209. Stereochemical Analysis of an Aromatic Triplet Di-π-methane Rearrangement[1])

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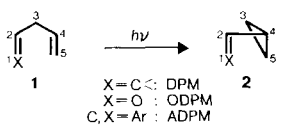
(22.IX.86)

It is shown that (−)-(*S*)-*N*,*N*-dimethyl-2-(1′-methylallyl)aniline ((−)-(*S*)-**4**), on direct irradiation in MeCN at 20°, undergoes in its lowest-lying triplet state an aromatic di-π-methane (ADPM) rearrangement to yield (−)-(1′*R*,2′*R*)- and (+)-(1′*R*,2′*S*)-*N*,*N*-dimethyl-2-(2′-methylcyclopropyl)aniline ((−)-*trans*- and (+)-*cis*-**7**) in an initial *trans*/*cis* ratio of 4.71 ± 0.14 and in optical yields of 28.8 ± 5.2% and 15 ± 5%, respectively. The ADPM rearrangement of (−)-(*S*)-**4** to the *trans*- and *cis*-configurated products occurs with a preponderance of the path leading to retention of configuration at the pivot atom (C(1′) in the reactant and C(2′) in the products) for (−)-*trans*-**7** and to inversion of configuration for (+)-*cis*-**7**, respectively. The results can be rationalized by assuming reaction paths which involve the occurrence of discrete 1,4- and 1,3-diradicals *(cf. Schemes 10, 12,* and *13)*. A general analysis of such ADPM rearrangements which allows the classification of these photochemical reactions in terms of borderline cases is presented *(Scheme 14)*. It is found that the optical yields in these 'step-by-step' rearrangements are determined by the first step, *i.e.* by the disrotatory bond formation between C(2) of the aromatic moiety and C(2′) of the allylic side chain leading to the generation of the 1,4-diradicals. Moderation of the optical yields can occur in the ring closure of the 1,3-diradicals to the final products, which may take place with different *trans*/*cis*-ratios for the individual 1,3-diradicals. Compounds (−)-*trans*-**7** as well as (+)-*cis*-**7** easily undergo the well-known photochemical *trans*/*cis*-isomerization. It mainly leads to racemization. However, a small part of the molecules shows *trans*/*cis*-isomerization with inversion of configuration at C(1′), which is best explained by a photochemical cleavage of the C(1′)–C(3′) bond.

1. Introduction. – As already established, the di-π-methane (DPM) rearrangement, which – depending upon the electronic excitation energy – may proceed *(Scheme 1)* in the singlet as well as in the triplet state, is one of the most investigated photo-induced skeletal transpositions of bichromophoric systems (*cf.* [1]). Other variation of the DPM rearrangement are the oxa-di-π-methane (ODPM) rearrangement – generally in the triplet state – if one vinyl moiety is replaced by an acyl group (*cf.* [2]) and aromatic di-π-methane (ADPM) rearrangement, if one or both vinyl moieties are replaced by aromatic rings (*cf.* [1] [3]).

Scheme 1



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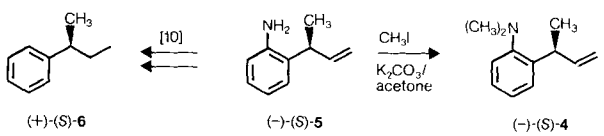
In this type of rearrangements, the stereochemical outcome at the pivot atom C(3), at which in the course of the reaction both bond cleavage and bond formation take place, is of decisive importance for establishing the mechanism of the process as well as an indicator for the effectiveness of chirality transfer in synthetic applications of these photochemical reactions (*cf.* [4]). In this respect, it was shown by *Zimmerman et al.* that the singlet-state DPM [5] (*cf.* [6]) and ADPM rearrangements [7] occur without loss of optical activity and with inversion of the configuration at C(3). On the other hand, triplet-state ODPM rearrangements can take place under racemization, partial or complete preservation of optical activity, accompanied by inversion or retention of configuration at C(3), depending, so far known, exclusively on the structural constraints of the ODPM system (*cf.* [2] [4]).

Within the scope of our investigation on triplet-state ADPM rearrangements of simple allylbenzene derivatives (*cf.* [3a] [3c–e]), it was of interest to disclose the stereochemical course of such skeletal transpositions leading to the corresponding cyclopropylbenzene derivatives by 1,2-migration of the benzene ring (*cf.* [3] [8] [9]). So far, no such stereochemical analysis has been attempted for an all-carbon DPM rearrangement in the triplet state. Moreover, the excitation energy in these ADPM systems is mainly within the aromatic moiety (*cf.* [3a] [3c–e])[3]) and the only structural constraint is due to the rigidity of the benzene ring.

2. ADPM Rearrangement of the Derivatives of *N,N*-Dimethyl-2-(1′-methylallyl)-aniline (4). – The ADPM system of choice was (–)-(*S*)-*N,N*-dimethyl-2-(1′-methylallyl)aniline ((–)-(*S*)-**4**), which can be obtained by dimethylation of (–)-(*S*)-2-(1′-methylallyl)aniline ((–)-(*S*)-**5**; *cf.* [10] [11])[4]). The absolute configuration of (–)-(*S*)-**5** had unequivocally been established by correlation with (+)-(*S*)-2-phenylbutane ((+)-(*S*)-**6**; *Scheme 2*).

Scheme 2



(+)-(*S*)-**6** (–)-(*S*)-**5** (–)-(*S*)-**4**

Furthermore, for this ADPM system, we expected an efficient rearrangement in the triplet state by irradiation, since the triplet energy of *N,N*-dimethylaniline ($E_T \geqq 69$ kcal mol^{-1} [12]) as a model compound is well below of that of the side chain, for which ethylene ($E_T \leqq 82$ kcal mol^{-1} [13]) and (*Z*)-butene ($E_T = 78.2$ kcal mol^{-1} [14]) may serve as borderline models[5]). From these values, we can conclude that intramolecular energy transfer to the side chain, where deactivation to the ground state can occur by isomerization around the C=C bond (*cf.* the T_1-ADPM rearrangement of *trans-N,N*-dimethyl-2-(2′-butenyl)-aniline [3d] and the failure of this rearrangement in solution in comparable cases like *trans*-2-(2-butenyl)anisole [3a] and -benzene [15]), should be minimized. Indeed, when (±)-**4** was irradiated in MeOH through quartz with a Hg high-pressure lamp, *trans*- and

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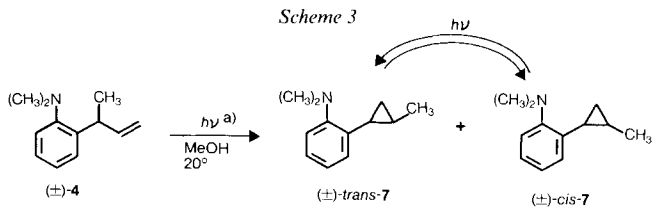
[3]) See also *Chapt. 2.*

[4]) Unless otherwise stated, all signs of rotations refer to the Na_D-line.

