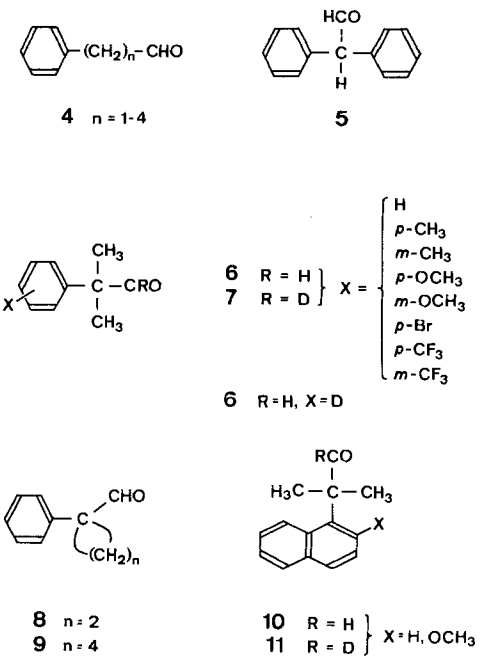
enantiomers *S*-**2** and *R*-**2** (in yields of ca. 88% and 12%, respectively), are formed. The quantum yield for **1** → **2** in hexane at 3130 Å is 0.61. The conclusion was drawn that, in a primary photochemical process, α-cleavage leads to intimately associated allyl-formyl radical-pair intermediates, from which carbon monoxide is eliminated with concurrent stereospecific transfer of the formyl hydrogen to the allyl radical component. The relative orientation of the partners in the incipient radical pairs, as preformed in the ground state conformers, determines the location of the transferred hydrogen in the olefinic products **2**. A concerted decay to the major product, *S*-**2**, as a competing singlet-excited state process, remains an additional mechanistic possibility.

Chart 1. *Representative Example of Earlier Results* [3]:
The Photodecarbonylation of R-(+)-*Laurolenal* (**1**)



This paper reports on work which aimed at gaining information concerning some of the hitherto unexplored aspects of this type of photoreaction. Specifically, the response of the unimolecular process of decarbonylation to structural modifications of the unsaturated aldehyde system, such as *the extension of the β,γ-double bond into an*

Chart 2. *α-Aryl Aldehydes Used for Investigation of Photolytic Decarbonylation*



aromatic ring[2]), *the incorporation of aldehyde and unsaturated moieties in an aliphatic chain* instead of a cyclic system, and *the substitution of the aromatic ring by electron donating and withdrawing groups*[2]), was to be examined. Preliminary experiments with phenyl aldehydes of types **4** and **5** [6] showed that irradiation of the α-phenyl aldehydes **4** (n = 1) and **5** resulted in rapid photo-decarbonylation to toluene and diphenylmethane, respectively, whereas aldehydes **4** (n = 2–4) exhibited, by comparison, only negligible tendencies towards elimination of carbon monoxide[3]). Consequently, the α-aryl aldehydes **6**–**11** were synthesised and investigated in more photochemical detail[4]).

Results

Syntheses of the Aldehydes (*Charts 3 and 4*). The reaction sequences **12** → **13** → **14** → **6**, **13** → **15** → **7** (Chart 3), **30** → **31** → **32** → **10** and **31** → **33** → **11** (Chart 4) served for the preparation of aldehydes of type **6**, **7**, **10** and **11**, with the exception of **6** (*p*-D and *p*-CF_3) and **7** (*p*-CF_3). Dialkylation of the arylacetates **12** and **30** (methyl or ethyl esters) with methyl iodide and sodium hydride in dimethylformamide was followed by lithium aluminium hydride and deuteride reductions to alcohols **14**, **15**, **32**, and **33**, respectively. Among the general methods available for the oxidation of primary alcohols to aldehydes, extensive investigation led to the preference of the following: the *Doering* oxidation using pyridine-sulfur trioxide complex and triethylamine in dimethylsulfoxide [8] for alcohols **14** and **15** (X = H, D, CH_3, OCH_3 and Br), **29** (n = 2 and 4) and **32** and **33** (X = H and OCH_3); oxidation with the *Fétizon* reagent (silver carbonate on celite) [9] for **14** and **15** (X = *p*- and *m*-CF_3).

Aldehyde **6** (*p*-D) was obtained by reductive debromination of the O-deuteriated *p*-bromophenyl alcohol **16** with lithium and deuterium oxide. Preliminary experiments with **14** (*p*-Br) under the same reaction conditions had shown that deprotonation by lithium is sufficiently slow to allow the non-deuteriated alcohol to function also as a proton source and thus to significantly lower the deuterium content in **6** (*p*-D).

p-Trifluoromethylphenyl acid (**13**) was prepared from *p*-trifluoromethylbenzoic acid (**17**) *via* the reaction sequence **17** →→ **21** (Chart 3). The cyanide **21** resisted attempted acid-catalysed hydrolysis, but yielded **13** on prolonged treatment with aqueous alkali. The synthesis of the phenylacetic acid **12** from *m*-trifluoromethylbenzoic acid (**22**) included the conventional steps **22** → **23** → **24** → **12**.

In the preparation of the cyclopropane and cyclopentane derivatives, **8** and **9**, known procedures, as summarized in Chart 4, were essentially followed [10] [11]. In order to avoid the poor yield of aldehyde **8** in the direct *Stephen* reduction of cyanide **26** (n = 2) [10], the latter was hydrolysed by alkali, followed by lithium aluminum hydride reduction of the resulting acid **27** and *Doering* oxidation [8] of the alcohol **29** (n = 2) to **8**. Acid-catalysed ethanolysis of the cyanide **29** (n = 4) [12] afforded ester **28** which was reduced to alcohol **29** (n = 4) and subsequently reoxidised to **9** as above.

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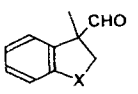
[2]) Further work, involving the systems **3a**–**d**, is in progress [2] [5].

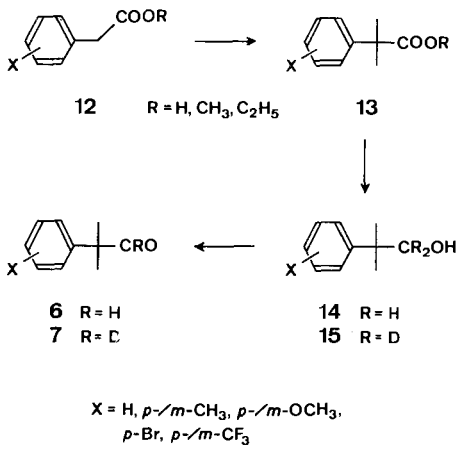


3 **a** X = CH_2; **b** X = NCH_3; **c** X = O; **d** X = S

[3]) The β-position of unsaturation as one of the necessary criteria for the (unimolecular) photodecarbonylation had been established previously for β,γ-unsaturated aldehydes [4]. From the preceding investigation [3] a further structural restriction emerged, *viz.*: in addition the reaction requires that overlap between the C_α–CO σ bond and the olefinic π system (or allylic stabilisation of the incipient radical on C_α upon the proposed photochemical α-cleavage) be possible.

[4]) Part of these results have been communicated in a preliminary form [7].

Chart 3. *Syntheses of Aldehydes of Type* **6** *and* **7**



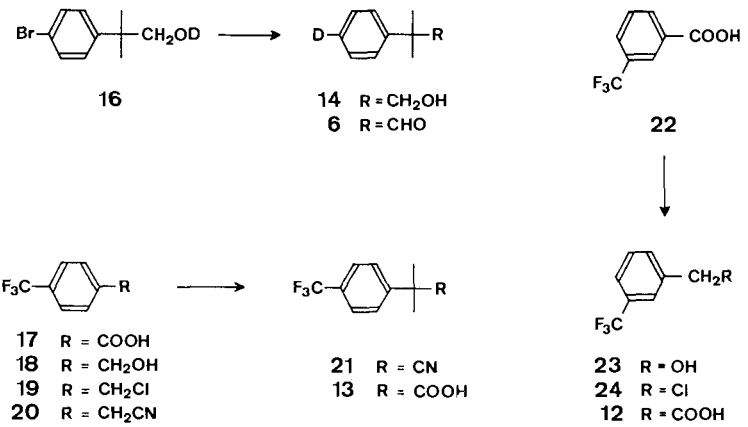
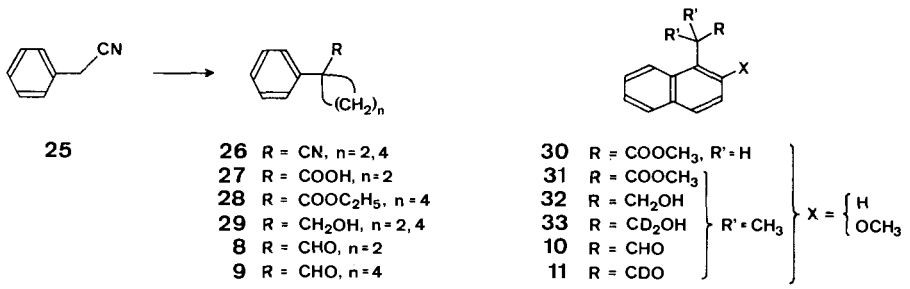


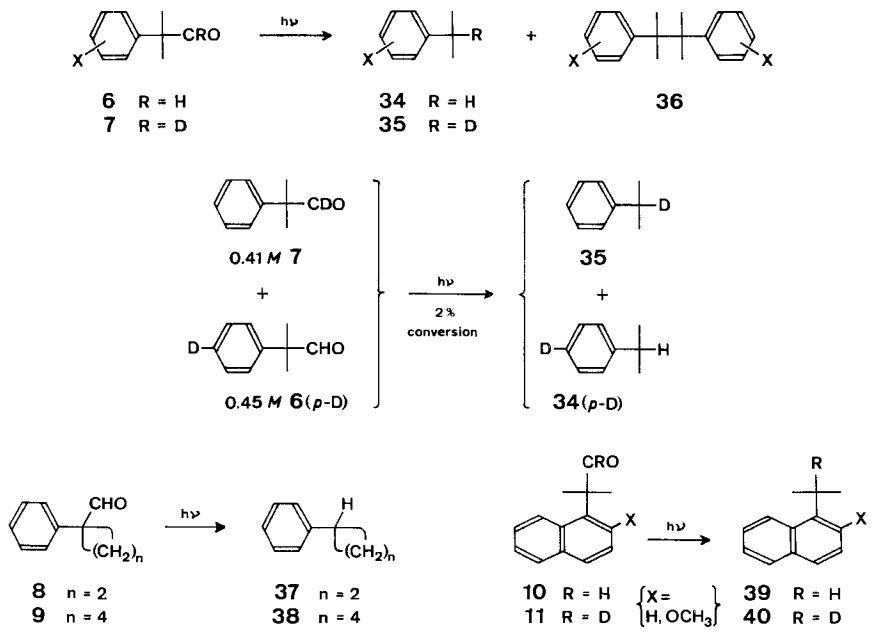
Chart 4. *Syntheses of Aldehydes* **8**–**11**



Irradiation of Aldehydes **6–11** *in Degassed Solutions* (*Chart 5*). Excitation of the $n \rightarrow \pi^*$ transition of aldehydes **6** (X = H, *p*- and *m*-CH_3, -OCH_3, -CF_3 and *p*-Br), in degassed iso-octane solutions with wavelength 3130 Å, afforded predominantly two products of decarbonylation[5]). The major product in each case was the corresponding cumene **34**. The amount of the minor components, 2,3-diphenyl-2,3-dimethyl-butanes **36**, was in some runs below ca. 0.5% and was then not determined accurately. Table 1 summarizes the composition of some representative reaction mixtures. The photodecarbonylation at 3130 Å of the deuterioaldehydes **7** (X = H, *p*- and *m*-CH_3, -OCH_3 and -CF_3) in pentane occurred with quantitative deuterium incorporation into the cumene products **35**[6]) for the most part. Only the formation of **35** (*p*-Br) in the photolysis of the *p*-bromo-deuterioaldehyde **7** in pentane involved a partial loss of deuterium (7%). Irradiation of aldehyde **7** (X = H) in the aromatic absorption band with wavelength 2537 Å again resulted in decarbonylation to **35** (with full retention of deuterium) and **36** (X = H for each).

The absence of an intermolecular hydrogen transfer process in the decarbonylation to **34** was ascertained in an experiment with 3130 Å using a solution of 0.45 M **6** (*p*-D; 59.8% d_1) and 0.41 M **7** (X = H) in pentane. Interruption of the irradiation after a conversion of 2% of the initial aldehydes, and mass spectrometric analysis of the photoproduct mixture, revealed the exclusive presence of d_0- and d_1-cumenes, **34** (X = H and *p*-D) and **35** (X = H). Random displacement and formation of d_2-cumenes had not occurred.

Chart 5. *Irradiation of Aldehydes* **6–11**



[5]) Other non-identified photoproducts generally amounted to less than 1–2% of the decarbonylation products.

[6]) Deuterium analyses were effected by mass spectrometry, with an average error $\lesssim \pm 1\%$.

The photolyses of aldehydes **8** and **9**, effected by 3130 Å in iso-octane, afforded mainly[5]) cyclopropyl-benzene (**37**) and cyclopentyl-benzene (**38**), respectively. Irradiation of the naphthyl aldehydes **10** and **11** (X = H for each) in pentane, at 2537 and 3130 Å, gave the isopropyl-naphthalenes **39** and **40** (X = H for each), respectively, with a loss of 3% of the initial isotope label in the latter case. The methoxynaphthyl aldehyde **10** (X = OCH_3) was photolysed in acetonitrile at 2537, 3130 and > 3270 Å, and in benzene at 3130 Å. Product **39** (X = OCH_3) was formed exclusively in each run. The deuterioaldehyde **11** (X = OCH_3) in acetonitrile, at wavelengths > 3270 Å, gave **40** (X = OCH_3) with a loss of 5% deuterium.

Deuterium isotope effects on the rate of decarbonylation were determined for the aldehydes **6**/**7**, X = H: 1.10, *p*-CH_3: 1.15, *m*-CH_3: 1.19, *p*-OCH_3: 1.40, *m*-CF_3: 1.13 (at 3130 Å in iso-octane), and for **10**/**11**, X = H: 1.06 (at 2537 Å in pentane).

Table 1. *Photolyses of Aldehydes* **6** (*X = H,* p- *and* m-CH_3, m-OCH_3, p-*Br*), **7** (*X = H*), **8**, **9** *and* **10** (*X = H, OCH_3*): *Composition of Mixture Produced* [a])

Aldehyde No.	(X)	Concentration [mole/l]	Wavelength [Å]	Composition of Mixture [%] Ar–C(H)–CRO[b]) (**6–10**)	Ar–C(H)–R[c]) (**34,35,37–39**)	[Ar–C$(CH_3)_2$]$_2$ (**36**)
6	(H)	0.011	3130	87	11	2
		0.040	3130	11	67	21
7	(H)	0.012	3130	16	81	3
		0.042	3130	20	73	7
		0.10	2537	47	50	3
6	(*p*-CH_3)	0.010	3130	63.2	26.8	0.2
	(*m*-CH_3)	0.010	3130	20.3	64.7	7.2[d])
	(*m*-OCH_3)	0.010	3130	79.3	12.6	4.0[d])
	(*p*-Br)	0.010	3130	46.3	38.2	1.2[d])
8		0.01	3130	95.4	1.0	
9		0.01	3130	86.1	10.7	
10	(H)	0.1	2537	55	45	
		0.1	3130	85	15	
10	(OCH_3)	0.05	2537	75	25	
		0.13	3130	80	20	
		0.1	> 3270	68	32	

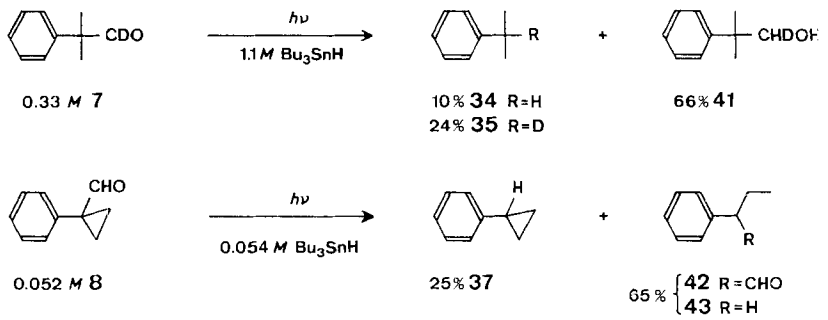
[a]) Number of light quanta absorbed differs in each run. Degassed solutions: **6–9** in iso-octane, **10** (X = H) in pentane, **10** (X = OCH_3) in acetonitrile.
[b]) R = H for **6** and **8–10**; R = D for **7**.
[c]) R = H for **34** and **37–39**; R = D for **35**.
[d]) Structure assignments based solely on analogy of VPC. retention times relative to those of **36** (X = H, *p*-CH_3, *p*-OCH_3).

*Attempted Quenching and Sensitisation Experiments; Effect of Added Tri-*n*-butylstannane* (*Chart 6*). The addition of naphthalene (0.34 and 0.80 M; irradiation at > 3270 Å) or *cis*-1,3-pentadiene (1.0 and 5.0 M; irradiation at 3130 Å) to degassed 0.05 M pentane solutions of **6** (X = H) did not change the rate of conversion to decarbonylation product. After a 55% conversion of aldehyde no *cis* → *trans* iso-

merisation of pentadiene by energy transfer was detectable. Irradiation of 0.08 M **6** in acetone at 2537 and 3130 Å did not effect any decarbonylation.

