Tabelle Z 2 (Fortsetzung)

I	II				III	IV	V	VI
	R^1	R^2	R^3	R^4				
								$C_{20}H_{16}N_6O$ (356,38)
Z 21	H	OCH_3	H	H	88,0	2	233–234	C 67,40 H 4,53 N 23,58
					73,2	N	4	C 67,22 H 4,34 N 23,56
								$C_{20}H_{16}N_6O$ (356,38)
Z 22	H	H	OCH_3	H	97,1	1	242–243	C 67,40 H 4,53 N 23,58
					80,7	K	3	C 67,28 H 4,32 N 23,65
								$C_{21}H_{18}N_6O$ (370,40)
Z 23	OCH_3	H	H	CH_3	97,3	2	240,5–241,5	C 68,09 H 4,90 N 22,69
					72,0	N	6/4	C 68,21 H 4,98 N 22,91
								$C_{21}H_{18}N_6O$ (370,40)
Z 24	H	OCH_3	H	CH_3	94,6	2	246–247	C 68,09 H 4,90 N 22,69
					71,0	N	4	C 68,38 H 4,92 N 22,56

Die Elementaranalysen wurden in der mikroanalytischen Abteilung (unter Leitung von Herrn Dr. *W. Padowetz*), die Elektronenspektren sowie die Fluoreszenzspektren in der physikalischen Abteilung (unter Leitung der Herren Dres. *H. Hürzeler* und *B. G. Somers*) der *CIBA-GEIGY AG*, Werk Klybeck, durchgeführt bzw. aufgenommen.

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294. The Photodecarbonylation of α-Aryl Aldehydes: 1-Formyl-1-methyl-indan and Heterocyclic Analogues[1])

by **H. Wolf**[2a]), **H.-U. Gonzenbach**[2b]), **K. Müller**[2c]), and **K. Schaffner**[3])

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(18. IX. 72)

Summary. The singlet photodecarbonylation of the indanyl aldehyde **7** – a benzohomologue of laurolenal (**1**) and also a conformationally rigid 'out-of-plane' analogue of the α-aryl aldehyde **4** previously studied [5] [6], – and of the heterocyclic derivatives **8–10** in degassed solutions, has

[1]) Photochemical Reactions, part 70 [1].

[2]) Taken in part from a) the doctoral thesis of *Wolf* [2], b) the diploma thesis of *Gonzenbach* [3] and c) of *Müller* [4].

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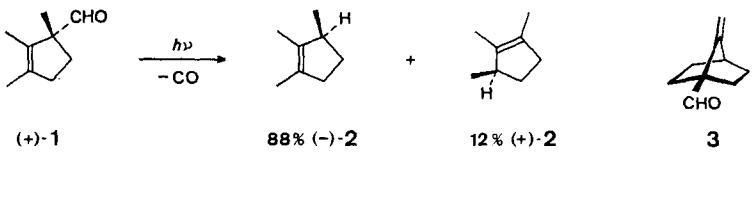
been investigated. While **7** decarbonylates uniformly to the methylindan **30** in close analogy to the examples studied previously, **8** and **9** decompose to the corresponding Δ^2-unsaturated compounds **33**, **35** in addition to decarbonylation to **32**, **34**. The results provide an independent indication for intermediate photolytically formed radical pairs (**a**) in which heteroatoms facilitate radical removal of hydrogen from C(2), and thus introduce disproportionation to give unsaturated products + CH_2O, competing with the otherwise exclusive alternative affording saturated products + CO.

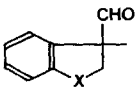
We have previously reported on the photodecarbonylation of cyclic β,γ-unsaturated and aliphatic α-aryl aldehydes which often occur with high quantum efficiency. Typical examples are (+)-**1** → (+)-**2** + (−)-**2** [5] and **4** → **5** + **6** [6] (Chart 1). The reaction was shown to be a singlet excited state process. It involves an intramolecular

Chart 1. *Previous Results: Photodecarbonylation of Cyclic β,γ-Unsaturated and Aliphatic α-Aryl Aldehydes [5] [6]*



transfer of the aldehydic hydrogen to the α-position concomitant with the elimination of carbon monoxide as the major path, and intramolecular hydrogen transfer to the γ-position in β,γ-unsaturated aldehydes and α-cleavage to free radicals in α-aryl aldehydes as minor routes[4]). Results with the conformationally rigid bicyclic aldehyde **3** indicated that a nonplanar conformation of the double bond and the C_α–CO bond is required for the unimolecular decarbonylation [5].

We now report results with a third series of aldehydes: the indanyl aldehyde **7** – a benzhomologue of **1** which represents a conformationally rigid 'out-of-plane' analogue of the α-aryl aldehyde **4** –, and the corresponding heterocyclic compounds **8–10**.



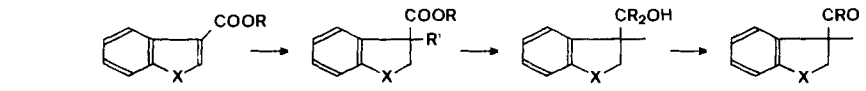
7 X = CH_2
8 X = O
9 X = S
10 X = NCH_3

Synthesis of Aldehydes 7–10. – The sequence of reactions employed for the preparation of the aldehydes **7–10** and the deuteriated analogues **7**(-d)–**10**(-d) are summarized in Chart 2. They include catalytic hydrogenation of compounds **11** [8] and **15** [9], and reduction of **24** [10] with sodium

[4]) A recent CIDNP study (chemically induced dynamic nuclear polarization) of the photolysis of the aryl aldehyde **4** (X = H) [7] revealed that reversible triplet α-cleavage to cumyl and formyl radicals occurs, evidently in competition with the decomposition of the predominant singlet excited state.

in ethanol to **12**, **16**, and **25**, respectively, and C_α-methylation of the methyl esters **12**, **17**, **21**, and **26**/**27** (obtained as a mixture from **25** with diazomethane, whereas thionyl chloride in methanol afforded selectively **26**). Reduction of the resulting products **13**, **18**, **22** and **28** to the corresponding hydroxymethyl and hydroxy-dideuterio-methyl compounds, **14**(-d), **19**(-d), **23**(-d), **29**(-d), was followed by oxidation to aldehydes **7**(-d) (using dimethylsulfoxide and acetic anhydride; *cf.* [11]) and **8**(-d), **9**(-d), and **10**(-d) (using pyridine-SO_3 complex in dimethylsulfoxide and triethylamine; *cf.* [12]).

Chart 2. *Synthesis of Aldehydes* **7**(-*d*)–**10**(-*d*)



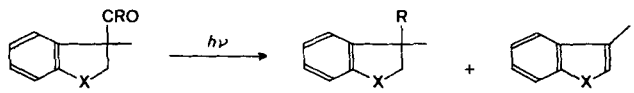
X = CH_2	**11** R = CH_3	**12** R = CH_3, R' = H **13** R = R' = CH_3	**14** R = H **14-d** R = D	**7** R = H **7-d** R = D
X = O	**15** R = H	**16** R = R' = H **17** R = CH_3, R' = H **18** R = R' = CH_3	**19** R = H **19-d** R = D	**8** R = H **8-d** R = D
X = S		**20** R = R' = H **21** R = CH_3, R' = H **22** R = R' = CH_3	**23** R = H **23-d** R = D	**9** R = H **9-d** R = D
X = NH	**24** R = H	**25** R = R' = H **26** R = CH_3, R' = H		
X = NCH_3		**27** R = CH_3, R' = H **28** R = R' = CH_3	**29** R = H **29-d** R = D	**10** R = H **10-d** R = D

Photochemical Results; Discussion. – Chart 3 and Table 1 summarize the results obtained on direct irradiation of aldehydes **7**(-d)–**10**(-d). The major photochemical characteristics of compounds **7**(-d)–**10**(-d) were analogous to those of the previously investigated β,γ-unsaturated and α-aryl aldehydes [5] [6] [13]. In carefully degassed solutions the indanyl aldehyde **7** smoothly decarbonylated to **30**. The singlet multiplicity of this reaction is probable although only indicated by negative quenching results. No effect was observed with 0.24 M 1,3-cyclohexadiene in pentane, and the rates of aldehyde conversion were essentially equal in pentane and in neat 1,3-pentadiene although only ca. 75% of product **30** was formed in the latter[5]). Similar to the series previously studied [5] [6] evidence in favor of a primary photochemical α-cleavage to a radical pair intermediate (*cf.* **b**, Chart 4) and its disproportionation to

[5]) The relatively high-lying triplet energies of the aldehydes precluded appropriate sensitization experiments (the O—O splittings of phosphorescence at 77 °K in ether/isopentane/ethanol glass were approximately the same for the aldehydes and their deoxo products, *e.g.* ca. 85 kcal/mole ($\tau \sim 5$ sec) for **8** and **32**, and ca. 79 kcal/mole ($\tau \sim 0.2$ sec) for **9** and **34**). With acetophenone and benzophenone the aldehydes **7** and **8** were converted to several compounds including small amounts of the decarbonylation products **30**/**31** and **32**/**33**, respectively, whereas **9**, with acetophenone, cleanly afforded 24% **34** and 76% **35** (*cf.* Table 1, runs no. 12 and 13, for the **34**/**35** product ratio on direct photolysis of **9**). These aldehydes competed also with benzhydrol for reaction with excited benzophenone. Presumably, these results are due to photochemical degradation of the aldehydes by reaction with the excited phenyl ketones (*e.g.*, hydrogen abstraction). Furthermore, irradiation of **8** at >3130 Å in neat acetone merely exhibited a light filter effect of the latter.