[5]) The quantum yield for the T_1-ADPM rearrangement of 2-allyl-*N,N*-dimethylaniline in MeOH is 0.030 ± 0.005 [3a].

Scheme 3



[a]) After 45 min of irradiation, 55% of (±)-**4** had been consumed to yield a mixture of 43% of (±)-*trans*-**7** and of 10% of (±)-*cis*-**7** (see *Exper. Part*).

cis-*N*,*N*-dimethyl-2-(2′-methylcyclopropyl)aniline ((±)-*trans*- and (±)-*cis*-**7**, respectively) were readily formed as the only products *(Scheme 3)*. The formation of (±)-*trans*-**7** and (±)-*cis*-**7** from (±)-**4** was effectively quenched in the presence of a 10- to 20-fold molar excess of isoprene (see *Exper. Part, Table 6*). Since the fluorescence of the aniline moiety is almost not quenched in this range of 1,3-diene concentration (see [3a]), we concluded that the ADPM rearrangement of (±)-**4** leading to (±)-*trans*/(±)-*cis*-**7** proceeds in the triplet state. On the other hand, the reversible photoisomerization of (±)-*trans*-**7** and (±)-*cis*-**7** could not be repressed in the presence of isoprene. However, GC showed that both stereoisomers were also present at very low conversion rates of (±)-**4**, *i.e.* both are genuine products of the photo-induced rearrangement of (±)-**4** (see below). Since the UV spectra of (±)-**4** as well as (±)-*trans*-**7** and (±)-*cis*-**7**[6]), which could be separated by flash chromatography on silica gel (see *Exper. Part*), were nearly identical *(Fig. 1)*, we could not repress the photochemical *trans*/*cis*-isomerization, even by filtering the light of excitation. However, irradiation of (±)-**4** in MeCN through a filter (*Jena*-glass; thickness 1.25 mm, T ≈ 10% at 303 nm) led to the most reproducible results.

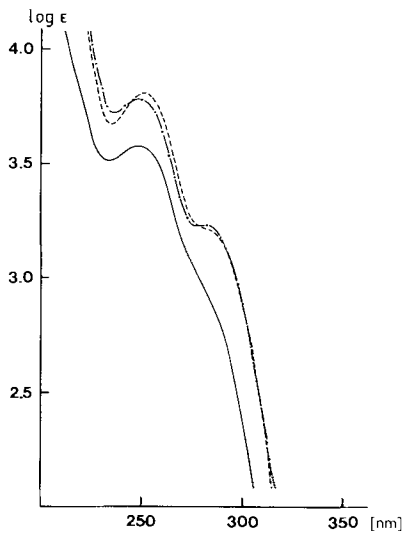


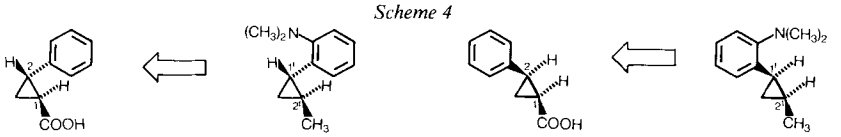
Fig. 1. *Long-wavelength part of the electronic-absorption spectra of* (±)-**4** (——), (±)-trans-**7** (–·–·–), *and* (±)-cis-**7** (– – –) *in EtOH*

[6]) *trans*- and *cis*-**7** are easily identified and distinguished by their ^{1}H-NMR spectra (CCl_4), especially with respect to the chemical shift of CH_3–C(2′) (1.24 ppm for *trans*- and 0.82 ppm for *cis*-**7**; see *Exper. Part*).

For a complete stereochemical analysis of the ADPM rearrangement of (−)-(*S*)-**4**, we needed to know the absolute configuration of *trans*- and *cis*-**7**. On the other hand, optically active *trans*- and *cis*-**7** of known absolute configuration would also allow to study the stereochemistry of the photochemically reversible *trans*/*cis*-isomerization.

We chose *trans*- and *cis*-2-phenylcyclopropanecarboxylic acids (*trans*- and *cis*-**8**, respectively; see *Scheme 4*) as starting materials for the synthesis of optically active *trans*- and *cis*-**7** of known absolute configuration. *Walborsky* and coworkers [16] have attributed the (1*S*,2*S*)-configuration to (+)-*trans*-**8** on the basis of its ozonolysis to (+)-(1*S*,2*S*)-cyclopropane-1,2-dicarboxylic acid. The highest observed $[\alpha]_D^{22}$-value of (+)-*trans*-**8** amounts to 311.7° and 314° (EtOH; *cf. Exper. Part*). The (1*S*,2*R*)-configuration of the *cis*-acid (+)-**8** has been established by the correlation *(inter alia)* with (−)-(1*R*,2*R*)-1,2-diphenylcyclopropane, accomplished by controlled inversion at C(1) [17]. The highest $[\alpha]_D^{20}$-value ($CHCl_3$) for (+)-*cis*-**8** has been estimated to be in the order of 30° (see *Exper. Part*).