When the naphthyl aldehydes **10** were irradiated at 3130 Å (for X = H, in pentane) and > 3270 Å (for X = OCH_3, in acetonitrile) in degassed solutions containing ca. 0.1 M 1,3-cyclohexadiene, the decarbonylation to the products **39** (X = H and OCH_3) occurred with unaltered efficiency, although in the case of **10** (X = H) simultaneous sensitised diene dimerisation [13] took place. Triplet sensitisation of each naphthyl aldehyde using acetophenone or benzophenone and light of 3660 Å and > 3270 Å, respectively, did not result in chemical reaction. That energy transfer did occur for the system naphthyl aldehyde **10** (X = H) – benzophenone was demonstrated by the fact that the photoreduction of benzophenone with benzhydrol to pinacol [14], upon excitation with wavelengths above 3270 Å, was entirely quenched by 0.045 M **10** (X = H).

Chart 6. *Photolysis of the Aldehydes* **7** *(X = H) and* **8** *in the Presence of Tri-n-butyl-stannane*



In the presence of tri-*n*-butylstannane, incorporation of hydrogen derived from it competes with the otherwise quantitative retention of the deuterium in the photodecarbonylation products **35** (X = H, *p*-CH_3, *p*- and *m*-OCH_3) and **40** (X = H). The results, as summarised in Table 2, show that the extent of hydrogen uptake remains constant over the range of 0.5–2.0 M stannane for the deuterioaldehydes **7**. The decarbonylation of the naphthyl deuterioaldehydes **11**, with added tri-*n*-butylstannane, occurred also with partial uptake of hydrogen ($\lesssim$ 5% for X = H, at 3130 Å; 53% for X = OCH_3, at > 3270 Å). Photoreduction to the primary alcohols, as an important competing process to decarbonylation, was observed in all the phenyl aldehydes **7**, whereas the reduction of the naphthyl analogues **11** was observable only to a very small extent. The ratio between decarbonylation and reduction of **7** (X = H), at different concentrations of reactants, is summarised in Table 3. It is noteworthy that the formation of bicumyl **36** (X = H) is entirely quenched by the stannane even at high aldehyde concentrations. Furthermore, reduction to alcohol did not occur when, instead of the stannane, isopropyl alcohol (10% in pentane) was added, which acts as a relatively good hydrogen donor in the photoreduction of saturated and α,β-unsaturated ketones and aldehydes.

The irradiation of the phenyl aldehyde **8**, at 3130 Å in the presence of the stannane, furnished a mixture of cyclopropylbenzene (**37**), *n*-propylbenzene (**43**) and 2-phenylbutanal (**42**). Periodical gas chromatographic (VPC.) analyses during the photolysis

Table 2. *Photolyses of Aldehydes* **7** *(X = H, p-CH_3, p- and m-OCH_3) and* **11** *(X = H, OCH_3) together with Tri-n-butylstannane in Degassed Solutions: Uptake of Hydrogen by the Decarbonylation Intermediates*

Aldehyde[a] No.	(X)		n-Bu_3SnH Concentration	Product of Decarbonylation[a] No.	(X)	
7	(H)	99% d_1[b]	0.24 M	**35**	(H)	77.0% d_1
			0.5 M 1.0 M 2.0 M	**35**	(H)	70.8% d_1
7	(*p*-CH_3)	98% d_1[b]	0.5 M 1.0 M 2.0 M	**35**	(*p*-CH_3)	76.9% d_1
7	(*p*-OCH_3)	99% d_1[b]	0.5 M 1.0 M 2.0 M	**35**	(*p*-OCH_3)	87.1% d_1
7	(*m*-OCH_3)	98% d_1[b]	0.5 M 1.0 M 2.0 M	**35**	(*m*-OCH_3)	70.3% d_1
11	(H)	99% d_1[b]	0.09 M 1.0 M	**40**	(H)	$\gtrsim$95% d_1
11	(OCH_3)	99% d_1[c]	0.14 M	**40**	(OCH_3)	47% d_1

[a]) See footnote 6.

[b]) Irradiation at 3130 Å in a turn-table reactor, aldehyde concentrations in pentane: 0.1 M **7**, 0.067 M **11** (X = H).

[c]) Irradiation at > 3270 Å, 0.051 M **11** (X = OCH_3) in benzene.

Table 3. *Irradiation of Aldehyde* **7** *(X = H) and Tri-n-butylstannane in Degassed Pentane Solution: Decarbonylation and Reduction*[a])

Aldehyde (X = H)	n-Bu_3SnH	Composition of Mixture Produced		
0.10 M **7**	0.16 M	64% **7**	20% **35** (X = H)	16% **41**
0.10 M **7**	0.32 M	58% **7**	17% **35** (X = H)	25% **41**
0.33 M **7**	1.1 M	29% **7**	24% **35** (X = H)	46% **41**

[a]) Irradiation at 3130 Å in a turn-table reactor.

indicated that the formation of **43** was due to photodecarbonylation of aldehyde **42**, and that cyclopropylbenzene (**37**) was not noticeably subjected to secondary photochemical reactions. 1-Phenyl-1-hydroxymethyl-cyclopropane (**29**, n = 2), 2-phenylbutan-1-ol, 2-phenyl-2-methylpropanal (**6**, X = H) and cumene (**34**, X = H) were not found among the reaction products.

Identification of Products. The cumenes **34** (X = H, *p*- and *m*-CH_3, *p*-Br), cyclopropylbenzene (**37**), cyclopentylbenzene (**38**) and *n*-propylbenzene (**43**) were identified by comparison with commercially available samples. The characterization of the cumenes **34** (X = *p*- [15] and *m*-OCH_3, *p*- and *m*-CF_3) and the 2,3-biphenyl-2,3-dimethyl-butane **36** (X = H [16], *p*-CH_3, *p*-OCH_3) by IR., NMR. and mass spectra sufficed to allow for unequivocal structural assignments. Photoproduct **39** (X = OCH_3)

was identified with 1-isopropyl-2-methoxy-naphthalene, which was synthesised from 1-acetyl-2-methoxy-naphthalene [17], and **39** (X = H) exhibited the expected spectral data and proved to be isomeric with a sample of 2-isopropylnaphthalene[7]). The deuteriated products of type **34** (*p*-D), **35**, **40** and **41** showed the appropriate IR., NMR. and mass spectra, and they were indistinguishable by VPC. from the non-deuteriated analogues. Product **42** was identical with 2-phenylbutanal prepared from commercially available ethyl 2-phenylbutyrate by the reduction-oxidation sequence described, *e.g.*, for **13** → **14** → **6** (X = H).

Quantum Efficiency of the Photodecarbonylations. The quantum yields of decarbonylation (Φ_{-CO}) for the aldehydes **6** and **8**–**10** are given in Table 4. Both the decrease of aldehyde and the increase of product concentration showed first-order kinetics up to at least 30% conversion in each case.

Table 4. *Quantum Yields of Photodecarbonylation of Aldehydes* **6**, **8**, **9** *and* **10** [a])

	Aldehyde No.	(X)	Φ_{-CO} 2537 Å	3130 Å	3340 Å
0.1M	**6**	(H)	0.64[b])	0.76[b])	
0.01M	**6**	(*p*-CH_3)		0.80[c])	
0.01M	**6**	(*m*-CH_3)		1.00[c])	
0.01M	**6**	(*p*-OCH_3)		1.04[c])	
0.01M	**6**	(*m*-OCH_3)		0.76[c])	
0.01M	**6**	(*p*-Br)		1.25[c])	
0.01M	**6**	(*p*-CF_3)		0.71[c])	
0.01M	**6**	(*m*-CF_3)		0.60[c])	
0.01M	**8**			0.02[c])	
0.01M	**9**			0.39[c])	
0.1M	**10**	(H)	0.29[b])	0.11[b])	
0.1M	**10**	(OCH_3)	0.073[b])	0.065[b])	0.11[b])

[a]) Degassed solutions; aldehydes **6**, **8** and **9** in iso-octane, **10** (X = H) in pentane, and **10** (X = OCH_3) in acetonitrile.

[b]) Measurements using ferri-oxalate actinometry [20] and VPC. for the determination of aldehyde concentrations; estimated error ± 0.02.

[c]) Measurements in turn-table reactor with aldehyde **6** (X = H) as standard; average error 8–10%.

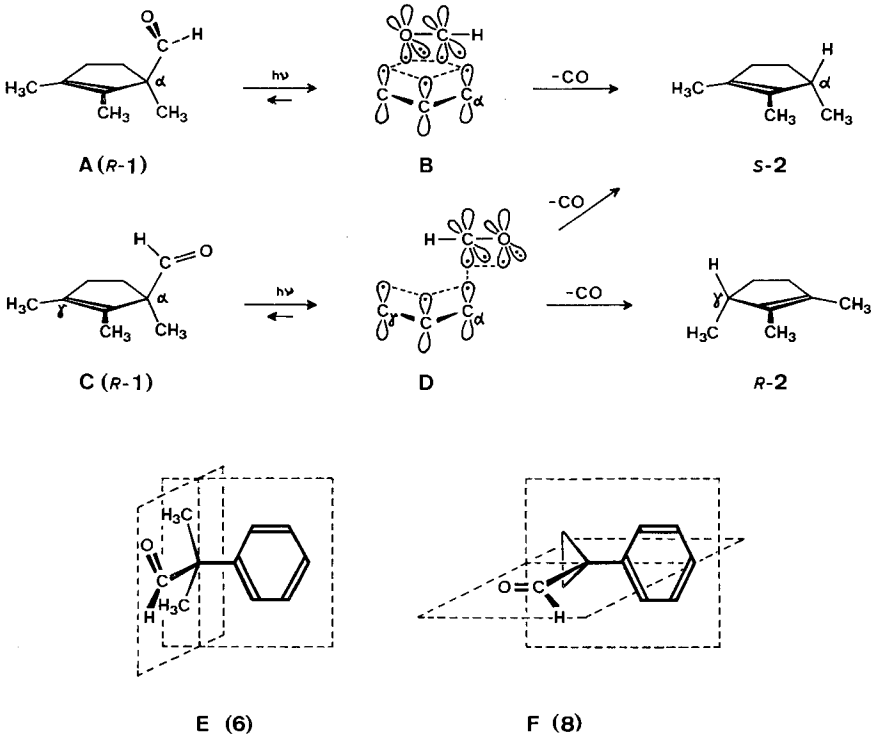
Discussion

The general aspects of the photocarbonylation of the cyclic β,γ-unsaturated aldehydes [3] [4] and the α-aryl aldehydes **6**–**11** under degassed conditions – concerning the singlet multiplicity of the reactive excited states, their unimolecular decay to products, the small deuterium isotope effect, and the limited interference of the stannane hydrogen – are all quite similar. These far-reaching analogies strongly suggest that the same basic reaction mechanism operates in both classes of compounds.

[7]) 2-Isopropylnaphthalene was synthesised from naphthalene and isopropyl *p*-toluenesulfonate according to a procedure which is claimed [18] to afford the 1-isopropyl isomer **39** (X = H) by distillative separation from unreacted naphthalene. In our preparation, however, the IR. spectrum lacks the strong bands at ca. 775 and 795 cm^{-1} which are characteristic for 1-alkylnaphthalenes, and the absorption pattern in the 700–900 cm^{-1} region agrees rather with the 2-isomeric structure [19]. It appears possible that the 1-isopropyl compound **39** (X = H) initially formed, isomerises under the temperature conditions of the separation.

The photodecarbonylation of the β,γ-unsaturated aldehyde *R*-(+)-laurolenal (**1**) has been shown to occur by two paths (see Chart 7) which were ascribed to represent predominantly the reactions of two rotameric aldehyde forms [3]. The major rotamer **A**, in which the oxygen is directed towards the olefinic β-carbon, furnishes product *S*-**2** either in a concerted decarbonylation process or *via* a closely associated formyl-allyl radical-pair intermediate **B**, whose relative spatial orientation remains as preformed in its rotameric aldehyde precursor **A** until carbon monoxide is eliminated and hydrogen is transferred to the α-carbon. It was proposed that some of the same product, *S*-**2**, as well as the enantiomer *R*-**2**, were formed from a minor rotamer (**C**), through an intermediary radical pair (**D**), in which the formyl hydrogen maintains a position about equidistant from the α- and γ-carbon atoms, and the oxygen is directed away from the centre above the allyl radical. The latter radical-pair intermediate is less closely associated than the former, and it is amenable to hydrogen uptake from tri-*n*-butyl stannane at the γ-carbon in a process which competes with the intramolecular transfer of formyl hydrogen to the same position.

Chart 7. *Proposed Mechanism of the Decarbonylation of* R-*Laurolenal* (**1**) [3]; *Conformations of Aldehydes* **6** (*with Maximum Exaltation of the* n → π^* *Transition*) *and* **8** (cf. [21] [22])



Assuming the same basic mechanism for the decarbonylation of α-aryl aldehydes – *i.e.* α-cleavage of the C_α-CO bond prior to the transfer of hydrogen – the constitutional and conformational differences between β,γ-unsaturated aldehydes such as **1** and aliphatic aryl aldehydes may be expected *a priori* to affect the results of photo-

decarbonylation of the latter in several ways. The aromatic system should prove unfavorable for the minor route involving hydrogen transfer to a γ-carbon (*cf.* **C** → *R*-**2**), although conformations resembling **C** may be preferred to those analogous to **A** (*vide infra*). It should also less effectively stabilise the incipient radical pair resulting from photolytic α-cleavage, and thus more readily allow for bimolecular reactions of, *e.g.*, the substituted benzyl component. One can conclude from the preceding investigation [3] that the aldehyde ground-state conformations do not essentially change on excitation and prior to the singlet cleavage process, and that a structural requirement for reaction is overlap between the C_α-CO σ-bond and the aromatic π-system[3]). The phenyl aldehydes now reported on seem to meet with this second condition when the results of conformational analyses of similar compounds, including the corresponding methyl ketone homologues by *Cookson* [21] and by *MacKenzie* [22], are consulted; these take into account the exaltation of the $n \rightarrow \pi^*$ absorptions observed for such ketones except for the cyclopropyl compound analogous to aldehyde **8**. The parallel trend of the UV. data for aldehydes **6**, **8** and **9**, suggests that the conclusions concerning the preferred conformations of methyl ketones [22] are qualitatively also applicable to the aldehyde series. On this basis, aldehydes **6** and **9** would fall into one category of conformers, and the cyclopropyl aldehyde **8** into another. Conformations **E** and **F** (Chart 7) are thus likely to most nearly approximate to the prevailing rotamers in the two types of aldehydes. In both cases then the C_α-CO σ-bond and the axis of the aromatic π-system are suitably oriented for orbital overlap. Similar conclusions, albeit also somewhat speculative, may be derived from the differences of the UV. spectra shown by the naphthyl aldehydes **10** and their respective decarbonylation products **39** (X = H and OCH_3 in each case).

The phenyl aldehydes **6** and **9** exhibit exalted $n \rightarrow \pi^*$ transitions at ca. 300 nm. With the exception of **6** (*m*-CF_3), for which $\varepsilon = 103$ in ethanol and 104 in iso-octane,

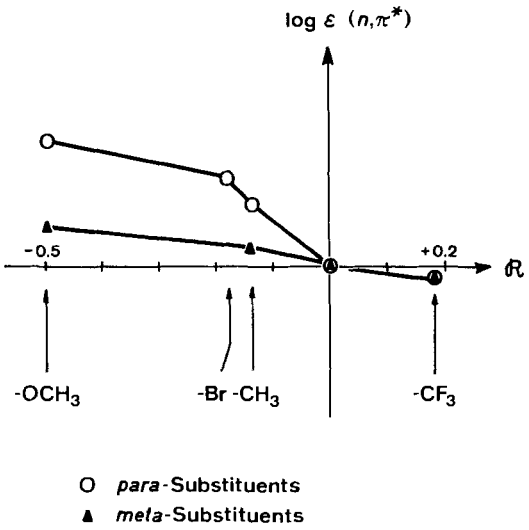


Fig. 1. Hammett *Correlation of the log* ε (n,π^*) *Values of Aldehydes* **6** *with Resonance Constants* ($\mathcal{R}$, [23])

the extinction coefficients are greater in ethanol [ε between 113 (for **6**, *p*-CF_3) and 301 (for **6**, *p*-OCH_3)] than in iso-octane [ε between 106 (for **6**, *p*-CF_3) and 190 (for **9**)], and in all cases the maxima do not shift significantly upon solvent change. A *Hammett* correlation of the logε (n, π^*) values of aldehydes **6** with resonance constants ($\mathcal{R}$) [23] gives approximately linear relationships in the *para*- and *meta*-substituted series (Fig. 1). Among the phenyl aldehydes investigated 1-formyl-1-phenyl-cyclopropane (**8**) constitutes the only exception which shows no important increase in intensity and a distinct solvent sensitivity of the $n \rightarrow \pi^*$ absorption [$\varepsilon = 48$ at 280 nm (shoulder) in ethanol, and $\varepsilon = 47$, 35, 31, and 22 at 283, 292, 302, and 312 nm, respectively, in iso-octane].

In the UV. spectra of the naphthyl aldehydes **10** (X = H and OCH_3) the aromatic absorptions are superimposed on the $n \rightarrow \pi^*$ transitions. In the aldehyde **10** (X = H) the intensities of the 292 and 313 nm bands are strongly enhanced in relation to those in the decarbonylation product **39** (X = H): $\Delta\varepsilon^{292}_{10\text{-}39} = 8900$ and $\Delta\varepsilon^{313}_{10\text{-}39} = 60$. It is interesting that the introduction of methoxyl in the C-2 position of naphthalene inverts the differences in absorption intensities between aldehyde and decarbonylation product, *i.e.* $\Delta\varepsilon^{292}_{39\text{-}10} = 119$, $\Delta\varepsilon^{ca.\,333}_{39\text{-}10} = 386$, $\Delta\varepsilon^{305}_{39\text{-}10} = 68$ (minimum).