30 and carbon monoxide was forthcoming in the study of the deuteriated aldehyde (**7**-d) which decarbonylated without loss of deuterium in pentane or isopropyl alcohol, irrespective of the excitation wavelength (2537 and $\geqslant$3130 Å), and with a negligible hydrogen/deuterium isotope effect of 1.09. In the presence of 0.1 M tri-*n*-butylstannane, 12% incorporation of external hydrogen occurred at the expense of the intramolecular deuterium transfer in **7**-d → **30**-d. The decarbonylation efficiencies of **7** in different solvents were quite similar, as shown in Table 2. We have previously proposed [5] [6] that the components of the incipient radical pair – formyl and indanyl radicals from **7** – arise photochemically in orientations already preformed in their homoconjugated excited state precursors, the extensive orbital overlap of which would be sufficiently carried over to provide optimum conditions for radical pair reactivity independent of solvation effects on the radical pair. The small isotope effect, the distinct yet small tendency to incorporate stannane hydrogen, and the minor solvent effects, unrelated to solvent viscosity, in the present series can be accomodated by this model of a stepwise reaction.

Chart 3. *Irradiation of Aldehydes* **7**(-*d*)-**10**(-*d*)



X = CH_2, R = H/D	**7** / **7**-d	**30** / **30**-d	**31**
X = O, R = H/D	**8** / **8**-d	**32** / **32**-d	**33**
X = S, R = H/D	**9** / **9**-d	**34** / **34**-d	**35**
X = NCH_3, R = H/D	**10** / **10**-d	**36** / **36**-d	**37**

The photochemical properties of the heterocyclic aldehydes **8**(-d) and **9**(-d) were quite similar to those described above for the indanyl aldehydes **7** and **7**-d (in degassed solutions), *with the exception that the decarbonylation to* **32** *and* **34**, *respectively, was accompanied by the formation of the corresponding dehydro products,* **33** *and* **35**[6]). Thus, using 1,3-cyclohexadiene and naphthalene, triplet quenching could not be achieved[5]), incorporation of stannane hydrogen competed to various extents (26% in **32**-d and 50% in **34**-d with ca. 0.1 M stannane) with the otherwise essentially quantitative intramolecular transfer of deuterium and the formation of the dehydro products **33** and **35**, and the hydrogen/deuterium isotope effects on the photolytic conversion were again quite small, 1.28 for **8**/**8**-d and 1.02 for **9**/**9**-d. The photolyses of the indolenyl aldehyde **10** invariably gave substantial amounts of amorphous precipitates which rendered quantitative evaluations of the product formation less

[6]) Photolysis without rigorous exclusion of air afforded dehydro products (**31**, **33**, **35**, **37**) from all four aldehydes (*cf.* Table 1: runs no. 2, 9, 12, 20). While degassing entirely suppressed this reaction for the indanyl and indolenyl aldehydes (**7** and **10**), the formation of ca. 5–10% dehydro products **32** and **34** from the benzo[*b*]furanyl and benzo[*b*]thiophenyl aldehydes **8** and **9**, respectively, persisted also in the absence of molecular oxygen.

Table 1. *Direct Irradiation of Aldehydes* **7**(-*d*)–**10**(-*d*) [a]

Run no.	Aldehyde	Solvent	Added n-Bu_3SnH	Wavelength	Products (percentage of converted aldehyde) [b]			
1	**7**	Pentane [c]	–	≥3130 Å	100% **30**			
2	**7**	Pentane [d]	–	≥3130 Å	53% **30**		47%	**31**
3	**7**-d	Pentane [c]	–	2537 Å	100% **30**-d	(≥99% d_1)		
4	**7**-d	Pentane [c]	–	≥3130 Å	100% **30**-d	(≥99% d_1)		
5	**7**-d	Isopropyl alcohol [c]	–	≥3130 Å	100% **30**-d	(≥99% d_1)		
6	**7**-d	Pentane [c]	0.1 M	≥3130 Å	100% **30**-d	(88% d_1)		
7	**8**	Pentane [c]	–	2537 Å	95% **32**		5%	**33**
8	**8**	Pentane [c]	–	≥3130 Å	94% **32**		6%	**33**
9	**8**	Pentane [d]	–	≥3130 Å	35% **32**		65%	**33**
10	**8**-d	Pentane [c]	–	≥3130 Å	95% **32**-d	(95% d_1)	5%	**33**
11	**8**-d	Pentane [c]	0.11 M	≥3130 Å	100% **32**-d	(74% d_1)		
12	**9**	Pentane [c]	–	≥3130 Å	93% **34**		7%	**35**
13	**9**	Pentane [e]	–	≥3130 Å	93% **34**		7%	**35**
14	**9**	Pentane [d]	–	≥3130 Å	37% **34**		63%	**35**
15	**9**-d	Pentane [c]	–	≥3130 Å	94% **34**-d	(≥99% d_1)	6%	**35**
16	**9**-d	Isopropyl alcohol [c]	–	≥3130 Å	94% **34**-d	(≥99% d_1)	6%	**35**
17	**9**-d	Pentane [c]	0.08 M	≥3130 Å	100% **34**-d	(50% d_1)		
18	**10**	Pentane [c]	–	2537 Å	~50% **36**			
19	**10**	Pentane [c]	–	≥3130 Å	~40% **36**			
20	**10**-d	Iso-octane [f]	–	≥3130 Å	~35% **36**-d	(≥99% d_1)	~33%	**37**

[a] Aldehyde concentration ca. 0.1 M; see Experimental Part for further details on runs no. 1–20 and for additional irradiation experiments.
[b] Aldehyde conversions 50–100% except for runs no. 6 (30%), 8 (40%), and 18 (28%).
[c] Solution degassed in three freeze-pump (10^{-5} Torr)-thaw cycles.
[d] Solution saturated with air oxygen.
[e] Solution degassed in five freeze-pump (10^{-5} Torr)-thaw cycles which included the introduction of argon into the sample tube after each pumping.
[f] Solution flushed with argon.

Table 2. *Solvent Effects on the Photodecarbonylation of Aldehyde* **7** [a]

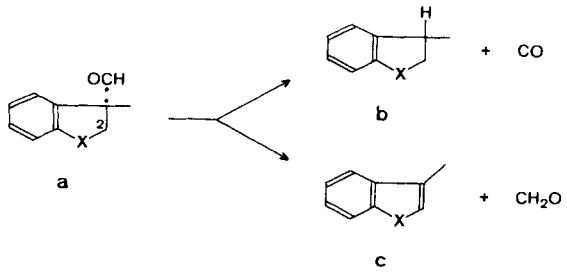
Solvent	Viscosity η	Φ_{rel} (**7** → **30**)
Pentane	0.24	1.0
Methanol	0.59	0.36
Benzene	0.65	0.76
Cyclohexane	1.02	1.0
Acetone	1.3	0.5
n-Tetradecane	2.18	0.53
Isopropyl alcohol	2.3	0.53
Cyclohexanol	68	0.75

[a] Degassed 0.058 M solutions. Irradiation at ≥3130 Å and 25° in a turn-table reactor.

reliable than in the other series. On irradiation of **10** in degassed solution formation of **36** as the only soluble product[6]) was observed, and the decarbonylation of **10**-d resulted in full retention of the deuterium in **36**-d (hydrogen/deuterium isotope effect 1.05 for **10**/**10**-d).

