# 20. Photosolvolysis of 2-Allylated Anilines to 2-Indanols

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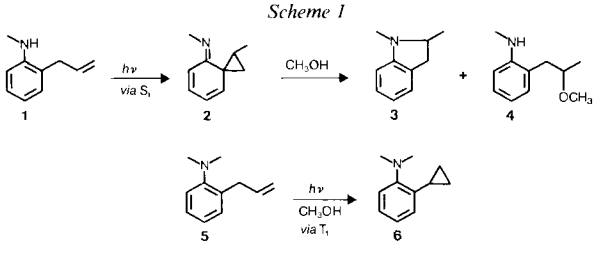
It is shown that 2-allylated anilines (*cf. Schemes 2–4, 7,* and *8*) on irradiation in protic solvents such as $H_2O$. MeOH, and EtOH in the presence of $H_2SO_4$ undergo a novel photosolvolysis reaction to yield specifically *trans*-2-hydroxy- and *trans*-2-alkoxy-1-methylindanes. Intermediates are presumably tricyclo[4.3.0.$0^{1,8}$]nona-2,4-dienes formed in an intramolecular [2*s* + 2*s*] cycloaddition reaction *(cf. Scheme 7)*. On the other hand, *N,N,N*-trimethyl-2-(1'-methylallyl)anilinium salts **18** *(Scheme 6)* and 2-(3'-butenyl)-*N,N*-dimethylaniline (**17**) lose on irradiation in MeOH or $H_2SO_4$/MeOH the ammonium group reductively to yield (1-methylallyl)benzene (**19**) and 1-methylindane (**20**), respectively.

We have already reported in detail on the photoreactivity of 2-allylanilines which is dependent on the degree of alkylation at the N-atom [1–4]. Non-alkylated and *N*-monoalkylated 2-allylanilines (*e.g.* **1**, *Scheme 1*) yield on irradiation in MeOH *via* an intramolecular CT-complex in the singlet state spiro[2.5]octadien-imines of type **2** which undergo rearrangement to the corresponding indolines (*e.g.* **3**) and solvolysis to 2-(2'-methoxyalkyl)anilines (*e.g.* **4**) [1–3].

*Scheme 1*




On the other hand, *N,N*-dialkyl-2-allylanilines (*e.g.* **5**) do not show this photochemical behaviour. However, they undergo in their triplet state a clean aromatic di-π-methane rearrangement to yield the corresponding 2-cyclopropylanilines (*e.g.* **6**) [1] [4]. Since the electronic nature of anilines can easily be changed by protonation, we were interested whether the described photoreactions of 2-allylated anilines could be quenched by protonation[4]).

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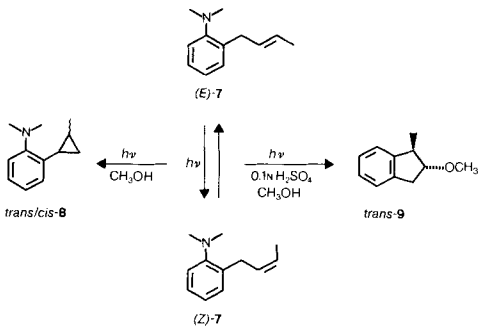
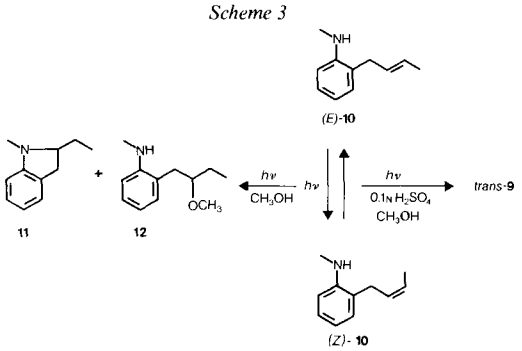
[4]) For acidities of anilinium ions in the ground and excited state, see [5] and literature cited therein.

*Scheme 2*




Direct irradiation of (*E*)-2-(2′-butenyl)-*N*,*N*-dimethylaniline ((*E*)-**7**) in MeOH with a high-pressure Hg lamp leads to rapid (*E*)/(*Z*)-isomerization and formation of the expected products (*trans*/*cis*-**8**; see *Scheme 2*) of the di-$\pi$-methane rearrangement [4]. Under the same conditions, however, in 0.1N $H_2SO_4$/MeOH again rapid (*E*)/(*Z*)-isomerization of (*E*)-**7** and the formation of a new product, namely *trans*-2-methoxy-1-methylindane (*trans*-**9**; isolated yield 43%) is observed. The *cis*-compound, prepared independently (see *Exper. Part*), could not be found in the reaction mixture (limit of detection $< 0.2\%$). This new photosolvolysis of (*E*)/(*Z*)-**7** occurred with the same rate in 5N $H_2SO_4$/MeOH which indicates that formation of *trans*-**9** is a reaction of the corresponding excited anilinium ion.

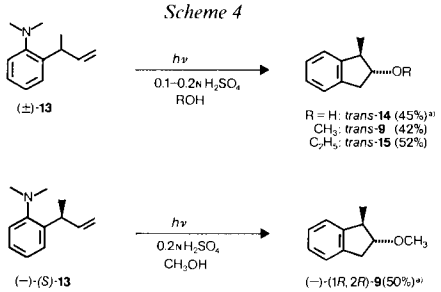
*Scheme 3*




This view is supported by the results obtained from the photolysis of the *N*-monomethylated aniline (*E*)-**10** (*Scheme 3*). Whereas irradiation in MeOH results in rapid (*E*)/(*Z*)-isomerization and formation of the mixture of indoline **11** and the MeOH-addition product **12** [2] a quenching of these products takes place in 0.1N $H_2SO_4$/MeOH. Again, rapid (*E*)/(*Z*)-isomerization and formation of *trans*-**9** as the sole product of photosolvolysis is observed.

To get more insight into the formation of the 2-indanol derivatives, we investigated the photochemical behaviour of (±)-*N*,*N*-dimethyl-2-(1′-methylallyl)aniline ((±)-**13**) which is isomeric with (*E*)/(*Z*)-**7**, however, devoid of stereoisomerism at the C=C bond. The results of irradiations in 0.1–0.2N $H_2SO_4$ in $H_2O$, MeOH, and EtOH are shown in *Scheme 4*.