Decarbonylation Quantum Efficiency; Reactions with Tri-n-*butylstannane Hydrogen.* The quantum yields of decarbonylation of the aliphatic phenyl aldehydes **6** are generally quite high (Table 4). The best linear *Hammett* correlation of the reaction efficiencies at 3130 Å in the *para*-substituted series (with the exception of the *p*-bromo derivative) was found using resonance constants ($\mathcal{R}$) [23], and in the *meta*-substituted series using σ_m^+ [24], a field constant with ca. 33% resonance effect (Fig. 2). The ϱ values

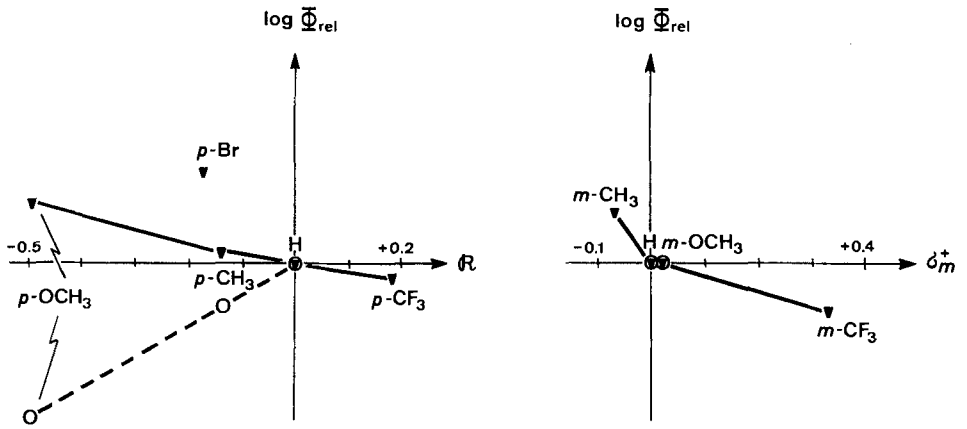


Fig. 2. Hammett *Correlations of the Quantum Efficiencies of Decarbonylation* (**6** → **34**) *at 3130* Å *and Uptake of Tri*-n-*butylstannane Hydrogen* (**7** → **35**)

obtained ($\varrho_p = -0.25$, $\varrho_m \sim -0.53$) can be satisfactorily reconciled with the proposed α-cleavage as the primary photochemical step to give an associated radical pair

(*cf.* Chart 8) with only moderate free dimethylbenzyl radical character[10]). The uptake of stannane hydrogen in the photoproducts **35** (X = H, *p*-CH_3, and *p*-OCH_3) (Table 2)[11]) shows an inverse dependence on the *para*-substitution, with a ϱ value of +0.70. This result appears plausible in terms of enhanced stabilisation of the radical-pair intermediate with increasing electron density available in the dimethylbenzyl moiety.

The quantum yield greater than unity of the decarbonylation of *p*-bromoaldehyde **6** suggests that the unimolecular reaction process is paralleled here by some radical chain initiation. Corroborative evidence is seen in the 7% hydrogen uptake in the reaction of the deuterioaldehyde **7** (*p*-Br) in pentane solution.

The cyclopropyl aldehyde **8** reacts with a strikingly low quantum yield, $\Phi_{-CO}^{3130} = 0.02$, although conformationally σ–π overlap between the C_α-CO bond and the aromatic system should be available (*cf.* **F**) as required for an efficient decarbonylation[3]). Among the factors which may contribute to lowering the reactivity in this case, two can be immediately accounted for. The dissociation energy of the C_α-CO bond of **8** – a cyclopropyl bond – can be estimated to exceed that of the other aldehydes (**6**, **9**, **10**) and thus make photolytic α-cleavage less favorable. Furthermore, reversible π-assisted cyclopropane opening, as an efficiently competing photoprocess, may well make an important contribution to the apparent photostability of **8**[12]).

The wavelength dependence of the decarbonylation quantum efficiencies of **6** (X = H) and **10** (X = H and OCH_3) deserves special attention. Of particular interest is the observation that the decarbonylation of the methoxynaphthyl aldehyde **10** (X = OCH_3) is also initiated by irradiation at > 3270 Å, *i.e.* in the long-wavelength absorption band, which corresponds to the aromatic L_b transition of methoxynaphthalene and is of lower energy than the carbonyl excited singlet state of, *e.g.*, the naphthyl aldehyde **10** (X = H). That the reaction again involves a predominantly unimolecular process is seen from the 95% retention of deuterium in the photolysis **11** → **40** (X = OCH_3 in both) in acetonitrile which still amounts to 47% in the presence of the stannane (Table 2)[13]). Barring the possibility that the carbonyl group is involved in the long-wavelength transition of **10** (X = OCH_3), *it would follow from*

[10]) By comparison, *Neale & Gross* [25] report a ϱ value of –1.36 for the hydrogen abstraction from substituted toluenes by the piperidinium radical, a free radical process.

[11]) The photolyses in the presence of tri-*n*-butylstannane were carried out at sufficiently low concentrations of aldehydes **7** in order to minimise the formation of products **34** arising from competitive hydrogen addition to free dimethylbenzyl radicals capable of recombination to bicumyls **36**.

[12]) For the photochemical cleavage of cyclopropyl methyl ketones in solution see *Marsh et al.* [26] and references therein. The reductive cleavage of **8** to **42** (Chart 6), in the presence of tri-*n*-butylstannane, may in fact originate from the interception by stannane hydrogen of the diradical formed upon photolytic fission of the three-membered ring in **8**. It is not possible, however, to distinguish this path from hydrogen abstraction by excited carbonyl oxygen as an alternative primary step; *cf.* [26] [27].

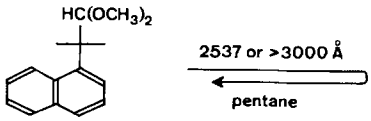
[13]) The relatively extensive uptake of stannane hydrogen in the photolysis of **11** (X = OCH_3) is in contrast to the corresponding results with the naphthyl analogue **11** (X = H). The difference may be due, at least in part, to greater steric hindrance to formation of a planar resonance-stabilised radical in the 2-methoxy series and hence a greater tendency towards dissociation of the photolytically formed associated radical-pair. A somewhat similar situation has been discussed for certain alicyclic β,γ-unsaturated aldehydes [3].

these results that the unimolecular decarbonylation is not a specific process of the aldehyde excited state but can also be induced by an appropriate π^*-excited system[14]). This fact has to be born in mind when evaluating the wavelength dependence of the quantum yield of, *e.g.*, aldehyde **6** (X = H) whose aromatic and $n \rightarrow \pi^*$ carbonyl absorption bands overlap only slightly. Decarbonylation upon aromatic $\pi \rightarrow \pi^*$ excitation at 2537 Å is less efficient than upon excitation in the $n \rightarrow \pi^*$ band at 3130 Å ($\Phi_{-CO}^{2537} = 0.64$, $\Phi_{-CO}^{3130} = 0.76$). An inherently less efficient reaction of the excited phenyl group or physical energy dissipation to ground state may here compete with intramolecular energy transfer from excited phenyl to aldehyde group which should be exothermal.

Reactive Excited State Multiplicity. Both the insensivity of the decarbonylation of phenyl aldehyde **6** (X = H) towards relatively high concentrations of the potential triplet quenchers naphthalene (0.8 M) and *cis*-1,3-pentadiene (5.0 M), and the failure of acetone sensitisation do not rigorously exclude the possibility that the reaction occurs at a higher rate than diffusion-controlled bimolecular triplet quenching, and from a triplet state which is energetically higher than that of acetone. The degree of aldehyde reduction to primary alcohol (**7**, X = H → **41**) in the presence of tri-*n*-butylstannane – *e.g.*, 60% **41** using 0.32 M stannane, with $\Phi_{-CO}^{3130} \sim 0.7$ without stannane – requires direct competition between reduction, which implicitly involves an excited state amenable to diffusion-controlled processes, and decarbonylation. It seems likely, therefore, that reduction and decarbonylation originate from the same excited state which would then necessarily have singlet multiplicity. An analogous situation has already been demonstrated for the β,γ-unsaturated aldehyde **1** [3]. There remains, however, the alternative that reduction occurs from the excited singlet state but that decarbonylation occurs from an extremely short-lived triplet state of the phenyl aldehyde.

Arguments in favor of the singlet multiplicity of the reactive excited state of the naphthyl aldehydes **10** (X = H and OCH_3) are less ambiguous. A photoreaction of the triplet excited carbonyl was *a priori* unlikely in view of the energetically favoured possibility of intramolecular energy transfer to the naphthalene[15]). Reaction of **10** (X = H) from its lowest triplet state is, in fact, ruled out for two reasons: (a) the failure of acetophenone to sensitise decarbonylation, and (b) the demonstration of

[14]) It is noted in this connection, however, that the dimethyl acetal derivative of **10** (X = H), **44**, remains unchanged upon irradiation at 2537 and > 3000 Å.



44

[15]) The naphthyl aldehyde **10** (X = H) in ether-isopentane-ethanol (5:5:2) (EPA) glass at 77 K exhibits phosphorescence which, by comparison with the emission of 1-isopropylnaphthalene (**39**, X = H), is very similar in band shape and lifetime but is slightly shifted to shorter wavelengths [**10**: τ = 2.50 s, onset ca. 452 nm, maxima at 470, 504 and 540 nm; **39**: τ = 2.06 s, onset ca. 458 nm, maxima at 475, 508 and 545 nm]. The phosphorescence intensity of the methoxynaphthyl aldehyde **10** (X = OCH_3) [**10**: τ = 2 s, onset ca. 470 nm, maxima at 498, 533 and 575 (shoulder) nm; **39**: τ = 5 s, onset ca. 470 nm, maxima at 498, 533 and 575 (shoulder) nm] is only 1/7th of the emission of **10** (X = H).

triplet quenching by 1,3-cyclohexadiene without affecting the decarbonylation. The same conclusion can be drawn for **10** (X = OCH_3) from the lack of acetophenone sensitisation. As cyclohexadiene did not quench the decarbonylation of **10** (X = OCH_3) nor did it undergo dimerisation, direct proof that any triplet energy transfer had occurred, is in this case, however, lacking[16]).

Conclusion. The results of the photodecarbonylation of α-aryl aldehydes can be accounted for by a mechanism which has been formerly proposed for cyclic β,γ-unsaturated aldehydes [3]. The present study thus shows that the process of unimolecular photodecarbonylation applies also to the aliphatic[17]) aryl aldehyde system and provides for wider application of this, in general, very smooth and efficient photoreaction.

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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 or satd. NaCl solution to the neutral point, drying over anhydrous $MgSO_4$, and removal of solvent by distillation over a *Vigreux* column at normal pressure (for phenyl derivatives) or by evaporation *in vacuo* in a rotatory evaporator.

Melting points (taken in open capillaries in an oil bath) and *boiling points* are not corrected. *Refraction indices* were measured on a *Zeiss* refractometer.

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), *q* (quartet) and *h* (heptet) for first-order multiplets, *m* for multiplets not described by other symbols, and *J* for coupling constants in cps. Proton integration of each signal is in agreement with the positions assigned.

Syntheses of Aldehydes 6–11. – *2-Phenyl-2-methyl-propanal* (**6**, *X* = *H*). 18.4 g of a 50% NaH (400 mmol) dispersion in mineral oil were added to 300 ml of anhydrous dimethylformamide. The mixture was kept under N_2, stirred, and cooled to ca. 10°. 56.4 g (400 mmol) of CH_3J and subsequently 16.4 g (100 mmol) of ethyl phenylacetate (**12**, R = C_2H_5, X = H)[18]) (dropwise addition over 1 h) were added. The hydrogen evolved was allowed to escape through a mercury seal. The mixture was warmed to room temperature, stirred for 14 h, then poured on to ice-cooled dilute HCl. The usual working up and distillation of the crude product gave, at 95–105°/10 Torr, 9.33 g (49% yield) of *ethyl 2-phenyl-2-methyl-proprionate* (**13**, *R* = C_2H_5, *X* = *H*). IR. (film): 703, 765, 1498, 1600, 1730. NMR. ($CDCl_3$): 1.17/*t* (3 H) + 4.11/*q* (2 H), *J* = 7.1, CH_2CH_3; 1.58/*s*, *gem*-$(CH_3)_2$; 7.3/*m*, arom. H. Mass spectrum: *m/e* = 192 (M^+, $C_{12}H_{16}O_2$), 119 (base peak). The residue after distillation was dissolved in ether; extraction with $NaHCO_3$ solution afforded 4.75 g (28%) of *2-phenyl-2-methyl-propionic acid* (**13**, *R* = *X* = *H*), m.p. 75–77°.

8.2 g (42.7 mmol) of ester **13** (R = C_2H_5, X = H) were added to a solution of 1.6 g (42.2 mmol) of $LiAlH_4$ in 300 ml of anhydrous ether. The mixture was heated under reflux for 0.5 h, then

[16]) That the triplet excited methoxynaphthyl aldehyde **10** (X = OCH_3) is less efficiently quenched by 1,3-cyclohexadiene than is **10** (X = H), is shown by the fact that concentrations of 0.4×10^{-3} M **10** (X = OCH_3) as compared with 0.9×10^{-4} M **10** (X = H) were necessary in order to quench 55% of the phosphorescence in 0.07 M cyclohexadiene in EPA glass at 77 K.

[17]) After the completion of our investigation of the phenyl aldehydes **6** [2], *Tonkyn & Cotter* [28] reported on the photolysis of an aliphatic homoallylic aldehyde, 2,2,4-trimethylpent-3-en-al, which resulted in decarbonylation as the major photochemical process.

[18]) Material available commercially from *Fluka AG*, Buchs (Switzerland).

cooled, treated with *Seignette* salt solution, and worked up as usual. Distillation of the crude product gave 5.5 g (85% yield) of *2-phenyl-2-methyl-propan-1-ol* (**14**, *X* = *H*). B.p. 105–109°/10 Torr. IR. (film): 702, 768, 1045, 1498, 1602, 3360. NMR. ($CDCl_3$): 1.33/*s*, *gem*-$(CH_3)_2$; 3.85/*s*, CH_2; 7.3/*m*, arom. H. Mass spectrum: *m/e* = 150 (M^+, $C_{10}H_{14}O$), 119 (base peak).

1.5 g (10 mmol) of alcohol **14** (X = H) were dissolved in 20 ml of $(CH_3)_2SO$ and 20 ml of acetic anhydride. After stirring for 14 h in the dark at room temperature, the solution was brought to *p*H 7–8 with 2N Na_2CO_3. Extraction with pentane and distillation furnished 0.70 g (47% yield) of a fraction, b.p. 70–80°/10 Torr, which contained 80% *2-phenyl-2-methyl-propanol* (**6**, *X* = *H*) and 15% starting material[19]. Pure **6** (X = H) was isolated by VPC. (SF-96, 133°). IR. (film): 697, 760, 838, 1495, 1605, 1720, 2715. UV. (C_2H_5OH): 259 (243), 297 (125); (iso-octane): 259 (260), 300 (135). NMR. ($CDCl_3$): 1.46/*s*, *gem*-$(CH_3)_2$; 7.3/*m*, arom. H; 9.50/*s*, CHO. Mass spectrum: *m/e* = 148 (M^+, $C_{10}H_{12}O$), 119 (base peak). – *2,4-Dinitrophenylhydrazone of* **6** (*X* = *H*): m.p. 144.5–145°. UV. (C_2H_5OH): 360 (22900).

$C_{16}H_{16}N_4O_4$ Calc. C 58.53 H 4.91% Found C 58.80 H 5.11%

A higher boiling fraction of the distillation (b.p. 115–130°/10 Torr) furnished 480 mg (23% yield) *1-methylthiomethoxy-2-methyl-2-phenyl-propane*. IR. (film): 699, 731, 767, 1075, 1490, 1600. NMR. ($CDCl_3$): 1.35/*s*, *gem*-$(CH_3)_2$; 1.99/*s*, S–CH_3; 3.57/*s*, CH_2-1; 4.58/*s*, –SCH_2O–; 7.3/*m*, arom. H. Mass spectrum: *m/e* = 210 (M^+, $C_{12}H_{18}OS$), 163, 132, 119 (base peak), 61.

2-Phenyl-2-methyl-propanal-1-d (**7**, X = H). Reduction of ester **13** (R = C_2H_5, X = H) with $LiAlD_4$ gave (90% yield) *2-phenyl-2-methyl-propan-1-ol-1,1-d_2* (**15**, *X* = *H*). B.p. 103–105°/10 Torr. IR. (film): 699, 759, 1498, 1601, 2091, 2198, 3360. Mass spectrum: 98% d_2[6])[20]).

Oxidation of alcohol **15** (X = H) according to *Albright & al.* [29] furnished (30% yield) *2-phenyl-2-methyl-propanal-1-d* (**7**, *X* = *H*). IR. (film): 700, 758, 1496, 1610, 1716, 2050, 2115. UV. (C_2H_5OH): 260 (198), 299 (140); (iso-octane): 259 (193), 300 (117). NMR. ($CDCl_3$): 1.47/*s*; *gem*-$(CH_3)_2$; 7.3/*m*, arom. H. Mass spectrum: 100% d_1[6])[20]).