The quantum yields of decarbonylation of the aldehydes **8** and **9** reveal a similar, yet more pronounced, trend in their dependence on wavelength (Table 3) to that of the aliphatic phenyl aldehyde **4** [6], with about unit efficiency at 3130 Å. As yet inexplicably, the indanyl aldehyde **7** exhibits clearly a reversed dependence, *viz.* a greater quantum yield on aromatic $\pi \rightarrow \pi^*$ excitation at 2537 Å than on $n \rightarrow \pi^*$ excitation at longer wavelength.

The appearance of a second path in the photolytic decomposition of the heterocyclic aldehydes **8** and **9**, in contrast to the uniform decarbonylation of **7** to the methylindan **30**, provides a further independent indication of intermediate radical pairs (*cf.* **a**) in the photodecarbonylation. The formation of the product pairs **32**/**33** and **34**/**35**, respectively, evidently reflects the competition between the disproportionation of such radical pairs **a** to products **b** and carbon monoxide on the one hand, and to products **c** and formaldehyde on the other. While the former, inherently more efficient, process (**a** → **b**) is observed as the exclusive mode of disproportionation in the indan system (and in the indoline system for which the estimation of the products



however, is less satisfactory), it is plausible that heteroatoms in **a** (X = O or S) facilitate sufficiently the removal of atomic hydrogen from position C(2) to induce the additional decomposition **a** → **c**.

Table 3. *Quantum Yields of the Photodecarbonylation of Aldehydes* **7**–**9**[a])

Aldehyde	Conversion	Φ at	
		2537 Å	3130 Å
7	7.4%	0.70	
7	13.5%		0.43
8	23.8%	0.48	
8	60.9%		1.03
9	24.4%	0.17	
9	68.9%		0.90

[a]) Quantum yields of aldehyde conversion (estimated error ± 0.08) in degassed 0.1 M pentane solutions, determined by potassium ferrioxalate actinometry [14].

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Experimental Part

General Remarks. – Unless stated otherwise, the *working up* of crude reaction mixtures involved extraction with ether, washing of the organic layer with H_2O or satd. aqueous NaCl solution to the neutral point, drying over anhydrous $MgSO_4$, and removal of solvent by distillation over a 25 cm *Vigreux* column at normal pressure (for indan and dihydrobenz[*b*]furan 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. *Refractive indices* were measured on a *Zeiss* refractometer.

Gas chromatograms (VPC.) were run on *Varian-Aerograph* A-90P3 models, using $10' \times 1/4''$ and $10' \times 3/8''$ columns (unless stated otherwise) and the following internal references: *n*–$C_{14}H_{28}$ for indan, *n*–$C_{15}H_{32}$ for dihydrobenzo[*b*]furan and indoline, and *n*–$C_{12}H_{26}$ for dihydrobenzo[*b*]-thiophene derivatives.

UV. spectra: λ_{max} are given in nm (ε values in parantheses). – *IR. spectra:* λ_{max} in cm^{-1}. – *NMR. spectra:* at 60 or 100 MHz. Chemical shifts are given in δ values, with $(CH_3)_4Si$ as internal standard. Abbreviations: *s* (singlet), *d* (doublet), *t* (triplet), and *q* (quartet) for first order 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. – *Mass spectra* (MS.) were run on *Hitachi-Perkin-Elmer* RMU-6A and RMU-6D instruments. The first mass given corresponds to the molecular ion, and the base peak is printed in italics.

UV.-Irradiations (see also footnotes to Table 1): The solutions were irradiated at room temperature in Pyrex (for wavelengths > 3000 Å) or quartz tubes (for 2537 Å) placed in a turntable reactor equipped with a magnetic stirrer and either a low-pressure mercury lamp (NK 6/20, *Quarzlampen GmbH*, Hanau; main emission at 2537 Å) in a water-cooled quartz jacket or a 125-W medium pressure mercury lamp (QM 125, *Meda Licht AG*, Basel) in a double-mantle Pyrex jacket. The inner mantle served for cooling with water, and the outer mantle (path length 15 mm) contained filter solutions for the following wavelength regions: ≥3130 Å (4.4 g KH-phthalate per liter H_2O; 0% transmission at 3000 Å, 94% at 3100 Å), >3270 Å (neat acetone; 0% transmission at 3200 Å, 50% at 3270 Å), >3400 Å (750 g NaBr + 8 g $Pb(NO_3)_2$ per liter H_2O; 0% transmission at 3400 Å, 94% at 3600 Å).

Syntheses of Aldehydes 7(-d)–10(-d). – *Methyl Indan-1-carboxylate* (**12**). 5 g Methyl 1-indene-1-carboxylate (**11**) [8] were hydrogenated on 1.25 g 10% Pd/charcoal in 100 ml C_2H_5OH. After uptake of 1 mole-equivalent of H_2, CH_2Cl_2 was added, the mixture filtered through celite, and the solvent evaporated *in vacuo* at 40°. Filtration through neutral Al_2O_3 (activity III) gave **12** (liquid; quantitative yield) which distilled at 115°/7 Torr. $n_D^{21.8} = 1.5280$. UV.: 260 (500), 266 (840), 273 (920). IR. (film): 755, 985, 1480, 1740, 2840. NMR. ($CDCl_3$): 2.1–2.6/*m*, H_2–C(2); 2.8–3.3/*m*, H_2–C(3); 3.69/*s*, H_3C–O; 4.1/*dd*, *J* = 7 and 14, H–C(1); 6.85–7.5/*m*, arom. H. MS.: 176 ($C_{11}H_{12}O_2$), *117*.

Methyl 1-Methyl-indan-1-carboxylate (**13**). 1.8 g (37.5 mmol) 50% NaH dispersion was freed from mineral oil with anhydrous petroleum ether and then added to 6.25 g (44 mmol) CH_3J in 20 ml dimethylformamide under N_2. A solution of 3.79 g (21.5 mmol) **12** in 25 ml dimethylformamide was dropped into the mixture with stirring and external water-cooling. The reaction mixture was stirred overnight at room temperature and then poured onto a mixture of ether, ice, and satd. $NaHCO_3$ solution. Working up was followed by distillation of the crude product (4.06 g of a slightly colored liquid which was essentially pure **13** according to IR. and VPC. [SE–30, 211°]) at 84°/7 Torr. IR. (film): 762, 1377, 1480, 1735, 2830. NMR. (CCl_4): 1.49/*s*, H_3C–C(1); 1.6–3.2/*m*, H_2–C(2) and H_2C–(3); 3.54/*s*, H_3C–O; 6.9–7.35/*m*, arom. H. MS.: 190 ($C_{12}H_{14}O_2$), *131*.

1-Hydroxymethyl-1-methyl-indan (**14**). 2.6 g (13.7 mmol) **13** were reduced with 800 mg $LiAlH_4$ in 20 ml boiling anhydrous ether for 2.5 h. After the excess hydride had been destroyed by the addition of dilute H_2SO_4, working up gave 2.5 g of a colourless liquid which distilled at 120°/8 Torr. VPC.: SE–30, 216°. $n_D^{21.5} = 1.5443$. IR. (film): 729, 761, 1480, 3360 (broad), 3550. NMR.

($CDCl_3$): 1.23/*s*, H_3C—(1); 1.5–2.4 and 2.75–3.05/2 *m*, H_2—C(2) and H_2—C(3); 3.46/s, H_2C—C(1); 7.0–7.2/*m*, arom. H. MS.: 162 ($C_{11}H_{14}O$), 144, *131*.

1-(Hydroxy-dideuteriomethyl)-1-methyl-indan (**14**-*d*). **13** was reduced with $LiAlD_4$ in place of $LiAlH_4$ as described above. $n_D^{22.3}$ = 1.5438. IR. (film): 725, 760, 770, 978, 1480, 2084, 2200, 3370 (broad), 3550. NMR. ($CDCl_3$): 1.23/*s*, H_3C—C(1); 1.5–2.4 and 2.8–3.05/2 *m*, H_2—C(2) and H_2—C(3); 7.0–7.2/*m*, arom. H. MS.: 164 ($C_{11}H_{12}D_2O$), *131* (100% d_2).

1-Formyl-1-methyl-indan (**7**). 1.3 g (8.02 mmol) **14** were dissolved in 24.4 ml $(CH_3)_2SO$ and 16.2 ml Ac_2O. After stirring at room temperature in the dark under N_2 for 26 h, 80 ml saturated aqueous Na_2CO_3 solution were added portionwise with external cooling. Stirring was continued for another hour before the mixture was poured onto pentane and worked up. Distillation of the crude product mixture (2.0 g) gave at ca. 40°/10 Torr *methyl acetoxymethyl sulfide* [IR. (film): 965, 1015, 1025, 1220, 1373, 1751] and at 120–140°/7 Torr a mixture of the following products which were isolated by VPC. (SE–30, 214°):

1) 34% *Starting material* **14**.