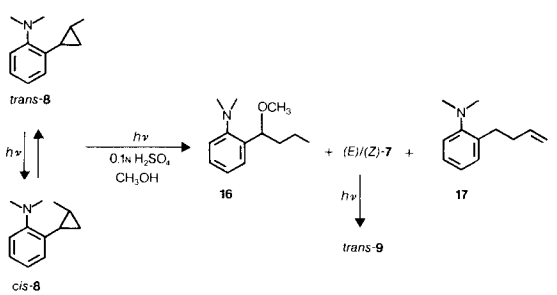
*Scheme 4*




a) Yield of purified material.

In all cases only the *trans*-2-indanol derivatives could be detected[5]). Since **13** rearranges photochemically in MeOH to the same di-$\pi$-methane products *trans/cis*-**8** [8], as obtained from (*E*)/(*Z*)-**7** (*cf. Scheme 2*), there exists, in principle, the possibility that these compounds are intermediates in the photosolvolysis reaction of (*E*)/(*Z*)-**7** and **13** in acidic media. However, the result of an irradiation of *trans*-**8** in 0.2N $H_2SO_4$/MeOH clearly show that 2-(1′-methoxybutyl)-*N*,*N*-dimethylaniline (**16**) is the main product of the photosolvolysis of *trans/cis*-**8** besides small amounts of (*E*)/(*Z*)-**7** and 2-(3′-butenyl)-*N*,*N*-dimethylaniline (**17**; *Scheme 5*). These compounds are typical products of reactions of the excited singlet state of phenylcyclopropanes (*cf.* [2] [9–11]). Small amounts of *trans*-**9** were also found in the reaction mixture. But there is no doubt that these arise from (*E*)/(*Z*)-**7** generated in the course of the photoreaction.

*Scheme 5*[a])




a) For product composition see *Table 2, Exper. Part.*

That, indeed, *trans/cis*-**8** can be excluded as precursors of *trans*-**9** follows also from the fact that irradiation of (–)-(*S*)-**13** in 0.2N $H_2SO_4$/MeOH yielded (–)-*trans*-**9**[6]) without loss of optical purity. Would have *trans/cis*-**8** been intermediates in the photoreaction, a loss of optical purity in the product should be the result since the di-$\pi$-methane rearrangement of (–)-(*S*)-**13** occurs with substantial decreases of optical activity of *trans/cis*-**8** [8].

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[5]) Relative configurations were determined by $^1$H-NMR spectroscopy with respect to *trans*-**9** (*cf. Exper. Part* and [6] [7]). The compounds of the *trans*-series exhibit for $CH_3$–C(1) a distinctly higher chemical shift (1.27, 1.28, and 1.34 ppm for **14**, **9**, and **15**, resp.) as compared to *cis*-**9** (1.15 ppm).

[6]) (–)-*trans*-**9** should have (1*R*,2*R*)-configuration, because the configuration at C(1′) of the starting material should not be changed in the course of the photoreaction. The sign of rotations of (–)-*trans*-**9** nicely correlates with that of (–)-(*S*)-1-methylindane of the same absolute configuration at C(1) [12].

Table 1. *[$H^+$] Dependence of the Photoreaction of* N,N-*Dimethyl-2-(1'-methylallyl)aniline* (**13**) *in MeOH*[a])

| pH[b]) in MeOH | Products [%][c]) | | | | |
|---|---|---|---|---|---|
| | **13** | *trans*-**9** | *trans*/*cis*-**8** | **16** | ΣProd. |
| 7.60 | 20.3 | – | 55.8 | – | 78.1 |
| 6.70 | 11.1 | – | 76.9 | – | 88.0 |
| 5.60 | 10.2 | – | 73.8 | – | 84.0 |
| 4.45 | 8.8 | – | 77.9 | 2.2 | 88.9 |
| 3.70 | 2.8 | 1.8 | 72.7 | 20.5 | 97.8 |
| 2.90 | 1.4 | 25.1 | 28.2 | 8.9 | 63.6 |
| 1.75 | 5.6 | 72.9 | 3.8 | 8.9 | 91.2 |
| 1.05 | 9.1 | 77.0 | – | 2.8 | 88.9 |
| 0.30 | 9.3 | 75.5 | – | – | 84.8 |

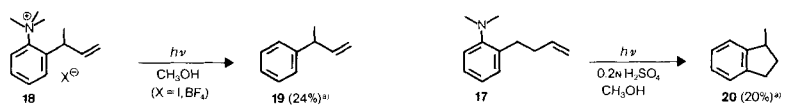
[a]) Analytical irradiations of $4.4 \times 10^{-2}$ M solutions of **13** in MeOH with a high-pressure Hg lamp through quartz during 30 min (merry-go-round apparatus).

[b]) pH in MeOH measured with a glass electrode calibrated with aqueous buffer solution (citric acid/NaOH) at pH 5 and adjusted by addition of $H_2SO_4$ to the solution of **13** in pure MeOH.

[c]) GC analyses with dodecane as internal reference.

*Table 1* shows the [$H^+$] dependence of the photoreaction of **13** in MeOH. Under slightly acidic conditions, only the formation of *trans*/*cis*-**8** and their photosolvolysis product **16** is observed. The more acidic the medium becomes the more the formation of these products is repressed and the generation of *trans*-**9** starts. In strongly acidic media, *trans*-**9** represents to sole photolysis product of **13**. Thus, *trans*-**9** is the photoproduct of protonated **13** and *trans*/*cis*-**8** are those of the free aniline.

*Scheme 6*




18 19 (24%)[a]) 17 20 (20%)[a])

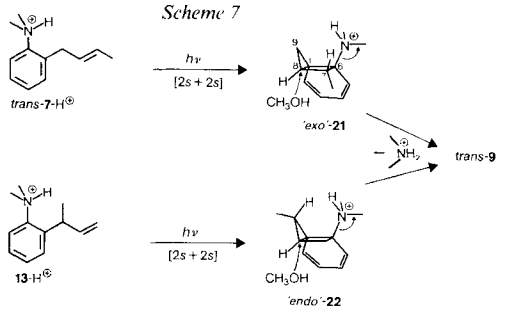
[a]) Yield of purified material.