2-Phenyl-2-methyl-propanal-4'-d (**6**, X = *p*-D). A solution of 2.51 g of *2-p*-bromophenyl-2-methyl-propan-1-ol (**14**, X = *p*-Br) in a few drops of acetone was saturated with deuterium oxide and evaporated to dryness *in vacuo*. The procedure was repeated four times. The IR. (film) of the *residue* (**16**) showed a ratio of 1:2.6 for the bands at 3340 and 2485 cm^{-1}. 2.26 g (9.8 mmol) of **16** were added to 0.42 g of a 36% Li (60 mmol) dispersion in paraffin in 100 ml anhydrous tetrahydrofuran and heated under reflux for 55 h with stirring; the reaction system was kept under Ar throughout. After cooling, the mixture was treated with 1.2 g (60 mmol) of D_2O and subsequently with satd. NH_4Cl solution. The usual working up and distillation of the crude product gave 1.01 g (69% yield) of *2-phenyl-2-methyl-propan-1-ol-4'-d* (**14**, *X* = p-*D*). B.p. 130°/10 Torr. IR. (film): 701, 764, 853, 1045, 1598, 2255, 2275, 3350. NMR. ($CDCl_3$): 1.36/*s*, *gem*-$(CH_3)_2$; 3.60/*s*, CH_2-1; 7.4/*m*, 4.35 arom. H. Mass spectrum: *m/e* = 151 (M^+, $C_{10}H_{13}DO$), 150 (M^+, $C_{10}H_{14}O$), 120 (base peak), 119; 59.8% d_1[6])[20]).

3.18 g (20 mmol) of pyridine-SO_3 complex in 25 ml $(CH_3)_2SO$ were added dropwise to a solution of 0.94 g (6.2 mmol) of alcohol **14** (*p*-D) and 6.50 g (64 mmol) of triethylamine in 20 ml $(CH_3)_2SO$ [8]. After stirring for 1 h at room temperature, the mixture was worked up and the crude product furnished on distillation 0.88 g (95% yield) of *2-phenyl-2-methyl-propanal-4'-d* (**6**, *X* = p-*D*). B.p. 105–120°/10 Torr. IR. (film): 702, 762, 836, 1495, 1735, 2255, 2280, 2695, 2795. Mass spectrum: *m/e* = 149 (M^+, $C_{10}H_{11}DO$), 148 (M^+, $C_{10}H_{12}O$), 120 (base peak), 119; 55.8% d_1[6])[20]).

2-p-Tolyl-2-methyl-propanal (**6**, X = *p*-CH_3). 20 g of a 50% NaH (400 mmol) dispersion in mineral oil was twice stirred up in pentane under N_2 and subsequently decanted. At 5–10° the NaH was combined with 600 ml anhydrous dimethylformamide and 57.0 g (400 mmol) of CH_3I, and 20 g (112 mmol) of ethyl *p*-tolylacetate (**12**, R = C_2H_5, X = *p*-CH_3) in 50 ml of dimethyl-

[19]) Oxidation method by *Albright & Goldman* [29]. In subsequent preparations of the aldehyde **6** (X = H), the *Doering* oxidation [8] gave better yields (ca. 90%). In preliminary experiments, oxidations of alcohol **14** (X = H) with pyridine-CrO_3 yielded small amounts of aldehyde with chiefly a 5:2 mixture of β,β-dimethyl-β-phenyl-ethyl alcohol and acetophenone; oxidation (a) with dimethyl azodicarboxylate [30] gave only traces of aldehyde, (b) with dicyclohexylcarbodiimide and pyridinium trifluoroacetate [31] gave ca. 30% aldehyde.

[20]) In VPC. the deuteriated compounds were indistinguishable from the non-deuteriated analogues.

formamide were added dropwise. The mixture was stirred under N_2 at room temperature for 46 h. The H_2 evolved was allowed to escape through a mercury seal. After treatment with C_2H_5OH and with satd. NH_4Cl solution, working up gave 8.5 g (42% yield) of *2-p-tolyl-2-methyl-propionic acid* (**13**, $R = H$, X = p-CH_3) and, after distillation of the neutral fraction, 14.1 g (56% yield) of *ethyl 2-p-tolyl-2-methyl-propionate* (**13**, R = C_2H_5, X = *p*-CH_3). B.p. 119–122°/10 Torr, $n_D^{23.5} = 1.4907$. IR. (film): 668, 730, 820, 1385, 1615, 1730. UV. (C_2H_5OH): 263 (320). NMR. ($CDCl_3$): 1.17/*t* (3 H) +4.12/*q* (2 H), J = 7.1, CH_2CH_3; 1.55/*s*, *gem*-$(CH_3)_2$; 2.31/*s*, arom. CH_3; 7.2/*AA'BB'* pattern, arom. H. Mass spectrum: *m/e* = 206 (M^+, $C_{13}H_{18}O_2$), 133 (base peak).

Ester **13** (R = C_2H_5, X = *p*-CH_3) was reduced with $LiAlH_4$. Distillation of the crude product furnished *2-p-tolyl-2-methyl-propan-1-ol* (**14**, X = p-CH_3) (81% yield). B.p. 122–125°/10 Torr; $n_D^{19.5} = 1.5215$. IR. (film): 606, 722, 816, 1458, 1512, 3350. UV. (C_2H_5OH): 264 (350). NMR. ($CDCl_3$): 1.24/*s*, *gem*-$(CH_3)_2$; 2.29/*s*, arom. CH_3; 3.40/*s*, CH_2-1; 7.1/*AA'BB'* pattern, arom. H. Mass spectrum: *m/e* = 164 (M^+, $C_{11}H_{16}O$), 133 (base peak).

Oxidation of alcohol **14** (X = *p*-CH_3) by *Doering*'s method [8] gave *2-p-tolyl-2-methyl-propanal* (**6**, X = *p*-CH_3) (89% yield). B.p. 120–140°/12 Torr; $n_D^{24.5} = 1.5098$. IR. (film): 723, 817, 846, 1470, 1515, 1730, 2795. UV. (C_2H_5OH): 265 (396), 297 (195); (iso-octane): 265 (359), 301 (148). NMR. ($CDCl_3$): 1.39/*s*, *gem*-$(CH_3)_2$; 2.31/*s*, arom. CH_3; 7.1/*AA'BB'* pattern, arom. H; 9.55/*s*, CHO. Mass spectrum: *m/e* = 162 (M^+, $C_{11}H_{14}O$), 133 (base peak). – *2,4-Dinitrophenylhydrazone of* **6** (X = p-CH_3): m.p. 166–167°. UV. (C_2H_5OH): 363 (22300).

$C_{17}H_{18}N_4O_4$ Calc. C 59.64 H 5.30 N 16.37% Found C 59.74 H 5.20 N 16.38%

2-p-Tolyl-2-methyl-propanal-1-d (**7**, X = *p*-CH_3). Reduction of the ester **13** (R = C_2H_5, X = *p*-CH_3) with $LiAlD_4$ gave *2-p-tolyl-2-methyl-propan-1-ol-1,1-d_2* (**15**, *p*-CH_3) (80% yield). B.p. 112–120°/10 Torr. IR. (film): 722, 818, 1516, 2082, 2193, 3360. UV. (C_2H_5OH): 265 (355). Mass spectrum: *m/e* = 166 (M^+, $C_{11}H_{14}D_2O$), 133 (base peak); 98% d_2[6])[20]).

Doering oxidation [8] of alcohol **15** (X = *p*-CH_3) gave *2-p-tolyl-2-methyl-propanal-1-d* (**7**, X = *p*-CH_3). IR. (film): 721, 818, 1515, 1713, 2043, 2116 cm^{-1}. UV. (C_2H_5OH): 266 (384), 299 (202); (iso-octane): 266 (358), 302 (153). Mass spectrum: *m/e* = 163 (M^+, $C_{11}H_{13}DO$), 133 (base peak); 99% d_1[6])[20]).

2-m-Tolyl-2-methyl-propanal (**6**, X = *m*-CH_3). Methylation of methyl *m*-tolylacetate (**12**, R = CH_3, X = *m*-CH_3)[18]) furnished *2-m-tolyl-2-methyl-propionic acid* (**13**, $R = H$, X = m-CH_3) (30% yield); *methyl 2-m-tolyl-2-methyl-propionate* (**13**, $R = CH_3$, X = m-CH_3) (53% yield). For the latter b.p. 116–124°/13 Torr; $n_D^{24} = 1.5007$. IR. (film): 708, 790, 1589, 1608, 1735. NMR. ($CDCl_3$): 1.57/*s*, *gem*-$(CH_3)_2$; 2.34/*s*, arom. CH_3; 3.63/*s*, CH_2-1; 7.2/*m*, arom. H. Mass spectrum: *m/e* = 192 (M^+, $C_{12}H_{16}O_2$), 133 (base peak).

Reduction of ester **13** (R = CH_3, X = *m*-CH_3) with $LiAlH_4$ gave *2-m-tolyl-2-methyl-propan-1-ol* (**14**, X = m-CH_3) (91% yield). B.p. 123–128°/13 Torr; $n_D^{26} = 1.5208$. IR. (film): 710, 788, 1047, 1590, 1609, 3370. UV. (C_2H_5OH): 264 (304). NMR. ($CDCl_3$): 1.30/*s*, *gem*-$(CH_3)_2$; 2.35/*s*, arom. CH_3; 3.57/*s*, CH_2-1; 7.2/*m*, arom. H. Mass spectrum: *m/e* = 163 (M^+, $C_{11}H_{16}O$), 133 (base peak).

Doering oxidation [8] of alcohol **14** (X = *m*-CH_3) furnished *2-m-tolyl-2-methyl-propanal* (**6**, X = *m*-CH_3) (97% yield). B.p. 113–118°/11 Torr; $n_D^{26.2} = 1.5084$. IR. (film): 707, 785, 810, 1365, 1492, 1588, 1608, 1732, 2697, 2795. UV. (C_2H_5OH): 265 (326), 298 (150); (iso-octane): 265 (290), 301 (120). NMR. (CCl_4): 1.41/*s*, *gem*-$(CH_3)_2$; 7.1/*m*, arom. H; 9.38/*s*, CHO. Mass spectrum: *m/e* = 162 (M^+, $C_{11}H_{14}O$), 133 (base peak). – *2,4-Dinitrophenylhydrazone of* **6** (X = m-CH_3): m.p. 144–144.5°; UV. (C_2H_5OH): 361 (19900).

$C_{17}H_{18}N_4O_4$ Calc. C 59.64 H 5.30 N 16.37% Found C 59.50 H 5.13 N 16.53%

2-m-Tolyl-2-methyl-propanal-1-d_1 (**7**, X = *m*-CH_3). Reduction of the ester **13** (R = CH_3, X = *m*-CH_3) with $LiAlD_4$ gave *2-m-tolyl-2-methyl-propan-1-ol-1,1-d_2* (**15**, X = m-CH_3) (97% yield). B.p. 113–118°/11 Torr. IR. (film): 707, 788, 1588, 1608, 2083, 2195, 3350. UV. (C_2H_5OH): 264 (250). Mass spectrum: *m/e* = 166 (M^+, $C_{11}H_{14}D_2O$), 133 (base peak); 98% d_2[6])[20]).

Doering oxidation [8] of the alcohol **15** (X = *m*-CH_3) afforded *2-m-tolyl-2-methyl-propanal-1,1-d* (**7**, X = m-CH_3) (82% yield). B.p. 110–115°/10 Torr. IR. (film): 706, 792, 1056, 1490, 1588, 1606, 2050, 2118. UV. (C_2H_5OH): 266 (340), 298 (158); (iso-octane): 265 (380), 299 (124). Mass spectrum: *m/e* = 163 (M^+, $C_{11}H_{13}DO$), 133 (base peak); 99% d_1[6])[20]).

2-p-Methoxyphenyl-2-methyl-propanal (**6**, X = *p*-OCH_3). A solution of 25.0 g (150 mmol) *p*-methoxyphenylacetic acid (**12**, R = H, X = *p*-OCH_3)[18] and 0.75 g of *p*-toluenesulfonic acid in 1 l CH_3OH was heated under reflux for 53 h, then concentrated *in vacuo* and taken up in ether. The solution was washed with 2N $NaHCO_3$ and satd. NaCl. Distillation of the crude product gave 25.4 g (94% yield) of *methyl p-methoxyphenylacetate* (**12**, R = CH_3, X = *p*-OCH_3). B.p. 96–99°/0.19 Torr; $n_D^{24.5}$ = 1.5125. IR. (film): 729, 823, 1047, 1290, 1516, 1588, 1617, 1740, 2835. UV. (C_2H_5OH): 277 (1430). NMR. (CCl_4): 3.55/*s*, CH_2; 3.67 + 3.77/2 *s*, two OCH_3; 7.0/*AA'BB'* pattern, arom. H.

Methylation of the ester **12** (R = CH_3, X = *p*-OCH_3) furnished *2-p-methoxyphenyl-2-methyl-propionic acid* (**13**, R = H, X = *p*-OCH_3) (77% yield) and *methyl 2-p-methoxyphenyl-2-methyl-propionate* (**13**, R = CH_3, X = *p*-OCH_3) (32% yield); b.p. 113–116°/0.8 Torr; $n_D^{23.5}$ = 1.5075. IR. (film): 835, 1515, 1585, 1615, 1735. UV. (C_2H_5OH): 276 (1800).

Reduction of the ester **13** (R = CH_3, X = *p*-OCH_3) with $LiAH_4$ gave *2-p-methoxyphenyl-2-methyl-propan-1-ol* (**14**, *X* = p-*OCH*$_3$) (84% yield). B.p. 117–118°/0.8 Torr; m.p. 44–44.8°; $n_D^{50.5}$ = 1.5176. IR. (film): 831, 1515, 1585, 1615, 3410. UV. (C_2H_5OH): 275 (2190). NMR. ($CDCl_3$): 1.29/*s*, *gem*-$(CH_3)_2$; 3.53/*s*, CH_2-1; 3.77/*s*, OCH_3; 7.1/*AA'BB'* pattern, arom. H. Mass spectrum: *m/e* = 180 (M^+, $C_{11}H_{16}O_2$), 149 (base peak), 121.

Oxidation of the alcohol **14** (X = *p*-OCH_3) with $(CH_3)_2SO$ and acetic anhydride[19] afforded on distillation (85–120°/12 Torr) four products which were isolated by VPC. (SE-32, 240°):

1) 64% *2-p-Methoxyphenyl-2-methyl-propanal* (**6**, X = *p*-OCH_3). IR. (film): 801, 834, 1038, 1258, 1519, 1584, 1613, 1728, 2700, 2800, 2835. UV. (C_2H_5OH): 275 (1710), 300 (301); (iso-octane): 276 (1280), 300 (150). NMR. ($CDCl_3$): 1.43/*s*, *gem*-$(CH_3)_2$; 3.79/*s*, OCH_3; 7.1/*AA'BB'* pattern, arom. H; 9.45/*s*, CHO. Mass spectrum: *m/e* = 178 (M^+, $C_{11}H_{14}O_2$), 149 (base peak), 121. – *2,4-Dinitrophenylhydrazone of* **6** (*X* = p-*OCH*$_3$): m.p. 144–146°. UV. (C_2H_5OH): 362 (18300).

$C_{17}H_{18}N_4O_4$ Calc. C 56.98 H 5.06% Found C 56.96 H 4.83%

2) 15% *2-p-Methoxyphenyl-2-methyl-propan-1-yl acetate*. IR. (film): 835, 1255, 1615, 1740, 2840. Mass spectrum: *m/e* = 222 (M^+, $C_{13}H_{18}O_3$), 163, 149 (base peak).

3) 17% *2-p-Methoxyphenyl-2-methyl-1-methylthiomethoxy-propane*. IR. (film): 832, 1070, 1616, 2835. Mass spectrum: *m/e* = 240 (M^+, $C_{13}H_{20}O_2S$), 163, 149 (base peak).

4) 4% *Unknown product.*

Doering oxidation [8] of the alcohol **14** (X = *p*-OCH_3) gave *aldehyde* **6** (*X* = p-*OCH*$_3$) in 94% yield; b.p. 143–148°/10 Torr.

2-p-Methoxyphenyl-2-methyl-propanal-1-d (**7**, X = *p*-OCH_3). Reduction of the ester **13** (R = CH_3, X = *p*-OCH_3) with $LiAlD_4$ furnished *2-p-methoxyphenyl-2-methyl-propan-1-ol-1,1-d_2* (**15**, X = *p*-OCH_3) (86% yield). B.p. 142–147°/10 Torr; m.p. 45–47°. IR. ($CHCl_3$): 831, 1034, 1579, 1612, 2085, 2195, 3570. UV. (C_2H_5OH): 273 (1700). Mass spectrum: *m/e* = 182 (M^+, $C_{11}H_{14}D_2O_2$), 149 (base peak); 98.3% d_2[6])[20]).

Doering oxidation [8] of the alcohol **15** (X = *p*-OCH_3) afforded *aldehyde* **7** (X = *p*-OCH_3) (97% yield). B.p. 134–137°/10 Torr. IR. (film): 786, 836, 1034, 1252, 1516, 1582, 1613, 1712, 2045, 2115, 2830. UV. (C_2H_5OH): 277 (1660), 300 (320, shoulder); (iso-octane): 278 (1760), 300 (265, shoulder). Mass spectrum: *m/e* = 179 (M^+, $C_{11}H_{13}DO_2$), 149 (base peak); 98.9% d_1[6])[20]).

2-m-Methoxyphenyl-2-methyl-propanal (**6**, X = *m*-OCH_3). *m*-Methoxyphenylacetic acid (**12**, R = H, X = *m*-OCH_3)[18] was esterified as described for **12** (R = H, X = *p*-OCH_3). *Methyl m-methoxyphenylacetate* (**12**, *R* = *CH*$_3$, *X* = *m-OCH*$_3$) was obtained (92% yield). B.p. 87–90°/0.25 Torr; n_D^{25} = 1.5137. IR. (film): 697, 776, 1052, 1261, 1497, 1588, 1738, 2835.