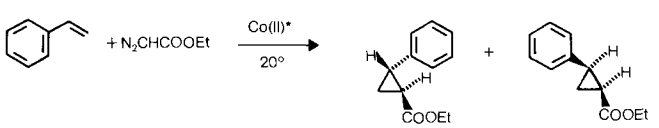
Scheme 4



(1*S*,2*S*)-**8** (1'*S*,2'*S*)-**7** (1*S*,2*R*)-**8** (1'*R*,2'*S*)-**7**

The optical resolution of (±)-*trans*- and (±)-*cis*-**8** (obtained from the reaction of ethyl diazoacetate and styrene and separation of the resulting mixture of the corresponding ethyl esters by kinetically controlled saponification [18]) turned out to be difficult and not reproducible[7]). Therefore, we attempted an asymmetric synthesis of *trans*- and *cis*-**8**. Besides several methods for the generation of optically active carbenoids for the syntheses of cyclopropane derivatives with optical yields of 8 to 30% [22–28] (*cf.* also [29–31]), the carbene-like addition of ethyl diazoacetate to styrene in the presence of an optically active Co(II) complex (derived from (−)-(2*E*,3*Z*)-camphorquinone dioxime; see *Exper. Part*) with optical yields of up to 72% is of special interest, since the ethyl esters **9** of *trans*- and *cis*-**8** are formed in a ratio of *ca.* 1:1 *(Scheme 5)* [32] (*cf.* also [33] [34]).

Scheme 5



(+)-(1*S*,2*S*)-**9** (+)-(1*S*,2*R*)-**9**

p: 0.36–0.60 0.36–0.78

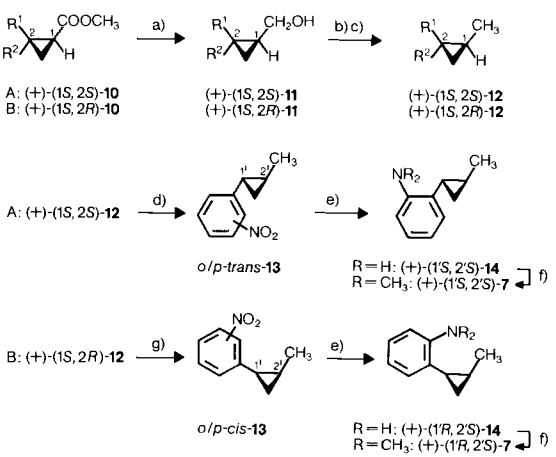
[7]) Recrystallizations of the quinine salt of (±)-*trans*-**8** from $MeOH/H_2O$ 3:1 [16] [17] [19] as well as from AcOEt, followed by a new formation of the dehydroabietylamine salt [20], gave only low optical yields of (+)-*trans*-**8**. Also, the brucine salt (recrystallization from acetone) and the (+)-1-phenylethylamine salt (recrystallization from MeOH, acetone, MeCN, and AcOEt) did not lead to a satisfactory optical resolution of (±)-*trans*-**8**. Similarly, the attempted optical resolution of (±)-*cis*-**8** *via* its brucine salt (recrystallization from MeOH or acetone [21]) or quinine salt (recrystallization from $MeOH/H_2O$ 3:1 [17] [19]) could only be achieved in low optical yields.

The highly air-sensitive Co(II) catalyst was prepared in gram quantities by a slightly modified form of the procedure described in [32] and was directly applied in the reaction of ethyl diazoacetate and styrene.

The optical purity (p) of (+)-*trans*-**9** and of (+)-*cis*-**9** varied in several runs *(cf. Table 2, Exper. Part)* from 0.36 to 0.78. The corresponding acids were obtained by kinetically controlled saponification and further purification by salt formation with dehydroabietylamine (for (+)-*trans*-**8**) or quinine (for (+)-*cis*-**8**). The acid (+)-(1*S*,2*S*)-**8**, thus obtained, showed $[\alpha]_D^{22} = 304.1 \pm 5.9°$ (EtOH) corresponding to $p = 0.976 + 0.019$[8]). The purified (+)-*cis*-**8** exhibited $[\alpha]_D^{22} = 23.9 \pm 1.0°$ ($CHCl_3$) corresponding to $p = 0.819 \pm 0.045$[9]).

The transformation of (+)-(1*S*,2*S*)-**8** into (+)-(1′*S*,2′*S*)-*N*,*N*-dimethyl-2-(2′-methylcyclopropyl)aniline ((+)-(1′*S*,2′*S*)-**7**) is outlined in *Scheme 6*. The methyl ester **10** of (+)-*trans*-**8** ($[\alpha]_D^{20} = 329.5 \pm 4.0°$ ($CHCl_3$)), obtained by reaction of **8** with CH_2N_2, was reduced with $LiAlH_4$ in Et_2O (*cf.* [35]) to the corresponding primary alcohol (+)-(1*S*,2*S*)-

Scheme 6



A: *trans*-series, $R^1 = H$, $R^2 = Ph$; B: *cis*-series, $R^1 = Ph$, $R^2 = H$.

[a]) $LiAlH_4/Et_2O$. [b]) MsCl/2,6-lutidine. [c]) $LiAlH_4$. [d]) HNO_3/Ac_2O, −60° (*o*/*p* = 7.5). [e]) Fe/HCl, $CaCl_2$, 100°; chromatographic separation of the *o*/*p*-isomers. [f]) MeI/Na_2CO_3, acetone, 20°. [g]) See d) (*o*/*p* = 5.3).

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[8]) The determination of the enantiomeric purity (e) of the corresponding methyl ester **10** *(cf. Scheme 6)* with Eu(hfc)$_3$ yielded e = 1.0 (see *Exper. Part*).

[9]) The methyl ester **10** *(cf. Scheme 6)* of (+)-*cis*-**8** ($[\alpha]_D^{20} = 34.7 \pm 1.3°$ ($CHCl_3$) and $48.3 \pm 1.3°$ (EtOH)) yielded with Eu(hfc)$_3$ $e = 0.848 \pm 0.013$. From this follows that enantiomerically pure (+)-*cis*-**10** should have $[\alpha]_D^{20} = 40.9 \pm 0.9°$ ($CHCl_3$; three independant measurements, see *Exper. Part*) and $57.0 \pm 2.4°$ (EtOH). These values differ from those published. It was reported [17] that (+)-*cis*-**8** with $[\alpha]_D^{20} = 15°$ ($CHCl_3$) yielded (+)-*cis*-**10** with $[\alpha]_D^{20} = 27°$ ($CHCl_3$), *i.e.* optically pure (+)-*cis*-**10** should have $[\alpha]_D^{20} = 54°$ ($CHCl_3$), based on $[\alpha]_D^{20} = 30°$ for the optically pure acid [17]. On the other hand, *Krieger* and *Landgrebe* [19] obtained from (+)-*cis*-**8** with $[\alpha]_D^{20} = 22.9°$ ($CHCl_3$) the corresponding methyl ester with $[\alpha]_D^{20} = 32.8°$ ($CHCl_3$). The maximum specific rotation for (−)-*cis*-**10** ($[\alpha]_D^{25} = -51°$ (EtOH)) was determined by epimerization and saponification to (+)-*trans*-**8**. With respect to these discrepancies, we rely on our values for specific rotations and optical purities of (+)-*cis*-**8**, its derivatives, and chemically correlated compounds.