The electronic behaviour of quaternary anilinium salts is similar to that of protonated anilines in acidic media. Therefore, we also tested the photochemical reactivity of *N,N,N*-trimethyl-2-(1'-methylallyl)anilinium salts (**18**) in MeOH as well as in 0.1N $H_2SO_4$ in MeOH and in $H_2O$ saturated with $Et_2O$ *(Scheme 6)*. In all cases not a trace of *trans*-**9** or *trans*-**14** could be detected in the reaction mixture. However, as a new product (1-methylallyl)benzene (**19**) was formed in up to 94% analytical yield (GC analyses with tridecane as internal reference), *i.e.* the anilinium salts **18** (X = I, $BF_4$) underwent a photo-*Emde* degradation [4] [13], known to occur also with *N,N,N*-trimethylanilinium iodide under direct excitation [14] [15] or with the bromide and chloride under sensitization with acetone [15]. Similarly, the direct irradiation of 2-(3'-butenyl)-*N,N*-dimethylaniline (**17**) in 0.2N $H_2SO_4$/MeOH did not give solvolysis products. Instead, 1-methylindane (**20**) was isolated as main reductive product of **17**. This finding clearly indicates that the excitation of protonated **17** leads to homolysis of the C(1)–N bond and formation of the corre-

sponding phenyl radicals which undergo a radical 1,5-cyclization to yield (1-indanyl)methyl radicals which abstract H-atoms from MeOH[7]).

Our findings are also in agreement with the observation of *Beckwith* and *Gara* [16] that treatment of 1-(3′-butenyl)-2-iodobenzene with $Bu_3SnH$ yields 1-methylindane (**20**) but no 1,2,3,4-tetrahydronaphthalene. That the photolysis of the anilinium salts **18** which should also react *via* homolysis of the C(1)-N bond does not lead to cyclization and formation of 1,2-dimethylbenzocyclobutene reflects the instability of (cyclobutyl)methyl radicals with respect to their ring opened forms (*cf.* [17]) and the fact that *endo*-cyclization of these radicals to the corresponding cyclopentyl radicals does not occur (*cf.* [18]).

*Scheme 7*




These observations and the fact that only *trans*-**9** is formed in the photosolvolysis of (*E*)/(*Z*)-**7**, (*E*)/(*Z*)-**10**, and **13** in acidic MeOH can be explained if one supposes the occurrence of congested intermediates of defined configuration which react with the nucleophilic solvent. These intermediates may arise from an intramolecular [2*s* + 2*s*] cycloaddition[8]) of the allylic side chain with the benzene ring (*cf. Scheme 7*)[9]). Concerted attack of a solvent molecule at C(8) of the tricyclo[4.3.0.0$^{1,8}$]nonadiene skeleton under ring opening and loss of the ammonium group at C(6) restores the aromatic system. From the *trans*-configuration of the products follows that the $CH_3$ groups must occupy the *'exo'*-position at C(7) and C(9) in the intermediates **21** and **22**, respectively. A $CH_3$ group in the *'endo'*-position at C(7) or C(9) would lead to sterically highly congested molecules because of non-bonding interaction with the solvated ammonium group at C(6). This view stipulates that (*E*)-**7** and (*E*)-**10** undergo the [2*s* + 2*s*] cycloaddition much faster than their (*Z*)-isomers which are in photochemical equilibrium with the (*E*)-forms under

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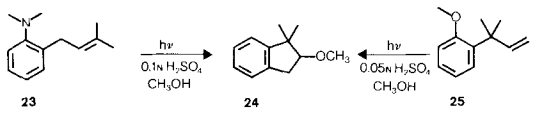
[7]) In agreement with this view is the finding that irradiation of **17** in [$^2H_2$]$SO_4$ in [*O*-$^2$H]methanol does not lead to $^2$H incorporation into **20**.

[8]) So far, we have not done any experiments which could characterize the involved electronic state of the anilinium ions. The cycloaddition may occur as a concerted one-step reaction in the excited singlet state or perhaps as a two-step reaction in the excited triplet state. The photo-*Emde* reaction [13] of **17** and **18** should be the result of the reactivity of the corresponding triplet states (*cf.* [13] [15]). This means that if the cycloaddition reaction of (*E*)/(*Z*)-**7**, (*E*)/(*Z*)-**10**, and **13** also starts from the corresponding excited triplet state it must occur more rapidly than the homolysis of the C(1)-N bond. Another possibility would be that the stepwise formation of the intermediates of type **21** and **22** is initiated by an intramolecular electron transfer from the allylic double bond as donor to the excited anilinium moiety as acceptor.

[9]) Whereas intramolecular 1,3-cycloadditions of alkenyl side chains to the excited benzene ring have been studied in the last years in great detail (*cf.* [19] and literature cited therein), scarcely nothing is known about intramolecular [2+2] cycloadditions with the exception of their occurrence in rigid polycyclic benzo systems (*cf.* [20]).

*Scheme 8*




the reaction conditions. However, that $CH_3$ groups in the *'endo'*-position at C(7) or C(9) in the tricyclo[4.3.0.0$^{1,8}$]nonadiene intermediates do not hinder the formation of these compounds is clearly shown by the photosolvolysis of *N,N*-dimethyl-2-(3'-methyl-2'-butenyl)aniline (**23**) and of 2-(1',1'-dimethylallyl)anisole (**25**) which both yield 2-methoxy-1,1-dimethylindane (**24**) on irradiation in acidic MeOH (*cf.* [4] and *Exper. Part*)[10]).

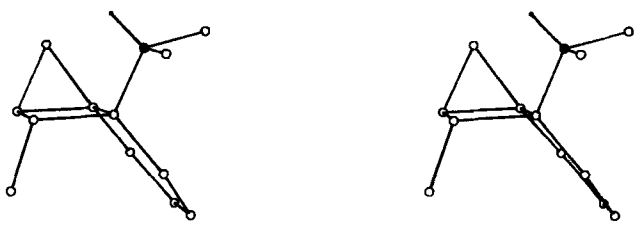
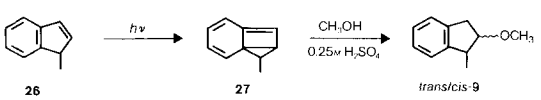


Figure. *Stereoscopic projection of* N,N-*dimethyl-(7-*exo-*methyltricyclo[4.3.0.0$^{1,8}$]nona-2,4-dien-6-yl)ammonium ion* (*'exo'*-**21**). View along the C(6)–C(1) bond. H-atoms except that of the ammonium group are omitted. Open circles: C; filled circle: N; dot: H. The postulated structure was generated with the RIMG program (*cf.* [24]) using X-ray data of bicyclo[2.1.0]pentane and bicyclo[4.2.0]octa-2,4-diene substructures searched for with the ROCSD program in the *Cambridge Structural Data Base*.