2) 9% *1-Acetoxymethyl-1-methyl-indan*. IR. (film): 762, 1240, 1480, 1745. NMR. ($CDCl_3$): 1.33/*s*, H_3C—C(1); 1.6–2.4/*m*, H_2—C(2); 2.03/*s*, H_3C—CO; 2.8–3.1/*m*, H_2—C(3); 4.08/*s*, H_2C—C(1); 7.18/*s*, arom. H. MS.: 204 ($C_{13}H_{16}O_2$), 164, *131*.

3) 34% *1-Methyl-1-(methylthiomethoxy-methyl)-indan*. IR. (film): 682, 732, 762, 1072, 1084. NMR. ($CDCl_3$): 1.30/*s*, H_3C—C(1); 1.5–2.5/*m*, H_2—C(2); 2.04/*s*, H_3C—S; 2.8–3.1/*m*, H_2—C(3); 3.50/*s*, H_2C—C(1); 4.60/*s*, H_2C—O,S; 7.17/*s*, arom. H. MS.: 222 ($C_{13}H_{18}OS$; weak), 174, 145, *131*. Acid-catalyzed hydrolysis (conc. HCl in CH_3OH) of this product furnished quantitatively the alcohol **14**.

4) 23% *1-Formyl-1-methyl-indan* (**7**). UV. (iso-octane): 261.5 (648; shoulder), 267 (885), 273.5 (880), ca. 300 (200; broad). IR. (film): 762, 1480, 1730, 2700. NMR. ($CDCl_3$): 1.40/*s*, H_3C—C(1); 1.6–2.15 and 2.37–2.8/2 *m*, H_2—C(2); 2.88–3.18/*m*, H_2C—C(3); 7.1–7.3/*m*, arom. H; 9.51/*s*, CHO. MS.: 160 ($C_{11}H_{12}O$), *131*[7]).

2,4-Dinitrophenylhydrazone of **7**: m.p. 146.5–148° (3 × cryst. from CH_2Cl_2—CH_3OH).

$C_{17}H_{16}O_4N_4$ Calc. C 59.99 H 4.74 N 16.47% Found C 59.84 H 4.88 N 16.30%

1-Deuterioformyl-1-methyl-indan (**7**-d). Oxidation of **14**-d with $(CH_3)_2SO$ and Ac_2O as described above furnished the following products (60 h reaction time):

1) ~1% *1-(Acetoxy-dideuteriomethyl)-1-methyl-indan*. IR. (film): 729, 760, 769, 1260, 1480, 1740, 2110, 2230.

2) 40% *1-Methyl-1-(methylthiomethoxy-dideuteriomethyl)-indan*. IR. (film): 684, 735, 761, 1054, 1074, 1090, 1098, 2073, 2175.

3) 14% *1-Deuterioformyl-1-methyl-indan* (**7**-*d*). UV. (iso-octane): 261.5 (630; shoulder), 267 (860), 273.5 (860), ca. 295 (220). IR. (film): 767, 1480, 1720, 2055, 2110. MS.: 161 ($C_{11}H_{11}DO$), *131* (100% d_1).

2,3-Dihydro-benzo[b]*furan-3-carboxylic acid* (**16**). 4.487 g (28.3 mmol) of benzo[*b*]furan-3-carboxylic acid (**15**) [9] were hydrogenated in an autoclave for 3 h at 45° and 3 at. H_2 on 630 mg Pd-on-charcoal[8]) in 550 ml C_2H_5OH. After filtration of the solution and evaporation of the solvent *in vacuo*, crystallization of the crude product from ether gave 4.422 g **16**. M.p. 95–97°. B.p. 150°/0.5 Torr. UV.: 282 (4160). IR. ($CHCl_3$): 1471, 1482, 1598, 1610, 1715, ca. 3300–2500 (broad), 3500. NMR. ($CDCl_3$): 4.3–5.02/*m*, H_2—C(2) and H—C(1); 6.8–7.5/*m*, arom. H. MS.: 164, 119, *91*.

$C_9H_8O_3$ Calc. C 65.85 H 4.91% Found C 65.86 H 4.89%

Methyl 2,3-Dihydrobenzo[b]*furan-3-carboxylate* (**17**). 4.42 g (27 mmol) **16** in 50 ml anhydrous CH_3OH were esterified with an excess of CH_2N_2 in ether. Evaporation of the solvent and distilla-

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[7]) In runs with ca. 100 mg of alcohol **14** and similar reaction times, the yields of aldehyde **7** were nearly doubled (*e.g.*, 7% **14**, 2% acetoxy compound, 50% methylthiomethoxy derivative, and 41% **7**).

[8]) When 10% Pd-on-charcoal was used, only a few percent of the acid **16** and 24% of its ethyl ester were formed. Similarly, hydrogenation of **15** in CH_3OH on 10% Pd catalyst gave 49% of the methyl ester **17** and insoluble materials.

tion of the crude oil gave 4.75 g **17**. B.p. 110°/0.5 Torr. UV.: 282 (2600). IR. (film): 751, 975, 1482, 1599, 1610, 1739, 2835. NMR. (CCl_4): 3.73/*s*, H_3C—O; 4.15–4.05/*m*, H_2—C(2) and H—C(1); 6.65–7.3/*m*, arom. H. MS.: 178, 119, *91*.

$C_{10}H_{10}O_3$ Calc. C 67.40 H 5.66 O 26.94% Found C 67.44 H 5.70 O 27.09%

Methyl 2,3-Dihydro-3-methylbenzo[b]*furan-3-carboxylate* (**18**). 561 mg (11.7 mmol) of 50% NaH dispersion were washed with petroleum ether in order to remove the mineral oil, and then covered with 30 ml of anhydrous tetrahydrofuran. Under vigorous stirring and external cooling solutions of 2.5 g (17.7 mmol) CH_3J and 2.0 g (11.3 mmol) **17**, each in 15 ml tetrahydrofuran, were simultaneously added dropwise. After the evolution of hydrogen had ceased, the mixture was stirred for 0.5 h, then poured onto icecooled aqueous NH_4Cl solution and extracted with ether. The organic layer was washed with satd. aqueous $Na_2S_2O_3$ solution. Working up yielded, after distillation, **1.**97 g **18**. B.p. 85°/0.2 Torr. UV.: 282 (2837). IR. (film): 752, 835, 985, 1481, 1598, 1735, 2830. NMR. ($CDCl_3$): 1.70/*s*, H_3C—C(3); 3.80/*s*, H_3C—O; 4.32+5.13/*AX* pattern, J = 9, H_2—C(3); 6.8–7.4/*m*, arom. H. MS.: 192, *133*, 105.

$C_{11}H_{12}O_3$ Calc. C 68.73 H 6.29 O 24.97% Found C 68.74 H 6.36 O 25.10%

2,3-Dihydro-3-hydroxymethyl-3-methyl-benzo[b]*furan* (**19**). A solution of 1.232 g (6.42 mmol) **18** in 10 ml anhydrous ether was slowly added under stirring to 4.94 mg (13 mmol) $LiAlH_4$ in 20 ml ether. After 1.5 h refluxing the mixture was poured onto satd. aqueous *Seignette* salt solution. Working up gave 974 mg of an amorphous solid which liquefied at 58°. B.p. 100°/0.2 Torr. UV.: 280 (2133). IR. ($CHCl_3$): 832, 975, 1460, 1480, 1600, 1610, 3600. NMR. ($CDCl_3$): 1.42/*s*, H_3C—C(3); 3.60+3.68/*AB* pattern, J = 11, H_2C—C(3); 4.21+4.61/*AX* pattern, J = 8.5, H_2—C(2); 6.8–7.3/*m*, arom. H. MS.: 164 ($C_{10}H_{12}O_2$), *133*, 105.

2,3-Dihydro-3-(hydroxy-dideuteriomethyl)-3-methyl-benzo[b]*furan* (**19**-d). Reduction of ester **18** with $LiAlD_4$ gave an amorphous solid which liquefied at 56–58°. B.p. 108°/0.3 Torr. IR. ($CHCl_3$): 835, 972, 1460, 1480, 1600, 1610, 2090, 2195, 2310, 3600. NMR. ($CDCl_3$): 1.33/*s*, H_3C—C(3); 4.12+4.53/*AX* pattern, J = 8.5, H_2—C(2); 6.7–7.3/*m*, arom. H. MS.: 166 ($C_{10}H_{11}DO_2$), *133*, 105 (100% d_2).