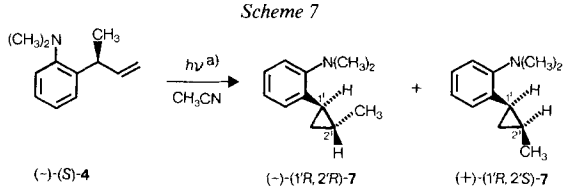
11 ($[\alpha]_D^{12} = 89.2 \pm 1.4°$ (EtOH)[10])). The methanesulfonyl derivative of (+)-(1*S*,2*S*)-**11**, formed in 2,6-lutidine with MsCl, yielded, on reduction with $LiAlH_4$, (+)-(1*S*,2*S*)-1-methyl-2-phenylcyclopropane ((+)-(1*S*,2*S*)-**12**) accompanied by 4-phenyl-1-butene as the main by-product (see *Exper. Part*).

Nitration of cyclopropylbenzenes leading to high *o*/*p*-ratios can be performed with HNO_3/Ac_2O at −60° [36–38]. Similarly, the nitration of the crude (+)-(1*S*,2*S*)-**12** yielded *o-trans*-**13**/*p-trans*-**13** in a ratio of 7.5:1. Without further purification, the mixture was reduced (Fe/HCl) to the *o*/*p*-mixture of the corresponding aniline derivatives (1′*S*,2′*S*)-**14** which were separated by chromatography (see *Exper. Part*). The *N*,*N*-dimethylation of (1′*S*,2′*S*)-**14** with MeI/Na_2CO_3 in acetone furnished the desired (+)-(1′*S*,2′*S*)-**7** with $[\alpha]_D^{25} = 41.0 \pm 0.4°$ (CCl_4) and in an optical purity of 0.976 ± 0.028 as determined for the starting material (+)-(1*S*,2*S*)-**8**.

The same reaction sequence was applied to the *cis*-acid (+)-(1*S*,2*R*)-**8** *(Scheme 6)*. The nitration of (+)-(1*S*,2*R*)-**12** yielded *o-cis*-**13**/*p-cis*-**13** in a ratio of 5.3:1. The isomers were separated by chromatography after reduction to the *o*/*p*-mixture of the corresponding aniline derivatives (1′*R*,2′*S*)-**14**. The *N*,*N*-dimethylation of the *o*-isomer led to the desired (+)-(1′*R*,2′*S*)-**7** with $[\alpha]_D^{25} = 155.2 \pm 2.1°$ (CCl_4) and e = 0.848 ± 0.024 as determined for (+)-(1*S*,2*R*)-**10**, *i.e.* $[\alpha]_D^{25} = 183.0 \pm 2.5$ (CCl_4) for the enantiomerically pure material.

The photolyses of (−)-(*S*)-**4** (p = 0.788 ± 0.051) in MeCN through a filter (*Jena*-glass) furnished, at conversion rates of 15 to 45%, (−)-*trans*-**7** in 12 to 20% yield and (+)-*cis*-**7** in 2.8 to 4.8% yield *(Scheme 7)*. The recovered reactant showed nearly no loss of optical purity (see *Table 3, Exper. Part*). The products which experienced a rapid loss of optical activity under the conditions of irradiation showed small but significant rotations. From the signs of rotation, the (1′*R*,2′*R*)- and (1′*R*,2′*S*)-configurations have been established for *trans*-**7** and *cis*-**7**, respectively *(Scheme 7)*.

Scheme 7



(−)-(*S*)-**4** (−)-(1′*R*,2′*R*)-**7** (+)-(1′*R*,2′*S*)-**7**

a) Filter: *Jena*-glass; 20°.

The linear regression obtained by plotting the optical yields of (−)-*trans*-**7** *vs.* rates of formation, after separation from the starting material and from (+)-*cis*-**7**, led to an initial p-value (p_0) of 0.288 ± 0.052[11]) *(cf. Fig. 2)*. The corresponding p_0-value for (+)-*cis*-**7** could only be estimated on the basis of the fact that the amount of (+)-*cis*-**7** was very small, so that only two [α]-value could exactly be measured. From these follows $p_0(cis) \approx 0.15$. If a third [α]-value with a greater uncertainty in measurement is also taken

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[10]) *Sugita* and *Inouye* [35] reported $[\alpha]_D^{12} = -46.6°$ (EtOH) for p = 0.513, which is in good agreement with our value ($[\alpha]_D^{20}$ (calc.) = 90.8° for p = 1.0).

[11]) Confidence limits are calculated for an error probability of 10%. All values are calculated for p = 1.0 of the starting material.

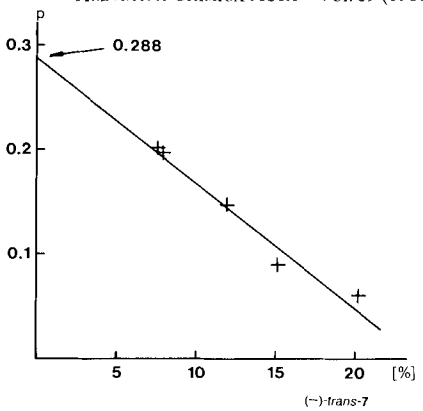


Fig. 2. *Optical purity of (−)-*trans-**7** vs. *its rate of formation*

into account, the confidence limits for p_0 can be estimated to be of the order of ±0.05, *i.e.* $p_0(cis) \approx 0.15 \pm 0.05$.

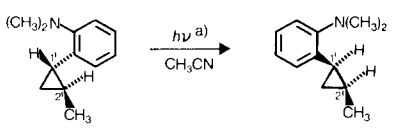
The initial *trans/cis*-ratio for the photoreaction of (−)-(*S*)-**4**, calculated by linear regression, is 4.71 ± 0.14 (= 82.5%) (−)-*trans*- and 17.5% (+)-*cis*-**7**) on the basis of 7 measurements *(cf. Table 7, Exper. Part)*.