The *Figure* shows a stereographic view of the skeleton of the postulated tricyclo[4.3.0.0$^{1,8}$]nonadiene intermediate from (*E*)-**7**. The interesting C(1)–C(8) and C(6)–N bonds which should be cleaved concertedly when the nucleophile attacks C(8) are in an *anticlinal*-to-*antiperiplanar* (if one takes into account the banana-like character of the C(1)–C(8) bond) orientation to each other. Moreover, both bonds are in a nearly parallel orientation with respect to the adjacent diene system. The electronic set-up in the intermediate should, therefore, be optimal for an *anti*-elimination reaction (*cf.* [22]) with anchimeric assistance of the adjacent diene and uptake of the nucleophile at C(8). *Morrison* and coworkers [7] [23] found that irradiation of 1-methylindene (**26**) in 0.25M $H_2SO_4$/MeOH leads to the formation of a 4:1 mixture of *trans*- and *cis*-**9** (*Scheme 9*). They postulated the tricyclic compound **27** as intermediate, formed by a disrotatory ring closure of **26**. Protonation of **27** at C(7) would generate the corresponding cyclohexadienyl cation which reacts with MeOH at C(8). The formation of *trans*/*cis*-**9** in this case may

*Scheme 9*

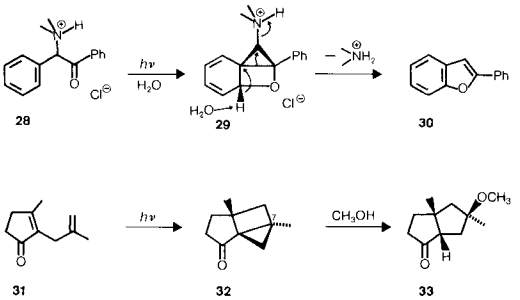



[10]) In the case of **25**, also the di-π-methane product and its consecutive photoproducts are formed. Compound **24** is also formed on irradiation of **25** in pure MeOH [4] [21].

be the result of the presence of *'exo'*- and *'endo'*-**27** or the unimolecular generation of 1-methylindan-2-yl cations by ionic rupture of the C(1)–C(8) bond with loss of stereochemistry.

To our knowledge, there are only two further reports in the literature concerning intramolecular photoreaction which are similar to those we described here. Already 20 years ago, *Sheehan* and *Wilson* [25] found that desylammonium salts such as **28** *(Scheme 10)* rearrange, on irradiation in $H_2O$, to 2-phenylbenzofuran (**30**). The tricyclic compound **29** has been postulated as intermediate.

*Scheme 10*




Recently, *Pattenden* and coworkers [26] reported that certain 2-allylated cyclopent-2-enones (*e.g.* **31**), instead of showing triplet di-$\pi$-methane reactivity, undergo in MeOH intramolecular [2 + 2] cycloaddition to yield tricyclic intermediates (*e.g.* **32**) which are attacked by MeOH at C(7) under opening of the three-membered ring and formation of the bicyclo[3.3.0]octane skeleton (*e.g.* **33**)[11]. This intramolecular photoreaction is suitable for the synthesis of cyclopentanoid natural products (*e.g.* hirsutane [26b]).

We thank Dr. *W. Bernhard* for mass spectra, Dr. *M. Cosandey* for $^{13}$C-NMR spectra, *F. Nydegger* for elemental analysis, and Dr. *H.-J. Ammann*, Central Research Units, *F. Hoffmann-La Roche & Co., Ltd*, CH-4002 Basle, for molecular modeling. Support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

## Experimental Part

*General.* See [2] [3] [27].

1. *Starting Anilines.* 1.1. *(E)/(Z)-2-(2'Butenyl)*-N-*methylaniline* ((*E*)/(*Z*)-**10**). Mixture of 87.4% of (*E*)- and 11.6% of (*Z*)-form [2].

1.2. *(E)/(Z)-2-(2'-Butenyl)*-N,N-*dimethylaniline* ((*E*)/(*Z*)-**7**). (*E*)/(*Z*)-2-(2'-Butenyl)aniline [27] (11.6 g, 0.079 mol), MeI (28.4 g, 0.2 mol), and $K_2CO_3$ (13.8 g, 0.079 mol) were stirred in acetone at r.t. for 72 h. Workup yielded 12.2 g (88%) of crude **7** which was distilled over a short column (b.p. 94°/9 Torr) to give 11.9 g of (*E*)/(*Z*)-**7** with 89.1% of the (*E*)- and 10.9% of the (*Z*)-form. UV (MeOH): 278 (sh, 3.06), 246 (3.67); min. 232 (3.61). UV (5N $H_2SO_4$/MeOH): 267 (2.58), 260 (2.68), 257 (sh, 2.62); min 265 (2.52), 234 (2.05). IR: 2840, 2740 ($(CH_3)_2$)N); 975 (CH=CH *trans*). $^1$H-NMR ($CCl_4$): 7.2–6.3 (*m*, 4 arom. H); 5.8–5.0 (*m*, H–C(2'), H–C(3')); 3.11 (small *m*, 2 H–C(1')); 2.62 (*s*, $(CH_3)_2$N); 1.8–1.55 (*m*, 3 H–C(4')).

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[11]) The C=O bond in **32** is nearly optimally disposed for an anchimeric assistance of the C(1)–C(7) bond rupture, *i.e.* the enol system acts in this case as 'leaving group'. This reaction should be catalyzable by acids.

1.3. N,N-*Dimethyl-2-(3'-methyl-2'-butenyl)aniline* (**23**). 2-(3'-Methyl-2'-butenyl)aniline [27] (1.0 g, 6.20 mmol), MeI (2.4 g, 16.9 mmol), and $K_2CO_3$ (2.34 g, 16.9 mmol) were stirred in acetone at r.t. for 36 h. Workup and distillation (120–125°/10 Torr) yielded 0.97 g (83%) of **23** in a purity (GC) of 97%. CC (benzene) gave **23** in a purity of 99% (GC). UV (cyclohexane): 211 (4.24), 249 (3.76); min. 233 (3.64). IR: 2820, 2775 ($(CH_3)_2N$); 768 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 7.1–6.7 (*m*, 4 arom. H); 5.24 (*t*, H–C(2')); 3.30 (*d*, 2 H–C(1')); 2.63 (*s*, $(CH_3)_2N$); 1.72 (br. *s*, 3 H–C(4'), $CH_3$–C(3')). MS: 189 (100, $M^+ + 1$), 174 (19), 144 (17), 134 (29), 132 (86), 118 (26), 91 (13). Anal. calc. for $C_{13}H_{19}N$ (189.30): C 82.48, H 10.12, N 7.40; found: C 82.37, H 10.23, N 7.47.