2,3-Dihydro-3-formyl-3-methyl-benzo[b]*furan* (**8**). 2.345 g (14.1 mmol) of alcohol **19** were dissolved in 25 g anhydrous $(C_2H_5)_3N$ and 50 ml anhydrous $(CH_3)_2SO$ were added. During 0.5 h a solution of 25 g pyridine-SO_3 complex in 100 ml $(CH_3)_2SO$ was dropped into the vigorously stirred mixture in the dark. Stirring was continued for 3 h before 1 l H_2O was added. Extraction with ether and washing of the organic layer with 2N H_2SO_4 was followed by the usual working up which, after distillation of the crude product, gave 2.102 g of a colorless oil (b.p. 85–90°/0.3 Torr) containing traces of $(C_2H_5)_3N$ separable from **8** by VPC. (SE—30/200°). UV.: 255 (138), 282 (2752), 300–330 (broad, 200–100). IR. (film): 751, 835, 980, 1460, 1480, 1598, 1610, 1726, 2700. NMR. ($CDCl_3$): 1.46/*s*, H_3C—C(3); 4.21+4.95/*AX* pattern, J = 9, H_2—C(2); 6.7–7.35/*m*, arom. H.; 9.60/*s*, CHO. MS. = 162, 133, *105*.

$C_{10}H_{10}O_2$ Calc. C 74.05 H 6.22 O 19.73% Found C 73.85 H 6.37 O 19.97%

2,4-Dinitrophenylhydrazone of **8**: m.p. 171–172°.

$C_{16}H_{14}N_4O_5$ Calc. C 56.14 H 4.12 N 16.37 O 23.37%
Found ,, 55.99 ,, 4.17 ,, 16.52 ,, 23.51%

2,3-Dihydro-3-deuterioformyl-3-methyl-benzo[b]*furan* (**8**-*d*). Oxidation as above of alcohol **19**-d gave **8**-d. B.p. 110–120°/0.1 Torr. IR. (film): 750, 835, 980, 1460, 1480, 1595, 1609, 1710, 2060, 2102, 2121. NMR. ($CDCl_3$): 1.50/*s*, H_3C—C(3); 4.29+5.02/*AX* pattern, J = 9.5, H_2—C(2); 6.75–7.4/*m*, arom. H. MS.: 163 ($C_{10}H_9DO_2$), 133, *105* (98% d_1).

Methyl 2,3-Dihydrobenzo[b]*thiophene-3-carboxylate* (**21**). 8.34 g (46.4 mmol) of 2.3-dihydrobenzo[*b*]thiophene-3-carboxylic acid (**20**) [15] were dissolved in 50 ml CH_3OH and esterified with an excess of CH_2N_2. Distillation of the crude oil at 110°/0.5 Torr gave 9.18 g **21**. IR. ($CHCl_3$): 1502, 1508, 1585, 1725 (broad), 2840. NMR. ($CDCl_3$): 3.25–3.9/*m*, H_2—C(2); 3.73/*s*, H_3C—O; 4.2–4.45/*m*, H—C(1); 6.85–7.5/*m*, arom. H. MS.: 196, 194, 137, *135*, 91.

$C_{10}H_{10}O_2S$ Calc. C 61.85 H 5.19 O 16.47 S 16.51%
Found ,, 62.00 ,, 5.07 ,, 16.74 ,, 16.22%

Methyl 2,3-Dihydro-3-methyl-benzo[b]*thiophene-3-carboxylate* (**22**). 110.8 mmol NaH, obtained by removing the mineral oil from 5.32 g 50% NaH dispersion with petroleum ether, were covered with anhydrous tetrahydrofuran and cooled to 0°. After addition of 10 g (70.4 mmol) CH_3J, a solution of 10.3 g (53.8 mmol) **21** in 30 ml tetrahydrofuran was added dropwise over 1 h with vigorous stirring under N_2, followed by the addition of another 5 g (35.2 mmol) CH_3J. The mixture was stirred for 2 h at room temperature, then poured onto cold satured aqueous NH_4Cl solution and extracted with ether. Washing of the extract with saturated aqueous $Na_2S_2O_3$ solution and working up gave a crude oil which distilled at 82–85°/0.07 Torr (8.7 g). UV.: 249 (6481), 289 (1966, broad shoulder). IR. (film): 750, 980, 1460, 1585, 1730. NMR. ($CDCl_3$): 1.60/*s*, H_3C—C(3); 3.70/*s*, H_3C—O; 3.15+3.97/*AX* pattern, $J = 11$, H_2—C(2); 6.9–7.3/*m*, arom. H. MS.: 210, 208, 151, *149*, 136, 134.

$C_{11}H_{12}O_2S$ Calc. C 63.45 H 5.81 S 15.37% Found C 63.36 H 5.96 S 15.37%

2,3-Dihydro-3-hydroxymethyl-3-methyl-benzo[b]*thiophene* (**23**). To a refluxing solution of 1.99 g (52.5 mmol) $LiAlH_4$ in 100 ml ether 5.213 g (25.06 mmol) **22** in 30 ml ether were added with stirring. Refluxing was continued for 1 h before the mixture was cooled and poured onto cold saturated aqueous *Seignette* salt solution. The working up and distillation of the crude product at 110°/0.06 Torr afforded 4.423 g **23**; m.p. 62–64.5°. UV.: 249 (8060), ca. 258 (6537, shoulder), ca. 290 (1880, broad shoulder). IR. ($CHCl_3$): 960, 1443, 1465, 1590, 3600. NMR. ($CDCl_3$): 1.35/*s*, H_3C—C(3); 3.10+3.40/*AB* pattern, $J = 11$, H_2—C(2); 3.50+3.62/broadened *AB* pattern, $J = 11$, H_2C—C(3); 7.0–7.25/*m*, arom. H. MS.: 182, 180, 151, *149*, 136, 134.

$C_{10}H_{12}OS$ Calc. C 66.65 H 6.71 S 17.79% Found C 66.54 H 6.79 S 17.65%

2,3-Dihydro-3-(hydroxy-dideuteriomethyl)-3-methyl-benzo[b]*thiophene* (**23**-*d*). The ester **22** was reduced to **23**-d with $LiAlD_4$, in place of $LiAlH_4$, as described above; m.p. 64°, b.p. 125–130°/0.08 Torr. IR. ($CHCl_3$): 969, 1441, 1462, 1588, 2080, 2195, 3600. NMR. ($CDCl_3$): 1.37/*s*, H_3C—C(3); 3.10+3.40/*AB* pattern, $J = 11$, H_2—C(2); 6.95–7.3/*m*, arom. H. MS.: 184, 182 ($C_{10}H_{10}D_2OS$), 151, *149*, 136, 134, (96,1% d_2).

2,3-Dihydro-3-formyl-3-methyl-benzo[b]*thiophene* (**9**). A solution of 41 g pyridine-SO_3 complex in 200 ml anhydrous $(CH_3)_2SO$ was slowly dropped into 4.181 g (23.2 mmol) **23** in 40 g of anhydrous $(C_2H_5)_3N$ and 15 ml $(CH_3)_2SO$ in the dark, with vigorous stirring and external cooling. Stirring was continued for 3 h at room temperature before 1 l H_2O was added and the mixture was extracted with ether. The extract was washed with 2N H_2SO_4 and worked up to yield 3.427 g **9** after distillation at 75°/0.1 Torr. The sample contained traces of $(C_2H_5)_3N$ which were removed by VPC. (SF–96, 200°). UV.: 251 (5856), ca. 260 (4850, shoulder), ca. 284 (1460, broad shoulder). IR. (film): 751, 833, 1442, 1460, 1584 ,1725, 2690. NMR. ($CDCl_3$): 1.45/*s*, H_3C—C(3); 3.15+3.78/*AB* pattern, $J = 11.5$, H_2—C(2); 6.85–7.25/*m*, arom. H.; 9.43/*s*, CHO. MS.: 180, 178, 151, *149*, 136, 134.

$C_{10}H_{10}OS$ Calc. C 67.38 H 5.66 S 18.00% Found C 67.52 H 5.58 S 17.87%

2,4-Dinitrophenylhydrazone of **9**: m.p. 129–130° (dec.).