Methylation of the ester **12** (R = CH_3, X = *m*-OCH_3) gave *2-m-methoxyphenyl-2-methyl-propionic acid* (**13**, *R* = *H*, *X* = m-*OCH*$_3$) (79% yield), m.p. 62.5° after three crystallisations from petroleum ether, and *methyl 2-m-methoxyphenyl-2-methyl-propionate* (**13**, *R* = *CH*$_3$, *X* = m-*OCH*$_3$) (17% yield). B.p. 99–103°/0.5 Torr; n_D^{23} = 1.5070. IR. (film): 702, 776, 1585, 1600, 1730. UV. (C_2H_5OH): 274 (1880). NMR. (CCl_4): 1.57/*s*, *gem*-$(CH_3)_2$; 3.65 + 3.80/2 *s*, two OCH_3; 7.1/*m*, arom. H. Mass spectrum: *m/e* = 208 (M^+, $C_{12}H_{16}O_3$), 149 (base peak), 121.

Reduction of the ester **13** (R = CH_3, X = *m*-OCH_3) with $LiAlH_4$ gave *2-m-methoxyphenyl-2-methyl-propan-1-ol* (**14**, *X* = m-*OCH*$_3$) (71% yield). B.p. 94–96°/0.25 Torr; n_D^{23} = 1.5276. IR. (film): 704, 780, 1049, 1582, 1601, 3380. UV. (C_2H_5OH): 272 (1590). NMR. (CCl_4): 1.31/*s*, *gem*-$(CH_3)_2$;

3.55/*s*, CH_2-1; 3.79/*s*, OCH_3; 7.0/*m*, arom. H. Mass spectrum: *m/e* = 180 (M^+, $C_{11}H_{16}O_2$), 149 (base peak), 121.

Doering oxidation [8] of the alcohol **14** (X = *m*-OCH_3) furnished *aldehyde* **6** (*X* = m-*OCH*$_3$) (78% yield). B.p. 94–97°/0.3 Torr; n_D^{23} = 1.5193. IR. (film): 702, 780, 1050, 1266, 1488, 1582, 1600, 1728, 2695, 2800, 2830. UV. (C_2H_5OH): 277 (1730), 300 (212, shoulder); (iso-octane): 277 (1690), 300 (150, shoulder). NMR. (CCl_4): 1.45/*s*, *gem*-$(CH_3)_2$; 3.79/*s*, OCH_3; 7.0/*m*, arom. H; 9.46/*s*, CHO. Mass spectrum: *m/e* = 178 (M^+, $C_{11}H_{14}O$), 149 (base peak), 121. – *2,4-Dinitrophenylhydrazone of* **6** (X = *m*-OCH_3): m.p. 141–141.2°; UV. (C_2H_5OH): 361 (23300).

$C_{17}H_{18}N_4O_4$ Calc. C 56.98 H 5.06 N 15.64% Found C 57.04 H 5.03 N 15.53%

2-m-*Methoxyphenyl-2-methyl-propanal-1-d* (**7**, X = *m*-OCH_3). Reduction of the ester **13** (R = CH_3, X = *m*-OCH_3) with $LiAlD_4$ gave *2*-m-*methoxyphenyl-2-methyl-propan-1-ol-1,1-d*$_2$ (**15**, *X* = m-*OCH*$_3$) (90% yield). B.p. 153–157°/10 Torr. IR. (film): 703, 784, 1583, 1601, 2082, 2190, 3380. UV. (C_2H_5OH): 274 (1675). Mass spectrum: *m/e* = 182 (M^+, $C_{11}H_{14}D_2O_2$), 149 (base peak); 96.5% d_2[6])[20]).

Doering oxidation [8] of the alcohol **15** (X = *m*-OCH_3) afforded *aldehyde* **7** (X = *m*-OCH_3) (84% yield). B.p. 134–137°/10 Torr. IR. (film): 701, 789, 880, 1047, 1256, 1490, 1582, 1600, 1712, 2050, 2118, 2828. UV. (C_2H_5OH): 278 (1690), 300 (160, shoulder); (iso-octane): 277 (1550), 300 (112, shoulder). Mass spectrum: *m/e* = 179 (M^+, $C_{11}H_{13}DO_2$), 149 (base peak); 98.2% d_1[6])[20]).

2-p-*Bromophenyl-2-methyl-propanal* (**6**, X = *p*-Br). Ethyl *p*-bromophenylacetate (**12**, R = C_2H_5, X = *p*-Br)[18] was methylated to *2*-p-*bromophenyl-2-methyl-propionic acid* (**13**, R = H, X = *p*-Br) (49% yield), m.p. 122–124°, and to *ethyl 2*-p-*bromophenyl-2-methyl-propionate* (**13**, R = C_2H_5, X = *p*-Br) (44% yield). B.p. 109–110°/0.6 Torr. IR. (film): 718, 755, 826, 1010, 1098, 1495, 1590, 1731. Mass spectrum: *m/e* = 272/270 (M^+, $C_{12}H_{15}BrO_2$), 199 (base peak), 179, 157, 118.

8.44 g (34.6 mmol) of acid **13** (R = H, X = *p*-Br) in 200 ml of anhydrous ether were reduced with 1.33 g (35 mmol) of $LiAlH_4$ in ether solution added dropwise. After 30 min heating under reflux, *Seignette* salt solution was added. By the usual working up 7.68 g (97%) of *2*-p-*bromophenyl-2-methyl-propan-1-ol* (**14**, *X* = p-*Br*) were obtained. B.p. 164–167°/10 Torr. IR. ($CHCl_3$): 826, 1010, 1045, 1493, 1592, 3450, 3610. UV. (EtOH): 267 (290). NMR. (CCl_4): 1.25/*s*, *gem*-$(CH_3)_2$; 3.42/*s*, CH_2-1; 7.3/*AA'BB'* pattern, arom. H. Mass spectrum: *m/e* = 230/228 (M^+, $C_{10}H_{13}BrO$), 199, 197 (base peak).

Doering oxidation [8] of the alcohol **14** (X = *p*-Br) gave *aldehyde* **6** (X = *p*-Br) (88% yield). B.p. 137–144°/10 Torr; $n_D^{21.4}$ = 1.5528. IR. (film): 719, 747, 820, 841, 1011, 1102, 1495, 1580, 1726, 2700, 2800. UV. (C_2H_5OH): 268 (328), 297 (195); (iso-octane): 269 (445), 302 (166). NMR. (CCl_4): 1.42/*s*, *gem*-$(CH_3)_2$; 7.3/*AA'BB'* pattern, arom. H; 9.40/*s*, CHO. Mass spectrum: *m/e* = 228/226 (M^+, $C_{10}H_{11}BrO$), 199, 197 (base peak), 171, 169, 118. – *2,4-Dinitrophenylhydrazone of* **6** (X = *p*-Br): m.p. 153.5–154°; UV. (C_2H_5OH): 358 (19200).

$C_{16}H_{15}BrN_4O_4$ Calc. C 47.19 H 3.71 Br 19.62 N 13.76%
Found ,, 47.18 ,, 3,76 ,, 19.69 ,, 13.72%

2-p-*Bromophenyl-2-methyl-propanal-1-d* (**7**, X = *p*-Br). Reduction of the ester **13** (R = C_2H_5, X = *p*-Br) with $LiAlD_4$ furnished *2*-p-*bromophenyl-2-methyl-propan-1-ol-1,1-d*$_2$ (**15**, *X* = p-*Br*) (90% yield), b.p. 155–165°/10 Torr. IR. ($CHCl_3$): 826, 896, 1011, 1492, 1590, 2090, 2200, 3610. UV. (C_2H_5OH): 269 (274). Mass spectrum: *m/e* = 232/230 (M^+, $C_{10}H_{11}BrD_2O$), 199, 197 (base peak), 118; 98.5% d_2[6])[20]).

Doering oxidation [8] of the alcohol **15** (X = *p*-Br) gave *aldehyde* **7** (X = *p*-Br) (94% yield). B.p. 142–147°/10 Torr. IR. (film): 717, 733, 829, 1009, 1493, 1588, 1712, 2050, 2115. UV. (C_2H_5OH): 269 (326), 298 (206); (iso-octane): 269 (338), 302 (176). Mass spectrum: *m/e* = 229/227 (M^+, $C_{10}H_{10}BrDO$), 199, 197 (base peak); 99.5% d_1[6])[20]).

2-p-*Trifluoromethylphenyl-2-methyl-propanal* (**6**, X = *p*-CF_3). 13.44 g (76.7 mmol) of *p*-trifluoromethylbenzyl alcohol (**18**) [b.p. 98–101°/11 Torr; IR. (film): 820, 1587, 1621, 3310[21]); UV. (C_2H_5OH): 264 (355)], obtained from *p*-trifluoromethylbenzoic acid (**17**)[18] by $LiAlH_4$ reduction (91% yield), in 25 ml of ether were added dropwise to a solution of 25.6 g (216 mmol) freshly distilled $SOCl_2$ in 30 ml of ether. After 14 h stirring at room temperature the product, p-*trifluoromethylbenzyl*

chloride (**19**) was isolated (82% yield) by direct distillation from the reaction mixture. B.p. 75–80°/10 Torr. IR. (film): 693, 755, 838, 1620[21]). NMR. ($CDCl_3$): 4.60/*s*, CH_2; 7.5/*AA'BB'* pattern, arom. H.

4.73 g (24.3 mmol) of chloride **19** were added dropwise to a boiling solution of 2.1 g (43 mmol) of NaCN in 12 ml of H_2O and 20 ml of C_2H_5OH[22]). After stirring for 3 h at reflux temperature the usual working up gave 3.42 g (73% yield) of p-*trifluoromethylbenzyl cyanide* (**20**). B.p. 112–118°/11 Torr; m.p. 45–46°. IR. ($CHCl_3$): 1621, 2250[21]). UV. (C_2H_5OH): 264 (448). Mass spectrum: *m/e* = 185 (M^+, $C_9H_6F_3N$), 166, 116 (base peak), 89.

Methylation of the cyanide **20** furnished *2-p-trifluoromethylphenyl-2-methyl-propionitrile* (**21**) (85% yield). B.p. 99–108°/10 Torr. IR. (film): 699, 842, 1518, 1583, 1602, 2235[21]). UV. (C_2H_5OH): 264 (412). Mass spectrum: *m/e* = 213 (M^+, $C_{11}H_{10}F_3N$), 198 (base peak), 178, 151.

5.9 g (27.7 mmol) of cyanide **21** were hydrolysed by boiling for 20 h with 90 ml of 20% aqueous NaOH and 30 ml C_2H_5OH to give *2-p-trifluoromethylphenyl-2-methyl-propionamide* [1.4 g; 22% yield; m.p. 138–141°; IR. ($CHCl_3$): 845, 1620, 1682, 3400, 3510[21])] and 5.05 g (78% yield) of *2-p-trifluoromethylphenyl-2-methyl-propionic acid* (**13**, R = H, X = *p*-CF_3). M.p. 73.5–74° after three crystallisations from ether-petroleum ether. IR. ($CHCl_3$): 1621, 1705, 1745, 3000 (very broad)[21]). UV. (C_2H_5OH): 263 (324).

Reduction of acid **13** (R = H, X = *p*-CF_3) with $LiAlH_4$ furnished *2-p-trifluoromethylphenyl-2-methyl-propan-1-ol* (**14**, X = *p*-CF_3) (88% yield). B.p. 123–129°/10 Torr; m.p. 35–36°. IR. (film): 711, 842, 1601, 3350[21]). UV. (C_2H_5OH): 264 (309). NMR. (CCl_4): 1.28/*s*, *gem*-$(CH_3)_2$; 3.43/*s*, CH_2-1; 7.5/*AA'BB'* pattern, arom. H. Mass spectrum: *m/e* = 218 (M^+, $C_{11}H_{13}F_3O$), 187 (base peak), 159.

6 g of carefully dried *Fétizon* reagent [9] (8.3 mmol of Ag_2CO_3 on celite dried for 4 h at 100° and 0.1 Torr) and 250 ml of anhydrous benzene were put into a flask equipped with dropping funnel, water separator, and magnetic stirrer. Benzene (30 ml) was distilled off under stirring, then 600 mg (2.75 mmol) of alcohol **14** (X = *p*-CF_3) in 30 ml of benzene were added dropwise and again 30 ml of solvent removed by distillation; the mixture was then kept for two days at reflux temperature under stirring. The black reaction mixture was filtered through celite and washed with 500 ml CH_2Cl_2. Evaporation of the solvent and distillation afforded 750 mg of a mixture (b.p. 115–125°/10 Torr) composed of 43% starting material and 55% *2-p-trifluoromethylphenyl-2-methyl-propanal* (**6**, X = *p*-CF_3). The latter was isolated by VPC. on SE-30 at 216°. IR. (film): 725, 845, 1581, 1618, 1726, 2700, 2800[21]). UV. (C_2H_5OH): 264 (396), 302 (113); (iso-octane): 265 (336), 303 (106). NMR. (CCl_4): 1.48/*s*, *gem*-$(CH_3)_2$; 7.5/*AA'BB'* pattern, arom. H; 9.52/*s*, CHO. Mass spectrum: *m/e* 216 (M^+, $C_{11}H_{11}F_3O$), 197, 187 (base peak), 159, 127, 69, 51. – *2,4-Dinitrophenylhydrazone of* **6** (X = *p*-CF_3): m.p. 159–160°; UV. (C_2H_5OH): 360 (21450).

$C_{17}H_{15}F_3N_4O_4$	Calc.	C 51.52	H 3.82	F 14.38	N 14.14%
	Found	,, 51.49	,, 3.92	,, 14.36	,, 14.19%

In a second experiment 100 mg (0.46 mmol) of alcohol **14** (X = *p*-CF_3) were oxidised as above, but using toluene instead of benzene. After 5 h reaction, then evaporation of the toluene, the residue gave, after distillation (b.p. 120–180°/10 Torr) and separation by VPC. (SE-30, 218°), 30% of starting material, 9% of *aldehyde* **6** (X = *p*-CF_3), and 49% of *2-p-trifluoromethylphenyl-propan-2-ol* [m.p. 25–30°; IR. (film): 712, 843, 1620, 3370; mass spectrum: *m/e* 204 (M^+, $C_{10}H_{11}F_3O$), 189 (base peak), 185, 173, 145].

2-p-Trifluoromethylphenyl-2-methyl-propanal-1-d (**7**, X = *p*-CF_3). Reduction of acid **13** (R = H, X = *p*-CF_3) with $LiAlD_4$ afforded *2-p-trifluoromethylphenyl-2-methyl-propan-1-ol-1,1-d_2* (**15**, X = *p*-CF_3) (88% yield). B.p. 122–129°/10 Torr; m.p. 34–36°. IR. (film): 704, 843, 1582, 1621, 2085, 2195, 3340[21]). UV. (C_2H_5OH): 258 (322), 263 (297). Mass spectrum: *m/e* = 220 (M^+, $C_{11}H_{11}D_2F_3O$), 201, 187 (base peak), 159; 94.6% d_2[6])[20]).

Alcohol **15** (X = *p*-CF_3) was oxidised using the procedure described for **14** (X = *p*-CF_3) in benzene. The resulting crude reaction product was subjected to a second oxidation furnishing (98% yield) a mixture (b.p. 120–130°/10 Torr) composed of 55% starting material and 40%

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[21]) The trifluoromethyl group of all *p*-substituted derivatives exhibits strong characteristic IR. bands at 1019 (sharp), 1069 (sharp), 1124 (broad), 1168 (broad) and 1329 (broad) cm^{-1}, all positions ± 4 cm^{-1}.

[22]) Method by *Fuson* & *Rabjohn* [32].

aldehyde **7** (*X* = p-CF_3). The latter was separated by VPC. (SF-96, 180°). IR. (film): 718, 843, 1582, 1619, 1718, 2052, 2118[21]). Mass spectrum: *m/e* = 217 (M^+, $C_{11}H_{10}DF_3O$), 198, 187 (base peak), 159; 98.5% d_1[6])[20]).

*2-*m-*Trifluoromethylphenyl-2-methyl-propanal* (**6**, *X* = m-CF_3). *m*-Trifluoromethylbenzoic acid (**22**)[18]) was converted stepwise into m-*trifluoromethylbenzyl alcohol* [**23**; 92% yield; b.p. 104–105°/14 Torr; IR. (film): 704, 798, 1598, 1618, 3310[23]); UV. (C_2H_5OH): 264 (542)] and m-*trifluoromethylbenzyl chloride* [**24**; 87% yield; b.p. 65–73°/10 Torr; IR. (film): 661, 702, 718, 806, 1495, 1600, 1618[23]); NMR. (CCl_4): 4.55/*s*, CH_2; 7.5/*m*, arom. H; mass spectrum: *m/e* = 176 (M^+, $C_8H_6ClF_3$), 157, 127 (base peak, $C_7H_5F_2$ by high resolution), 107] following the procedure described for **17** → **18** → **19**.

A solution of the *Grignard* reagent prepared from 6.45 g (33 mmol) of chloride **24** and 930 mg (38 gram-atoms) of Mg files in 250 ml anhydrous ether was heated under reflux for 2 h, treated with dry ice, and further heated for another 0.5 h. After acidification and extraction with ether, the organic layer was washed repeatedly with 2 N aqueous $NaHCO_3$. The combined aqueous portions furnished on acidification and working up 4.88 g (71%) of m-*trifluoromethylphenylacetic acid* (**12**, R = H, X = *m*-CF_3). M.p. 76–77.5° after three crystallisations from CH_2Cl_2-petroleum ether. IR. ($CHCl_3$): 918, 1493, 1598, 1620, 1715, 3000 (very broad)[23]).