1.4. *Anilines* **13** *and Salts* **18**. 1.4.1. *(±)*-N,N-*Dimethyl-2-(1'-methylallyl)aniline* ((±)-**13**). (±)-2-(1'-Methylallyl)aniline [2] [3] was dimethylated as described above in 76% yield (b.p. 110–120°/12 Torr). UV (MeOH): 247.5 (3.74), 282 (sh, 3.14); min. 235 (3.69). IR: 2825, 2785 ($(CH_3)_2N$); 948, 911 ($CH=CH_2$). $^1$H-NMR ($CCl_4$): 7.2–6.8 (*m*, 4 arom. H); 5.96 (*ddd*, H–C(2')); 5.1–4.8 (*m*, 2 H–C(3')); 4.3–3.9 (*quint.* like *m*, H–C(1')); 2.65 (*s*, $(CH_3)_2N$); 1.27 (*d*, $CH_3$–C(1')). MS: 176 (5, $M^+ + 1$). 175 (29, $M^+$), 161 (14), 160 (100), 158 (8), 146 (33), 145 (33), 144 (22), 134 (16). Anal. calc. for $C_{12}H_{17}N$ (175.28): C 82.23, H 9.78, N 7.99; found: C 82.30, H 9.88, N 7.99.

1.4.2. *(–)-(S)*-N,N-*Dimethyl-2-(1'-methylallyl)aniline* ((–)-**13**) [8]. (–)-(*S*)-2-(1'-Methylallyl)aniline [3] ($p = 0.79 \pm 0.06$) was dimethylated and distilled. $[\alpha]_D^{25} = -58.3 \pm 1.5°$ ($c = 2.19$, cyclohexane), $[\alpha]_D^{25} = -67.1 \pm 1.4°$ ($c = 7.13$, $CCl_4$). All other spectral data were identical with those of (±)-**13**.

1.4.3. *(±)*-N,N,N-*Trimethyl-2-(1'-methylallyl)anilinium Salts* (**18**). 1.4.3.1. *Iodide (X = I)*. Aniline (±)-**13** (1.5 g, 8.56 mmol) and MeI (5.0 g, 35.2 mmol) were boiled for 24 h. The salt formed was collected by filtration and residual **13** (1.2 g) again boiled with MeI (22 g, 0.155 mol) for 48 h. The salt was collected, combined with the first crop and washed several times with $Et_2O$ to yield 0.74 g (27%) of **18** (X=I); m.p. 173–174°. IR: 1636, 1486 (Ar), 1466, 1448, 1438, 1418, 1412, 1403, 1385, 1058, 1016, 1004, 930, 840, 795. $^1$H-NMR ($CDCl_3$/($D_6$)DMSO): 8.0–7.2 (*m*, 4 arom. H); 6.05 (*m*, H–C(2')); 5.3–4.8 (*m*, 2 H–C(3')); 4.20 (*dq*, H–C(1')); 4.03 (*s*, $(CH_3)_3N^+$); 1.53 (*d*, $J = 6.8$, $CH_3$–C(1')). Anal. calc. for $C_{13}H_{20}IN$ (317.22): C 49.22, H 6.36, N 4.42; found: C 49.30, H 6.39, N 4.51.

1.4.3.2. *Tetrafluoroborate (X = $BF_4$)*. The iodide (0.20 g, 0.63 mmol) and $AgBF_4$ (0.124 g, 0.63 mmol) were stirred in MeOH and the formed AgI separated by filtration. The tetrafluoroborate **18** (X = $BF_4$) was recrystallized from i-PrOH; m.p. 148–150°. $^1$H-NMR ($(D_6)$acetone): 8.1–7.3 (*m*, 4 arom. H), 6.15 (*m*, H–C(2')); 5.3–4.9 (*m*, 2 H–C(3')); 4.6–4.3 (*m*, H–C(1')); 3.88 (*s*, $(CH_3)_3N^+$); 1.48 (*d*, $J = 7.8$, $CH_3$–C(1')). Anal. calc. for $C_{13}H_{20}BF_4N$ (277.12): C 56.25, H 7.28, N 5.06; found: C 56.08, H 7.20, N 4.98.

1.5. *2-(3'-Butenyl)*-N,N-*dimethylaniline* (**17**). 1.5.1. *1-(3'-Butenyl)-2-nitrobenzene* (*cf.* [28]). To a mixture of 2-nitrotoluene (35 g, 0.255 mol), allyl bromide (31 g, 0.255 mol) and $Bu_4NHSO_4$ (8.7 g, 0.026 mol) was slowly added 50% NaOH soln. (60 ml). The mixture was stirred for 30 h at 60–70°. The org. material was extracted with $Et_2O$ and fractionated in a *Fischer* distillation column. The fraction at 125–130°/12 Torr yielded 7.49 g (15.6%) of the product in a purity of 94.3%. IR: 1647 (C=C); 1530, 1354 ($NO_2$); 1002, 922 ($CH=CH_2$); 751 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 8.0–7.1 (*m*, 4 arom. H); 6.1–5.5 (*m*, H–C(3')); 5.2–4.8 (*m*, 2 H–C(4')); 2.97 (*t*-like with f.s., 2 H–C(1')); 2.35 (*m*, 2 H–C(2')). Anal. calc. for $C_{10}H_{11}NO_2$ (177.21): C 67.78, H 6.26, N 7.90; found: C 67.44, H 5.99, N 7.70.

1.5.2. *2-(3'-Butenyl)aniline* (*cf.* [29]). The nitro compound (7.0 g, 0.037 mol) was reduced with Fe turnings in conc. HCl in the presence of $CaCl_2$ and the resulting aniline purified by CC (silica gel; hexane/$Et_2O$ 3:2). Distillation yielded 3.7 g (64%) of the pure aniline. IR: 3464, 3384 ($NH_2$); 1646 (C=C); 1003, 919 ($CH=CH_2$); 756 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 7.0–6.3 (*m*, 4 arom. H); 6.1–5.5 (*m*, H–C(3')); 5.2–4.8 (*m*, 2 H–C(4')); 3.38 (br. *s*, $NH_2$); 2.7–2.1 (*m*, 2 H–C(1'), 2 H–C(2')). MS: 148 (5, $M^+ + 1$), 147 (27, $M^+$), 134 (6), 133 (5), 120 (8), 119 (19), 107 (10), 106 (100), 105 (21). Anal. calc. for $C_{10}H_{13}N$ (147.22): C 81.59, H 8.90, N 9.51; found: C 81.37, H 9.01, N 9.66.

1.5.3. *Methylation*. The aniline (1.42 g, 9.65 mmol). MeI (1.37 g, 9.65 mmol), and $K_2CO_3$ (1.52 g, 11 mmol) were stirred in acetone (8 ml) for 40 h at r.t. The usual workup yielded a mixture of 41% of dimethylated, 31% of monomethylated, and 14% of non-methylated material. Separation by FC (hexane/$Et_2O$ 40:1) led to 0.31 g (17%) of pure **17** and to 0.31 g (19%) of the corresponding monomethylated aniline.