Since (−)-*trans*-**7** and (+)-*cis*-**7** underwent a rapid photoracemization in the course of the photoreaction of (−)-(*S*)-**4**, we were also interested to investigate the stereochemical outcome of these *trans/cis*-isomerizations.

When (+)-*trans*-**7** (p = 0.976 ± 0.028) was irradiated, the rapid formation of (+)-*cis*-**7** was observed. The *trans/cis*-ratio amounted to *ca.* 4.5 after 50 min of irradiation. Both diastereoisomers lost quickly their optical purity. The p_0 value for the formation of (+)-*cis*-**7** turned out to be 0.088 ± 0.031, *i.e.* the conversion of (+)-*trans*-**7** into (+)-*cis*-**7** is accompanied by an appreciable loss of optical activity. Since (+)-*cis*-**7** is (1′*R*,2′*S*)-configurated and (+)-*trans*-**7** (1′*S*,2′*S*)-configurated, it can be concluded that the isomerization occurs with a slight preponderance of the process leading to inversion of configuration at C(1′) and, correspondingly, retention of configuration at C(2′) *(Scheme 8)*. It is of importance to notice that (+)-*cis*-**7** derived photochemically from (−)-(*S*)-**4** is accompanied by (−)-*trans*-**7**. This means that (+)-*cis*-**7** is, indeed, the genuine product of the ADPM rearrangement of (−)-(*S*)-**4**, because the photoisomerization of (−)-*trans*-**7** would yield (−)-*cis*-**7** *(cf. Schemes 7* and *8)*.

Similar results were obtained, when (+)-*cis*-**7** (p = 0.848 ± 0.024) was irradiated in MeCN. The *trans/cis*-ratio attained after 20 min of irradiation amounted to *ca.* 3.5. The

Scheme 8

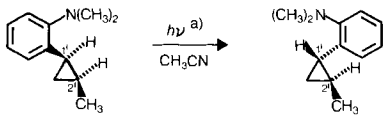


(+)-(1′*S*,2′*S*)-**7** (+)-(1′*R*,2′*S*)-**7**

a) Filter: *Jena*-glass; 20°.

only product[12]) formed was (+)-*trans*-**7** with a p_0-value of 0.12 ± 0.04[13]) and the (1′*S*,2′*S*)-configuration *(Scheme 9)*. Again, a slight dominance of the process that yields inversion of configuration at C(1′) and retention of configuration at C(2′) was observed. This process seems to be – within the limits of the accuracy of our measurements – slightly more effective for the *cis*/*trans*-isomerization of (+)-*cis*-**7** than for the reverse reaction of (+)-*trans*-**7**.

Scheme 9

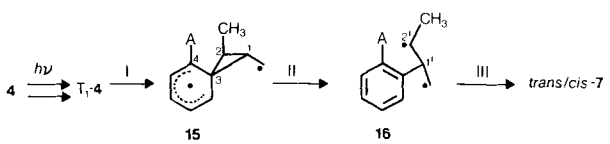


(+)-(1′*R*,2′*S*)-**7** (+)-(1′*S*,2′*S*)-**7**

[a]) Filter: *Jena*-glass; 20°.

3. Discussion. – The loss of > 70% in optical activity in the T_1-ADPM rearrangement of (−)-(*S*)-**4** is a reliable indication that the skeletal transposition of the allylic moiety proceeds in a non-concerted way, *i.e.* by involvement of discrete 1,4- and 1,3-diradicals according to the general scheme of ADPM rearrangements (*cf. Scheme 10* and [1] [3]). On the other hand, we should consider the fact that there is a remaining part of optical activity – emerging in the genuine ADPM product – which is due to surplus retention of configuration at the pivot atom (C(1′) in the reactant and C(2′) in the products) for the

Scheme 10



A = $(CH_3)_2N$

trans-product ((−)-(1′*R*,2′*R*)-**7**) and surplus inversion for the *cis*-product ((+)-(1′*R*,2′*S*)-**7**). Furthermore, we have to recognize the fact that the *trans*-product shows a higher genuine optical yield ($y = 28.8 \pm 5.2\%$) than its *cis*-isomer ($y \approx 15 \pm 5\%$)[14]). To rationalize these observations, we ought to analyze the outcome of bond formation and bond cleavage – especially with respect to the stereochemical consequences – in the individual *Steps I–III (cf. Scheme 10)* of the ADPM rearrangement of (−)-(*S*)-**4**.

From the estimates of the triplet energies of the two chromophors of **4** *(cf. Chapt. 2)*, we can conclude that the T_1-state of **4** is localized on the aromatic ring[15]). Thus, in *Step I* bond formation takes place by interaction of the T_1-state of the aromatic moiety with the

[12]) Prolonged irradiations led to increasing amounts of not distillable material.

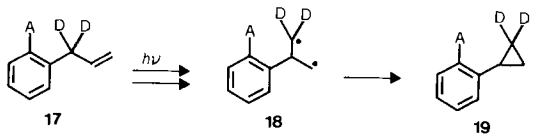
[13]) Only three measurements could be taken into account (see *Exper. Part*).

[14]) Uncertainty in the optical yield of the *cis*-product probably emerges from the difficulties in isolating and purifying the small amounts. However, there is no doubt that the *trans*-product is formed in a higher optical yield than the *cis*-product (*cf.* also *Table 3, Run 4* and *5*).

[15]) This follows also from a series of phosphorescence measurements of 3,3-diaryl-1-propenes, substituted in one aromatic moiety with π-donors and π-acceptors [39].