$C_{16}H_{14}N_4O_4S$ Calc. C 53.63 H 3.94 N 15.64% Found C 53.26 H 3.94 N 15.56%

2,3-Dihydro-3-deuterioformyl-3-methyl-benzo[b]*thiophene* (**9**-d). The dideuterioalcohol **23**-d was oxidized as described above. IR. (film): 751, 809, 1442, 1461, 1585, 1713, 2050, 2100. NMR. ($CDCl_3$): 1.48/*s*, H_3C—C(3); 3.20+3.80/*AB* pattern, $J = 11.5$, H_2—C(2); 7.0–7.25/*m*, arom. H. MS.: 181, 179 ($C_{10}H_9DOS$), 151, *149*, 136, 134 (100% d_1).

Indoline-3-carboxylic acid (**25**). 14.5 g (0.63 mol) Na were rapidly added in small pieces to a boiling solution of 7.8 g (48 mmol) indole-3-carboxylic acid (**24**) [10] in 145 ml anhydrous C_2H_5OH. 100 ml H_2O were added to the clear solution, the alcohol was removed by distillation *in vacuo*, and the aqueous solution extracted with ether in order to remove contaminating indole. After neutralization of the aqueous layer with conc. HCl and acidification with CH_3COOH, the precipitate was filtered off. 5.2 g of **25** crystallized from the filtrate upon standing at ca. 4°; m.p. 180–181° (dec.). The mother liquor was saturated with NH_4Cl and exhaustively extracted with ether in a *Kutscher-Steudel* extractor to yield another 980 mg **25**. Recristallization from 40% aqueous C_2H_5OH and sublimation at 140–150°/0.1 Torr gave an analytical sample of m.p. 181–182°.

UV.: 243 (8300), 294 (3800). IR. (KBr): 595, 760, 1469, broad structured bands between 1500–1700 and 1800–3500. NMR. (CD_3OD): ca. 3.3+3.6–3.85+4.0–4.3+6.6–7.4/4 *m*. MS.: 163, *118*, 90, 44.

$C_7H_9NO_2$ Calc. C 66.24 H 5.56 N 8.58% Found C 66.11 H 5.64 H 8.59%

Methylation of **25**. a) *With* CH_2N_2. 300 mg **25** were dissolved in CH_3OH and treated with ethereal CH_2N_2. After the esterification was complete according to TLC. (C_6H_6/C_2H_5OH 10:1), the solvents were evaporated and the residual mixture was separated by preparative TLC. (petroleum ether/ethyl acetate 5:1) into the following products:

1) 125 mg *Methyl indoline-3-carboxylate* (**26**). IR. (film): 750, 960, 1200, 1435, 1465, 1490, 1620, 1735, 3365. UV.: 243 (5250), 297 (1780). NMR. ($CDCl_3$): 3.6–4.2/*m*, H_2—C(2) and H—C(3); 3.75/*s*, H_3C—O; 6.5–7.5/*m*, arom. H. MS.: 177 ($C_8H_{11}NO_2$), 144, *118*, 91.

2) 89 mg *Methyl 1-methylindoline-3-carboxylate* (**27**). IR. (film): 750, 1200, 1260, 1495, 1608, 1740, 2840. NMR. ($CDCl_3$): 2.80/*s*, H_3C—N; 3.4–4.0/*m*, H_2—C(2) and H—C(3); 3.8/*s*, H_3C—O; 6.4–7.4/*m*, arom. H. MS.: 191 ($C_9H_{13}NO_2$), 158, *132*, 117, 91.

b) *With* $CH_3OH/SOCl_2$. 600 mg (5 mmol) $SOCl_2$ were slowly dropped into 2 ml anhydrous CH_3OH at $-15°$ before 163 mg (1 mmol) solid **25** were added. The mixture was stirred overnight while letting it warm up to room temperature. Slow addition of 2 g (20 mmol) $(C_2H_5)_3N$ was followed by working up with H_2O/ether to afford 128 mg pure **26**.

Methyl 1,3-Dimethylindoline-3-carboxylate (**28**). a) *From 27*. A solution of 100 mg (0.56 mmol) **27** in 2 ml anhydrous ether/dimethylformamide 1:1 was added to a mixture of 30 mg (0.62 mmol) NaH (from a 50% suspension in mineral oil which had been removed previously with petroleum ether) and 90 mg (0.62 mmol) CH_3J in 2 ml ether/dimethylformamide 1:1 under N_2. After stirring overnight at room temperature the reaction mixture was poured onto satd. aqueous $NaHCO_3$ solution and ice. Extraction with ether and purification of the crude product by preparative TLC. (petroleum ether/ethyl acetate 5:1) gave 76 mg **28**. UV.: 254 (7800), 305 (2400). IR. (film): 750, 1495, 1608, 1735. NMR. ($CDCl_3$): 1.55/*s*, H_3C—C(3); 2.80/*s*, H_3C—N; 3.10+3.90/*AB* pattern, $J = 9.5$, H_2—C(2); 3.70/*s*, H_3C—O; 6.4–7.3/*m*, arom. H. MS.: 205, *146*, 131.

$C_{12}H_{15}NO_2$ Calc. C 70.22 H 7.37 N 6.82% Found C 70.43 H 7.41 N 6.55%

b) *From* **26**. Methylation of 300 mg (1.7 mmol) **26** with 700 mg (4 mmol) CH_3J and 200 mg (4 mmol) NaH (from a 50% suspension in mineral oil which had been removed previously with petroleum ether) for 4 days in 10 ml refluxing anhydrous ether and working up with satd. aqueous NH_4Cl solution/ice/ether afforded 265 mg of an oil which proved to be identical with **28** by TLC. (petroleum ether/ethyl acetate 5:1) and IR.

A similar run in boiling tetrahydrofuran gave 81% **28** after 2 h.

1,3-Dimethyl-3-hydroxymethyl-indoline (**29**). A solution of 2.4 g (11.8 mmol) **28** in 10 ml anhydrous ether was slowly dropped into 285 mg (7.1 mmol) $LiAlH_4$ in 10 ml ether. The mixture was refluxed for 1 h, then poured onto 50 ml satd. aqueous *Seignette* salt solution and extracted with ether. Chromatography of the crude reaction product on silicagel with petroleum ether/ethyl acetate 2:1 yielded 660 mg starting material **28** and 400 mg **29**. UV.: 255 (8500), 301 (2400). IR. (film): 745, 1260, 1495, 1608, 3350 (broad). NMR. ($CDCl_3$): 1.32/*s*, H_3C—C(3); 2.75/*s*, H_3C—N; 2.95+3.40/*AB* pattern, $J = 9$, H_2—C(2); 3.60/*s*, H_2C—C(3); 6.4–7.3/*m*, arom. H. MS.: 177 ($C_{11}H_{13}NO$), *146*, 131.

1,3-Dimethyl-3-(hydroxy-dideuteriomethyl)-indoline (**29**-*d*). Reduction of **28** using $LiAlD_4$, in place of $LiAlH_4$, as described for **29** gave, after column chromatography, **29**-d.

1,3-Dimethyl-3-formyl-indoline (**10**). 360 mg (2 mmol) **29** in 5 ml $(CH_3)_2SO$ were added to a mixture of 5 ml $(CH_3)_2SO$, 1.05 g (6.6 mmol) pyridine—SO_3 complex, and 3.3 g (33 mmol) $(C_2H_5)_3N$. The mixture was stirred for 3 h in the dark at room temperature, then treated with 50 ml 1 N HCl and extracted with ether. Chromatography of the crude product on silicagel with petroleum ether/ethyl acetate 2:1 gave 93 mg **10**. UV.: 252 (5760), 300 (1590). IR. (film): 740, 755, 1495, 1608, 1725, 2700. NMR. ($CDCl_3$): 1.44/*s*, H_3C—C(3); 2.78/*s*, H_3C—N; 3.12+3.80/*AB* pattern, $J = 9$, H_2—C(2); 6.4–7.4/*m*, arom. H; 9.50/*s*, CHO. MS.: 175 ($C_{11}H_{13}NO$), *146*, 131, 771.

3-Deuterioformyl-1,3-dimethyl-indoline (**10**-*d*). Oxidation of **29**-d and working up as described for **29** → **10** gave **10**-d. MS.: 100% d_1.

UV.-Irradiation of 1-Formyl-1-methyl-indan (7) and 1-Deuterioformyl-1-methyl-indan (7-d): – See Table 1 for the results of direct irradiations of **7** and **7**-d. The mixture of *1-methylindan* (**30**) [16] and *1-methylindene* (**31**) [17] was analyzed by VPC. on a 20% SF-96 column at 160°.

1-Deuterio-1-methyl-indan (**30**-d). IR. (film): 737, 753, 1376, 1482, 2105, ca. 2150 (broad). NMR. (CCl_4): 1,27/*t*, *J* = 0,9, H_3C—C(1).