9.35 g (42.9 mmol) of *methyl* m-*trifluoromethylphenylacetate* [**12**, R = CH_3, X = *m*-CF_3; b.p. 104–105°/13 Torr; $n_D^{20.6}$ = 1.4482; IR. (film): 703, 803, 1498, 1599, 1745[23]); UV. (C_2H_5OH): 264 (520); NMR. (CCl_4): 3.62/*s*, CH_2; 3.69/*s*, OCH_3; 7.5/*m*, arom. H; mass spectrum: *m/e* = 218 (M^+, $C_{10}H_9F_3O_2$), 159 (base peak)], prepared (83% yield) from **12** (R = H, X = *m*-CF_3) as described for **12** (R = H, X = *p*-OCH_3), were methylated according to the procedure described for **12** (R = C_2H_5, X = *p*-CH_3). The resulting *methyl 2-*m-*trifluoromethylphenyl-2-methyl-propionate* (**13**, R = CH_3, X = *m*-CF_3) was obtained in 86% yield. B.p. 105–110°/10 Torr; n_D^{20} = 1.4509. IR. (film): 706, 804, 1494, 1596, 1613, 1736[23]). UV. (C_2H_5OH): 264 (544). NMR. (CCl_4): 1.59/*s*, *gem*-$(CH_3)_2$; 3.64/*s*, OCH_3; 7.5/*m*, arom. H. Mass spectrum: *m/e* = 246 (M^+, $C_{12}H_{13}F_3O_2$), 187 (base peak), 159.

Reduction of the ester **13** (R = CH_3, X = *m*-CF_3) with $LiAlH_4$ gave *2-*m-*trifluoromethylphenyl-2-methyl-propan-1-ol* (**14**, X = *m*-CF_3) (79% yield). B.p. 116–120°/11 Torr; n_D^{19} = 1.4662. IR. (film): 709, 719, 804, 1050, 1496, 1597, 1615, 3340[23]). NMR. (CCl_4): 1.30/*s*, *gem*-$(CH_3)_2$; 3.47/*s*, CH_2-1; 7.5/*m*, arom. H. Mass spectrum: *m/e* = 218 (M^+, $C_{11}H_{13}F_3O$), 187 (base peak), 159, 127.

Oxidation of the alcohol **14** (X = *m*-CF_3) with the *Fétizon* reagent [9] in toluene afforded, after 18 h reaction, a mixture (b.p. 95–105°/10 Torr) composed of 13% starting material and 85% *aldehyde* **6** (*X* = m-CF_3) (65% yield). The latter was separated by VPC. (SE-30, 190°); $n_D^{19.3}$ = 1.4577. IR. (film): 704, 803, 862, 1493, 1614, 1735, 2700, 2801[23]). UV. (C_2H_5OH): 263 (689), 301 (118); (iso-octane): 263 (560), 301 (110). NMR. (CCl_4): 1.49/*s*, *gem*-$(CH_3)_2$; 7.5/*m*, arom. H; 9.48/*s*, CHO. Mass spectrum: *m/e* = 216 (M^+, $C_{11}H_{11}F_3O$), 197, 187 (base peak), 159, 127. – *2,4-Dinitrophenylhydrazone of* **6** (*X* = m-CF_3): m.p. 129–129.5°. UV. (C_2H_5OH): 358 (21 800).

$C_{17}H_{15}F_3N_4O_4$	Calc.	C 51.52	H 3.82	F 14.38	N 14.14%
	Found	,, 51.65	,, 3.87	,, 14.22	,, 14.23%

*2-*m-*Trifluoromethylphenyl-2-methyl-propanal-1-d* (**7**, X = *m*-CF_3). Reduction of ester **13** (R = CH_3, X = *m*-CF_3) with $LiAlD_4$ furnished *2-*m-*trifluoromethylphenyl-2-methyl-propan-1-ol-1,1-d*$_2$ (**15**, X = *m*-CF_3) (91% yield). B.p. 124–128°/10 Torr. IR. (film): 706, 801, 1593, 1612, 2085, 3340[23]). UV. (C_2H_5OH): 263 (664). Mass spectrum: *m/e* = 220 (M^+, $C_{11}H_{11}D_2F_3O$), 187 (base peak), 159, 127; 95.3% d_2[6])[20]).

Oxidation of alcohol **15** (X = *m*-CF_3), as described for **14** (X = *m*-CF_3), gave (84% yield) a mixture (b.p. 110–120°/10 Torr) composed of 38% of starting material and 51% of *aldehyde* **7** (*X* = m-CF_3); the latter was isolated by VPC. (SE-30, 220°). IR. (film): 704, 802, 850, 1593, 1612, 1719, 2046, 2108[23]). UV. (C_2H_5OH): 264 (555), 300 (103); (iso-octane): 264 (528), 302 (104). Mass spectrum: *m/e* = 217 (M^+, $C_{11}H_{10}DF_3O$), 198, 187 (base peak), 159, 151, 127; 98.3% d_1[6])[20]).

1-Phenyl-1-formyl-cyclopropane (**8**). 14.9 g (120 mmol) of benzyl cyanide (**25**)[18]) were alkylated with 1,2-dibromoethane and $NaNH_2$ in ether [11]. 7.55 g (44% yield) of *1-phenyl-1-cyano-cyclo-*

[23]) The trifluoromethyl group of all *m*-substituted derivatives exhibits strong characteristic IR. bands at 1078 (sharp), 1098 (sharp), 1128 (broad), 1166 (broad) and 1333 (broad) cm^{-1}, all positions ± 4 cm^{-1}.

propane (**26**, $n = 2$) were obtained; b.p. 65–74°/0.4 Torr. IR. (film): 701, 759, 949, 1503, 1602, 2338. NMR. ($CDCl_3$): 1.55/*AA'BB'* pattern, cyclopropyl H; 7.3/*m*, arom. H. (Lit.: b.p. 137°/30 Torr [10], 110–113°/1 Torr [33].)

5.59 g (39.1 mmol) of cyanide **26** (n = 2) were hydrolysed by heating under reflux for 22 h in a solution of 30 g KOH in 90 ml CH_3OH and 10 ml H_2O. The solution was diluted with H_2O, the CH_3OH evaporated, and acidified. The usual working up gave 6.0 g (95% yield) of crystalline *1-phenyl-1-carboxy-cyclpropane* (**27**). M.p. of crude product 76–79° (lit.: 86–87° [11]). IR. ($CHCl_3$): 950, 1496, 1589, 1602, 1680, 2900 (very broad).

Reduction of the acid **27** with $LiAlH_4$ furnished in 78% yield *1-phenyl-1-hydroxymethyl-cyclopropane* (**29**, $n = 2$). B.p. 74–80°/0.3 Torr (lit.: 117–122°/12 Torr [10]). IR. (film): 699, 760, 1031, 1495, 1587, 1601, 3350. NMR. (CCl_4): 0.75/*AA'BB'* pattern, cyclopropyl H; 3.45/*s*, CH_2-1'; 7.2/*m*, arom. H.

Oxidation of the alcohol **29** (n = 2) with pyridine-SO_3 complex and triethylamine in $(CH_3)_2SO$ [8] afforded the *aldehyde* **8** (82% yield). B.p. 115–122°/10 Torr (lit.: 104–106°/12 Torr [10]); $n_D^{25.5} = 1.5405$. IR. (film): 701, 721, 764, 898, 1501, 1582, 1603, 1712, 2695, 2818. UV. (C_2H_5OH): 258 (209), 280 (48, shoulder); (iso-octane): 258 (196), 283 (47), 292 (35), 302 (31), 312 (22), 324 (9). NMR. ($CDCl_3$): 1.1–1.8/*AA'BB'* pattern, cyclopropyl H; 7.3/*m*, arom. H; 9.30/*s*, CHO. Mass spectrum: *m/e* = 146 (M^+, $C_{10}H_{10}O$, base peak), 117, 115, 91.– *2,4-Dinitrophenylhydrazone of* **8**: m.p. 188–189° (lit.: 189° [10]).

1-Phenyl-1-formyl-cyclopentane (**9**). Alkylation of benzyl cyanide (**25**) with 1,4-dibromobutane [11] gave *1-phenyl-1-cyano-cyclopentane* (**26**, $n = 4$) (69% yield), b.p. 110–125°/10 Torr. IR. (film): 659, 754, 1488, 1587, 2212. (Lit.: b.p. 148–153°/20 Torr [10], 148–159°/20 Torr [12], 145–160°/25–30 Torr [34].)

On acid-catalysed ethanolysis [12] the cyanide **26** (n = 4) afforded *1-phenyl-1-carboxy-cyclopentane* (1.4% yield) (m.p. 156–158°; lit.: m.p. 156–158° [12], and 158–159° [11]) and *1-phenyl-1-methoxycarbonylcyclopentane* (**28**) (84% yield), b.p. 105–107°/10 Torr. IR. (film): 701, 783, 1495, 1580, 1601, 1728. NMR. (CCl_4): 1.11/*t* (3 H) + 4.01/*q* (2 H), J = 7, CH_2CH_3; 1.8/*m* (6 H) + 2.6/*m* (2 H), cyclopentyl H; 7.2/*m*, arom. H. (Lit.: b.p. 118–120°/0.75 Torr [12], 142–144°/10 Torr [10].)

Reduction of the ester **28** with $LiAlH_4$ gave *1-phenyl-1-hydroxymethyl-cyclopentane* (**29**, $n = 4$) (67% yield), b.p. 103–105°/10 Torr. IR. (film): 701, 718, 1050, 1498, 1579, 1601, 3380. UV. (C_2H_5OH): 258 (206). NMR. (CCl_4): 1.7–2.0/*m*, cyclopentyl H; 3.36/*s*, CH_2OH; 7.2/*m*, arom. H. Mass spectrum: *m/e* = 176 (M^+, $C_{12}H_{16}O$), 146, 145 (base peak), 144, 91. Lit.: b.p. 142–144°/10 Torr [10].

Doering oxidation [8] of the alcohol **29** (n = 4) gave, in quantitative yield, a mixture (b.p. 145–155°/10 Torr) composed of 25% of starting material and 70% of *aldehyde* **9**. The latter was isolated by VPC. on SE-30 (250°). IR. (film): 702, 760, 1493, 1579, 1600, 1723, 2805, 2790. UV. (C_2H_5OH): 261 (470), 300 (234); (iso-octane): 262 (355), 300 (190). NMR. ($CDCl_3$): 1.7/*m* (6 H) + 2.5/*m* (2 H), cyclopentyl H; 7.3/*m*, arom. H; 9.39/*s*, CHO. Mass spectrum: *m/e* = 174 (M^+, $C_{12}H_{14}O$), 145 (base peak), 91. – *2,4-Dinitrophenylhydrazone of* **9**: m.p. 167° (lit.: m.p. 167–168° [35]); UV. (C_2H_5OH): 364 (20000).

2-(1-Naphthyl)-2-methyl-propanal (**10**, $X = H$). Methylation of methyl 1-naphthylacetate (**30**, X = H), m.p. 81–82.5°, to *methyl 2-(1-naphthyl)-2-methyl-propionate* (**31**, $X = H$) was achieved in 83% yield. M.p. 81–82.5°; b.p. 105–108°/0.02 Torr. UV. (C_2H_5OH): 270 (5450), 281 (6440), 291 (4470), 312 (280). IR. (CCl_4): 860, 920, 1252, 1342, 1362, 1385, 1432, 1512, 1600, 1730, 3040. NMR. ($CDCl_3$): 1.75/*s*, *gem*-$(CH_3)_2$; 3.53/*s*, OCH_3; 7.15–7.5 (4 H) + 7.6–7.9 (3 H)/2 *m*, arom. H. Mass spectrum: *m/e* = 228 (M^+), 169 (base peak).

$C_{15}H_{16}O_2$ Calc. C 78.52 H 7.06% Found C 78.68 H 7.18%

Reduction of the ester **31** (X = H) with $LiAlH_4$ gave *2-(1-naphthyl)-2-methyl-propan-1-ol* (**32**, $X = H$) (87% yield), b.p. 124°/0.04 Torr (viscous oil). IR. (film): 775, 805, 1365, 1395, 1510, 1600, 3040, 3090, 3360. NMR. ($CDCl_3$): 1.60/*s*, *gem*-$(CH_3)_2$; 4.05/*s*, CH_2-1; 7.2–8.0 (6 H) + 8.2–8.5 (1 H)/2 *m*, arom. H. Mass spectrum: *m/e* = 200 (M^+, $C_{14}H_{16}O$), 169 (base peak).

Doering oxidation [8] of the alcohol **32** (X = H) gave aldehyde **14** (X = H) (80% yield), b.p. 110°/0.4 Torr (liquid). UV. (C_2H_5OH): 270 (14400), 281 (17100), 292 (11300), 313 (990); (pentane): 313 (298). IR. (film): 778, 805, 1360, 1390, 1510, 1600, 1725, 2690, 2790, 3040. NMR.

($CDCl_3$): 1.58/*s*, *gem*-$(CH_3)_2$; 7.3–7.5 (4 H) + 7.6–7.9 (3 H)/2 *m*, arom. H; 9.62/*s*, CHO. Mass spectrum: *m/e* = 198 (M^+), 169 (base peak).

$C_{14}H_{14}O$ Calc. C 84.81 H 7.12% Found C 84.80 H 7.16%

2-(1-Naphthyl)-2-methyl-propanal-1-d (**11**, X = H). Reduction of the ester **31** (X = H) with $LiAlD_4$ afforded *2-(1-naphthyl)-2-methyl-propan-1-ol-1,1-d_2* (**33**, X = H). IR. (film): 778, 801, 1363, 1385, 1395, 1510, 1600, 2085, 2200, 3030, 3090, 3360 (broad). NMR. ($CDCl_3$): 1.60/*s*, *gem*-$(CH_3)_2$; 7.2–8.0 (6 H) + 8.2–8.5 (1 H)/2 *m*, arom. H. Mass spectrum: *m/e* = 202 (M^+, $C_{14}H_{14}D_2O$), 169 (base peak); 99% d_2 [6])[20]).

Doering oxidation [8] of the alcohol **33** (X = H) furnished *aldehyde* **11** (*X = H*). IR. (film): 779, 802, 1360, 1380, 1395, 1510, 1600, 1714, 2040, 2102, 3040. NMR. ($CDCl_3$): 1.63/*s*, *gem*-$(CH_3)_2$; 7.3–7.5 (4 H) + 7.6–7.9 (3 H)/2 *m*, arom. H. Mass spectrum: *m/e* = 199 (M^+, $C_{14}H_{13}DO$), 169 (base peak); 100% d_1[6])[20]).

2-(2-Methoxy-1-naphthyl)-2-methyl-propanal (**10**, X = OCH_3)[24]). (2-Hydroxy-1-naphthyl)-acetic acid, m.p. 148–150 (lit.: m.p. 151° [37])[25]), was methylated (91% yield) with CH_2N_2 to *methyl (2-methoxy-1-naphthyl)-acetate* (**30**, *X = OCH₃*). M.p. after crystallisation from pentane 67–68°. UV. (C_2H_5OH): 236 (15200), 282 (4300), 293 (3500), 323 (1720), 337 (1970). IR. ($CHCl_3$): 965, 1025, 1090, 1160, 1250, 1265, 1515, 1600, 1630, 1740, 2830, 3050. NMR. (CCl_4): 3.58 + 3.90/2 *s*, two OCH_3; 3.99/*s*, CH_2; 7.1–7.9/*m*, arom. H. Mass spectrum: *m/e* = 230 (M^+, $C_{14}H_{14}O_3$), 171 (base peak).

10 g (210 mmol) of NaH were suspended in 100 ml of abs. tetrahydrofuran, 25 g (175 mmol) of CH_3I were added and, with stirring under N_2, 15 g (65 mmol) of ester **30** (X = OCH_3) in 120 ml of abs. tetrahydrofuran were dropped slowly into the mixture at 0°. After stirring for 4 days at room temperature the mixture was heated under reflux for 1 h and then poured onto ice-cold satd. NH_4Cl solution. The crude mixture from the usual working contained 41% of **31** (X = OCH_3) and 59% of monomethylated product, according to NMR. analysis. The methylation procedure was repeated four times (total reaction time 23 days) until a yield of 95% of crude *methyl 2-(2-methoxy-1-naphthyl)-2-methyl-propionate* (**31**, *X = OCH₃*) was obtained[26]). Distillation at 115–120°/0.06 Torr gave 12 g (72% yield) of a solid material, which after crystallisation from pentane had m.p. 58°. UV. (C_2H_5OH): 282 (4900), 293 (3920), 322 (1875), 334 (1120). IR. ($CHCl_3$): 860, 1070, 1130, 1150, 1270, 1510, 1600, 1620, 1725, 2830. NMR. ($CDCl_3$): 1.85/*s*, *gem*-$(CH_3)_2$; 3.58 + 3.83/2 *s*, two OCH_3; 7.1–7.4 (3 H) + 7.6–8.1 (3 H)/2 *m*, arom. H. Mass spectrum: *m/e* = 258 (M^+, $C_{16}H_{18}O_3$), 199 (base peak).