S_0-state of the allylic side chain to yield the 1,4-diradicals **15**[16]). These diradicals may exist still in the triplet state or revert to the singlet ground state. However, based on the fact that cyclopropane-1,2-dimethyl diradicals – comparable to **15** – undergo, in their ground state, *Grob* fragmentation to the corresponding 1,4-diens (*cf.* [1b] [44]), we suppose *Step II* to occur still on the triplet hyperface to yield the 1,3-diradicals **16**. Whereas *Step I* might be directly reversible, *i.e.* on the triplet hypersurface, or indirectly reversible, *i.e. via* intersystem crossing of **15**, to the singlet ground state which will then revert by *Grob* fragmentation to **4** in the ground state[17]). *Step II* should be irreversible, especially on the triplet hypersurface (*cf.* [1b] [46]). Otherwise for (−)-(*S*)-**4**, a certain extent of racemization would be expected upon irradiation leading to ADPM reactivity. This is, however, not the case within the limits of our measurements. To establish this fact for another T_1-ADPM rearrangement, we synthetized (see *Exper. Part*) and irradiated 2-([1′,1′-$^2H_2$]-allyl)-*N*,*N*-dimethylaniline (**17**) in MeOH to > 50% conversion to the expected 2-([2′,2′-$^2H_2$]cyclopropyl)-*N*,*N*-dimethylaniline (**19**; *Scheme 11*). The recovered starting material showed no trace of the ^2H label at C(3′) (^2H-NMR). If the symmetrical 1,3-diradical **18** would have reacted back to **17** to some extent, the label would have been detected also at C(3′). This experiment demonstrates again that *Step II (Scheme 10)* is the decisive step in ADPM rearrangements. However, it might be complicated by competing reactions of **15** back to **4** *via* the triplet or singlet channel.

Scheme 11



17 **18** **19**

A = $(CH_3)_2N$

The final *Step III* may still occur on the triplet hypersurface or after intersystem crossing in the singlet state of **16**, and will lead to the *trans*- and *cis*-isomers of **7** (*cf.* [47] [48]).

The four possible conformers of (−)-(*S*)-**4**, which may undergo the ADPM rearrangement, are shown below[18]). Bond formation between C(2) and C(2′) in the T_1-state of the

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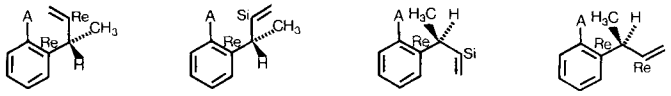
[16]) This statement underlines the point that the T_1-photoreaction of **4** would not follow the NEER principle (*cf.* [40]), *i.e.* the allylic side chain will retain its torsional freedom in the T_1-state of **4**. We can consider T_1-*N*,*N*-dimethylaniline as a model for triplet-excited **4**. The first-order decay rate of the T_1-state of *N*,*N*-dimethylaniline at 20° is in the order of $(1.5–3.0)\cdot 10^6 s^{-1}$ depending on the solvent (*cf.* [12b] [41] and lit. cited therein). This may give the lowest limit for the rate of bond formation between C(2) and C(2′) in T_1-**4** and should be compared with the rate of rotations around the C(2)–C(1′) and the C(1′)–C(2′) bonds, which may possess rotational barriers of 3 to 6 kcal mol^{-1} (*cf.* [42]). If we assume a normal ln A value of 28.3 for torsional motions (*cf.* [43]), we find for k(rot) $(60–10\,000)\cdot 10^6 s^{-1}$ at 20°, which is well above the decay rate of T_1-*N*,*N*-dimethylaniline. This means that the T_1-state of **4** will await the optimal conformation of the allylic side chain for bond formation.

[17]) Such mechanisms might also be responsible for the photochemical (*E*)/(*Z*)-isomerization of 2-butenylbenzenes and related compounds (*cf.* [1] [3] [45]).

[18]) The first of the configurational prefixes attached to the compound numbers refers to the s-*cis*- (*c*) or s-*trans*-orientation (*t*) around the C(2)–C(1′) bond and the second one around the C(1′)–C(2′) bond. The relative topicities (*Re*, *Si*) at C(2) and C(2′) are indicated with respect to the part above the plane of paper (= π-plane).



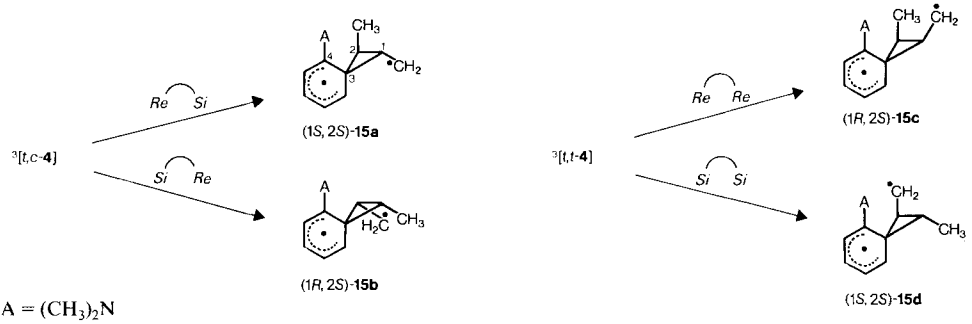
c,c-**4** *c,t*-**4** *t,c*-**4** *t,t*-**4**

A = $(CH_3)_2N$

aromatic part of the molecules can – for steric reasons – solely occur in a disrotatory mode to yield the corresponding spiro[2.5]octadiendiyl intermediates *(cf. Scheme 12)*. The disrotatory combination of the topicities at C(2) and C(2′) shows that *c,c*-**4** and *t,t*-**4** and, on the other hand, *c,t*-**4** and *t,c*-**4** will lead to the same configuration at C(1) and C(2) of the intermediates **15**. The steric interference of the $(CH_3)_2N$ group at C(1) and the C(2′)–C(3′) or the C(2′)–H bonds in *c,c*-**4** and *c,t*-**4**, respectively, disfavours these conformers. We will, therefore, restrict our discussions to the reaction of *t,c*-**4** and *t,t*-**4**.

The expected structures derived from these conformers are presented in *Scheme 12*. In both cases, a *trans*- and *cis*-configurated intermediate 1,4-diradical **15** should be formed.

Scheme 12[a])



A = $(CH_3)_2N$

[a]) *Re⌒Si etc.* describe the combination of topicities at C(2) and C(2′).