**17**. IR: 2790 ($(CH_3)_2N$); 1643 (C=C); 998, 913 ($CH=CH_2$); 750 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 7.2–6.6 (*m*, 4 arom. H); 6.1–5.5 (*m*, H–C(3')); 5.2–4.8 (*m*, 2 H–C(4')); 2.9–2.1 (*m*, 2 H–C(1'), 2 H–C(2')); 2.64 (*s*, $(CH_3)_2N$). MS: 175 (53, $M^+$); 160 (14), 135 (12), 134 (100), 132 (19). Anal. calc. for $C_{12}H_{17}N$ (175.28): C 82.23, H 9.78, N 7.99; found: C 82.09, H 10.01, N 8.01.

*2-(3'-Butenyl)*-N-*methylaniline*. IR: 3445 (NH); 2818 ($CH_3N$); 1642 (C=C). $^1$H-NMR ($CCl_4$): 3.44 (br. *s*, NH); 2.85 (*s*, $CH_3NH$); other signals as in **17**. MS: 161 (26, $M^+$), 120 (100). Anal. calc. for $C_{11}H_{15}N$ (161.25): C 81.94, H 9.38, N 8.69; found: C 81.91, H 9.44, N 8.80.

2. *Irradiations of the Anilines in Acidic Media.* Prep. irradiations with a high-pressure Hg lamp (type *125 HPK, Philips*) through quartz in a 150- or 250-ml irradiation apparatus (*H. Mangels*, Roisdorf/BRD) or in 90-ml half-cylindrical cuvettes at 16–20° under $N_2$. Anal. irradiations were performed in a merry-go-round apparatus (model *DEMA 125, H. Mangels*) with the 125-HPK lamp.

2.1. *Irradiations of (E)/(Z)-***7**. The aniline (0.25 g, 1.43 mmol) was dissolved in 0.1N $H_2SO_4$/MeOH (100 ml) and irradiated for 80 min to yield (GC) a mixture with 26% of (*E*)-**7**, 25% of (*Z*)-**7**, and 48% of trans-*2-methoxy-1-methylindane* (*trans*-**9**). Three further products were recognized in the GC (total 1.5%); however, none of these represented *cis*-2-methoxy-1-methylindane (*cis*-**9**). Indane **9** was extracted with $Et_2O$ and purified by TLC (toluene) and by distillation (120°/12 Torr); yield 0.10 g (43%). IR: 3075, 3045, 3025 (Ar); 2830 ($CH_3O$); 1113 ($CH_3OAr$); 746 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 7.05 (br. *s*, 4 arom. H); 3.63 (*q*-like, *J* (2,1 *trans*) ≈ *J* (2,3 *trans*) ≈ *J* (2,3 *cis*) ≈ 6.5, H–C(2)); 3.33 (*s*, $CH_3O$–C(2)); 3.3–2.5 (*m*, H–C(1), 2 H–C(3)); 1.28 (*d*, *J* = 7, $CH_3$–C(1)). $^{13}$C-NMR ($CDCl_3$; 25.2 MHz): 145.4 (*s*, C(3a)); 139.4 (*s*, C(7a)); 126.5 (*d*, C(5), C(6)); 124.4 (*d*, C(4)); 123.2 (*d*, C(7)); 89.4 (*d*, C(2)); 57.0 (*q*, $CH_3O$–C(2)); 45.0 (*d*, C(1)); 37.1 (*t*, C(3)); 17.8 (*q*, $CH_3$–C(1)). MS: 162 (100, $M^+$), 147 (50), 131 (45), 130 (94), 129 (40), 119 (27), 117 (42), 115 (49), 104 (18), 91 (28).

The photoreaction of (*E*)/(*Z*)-**7** occurred at the same rate in 5N $H_2SO_4$/MeOH.

2.2. *Irradiations of (E)/(Z)-***10**. The aniline (38.1 mg, 0.236 mmol) was dissolved in 0.1N $H_2SO_4$/MeOH (15 ml) and irradiated for 45 min to yield a mixture of 18% of (*E*)-**10**, 20% of (*Z*)-**10**, and 60% of *trans*-**9**. The isomeric *cis*-**9** could not be detected (cap. GC). However, traces (~0.2%) of *2-ethyl-1-methylindoline* (**11**) and *2-(2'-methoxybutyl)-*N*-methylaniline* (**12**) (*cf.* [2]) were present.

The photoreaction was slower by a factor of 1.5 in 5N $H_2SO_4$/MeOH. Again, *trans*-**9** was the sole product.

2.3. *Irradiation of* N,N-*Dimethyl-2-(3'-methyl-2'-butenyl)aniline* (**23**). A $10^{-2}$ M soln. of **23** in 0.1N $H_2SO_4$/MeOH was irradiated for 15 min to yield a mixture of 36.5% of *2-methoxy-1,1-dimethylindane* (**24**) [4] [21] and 57.5% of **23**. In addition, seven further products of less than 1% each were formed.

**24**. IR: 3079, 3030 (Ar); 2828 ($CH_3O$); 1389, 1368 (> $C(CH_3)_2$); 1229, 1129, 1112 ($CH_3OAr$); 772 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 7.04 (br. *s*, 4 arom. H); 3.65 (*dd*, *J* (2,3) = 8.5, 6.5, H–C(2)); 3.40 (*s*, $CH_3O$–C(2)); 3.08 (*dd*, *J*(3,3) = 15, *J* (3,2) = 6.5, H–C(3)); 2.71 (*dd*, *J* (3,3) = 15, *J* (3,2) = 8.5, H–C(3)); 1.30, 1.06 (2*s*, 2 $CH_3$–C(1)). $^{13}$C-NMR ($CDCl_3$, 25.2 MHz): 150.3 (*s*, C(7a)); 138.0 (*s*, C(3a)); 126.7 (*d*, C(4)); 126.4 (*d*, C(5)); 124.6 (*d*, C(7)); 122.0 (*d*, C(6)); 90.1 (*d*, C(2)); 57.9 (*q*, $CH_3O$–C(2)); 46.2 (*s*, C(1)); 35.3 (*t*, C(3)); 26.7, 22.1 (2 *q*, 2 $CH_3$–C(1)). MS: 176 (100, $M^+$), 161 (99), 131 (20), 129 (75).