Dependence of Decarbonylation Efficiency on Solvent. 0.06 M Solutions of **7** in various solvents were degassed and simultaneously irradiated at ≥3130 Å in a turn-table reactor; see Table 2 for the results.

Attempted Triplet Quenching. The photodecarbonylation of **7** in neat degassed 1,3-pentadiene at ≥3130 Å proceded essentially at the same rate as a parallel run in pentane, but only ca. 75% of the theoretical amount of product **30** was formed at 60% conversion of aldehyde.

Two degassed pentane solutions, which contained a) 0.052 M **7** and b) 0.052 M **7** + 0.236 M 1,3-cyclohexadiene, were simultaneously photolyzed at ≥3130 Å in a turn-table reactor. After 2 h, 63% and 68% of **7**, respectively, had reacted.

Triplet Sensitization. a) *With Acetophenone.* Degassed solutions of a) 0.0032 M **7** and b) 0.0032 M **7** + 0.13 M acetophenone in pentane were simultaneously irradiated at >3400 Å in a turn-table reactor. At 5% conversion to 100% **30** in run a), the aldehyde in run b) had completely reacted to give a mixture of products among which **30** and **31** were identified in very small amounts only.

b) *With Benzophenone.* The photolysis of degassed solutions of a) 0.018 M **7** and b) 0.018 M **7** + 0.45 M benzophenone in benzene at >3270 Å in a turn-table reactor resulted in a 14% conversion of **7** into **30** (run a) and a 100% conversion of **7** into several products including traces of **30** and **31** (run b).

Quenching of Photolytic Benzpinacol Formation from Benzophenone by **7**. Two degassed *t*-butyl alcohol solutions of a) 0.204 M benzophenone + 0.081 M benzhydrol and b) 0.207 M benzophenone + 0.070 M benzhydrol + 0.033 M **7** were simultaneously irradiated for 14 h at >3270 Å in a turn-table reactor. The yields of benzpinacol were a) 295.5 mg and b) 163.5 mg.

UV.-Irradiation of 2,3-Dihydro-3-formyl-3-methyl-benzo[*b*]furan (8) and 2,3-Dihydro-3-deuterioformyl-3-methyl-benzo[*b*]furan (8-d). – See Table 1 for the results of direct irradiations of **8** and **8**-d. The product mixtures of *2,3-dihydro-3-methyl-benzo*[b]*furan* (**32**) and *3-methyl-benzo*[b]*furan* (**33**) [18] were inseparable by VPC. and were analyzed by NMR.

For comparative purposes, **32** was prepared as follows: 2 g (15.1 mmol) **33** were hydrogenated in an autoclave on 500 mg 10% Pd-charcoal catalyst in 400 ml CH_3OH for 5 h at 55° and 5 at. H_2. Distillation of the crude product at 60°/0.5 Torr gave 800 mg **32**. UV.: 283 (2765), ca. 287 (2050, shoulder). IR. (film): 750, 835, 965, 1225, 1460, 1481, 1600, 1610. NMR. ($CDCl_3$): 1.29/*d*, *J* = 7, H_3C—C(3); 3.48/six broadened lines, H—C(3); 4.01 + 4.61/2 '*t*', H_2—C(2); 6.65–7.15/*m*, arom. H. MS.: 134 ($C_9H_{10}O$), *119*, 91.

The composition of the product in irradiation run no. 8 (Table 1) remained unchanged during the fivefold period required for full photochemical conversion.

Attempted Triplet Quenching. 0.052 M Solutions of **8** in pentane, which contained a) 0 M, b) 0.163 M, and c) 0.3 M 1,3-cyclohexadiene, were degassed and irradiated in a turn-table reactor at >3270 Å. After 3 h, the aldehyde conversions were a) 10%, b) 12%, and c) 10%. Photodimerization of the diene was not observed in runs b) and c).

Also no quenching effect was found in a similar series of runs (hexane solution) with 0.11 M naphthalene.

Triplet Sensitization. A degassed pentane solution of 0.12 M **8** and 0.14 M acetophenone was photolyzed at >3400 Å to full conversion. The product mixture was composed of only small amounts of **32** and **33** and several unidentified products in larger quantities according to VPC.

Two degassed benzene solutions of a) 0.02 M **8** and b) 0.02 M **8** + 0.35 M benzophenone were irradiated for 3 h in a turn-table reactor at >3270 Å. The aldehyde conversion in run a) was 22.5% (→**32** + **33**). In run b) 94% of **8** were transformed but only gave traces of **32** and **33**. Among the remaining unidentified products no benzpinacols could be found by MS.

Quenching of Photolytic Benzpinacol Formation from Benzophenone by **8**. Two degassed *t*-butyl alcohol solutions of a) 0.206 M benzophenone + 0.152 M benzhydrol + 0.058 M **8** were irradiated in a turn-table reactor for 24 h at >3270 Å. The yields of benzpinacol were a) 238.5 mg and b) 73.1 mg.

UV.-Irradiation of 2,3-Dihydro-3-formyl-3-methyl-benzo[*b*]thiophene (9) and 2,3-Dihydro-3-deuterioformyl-3-methyl-benzo[*b*]thiophene (9-d): – See Table 1 for the results of direct irradiations of **9** and **9**-d. The mixture of products *2,3-dihydro-3-methyl-benzo*[b]*thiophene* (**34**) and *3-methylbenzo*[b]*thiophene* (**35**) [19] was analyzed by VPC. on a *Perkin-Elmer* 226 chromatograph with a 150′ capillary column QF-1 at 145°.

For comparative purposes, **34** was prepared as follows: 3.608 g (20 mmol) of 3-methylbenzo[*b*]thiophene 1,1-dioxide [20] and 7.381 g (180 mmol) $LiAlH_4$ were dissolved in 250 ml anhydrous dioxan. The solution was stirred for 24 h at 95°, then cooled and poured onto satd. aqueous NH_4Cl solution. After the addition of satd. aqueous *Seignette* salt solution, working up afforded a 1:2:1 mixture of *2-phenylpropan-1-ol*, *2,3-dihydro-3-methyl-benzo*[b]*thiophene* (**34**), and *3-methyl-benzo*[b]*thiophene* (**35**). **34** was isolated by VPC. on an Apiezon-L column at 220°. IR. (film): 694, 748, 930, 1440, 1460, 1587. NMR. ($CDCl_3$): 1.33/*d*, *J* = 6, H_3C—C(3); 2.8–3.1 and 3.3–3.7/2 *m*, H_2—C(2) and H—C(3); 6.9–7.2/*m*, arom. H. MS.: 152, 150, 137, *135*, 91.

$C_9H_{10}S$ Calc. C 71.98 H 6.71% Found C 72.08 H 6.51%

The product composition of irradiation run no. 13 (Table 1) remained unchanged when the period required for full photochemical conversion was severalfold increased.

Attempted Triplet Quenching. Degassed 0.052 M solutions of **9** in pentane, which contained a) no quencher, b) 0.092 M and 0.21 M naphthalene, and c) 0.13 M and 0.38 M 1,3-cyclohexadiene, were simultaneously irradiated at >3270 Å in a turn-table reactor. After ca. 25% conversion no quenching effect was observed in runs b) and c), and no photodimerization of the diene was found in run c).

Triplet Sensitization. a) *With Acetophenone.* Degassed solutions of a) 0.012 M **9** and b) 0.0139 M **9** + 0.05 M acetophenone in pentane were simultaneously photolyzed at >3400 Å in a turn-table reactor. At 30% conversion of aldehyde in run a) the sensitized run b) showed full conversion.

Degassed solutions of a) 0.09 M **9** and b) 0.082 M **9** + 0.11 M acetophenone in pentane were photolyzed at >3270 Å. When in run a) 80% of the aldehyde were converted to 86% **34** and 14% **35**, run b) afforded 24% **34** and 76% **35** at full conversion of **9**.

b) *With Benzophenone.* Degassed solutions of a) 0.014 M **9** and b) 0.014 M **9** + 0.456 M benzophenone in benzene were simultaneously irradiated at >3270 Å in a turn-table reactor. At 33% conversion of aldehyde **9** to products **34** and **35** in run a), 88% aldehyde were consumed in run b) but only ca. 50% of the theoretical yield of **34** and **35** were obtained.

Quenching of Photolytic Benzpinacol Formation from Benzophenone by **9**. Two degassed *t*-butyl alcohol solutions of a) 0.204 M benzophenone + 0.081 M benzhydrol and b) 0.206 M benzophenone + 0.07 M benzhydrol + 0.049 M **9** were irradiated for 14 h at >3270 Å in a turn-table reactor. The yields of benzpinacol were a) 295.5 mg and b) 86.3 mg.