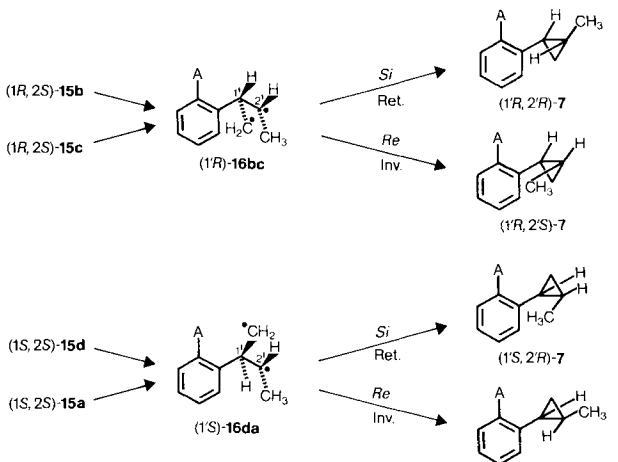
The two *trans*- (**15a** and **15d**) and *cis*-forms (**15b** and **15c**) are distinguished by the relative position of the $(CH_3)_2N$ group at C(4) with respect to the substituents at the cyclopropane subunit. Molecular models indicate that the *Re,Si*-combination of ^{3}[*t,c*-**4**] results in a peri-motion[19]) of CH_3–C(1′) with respect to the $(CH_3)_2N$ group at C(1) and a *trans*-motion of CH_2(3′) in relation to CH_3–C(1′). The opposite combination (*Si,Re*) leads to a peri-motion of H–C(1′) in relation to $(CH_3)_2N$ with concomitant *cis*-motion of CH_2(3′) and CH_3–C(1′). The motions in the other excited conformer (^{3}[*t,t*-**4**]), induced by the C(2)–C(2′) bond formation, cause a strong peri-interaction ($(CH_3)_2N$, CH_3–C(1′)) and *cis*-interaction (CH_3–C(1′), CH_2(3′)) in the *Re,Re*-mode, whereas the *Si,Si*-mode of combination only yields H–C(1′), $(CH_3)_2N$ peri-interaction and *trans*-orientation of CH_3–C(1′), CH_2(3′). Since the strong peri-interaction between CH_3–C(1′) and $(CH_3)_2N$ should dominate the other steric interactions, we can conclude that the formation of (1*R*,2*S*)-**15b** should be favoured over the formation of (1*S*,2*S*)-**15a** and, on the other

[19]) The steric situation in the transition state of bond formation between C(2) and C(2′) resembles that of a peri-substituted naphthalene.

hand, the formation of (1*S*,2*S*)-**15d** over that of (1*R*,2*S*)-**15c**. No loss of optical activity will occur so far in the different reaction paths, *i.e.* the configurational information of the starting material will be fully transferred to the 1,4-diradicals **15a–d**.

The next step *(Step II, cf. Scheme 10)* will lead to the cleavage of the C(2)–C(3) bond in **15a–d** to yield the diastereoisomeric 1,3-diradicals **16** *(Scheme 13)*. The intermediates **15b** and **15c** as well as **15a** and **15d** will, in principle, yield the same 1,3-diradicals, namely (1′*R*)-**16bc** and (1′*S*)-**16da**, respectively[20]). If free rotation around the C(1′)–C(2′) bond is allowed, the two 1,3-diradicals become enantiomeric. In this case, we expect both 1,3-diradicals to cyclize to **7** with the same *trans*/*cis*-ratio. However, if the two 1,3-diradicals still have a certain configurational memory of their precursors, the cyclization to **7** may occur with different *trans*/*cis*-ratios. Since the cyclization of (1′*R*)-**16bc** and (1′*S*)-**16da** leads to the enantiomers of *trans*- and *cis*-**7** (see *Scheme 13*), we should expect variations

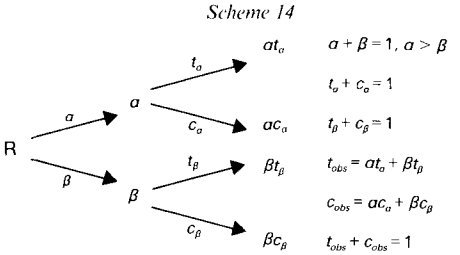
Scheme 13[a])



[a]) Locants are chosen so that they correspond to those in the products.

in the optical purity of the *trans*- and *cis*-product depending on the rotational behaviour of (1′*R*)-**16bc** and (1′*S*)-**16da**. The borderline cases may be described more precisely by using the relations and definitions shown in *Scheme 14*. If we call α/β the ratio with which an optically active compound R reacts to two stereoisomeric intermediates, and t_α/c_α and

Scheme 14



[20]) The originally formed 1,3-diradicals **16b** and **16c** (**16d** and **16a**) differ in the conformation around the C(2)–C(1′) bond.

t_β/c_β the ratios with which these intermediates or their consecutive products are transformed into the final products (t_{obs} and c_{obs}), we can calculate the corresponding optical purities: $p^t_{obs} = (\alpha t_\alpha - \beta t_\beta)/t_{obs}$ and $p^c_{obs} = (\alpha c_\alpha - \beta c_\beta)/c_{obs}$[21]).

Our first borderline case discussed above corresponds to $t_\alpha/c_\alpha = t_\beta/c_\beta$, *i.e.* both intermediates yield the enantiomeric products with the same *trans*/*cis*-ratio. The corresponding optical purities are: $p^t_{obs} = p^c_{obs} = \alpha$–$\beta$. We may call this the average optical purity $p_{av} = \alpha$–β. In this case, the p-values are only determined by the first step of the reaction, *i.e.* by α/β. The greater α/β is, the greater will be the optical purity (optical yield) of the resulting diastereoisomers.

Our second borderline case discussed above is described by $t_\alpha/c_\alpha \neq t_\beta/c_\beta$ and may be subdivided in the special cases: *a)* If we assume that $t_\alpha/c_\alpha > t_\beta/c_\beta$, we find that $p^t_{obs} > p_{av} > p^c_{obs}$. This means that the greater the difference between the two *trans*/*cis* ratios is, the greater will be the difference of the optical purities of the products. However, the total optical purity ($p^t_{obs} \cdot t_{obs} + p^c_{obs} \cdot c_{obs}$) cannot exceed p_{av}.

b) One of the diastereoisomeric products will become racemic when $\alpha t_\alpha = \beta t_\beta$ ($p^t_{obs} = 0$) or $\alpha c_\alpha = \beta c_\beta$ ($p^c_{obs} = 0$). The maximum optical purity of the second compound will then be given by $p^c_{obs} = p_{av}/c_{obs}$ or $p^t_{obs} = p_{av}/t_{obs}$. It follows that by a given α/β-ratio the maximum optical purity to be observed will depend on the difference of the two *trans*/*cis*-ratios. The greater it is, the greater will be the observed optical purity.

c) In the case of $t_\alpha = 1$ ($c_\alpha = 0$), the optical purity of the *trans*-compound will be given by $p^t_{obs} = (\alpha - \beta t_\beta)/t_{obs} = (p_{av} + \beta c_\beta)/t_{obs}$. It follows that the smaller t_β/c_β is, the greater will be p^t_{obs} by a given α/β ratio. In any case, the *cis*-product will be optically pure ($p^c_{obs} = 1$).