2.4. *Irradiations of* N,N-*Dimethyl-2-(1'-methylallyl)aniline* (**13**). 2.4.1. *(±)-***13** *in MeOH*. The aniline (164 mg, 0.935 mmol) was dissolved in 0.2N $H_2SO_4$/MeOH (90 ml) and irradiated for 60 min to yield a mixture of 31% of **13** and 39% of *trans*-**9**. The *cis*-**9** could not be detected. Two by-products were formed in *ca.* 1% each. Workup and distillation (90–100°/12 Torr) yielded 44 mg (42% with respect to reacted (±)-**13**) of pure *trans*-**9** which was identical with the material described under *2.1*. Anal. calc. for $C_{11}H_{14}O$ (162.23): C 81.44, H 8.70; found: C 81.29, H 8.77.

2.4.2. *(−)-(S)-***13** *in MeOH*. The (−)-aniline (175 mg, 1.0 mmol) was dissolved in 0.2N $H_2SO_4$/MeOH (150 ml) and irradiated for 20 min. The usual workup and prep. TLC (hexane/$Et_2O$ 5:1) yielded, after distillation (110°/12 Torr), 81 mg (50%) of pure (−)-*trans*-**9** of (1*R*,2*R*)-configuration. $[\alpha]_D^{25} = -56.2 \pm 0.9°$ (*c* = 1.15, $CCl_4$). Enantiomeric purity (*e*) according to $Eu(hfc)_3$ experiments in 1,1,2-trichloro-1,2,2-trifluoroethane: *e* = 0.79 ± 0.01. All other spectra were identical with those of authentic racemic material.

To the aq. soln. from the extraction of (−)-*trans*-**9** was added NaOH and the basic soln. purged with $N_2$. $Me_2NH$ in the $N_2$ stream was trapped with liquid $N_2$. The condensate was treated with 3 ml of a sat. soln. of picric acid in EtOH to yield, after recrystallization, from EtOH, 24 mg (9%) of dimethylammonium picrate; m.p. 158° ([30]: 158°). $^1$H-NMR ($(D_6)$acetone): 8.68 (*s*, 2 arom. H); 3.48 (br. *s*, $NH_2$); 2.93 (*s*, $(CH_3)_2NH_2^+$).

2.4.3. *(±)-***13** *in $H_2O$/$Et_2O$*. The aniline (292 mg, 1.67 mmol) was dissolved in 0.1N aq. $H_2SO_4$ saturated with $Et_2O$[12]) and irradiated for 50 min. Extraction with $Et_2O$ yielded, after distillation, 72 mg (29%) of trans-*1-methyl-2-indanol* (*trans*-**14**). After basification of the aq. soln., 35% of the starting aniline were recovered. The *cis*-isomer of **14** could not be detected. IR: 3340 (OH); 3075, 3050, 3025 (Ar); 1086, 1069 (C–O); 745 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 7.07 (br. *s*, 4 arom. H); 3.98 (*q*-like, *J* (2,3 *cis*) ≈ *J* (2,3 *trans*) ≈ *J* (2,1 *trans*) ≈ 6.5, H–C(2)); 3.3–2.5 (*m*, H–C(1), 2 H–C(3)); 2.20 (br. *s*, OH); 1.27 (*d*, *J* = 7.5, $CH_3$–C(1)). MS: 149 (5, $M^+$ + 1), 148 (54, $M^+$), 133 (16), 130 (11), 129 (7), 128 (5), 120 (14), 119 (100), 117 (8), 115 (16), 105 (20), 91 (19). Anal. calc. for $C_{10}H_{12}O$ (148.21): C 81.04, H 8.16; found: C 80.79, H 8.31.

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[12]) Without saturation with $Et_2O$ the aq. soln. of **13** became turbid after some seconds of irradiation, and the photoreaction slowed down.

2.4.4. *(±)-***13** *in EtOH.* The aniline (310 mg, 1.77 mmol) was dissolved in 0.1N $H_2SO_4$/EtOH (300 ml) and irradiated for 65 min. The isolated neutral compound was purified by FC (pentane/$Et_2O$ 10:1) and distillation (122–127°/12 Torr) to yield 163 mg (52%) of trans-*2-ethoxy-1-methylindane* (*trans*-**15**). IR: 3072, 3046, 3028 (Ar); 2873 ($RCH_2O$); 1117 ($RCH_2OAr$); 746 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 7.15 (br. *s*, 4 arom. H); 3.80 (*q*-like, *J* (2,3 *cis*) ≈ *J* (2,3 *trans*) ≈ *J* (2,1 *trans*) ≈ 6.4, H–C(2)); 3.60, 3.57 (*AB*, $CH_3CH_2O$–C(2)); 3.4–2.6 (*m*, H–C(1), 2 H–C(3)); 1.34 (*d*, *J* = 6.9, $CH_3$–C(1)); 1.24 (*t*, *J* = 6.5, $CH_3CH_2O$–C(2)). MS: 177 (9, $M^+$ + 1), 176 (82, $M^+$), 147 (15), 135 (31), 133 (26), 131 (30), 130 (100), 129 (26), 120 (52), 119 (89). Anal. calc. for $C_{12}H_{16}O$ (176.26): C 81.77, H 9.15; found: C 81.69, H 9.06.

2.5. *Irradiation of* N,N,N-*Trimethyl-2-(1'-methylallyl)anilinium Salts* (**18**). 2.5.1. *Iodide (X = I) in MeOH.* The salt (440 mg, 1.39 mmol) was irradiated in MeOH (150 ml) for 20 min. The mixture consisted of 79% of *(1-methylallyl)benzene* (**19**)[13]), 3% of reactant, and of several unknown products in low concentration. The indane was isolated by prep. TLC (hexane/$Et_2O$ 10:1) and CC on silica gel impregnated with 10% $AgNO_3$ (pentane). Distillation (50°/0.02 Torr) yielded 43 mg (24%) of **19**. IR: 1640 (C=C); 1604, 1495 (Ar); 1000, 915 (CH=$CH_2$); 759, 703 (5 adjac. arom. H). $^1$H-NMR ($CCl_4$): 7.3–6.9 (*m*, 5 arom. H); 6.2–5.7 (*m*, H–C(2)); 5.2–4.8 (*m*, 2 H–C(3)); 3.6–3.2 (*m*, H–C(1)); 1.37 (*d*, *J* = 7.2, $CH_3$–C(1)).

2.5.2. *Tetrafluoroborate (X = $BF_4$) in MeOH.* A $10^{-2}$M soln. of the salt in MeOH was irradiated for 120 min. The sole product which could be detected (cap. GC using tridecane as reference) was **19** in 94% yield.