Reduction of the ester **31** (X = OCH_3) with $LiAlH_4$ gave *2-(2-methoxy-1-naphthyl)-2-methyl-propan-1-ol* (**32**, *X* = OCH_3) (85% yield). B.p. 115°/0.05 Torr (liquid). IR. ($CHCl_3$): 1040, 1060, 1510, 1600, 1620, 2830, 3510 (broad). NMR. ($CDCl_3$): 1.85/*s*, *gem*-$(CH_3)_2$; 3.87/*s*, CH_2-1; 3.90/*s*, OCH_3; 7.05–7.9 (5 H) + ca. 8.3 (1 H)/2 *m*, arom. H. Mass spectrum: *m/e* = 230 (M^+, $C_{15}H_{18}O_2$), 199 (base peak).

Doering oxidation [8] of alcohol **32** (X = OCH_3) furnished *aldehyde* **10** (*X = OCH₃*) (64% yield). B.p. 115°/0.02 Torr; m.p., after crystallisation from pentane, 77–78°. UV. (C_2H_5OH): 284 (6300), 295 (shoulder), 322 (shoulder), 336 (2000). IR. ($CHCl_3$): 860, 910, 1070, 1330, 1370, 1460, 1510, 1598, 1623, 1720, 2700, 2830. NMR. ($CDCl_3$): 1.70/*s*, *gem*-$(CH_3)_2$; 3.83/*s*, OCH_3; 7.1–7.55 (3 H) + 7.65–7.9 (2 H) + 8.0–8.3 (1 H)/3 *m*, arom. H; 9.55/*s* CHO. Mass spectrum: *m/e* = 228 (M^+), 199 (base peak). $C_{15}H_{16}O_2$ Calc. C 78.93 H 7.06% Found C 79.00 H 7.04%

2,4-Dinitrophenylhydrazone of **10** (X = OCH_3): m.p. 171°; UV. (C_2H_5OH): 365 (21200).

$C_{21}H_{20}N_4O_5$ Calc. C 61.76 H 4.94 N 13.72% Found C 61.76 H 4.95 N 13.67%

2-(2-Methoxy-1-naphthyl)-2-methyl-propanal-1-d (**11**, X = OCH_3)[24]). Reduction of ester **31** (X = OCH_3) with $LiAlD_4$ gave *2-(2-methoxy-1-naphthyl)-2-methyl-propan-1-ol-1,1-d_2* (**33**, X = OCH_3) (87% yield). B.p. 120°/0.05 Torr (liquid). IR. ($CHCl_3$): 910, 980, 1030, 1065, 1105, 1310, 1370, 1460, 1510, 1600, 1620, 2100, 2210, 2840, 3510 (broad). NMR. ($CDCl_3$): 1.65/*s*, *gem*-$(CH_3)_2$;

[24]) Preliminary work by *Nobs* [36].

[25]) Synthesised according to the procedure by *Furman et al.* [37].

[26]) The second methylation step in dimethylformamide and phosphoryl tri-dimethylamide as solvents proceeded considerably slower even than in tetrahydrofuran.

3.90/*s*, OCH_3; 7.1–7.8/*m*, arom. H. Mass spectrum: *m/e* = 232 (M^+, $C_{15}H_{16}D_2O_2$), 199 (base peak); 98% d_2[6] [20]).

Doering oxidation [8] of alcohol **33** (X = OCH_3) furnished *aldehyde* **11** (*X* = *OCH*$_3$) (38% yield). B.p. 115°/0.04 Torr; m.p., after crystallisation from pentane, 77–78°. IR. ($CHCl_3$): 900, 1030, 1070, 1330, 1370, 1385, 1460, 1510, 1600, 1620, 1710, 2080, 2120, 2830. NMR. ($CDCl_3$): 1.70/*s*, *gem*-$(CH_3)_2$; 3.83/*s*, OCH_3; 7.15–7.55 (3 H) + 7.7–7.9 (2 H) + 8.05–8.3 (1 H)/3 *m*, arom. H. Mass spectrum: *m/e* = 229 (M^+, $C_{15}H_{15}DO_2$), 199 (base peak); 99% d_1[6] [20]).

Photolyses of Aldehydes 6 and 7. – a) *Semipreparative Runs with Degassed Solutions; Identification of Products.* 5–7 ml of 0.04–0.06 M pentane solutions of each aldehyde were degassed in Pyrex tubes in two freeze-thaw cycles at 10^{-5} Torr and irradiated in a turn-table reactor, equipped with magnetic stirring and a central 125-W medium-pressure mercury lamp (QM 125 *Meda Licht AG*, Basel), placed in a double Pyrex immersion well. The inner jacket was water-cooled, and the outer jacket contained a filter solution of 0.60 g K_2CrO_4 + 0.17 g KOH/15 l H_2O (path length 15 mm; transmission 8% at 275 nm, 79% at 313 nm, 7% at 375 nm, measured in a quartz cell). The solvent of each tube was carefully evaporated, and analytical samples of the following photoproducts were collected by VPC. (see also Table 1).

From **6** and **7** (X = H): *cumene* (*2-phenylpropane;* **34**, *X* = *H*), which was identified by comparison with an authentic sample[18]), using VPC., IR., NMR. and mass spectra; *2-phenylpropane-2-d* (**35**, *X* = *H*), IR. ($CHCl_3$): 1028, 1494, 1602, 2135, 2205; NMR. (CCl_4): 1.26/*t*, *J* = 0.9, $CD(CH_3)_2$; 7.14/*m*, arom. H; mass spectrum: *m/e* = 121 (M^+, $C_9H_{11}D$), 106 (base peak); 99.7% d_1[6] [20]); and *2,3-diphenyl-2,3-dimethyl-butane* (**36**, X = H), m.p. 115.5–116.5° ([14]: m.p. 118.5–119.5°); mass spectrum: *m/e* = 238 (M^+, $C_{18}H_{22}$), 119 (base peak).

From **6** and **7** (X = *p*-CH_3): *2-*(p-*tolyl*)*-propane* (**34**, X = *p*-CH_3), which was identified by comparison with an authentic sample[18]), using VPC., IR., NMR., and mass spectra; *2-*(p-*tolyl*)*-propane-2-d* (**35**, X = *p*-CH_3), IR. (film): 722, 803, 820, 1112, 1516, 2138; mass spectrum: *m/e* = 135 (M^+, $C_{10}H_{13}D$), 120 (base peak); 98.9% d_1[6] [20]); and *2,3-di-*(p-*tolyl*)*-2,3-dimethyl-butane* (**36**, X = *p*-CH_3), m.p. 155–157°; mass spectrum: *m/e* = 266 (M^+, $C_{20}H_{26}$), 133, 78 (base peak).

From **6** and **7** (X = *m*-CH_3): *2-*(m-*tolyl*)*-propane* (**34**, X = *m*-CH_3), which was identified by comparison with an authentic sample[18]), using VPC., IR., NMR., and mass spectra; and *2-*(m-*tolyl*)*-propane-2-d* (**35**, *X* = m-*CH*$_3$), IR. (film): 705, 780, 1589, 1608, 2115, 2150; mass spectrum: *m/e* = 135 (M^+, $C_{10}H_{13}D$), 120 (base peak); 99.0% d_1[6] [20]).

From **6** and **7** (X = *p*-OCH_3): *2-*(p-*methoxyphenyl*)*-propane* (**34**, X = *p*-OCH_3) [13], IR. (film): 684, 828, 1036, 1512, 1583, 1613, 2823; UV. (C_2H_5OH): 279 (1600); mass spectrum: *m/e* = 150 (M^+, $C_{10}H_{14}O$), 135 (base peak); *2-*(p-*methoxyphenyl*)*-propane-2-d* (**35**, *X* = p-*OCH*$_3$), IR. (film): 680, 827, 1037, 1510, 1580, 1612, 2132, 2825; mass spectrum: *m/e* = 151 (M^+, $C_{10}H_{13}DO$), 136 (base peak); 99.4% d_1[6] [20]); and *2,3-di-*(p-*methoxyphenyl*)*-2,3-dimethyl-butane* (**36**, X = *p*-OCH_3), m.p. 182–184°; UV. (C_2H_5OH): 276 (3135); mass spectrum: *m/e* = 298 (M^+, $C_{20}H_{26}O_2$), 149 (base peak), 121.

From **6** and **7** (X = *m*-OCH_3): *2-*(m-*methoxyphenyl*)*-propane* (**34**, X = *m*-OCH_3), IR. (film): 702, 778, 1053, 1486, 1583, 1601, 1610, 2825; UV. (C_2H_5OH): 273 (1580); mass spectrum: *m/e* = 150 (M^+, $C_{10}H_{14}O$), 135 (base peak), 105; and *2-*(m-*methoxyphenyl*)*-propane-2-d* (**35**, *X* = m-*OCH*$_3$), IR. (film): 700, 776, 1052, 1487, 1583, 1601, 1611, 2132, 2822; mass spectrum: *m/e* = 151 (M^+, $C_{10}H_{13}DO$), 136 (base peak), 106; 98.5% d_1[6] [20]).

From **6** and **7** (X = *p*-Br): *2-*(p-*bromophenyl*)*-propane* (**34**, X = *p*-Br) [38] which was identified with an authentic sample[18]), using VPC., IR., NMR. and mass spectra; and *2-*(p-*bromophenyl*)*-propane-2-d* (**35**, X = *p*-Br), IR. (film): 716, 753, 803, 822, 1010, 1489, 1591, 2135; mass spectrum: *m/e* = 201 (M^+, $C_9H_{10}BrD$), 199, 186, 184, 105 (base peak); 93.0% d_1[6] [20]).

From **6** and **7** (X = *p*-CF_3): *2-*(p-*trifluoromethylphenyl*)*-propane* (**34**, X = *p*-CF_3), IR. ($CHCl_3$): 840, 1619[21]); mass spectrum: *m/e* = 188 (M^+, $C_{10}H_{11}F_3$), 173 (base peak); and *2-*(p-*trifluoromethyl*-*phenyl*)*-propane-2-d* (**35**, X = *p*-CF_3), IR. ($CHCl_3$): 840, 1620, 2140[21]); mass spectrum: *m/e* = 189 (M^+, $C_{10}H_{10}DF_3$), 174 (base peak); 98.5% d_1[6] [20]).

From **6** and **7** (X = *m*-CF_3): *2-*(m-*trifluoromethylphenyl*)*-propane* (**34**, X = *m*-CF_3), IR. ($CHCl_3$): 900, 1596, 1614[21]); mass spectrum: *m/e* = 188 (M^+, $C_{10}H_{11}F_3$), 173 (base peak); and *2-*(m-*trifluoro*-*methylphenyl*)*-propane-2-d* (**35**, X = *m*-CF_3), IR. ($CHCl_3$): 900, 1595, 1613, 2140[21]); mass spectrum: *m/e* = 189 (M^+, $C_{10}H_{10}DF_3$), 174 (base peak); 99.2% d_1[6] [20]).

b) **6** (*X = H*) *together with Isopropyl Alcohol at 3130 Å.* A 0.01 M solution of **6** (X = H) in iso-octane containing 10% isopropyl alcohol was irradiated in two tubes, one degassed and one open, as described in a). In each run the composition of the product did not differ qualitatively from those in pure iso-octane (see Table 1); *no* alcohol **14** (X = H) was formed (VPC. analysis).

c) **6** (*X* = p-*D*) *together with* **7** (*X = H*) *at 3130 Å.* A degassed solution of 81 mg **6** of (X = *p*-D; 0.453 M) and 74 mg of **7** (X = H; 0.414 M) in 1.2 ml pentane was irradiated as described in a). The deuterium content of the aldehydes before irradiation was 22.8% d_0 and 77.2% d_1. The photolysis was discontinued at an aldehyde conversion of 2%, and the *aldehydes* and *cumene products* (**35**, *X = H*, and **34**, *X* = p-*D*) were isolated by VPC. for mass spectrometric analysis. The deuterium contents were 22.2% d_0 and 77.8% d_1 for the aldehydes and 49.0% d_0, 50.5% d_1, and $<0.5\%$ d_2 for the cumenes[6][20].

d) **7** (*X = H*) *at 2537 Å.* 4 ml of a 0.1 M solution of **7** (X = H) in pentane were degassed in a quartz tube and irradiated with a low-pressure mercury lamp (NK 6/20, *Quarzlampen GmbH*, Hanau; main emission at 2537 Å). After 16 h VPC. analysis on a 20% SF-96 column, 5′ × 1/4″, at 200° showed 47% starting material, 50% **35** (X = H), and 3% **36** (X = H) (*cf.* Table 1). Deuterium content of **35** (X = H): > 98% d_1[6][20].

e) *Aldehydes* **7** *together with Tri*-n-*butylstannane at 3130 Å.* Degassed solutions of aldehydes **7** (X = H, *p*-CH_3, *p*- and *m*-OCH_3) and freshly prepared [39] *n*-Bu_3SnH (b.p. 115–117°/10 Torr) were irradiated as described in a). Samples of products **35** were isolated, by VPC. on a 20% SF-96 column, 5′ × 3/8″, for mass spectrometric determination of the deuterium content. For results see Tables 2 and 3.

f) *Relative Decarbonylation Efficiencies of Aldehydes* **6** *and* **7**. Six samples of each aldehyde in ca. 0.01 M iso-octane solution, containing an appropriate alkane as internal VPC. reference, were degassed in Pyrex tubes and irradiated for 5, 10, 15, 20, 25, and 30 min, respectively, as described in a). The decrease of aldehyde concentration was measured in each case by 2–3 VPC. injections. The relative efficiencies of decarbonylation were determined by the use of log [**10**]/*t* diagrams. For the results see Table 5.

Table 5. *The Photodecarbonylation of Aldehydes* **6–9**: *Relative Efficiences*[a]

Aldehyde No.	(X)	VPC. Column Temperature[b]	Φ^{rel}_{-CO}[c]	Deuterium Isotope Effect Φ_{-CO} (**6**)/Φ_{-CO} (**7**)
6	(H)	172° [d]	1.00	1.10
7	(H)	172° [d]	0.91	
6	(*p*-CH_3)	182° [d]	1.05	1.15
7	(*p*-CH_3)	182° [d]	0.91	
6	(*m*-CH_3)	181° [d]	1.31	1.19
7	(*m*-CH_3)	181° [d]	1.10	
6	(*p*-OCH_3)	202° [e]	1.37	1.40
7	(*p*-OCH_3)	202° [e]	0.98	
6	(*m*-OCH_3)	200° [e]	1.00	
6	(*p*-Br)	218° [f]	1.64	
6	(*p*-CF_3)	180° [d]	0.93	
6	(*m*-CF_3)	180° [d]	0.79	1.13
7	(*m*-CF_3)	180° [d]	0.70	
8		176° [d]	0.03	
9		210° [f]	0.51	

[a] Ca. 0.01 M aldehyde in degassed iso-octane solution; irradiation at 3130 Å.
[b] 20% SF-95 column, 5′ × 3/8″.
[c] ± 5%. – Internal VPC. references: [d] *n*-$C_{13}H_{28}$; [e] *n*-$C_{15}H_{32}$; [f] *n*-$C_{16}H_{34}$.

g) **6** (*X = H*) *in Acetone at 2537 and 3130 Å.* A $0.8 \cdot 10^{-2}$M solution of **6** (X = H) in acetone (internal VPC. reference: *n*-$C_{17}H_{36}$) was degassed in a quartz cell and irradiated consecutively with a low-pressure and a medium-pressure mercury lamp (through aqueous 0.44% KH-phthalate solution, cut-off at ca. 3040 Å). VPC. analysis, after each irradiation period, revealed no change in the initial aldehyde concentration.

h) **6** (*X = H*) *together with Naphthalene or with 1,3-Pentadiene.* Three 2-ml solutions each of 0.0503M **6** (X = H), *n*-$C_{13}H_{28}$ (VPC. reference), and naphthalene (0.80, 0.34, and 0M) and *cis*-1,3-pentadiene (5, 1, and 0M), respectively, were degassed in Pyrex tubes and irradiated in a turn-table reactor as described in a), but using as filter solution acetone-H_2O 1:5 (cut-off at 3270 Å). After 4 h irradiation, VPC. analysis showed that the decarbonylation of aldehyde was quantitatively the same in all samples. Furthermore, no *cis* → *trans* isomerisation of pentadiene was detectable using a 20% TCEP column, 20′ × 1/4″, at 40°.

Photolyses of Aldehyde 8. – a) **8** *in Iso-octane at 3130 Å.* Results are summarised in Tables 1 and 5. The decarbonylation product, *cyclopropylbenzene* (**37**), was identified by comparison with an authentic sample[18]) using VPC. retention time, IR. and mass spectra.

b) **8** *with Tri*-n-*butylstannane at 3130 Å.* The results of the irradiation of 0.052M **8** with 0.054M *n*-Bu_3SnH in pentane are summarised in Table 6. After 135 min an additional portion (0.59M) of stannane had been added. *Cyclopropylbenzene* (**37**) and n-*propylbenzene* (**43**) were identified by comparison with commercial samples (VPC., IR., mass spectra)[18]). By VPC. on 20% SF-96 (5 × 3/8″, 172°), 15% SE-52 (5′ × 1/4″, 145°), and 15% UCON 1715 (5′ × 1/4″, 118° and 140°) columns the *2-phenylbutanal* (**42**) obtained was indistinguishable from a sample prepared from ethyl 2-phenylbutyrate[18]) by reduction with $LiAlH_4$ and oxidation of the resulting 2-phenylbutan-1-ol with pyridine-SO_3 complex and triethylamine [8]. Using the same VPC. conditions, 1-phenyl-1-hydroxymethyl-cyclopropane (**29**, n = 2), 2-phenyl-butan-1-ol, 2-phenyl-2-methylpropanal (**6**, X = H), and cumene (**34**, X = H) could not be detected in the photomixture.