UV.-Irradiation of 1,3-Dimethyl-3-formyl-indoline (10) and 3-Deuterioformyl-1,3-dimethyl-indoline (10-d). – In all photolyses of **10** and **10**-d described below amorphous yellow to dark brown precipitates formed which were not further investigated. See Table 1 for the results of direct irradiations other than those described below. The formation of product **36** was analyzed by VPC. (SE-30 and UCON-1715 columns).

1,3-Dimethylindoline (**36**). UV.: 252 (7250), 299 (2240). IR. (film): 730, 742, 755, 1490, 1608, 2790, 2850, 2950, 3020, 3040. NMR. ($CDCl_3$): 1.30/*d*, *J* = 6, H_3C—C(3); 2.74/*s*, H_3C—N; 2.7–3.65/*m*, H_2—C(2) and H—C(3); 6.4–7.2/*m*, arom. H. MS.: 147 ($C_{10}H_{13}N$), *132*, 117. For comparative purposes (by IR., VPC., and TLC.) **36** was prepared from 3-methylindole (skatole), 2 g (15.2 mmol) of which were dissolved in 100 ml CH_3OH and treated with 50 ml 31% HBF_4. The mixture was filtered through celite and 200 mg PtO_2 were added to the filtrate, followed by hydrogenation with stirring. After the absorption of 1.5 equiv. H_2 (5 h) the catalyst was removed and the filtrate was poured onto cold satd. aqueous NH_4Cl solution. The working up gave a red oil, the ethereal solution of which was filtered through neutral Al_2O_3 to yield 1.95 g *3-methylindoline*. UV.: 243 (5250), 291 (2630). IR. (film): 745, 1240, 1465, 1490, 1608, 2860, 2920, 2950, 3020, 3040, 3370. After washing off the mineral oil from 250 mg 50% NaH (5 mmol) suspension with petroleum ether, the residue was mixed with 700 mg (5 mmol) CH_3J and 600 mg (4.5 mmol) 3-methylindoline in 20 ml anhydrous ether. After reflux for 6 h and the usual working up, 117 mg **36** were isolated from the crude product mixture by VPC. on a SE-52 column at 220°.

10 *in Iso-octane at* ≥ 3130 Å. a) A 0.008 M iso-octane solution was flushed with argon for 15 min. The container tube was then closed with a rubber cap. The results of the irradiation, as obtained by VPC. analysis (SE-30 column at 190°) of 10 μl samples which were periodically removed with a syringe filled with iso-octane vapor, are plotted in Figure 1a.

Product **37** (*1,3-dimethylindole*) was isolated by VPC. and identified by IR., VPC., and TLC. (petroleum ether-ethyl acetate 5:1) with a sample prepared as follows: A small piece of Na, followed by 10 mg $Fe(NO_3)_3 \cdot H_2O$, were added to 400 ml anhydrous NH_3 which had been condensed using a dry ice-isopropyl alcohol bath. When the NH_3 solution had turned from the initially blue to a light grey color, 3 g (0.13 mol) Na were added in small pieces. After 0.5 h a solution of 12.5 g (95.4 mmol) 3-methylindole (skatole) in 50 ml anhydrous ether were introduced in 10 ml portions with vigorous magnetic stirring which was continued for 1 h. A solution of 15 g (106 mmol) CH_3J in 30 ml ether was then added and the vigorously stirred mixture was refluxed for 1 h before the NH_3 was evaporated over a period of 4 h. The residue was taken up in satd. aqueous NH_4Cl solution. The usual working up gave a yellow oil which, after filtration through neutral Al_2O_3, was a mixture of 35% starting material and 65% *1,3-dimethylindole* (**37**) (material balance 92%). **37** was isolated by VPC. UV.: 291 (3160). IR. ($CHCl_3$): 1010, 1325, 1370, 1390, 1470, 1485, 1570, 1618, 2815, 2875, 2910, 3000. NMR. ($CDCl_3$): 2.32/*s*, H_3C—C(3); 3.71/*s*, H_3C—N; 6.80/*s*, H—C(2); ca. 7.1/*m* + 7.55/*bd*, $J \sim 8$, arom. H. MS.: 145 ($C_{10}H_{11}N$), *144*, 130, 115, 77.

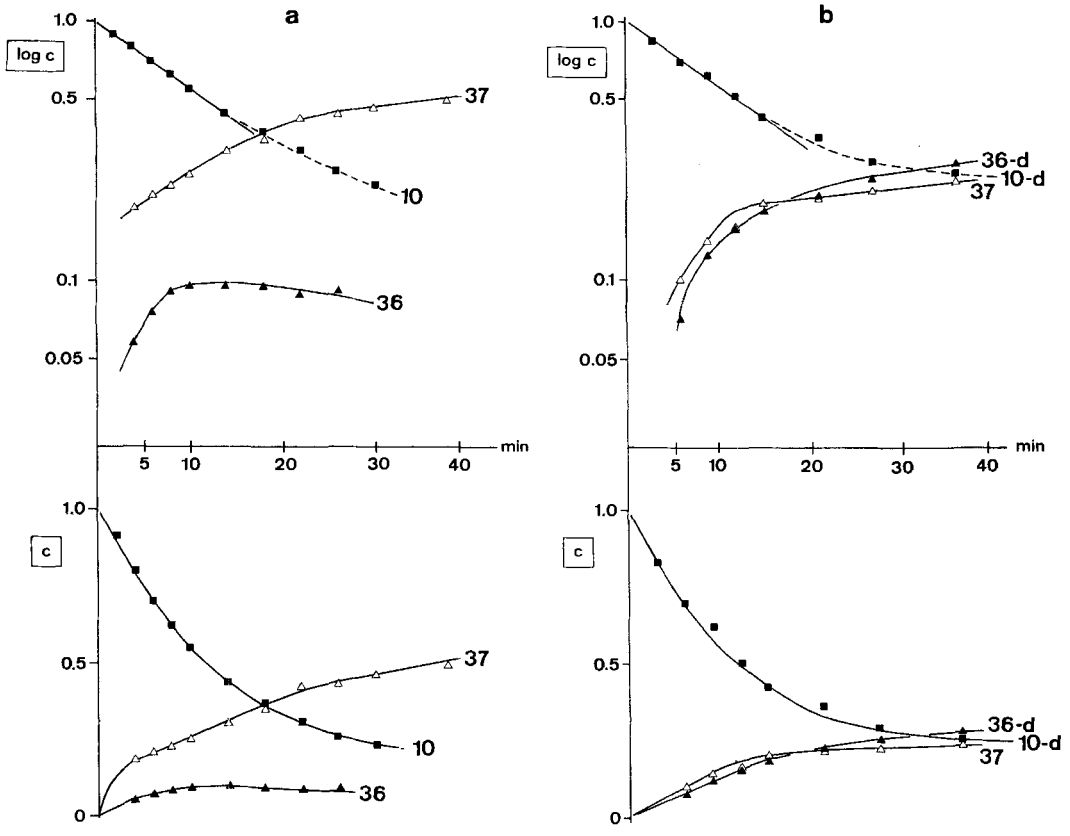

Figure 1. *Photolysis of* (*a*) **10** *and* (*b*) **10**-*d in Iso-octane at* ≥ 3130 *Å*. Solutions flushed with argon prior to irradiation.

b) A 0.04 M pentane solution was sealed in a Pyrex tube without prior degassing and photolyzed to 72% conversion. Only a trace of **36** and no other soluble products could be detected in the solution by VPC.

10-*d in Iso-octane at* ≥ 3130 *Å*. A 0.02 M solution was flushed with argon for 15 min. The container tube was then closed with a rubber cap and irradiated to ca. 75% conversion. VPC. analysis (SE-30 column at 190°) of 10 μl samples which were periodically removed with a syringe filled with iso-octane vapor, gave the results plotted in Figure 1b. The solution was centrifuged from the precipitate and concentrated *in vacuo*. Ca. 500 γ samples of **10**-d, **36**-d, and **37** were isolated by VPC. and analyzed by MS. (**10**-d and **36**-d: $\geq 99\%$ d_1; **37**: 100% d_0).

Quantum Yield Determinations of the Photodecarbonylation of Aldehydes **7**–**9**. The experimental details – optical unit and actinometry – have been described previously ([6]: p. 895). For further details and the results see Table 3.

Microanalyses were carried out by Mr. *W. Manser* of the Microanalytical Laboratory, ETH Zürich. 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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