2.6. *Irradiation of 2-(3'-Butenyl)-*N,N-*dimethylaniline* (**17**). 2.6.1. *In MeOH.* The aniline (300 mg, 1.71 mmol) was irradiated in 0.2N $H_2SO_4$/MeOH (150 ml) for 60 min. Addition of 50 ml of sat. NaCl soln. and extraction with pentane yielded, after distillation (50°/0.02 Torr), 45 mg (20%) of *1-methylindane* (**20**). The compound was identical in all aspects with an authentic sample (*cf.* [12a]).

2.6.2. *In [O-$^2$H]Methanol.* The aniline (153 mg, 0.873 mmol) was dissolved in a soln. of 0.75 g of $D_2SO_4$ in 125 ml of [*O*-$^2$H]Methanol and irradiated for 60 min. Workup as described above yielded 30 mg (26%) of **20**. IR and $^1$H-NMR: no $^2$H had been incorporated (neither at $CH_3$–C(1) nor at C(1)). Incorporation in the aromatic moiety amounted to about 7%.

2.7. *Irradiation of* trans-N,N-*Dimethyl-2-(2'-methylcyclopropyl)aniline* (*trans*-**8**; *Table 2*). This compound (175.3 mg, 1.00 mmol; *cf.* [4] [8]) was irradiated in 0.1N $H_2SO_4$/MeOH (90 ml) for 50 min. The main product, namely N,N-*Dimethyl-2-(1'-methoxybutyl)aniline* (**16**) was isolated by extraction with $Et_2O$ after basification. Prep. GC at 120° and distillation at 60°/0.03 Torr yielded 25 mg of **16**. IR: 2822 ($CH_3O$); 2783 (($CH_3)_2N$); 1595, 1577, 1487 (Ar); 1095 (C–O–C); 753 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 7.4–6.8 (*m*, 4 arom. H); 4.60 (*m*, H–C(1')); 3.07 (*s*, $CH_3O$–C(1')); 2.62 (*s*, $(CH_3)_2N$); 2.7–1.1 (*m*, 2 H–C(2'), 2 H–C(3')); 1.1–0.7 (*m*, 3 H–C(4')). MS: 208 (2, $M^+$ + 1), 207 (10, $M^+$), 193 (14), 192 (100), 176 (12), 164 (12). Anal. calc. for $C_{13}H_{21}NO$ (207.32): C 75.32, H 10.21, N 6.76; found: C 75.40, H 10.31, N 6.79.

Table 2. *Irradiation of* trans-**8**. Product composition in dependence of time (GC, %).

| Compound | Irradiation time [min] | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 22 | 31 | 40 | 50 |
| *trans*-**8** | 98.3 | 46.0 | 21.9 | 11.6 | 7.4 | 4.2 |
| *cis*-**8** | – | 13.9 | 14.4 | 11.2 | 6.8 | 4.0 |
| **16** | – | 12.2 | 29.7 | 36.0 | 47.2 | 51.8 |
| (*Z*)-**7** | – | 3.0 | 5.0 | 5.6 | 5.8 | 5.8 |
| (*E*)-**7** | – | 1.6 | 2.7 | 3.1 | 3.4 | 3.8 |
| **17** | – | 4.2 | 5.3 | 6.0 | 5.2 | 6.1 |
| *trans*-**9** | – | 1.1 | 2.0 | 3.2 | 7.0 | 7.2 |
| Not identified products | 1.7 | 12.5 | 16.1 | 14.8 | 16.2 | 14.5 |

3. trans- *and* cis-*2-Methoxy-1-methylindane* (*trans*- and *cis*-**9**). 3.1. trans/cis-*1-Methyl-2-indanol* (*trans*/*cis*-**14**). 1-Methyl-2-indanone (1.0 g, 6.84 mmol) [31] dissolved in $Et_2O$ (5 ml) was added dropwise to a stirred soln. of $LiAlH_4$ (0.23 g, 6 mmol) in $Et_2O$ (10 ml) at r.t. Workup after stirring for an additional hour and distillation (150–160°/11 Torr) yielded 1.0 g (99%) of a mixture of 67% of *trans*-**14** (*cf.* [6] [7]) and 29% of *cis*-**14**[14]). IR: 3330

[13]) Anal. irradiations of **18** (X = I) in 0.1N $H_2SO_4$/MeOH and in $H_2O$ saturated with $Et_2O$ gave also solely **19** in 68 and 86% yield, respectively (cap. GC using tridecane as reference).

[14]) *cis*-**14** described by *Marshall* and *Prager* [32] should have *trans*-configuration according to the published $^1$H-NMR data.

(br., OH); 1070 (C–O–H); 745 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 6.99 (br. *s*, 4 arom. H); 4.5–4.1 (*m*, H–C(2)); 3.9–2.6 (*m*, OH, 2 H–C(3), H–C(1)); 1.30, 1.19 (2*d*, $J \approx 7$, together 3 H, $CH_3$–C(1) in *trans*- and *cis*-**14**).

3.2. *Methylation of* trans/cis-**14** (*cf.* [33]). The indanol mixture (0.85 g, 5.74 mmol) and $Bu_4NHSO_4$ (50 mg, 0.15 mmol) were distributed between petroleum ether (2.5 ml) and 50% NaOH (1.2 ml) by stirring for 40 min. Then, $Me_2SO_4$ (2.17 g, 17.2 mmol) was slowly added and the mixture stirred for 2.5 h. Workup yielded 0.46 g (50%) of a mixture of 70% of *trans*-**9** and 26% of *cis*-**9**. The mixture was separated 2 times by prep. TLC ($CH_2Cl_2$). The faster moving isomer represented *cis*-**9** and the slower moving one *trans*-**9**.

*cis*-**9** (containing 7% of *trans*-**9**). IR: 3065, 3040, 3020 (Ar); 2825 ($CH_3O$); 1130 (>C–O–$CH_3$); 759 (4 adjac. arom. H). $^1$H-NMR ($CCl_4$): 7.05 (br. *s*, 4 arom. H); 4.04 (*q*-like, $J$ (2,1 *cis*) $\approx J$ (2,3 *cis*) $\approx J$ (2,3 *trans*) $\approx 6$, H–C(2)); 3.33 (*s*, $CH_3O$–C(2)); 3.5–2.8 (*m*, H–C(1), 2 H–C(3)); 1.15 (*d*, $J = 7.5$, $CH_3$–C(1)). MS: 162 (100, $M^+$), 147 (29), 131 (25), 130 (86), 129 (24), 119 (13), 117 (23), 115 (26).

*trans*-**9** (containing 0.2% of *cis*-**9**) (*cf.* [7]). All spectra were identical with those of 2-methoxy-1-methylindane obtained by photolysis of **13** in 0.1N $H_2SO_4$/MeOH (see *2.4*).

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