Table 6. *Photolysis of Aldehyde* **8** *with Tri*-n-*butylstannane*[a])

Compound	% after an Irradiation Time of		
	15 min	135 min	195 min[b])
1-Phenyl-1-formyl-cyclopropane (**8**)	97.3	86.5	80.1
Cyclopropylbenzene (**37**)	2.0	3.4	4.8
n-Propylbenzene (**43**)	0.3	0.7	1.8
2-Phenylbutanal (**42**)	0.1	8.0	7.7

[a]) 0.052M **8**; irradiation at 3130 Å; see text for [*n*-Bu_3SnH] and analytical VPC. conditions.
[b]) Further addition of *n*-Bu_3SnH, see text.

Photolyses of Aldehyde 9. See Tables 1 and 5 for the results of the irradiations of **9** at 3130 Å in degassed solution. The decarbonylation product, *cyclopentylbenzene* (**38**), was identified by comparison with an authentic sample[18]) using VPC. retention time, IR. and mass spectra.

Photolyses of Aldehydes 10 and 11 (*X* = H). – a) **10** (*X = H*) *at 2537 Å.* Two quartz tubes with 5 ml of 0.5M solutions of **10** (X = H) in pentane and isopropyl alcohol, respectively, were degassed and irradiated with a low-pressure mercury lamp in a turn-table reactor. VPC. analysis showed that only one product, **39** (X = H), had been formed, with a ca. 45% conversion of aldehyde in pentane and ca. 60% in isopropyl alcohol. *1-Isopropylnaphthalene* (**39**, *X = H*) was isolated by VPC. on a 20% SE-52 column, 5′ × 3/8″, at 260°. The IR. spectrum was identical with that reported in the literature [19b]. NMR. ($CDCl_3$): 1.40/*d* (6 H) + 3.73/*h* (1 H), *J* = 7, $CH(CH_3)_2$; 7.25–8.1/*m*, aromat. H. Mass spectrum: *m/e* = 170 (M^+, $C_{13}H_{14}$), 155 (base peak). UV. (C_2H_5OH): 273 (4200), 283 (5100), 293 (3600), 313 (386)[27]).

[27]) 1-Isopropylnaphthalene (**39**, X = H) differed in VPC., IR. and NMR. from the product prepared according to the procedure by *Hickinbottom et al.* [18][7]).

b) **10** (*X = H*) *at 3130 Å*. 10 ml of a 0.08 M solution of **10** (X = H) in pentane were degassed in a Pyrex tube and irradiated at 3130 Å to ca. 40% conversion of aldehyde. According to VPC. product **39** (X = H) was formed exclusively (identification by NMR. and mass spectrum).

c) **11** (*X = H*) *at 2537 Å*. Two quartz tubes with 5 ml of 0.1 M solution of **11** (X = H) in pentane and isopropyl alcohol, respectively, were degassed and irradiated as described in a). After ca. 75% and 80% conversions of aldehyde the product of each run, *1-(1'-deuterioisopropyl)-naphthalene* (**40**, *X = H*), was isolated by VPC. IR. (film): *inter alia* 2150. NMR. ($CDCl_3$): 1.43/*s*, $CD(CH_3)_2$; 7.2–8.0/*m*, arom. H. Mass spectrum: *m/e* = 171 (M^+, $C_{13}H_{13}D$), 156 (base peak); 97% d_1 in both runs[6] [20]).

d) *Deuterium Isotope Effect on the Decarbonylation of* **10** *and* **11** (*X = H*) *at 2537 Å*. Ca. 0.06 M solutions of each aldehyde in pentane (VPC. reference: *n*-$C_{14}H_{30}$) were degassed in quartz tubes and irradiated in a turn-table reactor with a low-pressure mercury lamp until a conversion of ca. 60% was reached. Quantitative VPC. analysis gave, after correction for the difference in absorbance, a ratio of 1.06 for aldehyde conversion (**11**/**10**) and product formation (**39**/**40**, X = H).

e) **11** (*X = H*) *with Tri-n-butylstannane at 2537 Å*. Two pentane solutions, 0.067 M **11** (X = H) with 0.09 M of *n*-Bu_3SnH and 0.1 M **11** (X = H) with 1.0 M *n*-Bu_3SnH, respectively, were degassed and irradiated as described in a). Primary alcohol was formed in very small amounts besides the major product **40** (X = H) at a ca. 65% conversion of aldehyde. The hydrocarbon was isolated by VPC. Mass spectrum: $\gtrsim$95% d_1[6] [20]) in both runs.

f) **10** (*X = H*) *with 1,3-Cyclohexadiene at 3130 Å*. Three Pyrex tubes with 5 ml of pentane solutions [no. 1: 0.06 M **10** (X = H), no. 2: 0.06 M **10** (X = H) with 0.066 M 1,3-cyclohexadiene, no. 3: with 0.066 M 1,3-cyclohexadiene] were degassed and irradiated in a turn-table reactor with a medium-pressure mercury lamp housed in a water-cooled Pyrex finger. VPC. analysis after a ca. 20% conversion of aldehyde showed that decarbonylation to **39** (X = H) had proceeded to the same extent in tubes no. 1 and 2; the diene solution in no. 3 had remained unchanged (no dimer formation [13]), and in no. 2 appreciable formation of *diene dimers* was observed in addition to decarbonylation.

g) **10** (*X = H*) *with Acetophenone (at 3660 Å) and with Benzophenone (at > 3270 Å)*. A degassed pentane solution of 0.062 M **10** (X = H), 0.068 M acetophenone, and *n*-$C_{14}H_{30}$ (reference for VPC. analysis) was irradiated at 3660 Å (wave length not absorbed by aldehyde; isolated from an *Osram* HBO 500-W high-pressure mercury lamp through a *Bausch & Lomb* 500-mm grating monochromator). No decrease in aldehyde concentration nor formation of **39** (X = H) was detectable after a prolonged irradiation period (18 h).

A similar experiment to achieve sensitised decarbonylation, using benzophenone and a medium-pressure mercury lamp and acetone filter, was equally unsuccessful. Triplet energy transfer from benzophenone to **10** (X = H) was demonstrated as follows: two solutions of 0.2 M benzophenone, no. 1 with 0.07 M diphenylcarbinol and 0.045 M aldehyde **10** (X = H), and no. 2 with 0.07 M diphenylcarbinol, in *t*-butyl alcohol were degassed in Pyrex tubes and irradiated in a turn-table reactor with a medium-pressure mercury lamp through an acetone filter (cut-off at ca. 3270 Å). In run no. 2 there was 52% conversion to benzopinacol (m.p. 184–185°); in run no. 1, essentially no reaction had occurred.

Photolyses of Aldehydes 10 and 11 (X = OCH_3). – a) **10** (*X = OCH_3*) *at 2537 Å*[24]). Three quartz tubes with 2 ml of a 0.05 M solution of **10** (X = OCH_3) in acetonitrile were each degassed and irradiated with a low-pressure mercury lamp in a turn-table reactor. VPC. analysis on 20% SE-30 (at 250°) and Apiezon-L columns (at 290°) showed that *product* **39** (*X = OCH_3*) was formed exclusively and that the decrease of aldehyde was linear in the log [**10**]/*t* diagram. The product was identified with a sample of *1-isopropyl-2-methoxy-naphthalene* (**39**, *X = OCH_3*) [by VPC., m.p. (48°), IR., NMR. (1.5/*d* (6 H) + 3.95/*h* (1 H), *J* = 7, $CH(CH_3)_2$; 3.85/*s*, OCH_3; 7.15–8.25/*m*, arom. H), and mass spectra (*m/e* = 200 (M^+, $C_{14}H_{16}O$), 185 (base peak)], which was synthesised according to a known procedure [16].

b) **10** (*X = OCH_3*) *at 3130 Å in Benzene and at > 3270 Å in Isopropyl Alcohol and in Acetonitrile*. Ca. 0.1 M degassed solutions were irradiated to give only *product* **39** (*X = OCH_3*) in each case. The rate of decarbonylation in acetonitrile at > 3270 Å was ca. twice as fast as that in isopropyl alcohol.

c) **11** (*X = OCH_3*) *at > 3270 Å in Isopropyl Alcohol and in Acetonitrile*. Ca. 0.09 M degassed solutions were irradiated to ca. 80% aldehyde conversion in acetonitrile and ca. 38% in isopropyl

alcohol. In each case *1-(1'-deuterioisopropyl)-2-methoxy-naphthalene* (**40**, X = OCH_3) was isolated by VPC. (SE-30 column at 230°). IR. ($CHCl_3$): 970, 1020, 1030, 1080, 1150, 1330, 1460, 1510, 1600, 1625, 2830, 2860. NMR. ($CDCl_3$): 1.55/*s*, $C(CH_3)_2$; 4.05/*s*, OCH_3; 7.3–8.3/*m*, arom. H. Mass spectrum: *m/e* = 201 (M^+, $C_{14}H_{15}DO$), 186 (base peak); 94% d_1 (from acetonitrile), 95.5% d_1 (from isopropyl alcohol)[6][20].

d) **11** (*X = OCH₃*) *with Tri-n-butylstannane at >3270 Å*[24]. A degassed solution of 0.14 M n-Bu_3SnH with 0.051 M **11** (X = OCH_3) in benzene was irradiated to ca. 90% aldehyde conversion. On separation by VPC. (NPGS column at 260°) most of the decarbonylation product was reductively dealkylated by the excess stannane to give *2-methoxynaphthalene*. The isotope content of the intact *photoproduct* **40** (*X = OCH₃*) was 47% d_1[6][20].

e) **10** (*X = OCH₃*) *with Acetophenone at 3660 Å*[24]. A solution of 0.09 M **10** (X = OCH_3) with 0.23 M acetophenone in benzene was degassed and irradiated with wavelength 3660 Å (no light absorption by aldehyde). No decrease in aldehyde concentration nor formation of **39** (X = OCH_3) was detectable after prolonged irradiation (48 h).

f) **10** (*X = OCH₃*) *with 1,3-Cyclohexadiene*. Three Pyrex tubes with 5 ml acetonitrile solutions of 0.05 M **10** (X = OCH_3), 0.1 M 1,3-cyclohexadiene, and 0.05 M **10** (X = OCH_3) with 0.1 M 1,3-cyclohexadiene, respectively, were degassed and irradiated in a turn-table reactor at 3130 Å. After a ca. 20% conversion of aldehyde VPC. analysis showed that decarbonylation to **40** (*X = OCH₃*) had proceeded to the same extent in tubes no. 1 and 3, and that the diene concentration in tubes no. 2 and 3 had remained unchanged (no dimer formation [13]).

Quantum Yield Determinations of the Photodecarbonylation of Aldehydes 6 (X = H) and 10 (X = H and OCH_3). – The irradiation unit consisted of an optical bench with an *Osram* HBO 500-W high-pressure mercury lamp. Its light emission was focussed by an appropriate system of mirror, quartz lenses, and a water-cooled quartz cell on the entrance slit of a *Bausch and Lomb* 500-mm grating monochromator. The $\lesssim$50-Å band exit beam passed through two quartz cells (each with 1 cm length). For the irradiations, the degassed aldehyde solution was placed in the first cell, and actinometry solution in the second cell. The incident light intensity was monitored before and after each irradiation experiment, using actinometry solution in the first cell. The ferrioxalate method described by *Parker & Hatchard* [20] was employed for actinometry (0.15 M $FeK_3[(COO)_2]_3$ solution; $\Phi_{Fe^{2+}} = 1.24$ at 2537, 3130, and 3340 Å; photometric determination of the Fe^{2+}-1,10-phenanthroline complex at 5100 Å, $\varepsilon = 11100$).

a) **6** (*X = H*): 0.1 M solution in iso-octane with n-$C_{11}H_{24}$ as internal reference; ca. 23% conversion at 2537 Å and ca. 12% conversion at 3130 Å; VPC. analysis on a 20% SE-52 column at 180°.

b) **10** (*X = H*): 0.1 M solution in pentane with n-$C_{14}H_{30}$ as internal reference; ca. 26% conversion at 2537 Å and ca. 18% conversion at 3130 Å; VPC. analysis on a 20% SE-52 column at 230°.

c) **10** (*X = OCH₃*): 0.1 M solution in acetonitrile with n-$C_{12}H_{26}$ as internal reference; ca. 10% conversion at 2537 Å, ca. 12% conversion at 3130 Å, and ca. 17% conversion at 3340 Å; VPC. analysis on a 20% SE-52 column at 280°.

The results are given in Table 4 (p. 876).

Phosphorescence of Aldehydes 10 (X = H and OCH_3). – Measurements were conducted with a modified *Aminco-Bowman* fluorophosphorimeter equipped with a phosphoroscope-stepper motor unit and a sample holder designed to ensure a reproducible position of the sample tube in the phosphoroscope. Lifetimes were determined from decay curves using an oscilloscope.

For the comparison of the phosphorescence intensities, excitation at 2820 Å was used and the aldehyde **10** (X = H and OCH_3) concentrations ($\sim 10^{-4}$ M) chosen were such that the integrated areas of the emission spectra were similar. The intensity ratio was calculated by correcting for differences in integrated areas, absorbance of the solutions at the excitation wavelength, and photomultiplier sensitivity. The results are given in footnote 15.

For the phosphorescence quenching experiments with 0.07 M 1,3-cyclohexadiene, excitation at 3130 Å (for **10**, X = H) and 3350 Å (for **10**, X = OCH_3) was used, and the aldehyde concentration adapted for ca. 55% quenching of the emission in both experiments. The result is given in footnote 16.

2-(1-Naphthyl)-1-methyl-propanal Dimethyl Acetal (44): Preparation and Irradiation. – 880 mg (4.4 mmol) of aldehyde **10** (X = H) were treated for 15 h with 137 (0.97 mmol) of

p-toluenesulfonic acid in 50 ml of CH_3OH. The cooled solution was poured onto satd. $NaHCO_3$ solution and extracted with ether. The usual working up gave a crude product which contained ca. 90% of the *acetal* **44**. Samples for identification and irradiation purposes were isolated by VPC. on a 20% SE-30 column at 210°. UV. (C_2H_5OH): 272 (690), 284 (8083), 294 (5643), 304 (1144), 315 (457). IR. (film): 780, 805, 1075, 1110, 1601, 2820. NMR. (CCl_4): 1.6/*s*, *gem*-$(CH_3)_2$; 3.18/*s*, two OCH_3; 5.03/*s*, CH-1; 7.2–7.95 + 8.2–8.5/2 *m*, arom. H. Mass spectrum: m/e = 244 (M^+), 169, 141, 75 (base peak).

$C_{16}H_{20}O_2$ Calc. C 78.65 H 8.25% Found C 78.59 H 8.24%

A 0.08 M solution of **44** in pentane was degassed in a quartz tube and irradiated at 2537 Å with a low-pressure mercury lamp. VPC. analysis indicated no chemical change after extensive irradiation.

A similar experiment was carried out at > 3000 Å using a Pyrex tube and a medium-pressure mercury lamp. Again no reaction was observed.

Microanalyses were carried out by Mr. *W. Manser* of the Microanalytical Laboratory, ETH Zurich. NMR. spectra were measured in our Instrumental Division (Prof. *W. Simon*). We thank PD Dr. *J. Seibl* for the measurement and interpretation of the mass spectra.

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88. Hormon-Rezeptor-Beziehungen: Synthese und Eigenschaften von N^{ε}-Dansyllysin^{21}-adrenocorticotropin-(1-24)-tetrakosipeptid

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(22. II. 71)

Summary. We are investigating interactions between hormones and their potential receptor molecules by means of biologically active, synthetic hormone derivatives. The substituents are so chosen that they can supply quantitative information about specific contacts or convert the hormone to an 'affinity marker'. We describe the synthesis of N^{ε}-dansyllysine^{21}-adrenocorticotropin-(1–24)-tetrakosipeptide. In fat cells and in adrenal cells of the rat the dansyl substituent does not seem to impair the interaction between the peptide moiety and its biological receptors. It allows for affinity studies by fluorescence depolarisation and for measurement of intramolecular and intermolecular distances by means of energy transfer (fluorescence sensibilisation).

Potentielle Rezeptormolekeln. Das gängige Konzept der Hormonwirkung über zelluläre Rezeptoren ruft nach Identifizierung von Rezeptormolekeln und nach Aufklärung des chemischen Mechanismus der Hormon-Rezeptor-Wechselwirkung [1]. Weder das eine noch das andere ist bisher gelungen. Zur Zeit untersuchen wir diesen Problemkreis mittels synthetischer Derivate von Peptid- und andern Hormonen (z. B. Diazoacetylcholin [2]). Wir gehen dabei von folgenden Annahmen aus: eine Rezeptormolekel muss imstande sein

1. ihr Hormon spezifisch zu erkennen (sog. Diskriminatorwirkung), und als Folge davon

2. ein physikalisches oder chemisches Signal erzeugen (sog. «Transducer»-Wirkung), welches die erste einer ganzen Serie biochemischer Reaktionen auslöst, die zur bekannten physiologischen Wirkung des Hormons führt.

Jede in der Erfolgszelle vorhandene (Makro-)Molekel, die imstande ist, ein Hormon spezifisch zu binden, könnte im Prinzip zur Unterscheidung zwischen verschiedenen Hormonen und somit als Diskriminator dienen: sie ist eine *potentielle Rezeptormolekel.* Ob sie auch tatsächlich eine Rezeptormolekel ist, hängt von ihrer Fähigkeit ab, das oben erwähnte Signal zu erzeugen. Unser Vorgehen zielt darauf hin, durch Bindungsstudien potentielle Rezeptoren aufzufinden und danach durch Signalstudien zu versuchen, sie als tatsächliche Rezeptoren zu identifizieren oder auszuschliessen.