We also can apply *Scheme 14* to understand the interdependence of the configurational changes (preponderant formation of molecules with retention or inversion of configuration) at the pivot atom (C(1') in the reactant and C(2') in the products) in the ADPM rearrangement investigated. In this case, α and β denote the (*R*)- or (*S*)-configuration created at the new C-centre of importance (C(1) in *Scheme 12*) in the first step of the reaction. The following two reaction steps are of importance with respect to the change of the configuration at the pivot atom, which may occur with retention (*e.g.* indicated by t_α or c_β) or inversion (*e.g.* indicated by t_β or c_α). Now, we can see that, as long as $\alpha t_\alpha > \beta t_\beta$ and hence $t_\alpha/t_\beta > \beta/\alpha$ (see *Scheme 14*), the *trans*-product will be formed with a preponderance of the molecules showing retention of configuration at C(2'). The accompanying *cis*-product may show inversion at C(2') in the case that $\alpha c_\alpha > \beta c_\beta$ and correspondingly $c_\alpha/c_\beta > \beta/\alpha$. Thus, all optically active DPM systems of the type described here, where by a given α/β-ratio $t_\alpha/t_\beta \approx c_\alpha/c_\beta$ or $t_\alpha/c_\alpha \approx t_\beta/c_\beta$ and both ratio are $> \beta/\alpha$, will yield the two diastereoisomeric cyclopropane derivatives with opposite configuration at the pivot atom. This should, in general, be the case, because without additional molecular constraints the rotational behaviour of the crucial intermediate 1,3-diradicals of type **16** *(cf. Scheme 13)* will be similar, *i.e.* $t_\alpha/c_\alpha \approx t_\beta/c_\beta$. However, great differences in the rotational behaviour may lead to $\beta c_\beta > \alpha c_\alpha$ in the case that $\alpha t_\alpha > \beta t_\beta$. Here, we obtain $t_\alpha/t_\beta > \beta/\alpha > c_\alpha/c_\beta$ or $t_\alpha/c_\alpha > \beta/\alpha > t_\beta/c_\beta$, *i.e.* both diastereoisomeric cyclopropane derivatives will be formed with the same configuration (retention in the case discussed) at the pivot atom.

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[21]) A comparison of *Scheme 13* and *14* shows that αt_α additionally designates the (1'*R*,2'*R*)-configuration of **7** and αc_α the (1'*R*,2'*S*)-configuration *etc.*

Now, we can turn to the results obtained for the ADPM rearrangement of (−)-(*S*)-**4**. From $p^t_{obs} = 0.288 \pm 0.052$ for (−)-(1′*R*,2′*R*)-**7** and $p^c_{obs} \approx 0.15 \pm 0.05$ for (+)-(1′*R*,2′*S*)-**7**, and $t_{obs}/c_{obs} = 4.71 \pm 0.14$, we can conclude that the rearrangement occurred according to the case *a* discussed above, *i.e.* $t_\alpha/c_\alpha > t_\beta/c_\beta$. These data also lead to the conclusion that t_α/c_α will not strongly deviate from t_β/c_β, and hence the *trans*- and *cis*-configurated cyclopropane derivatives should show opposite configuration at the pivot atom (C(2′)). With the yields of the enantiomers given in *Table 1*, the following values for 20° can be calculated:

$\alpha/\beta = 63.2/36.8 = 1.72$ leading to $p_{av} = 0.264$;

$t_\alpha/c_\alpha = 53.1/10.1 = 5.3$, and $t_\beta/c_\beta = 29.4/7.4 = 4.0$.

$\alpha/\beta = 1.72$ means for the conformers of (−)-(*S*)-**4** that *t,c*-**4** in the triplet state prefers ring closure on the side (*Si,Re*) opposite to that including CH_3–C(1′) (→(1*R*,2*S*)-**15b**), whereas *t,t*-**4** in the triplet state preferentially undergoes ring closure just on the side (*Si,Si*) including CH_3–C(1′) (→(1*R*,2*S*)-**15c**). This is a contradiction for steric reasons which can be suspended, if we assume that *t,c*-**4** is the strongly preferred conformer for the ADPM rearrangement in the triplet state with a 1.72:1 ratio in favour of the *Si,Re* bond formation in the first step *(Step I, Scheme 10)*. On the other hand, if we assume that, on steric grounds, ring closure will exclusively occur on the side of the molecules opposite to that including CH_3–C(1′), 1.72:1 should be the ratio of conformers ([*t,c*-**4**]/[*t,t*-**4**]) having undergone the ADPM rearrangement[22]).

Table 1. *Initial Percentage of Enantiomers of* (−)-trans-**7** *and* (+)-cis-**7** *Formed in the ADPM Rearrangement of* (−)-(S)-**4**[a])

Diastereoisomer[b])	Enantiomer	Yield[c]) [%]
(−)-*trans*-**7**	(−)-(1′*R*,2′*R*)-**7**	53.1 ± 2.7
	(+)-(1′*S*,2′*S*)-**7**	29.4 ± 2.5
(+)-*cis*-**7**	(+)-(1′*R*,2′*S*)-**7**	10.1 ± 1.0
	(−)-(1′*S*,2′*R*)-**7**	7.4 ± 1.0

[a]) In MeCN at 20° *(cf. Scheme 7)*.

[b]) Initial *trans/cis*-ratio for **7** = 4.71 ± 0.14.

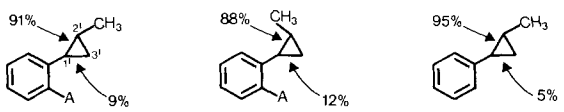
[c]) Calculated according to the assumption that $p = [\alpha]/[\alpha]_0 = (e_+ - e_-)/(e_+ + e_-)$ *(cf. Chapt. 2)*.

Photochemically induced stereomutations of cyclopropane derivatives are well-known and may occur under direct irradiation or in the presence of triplet sensitizers (*cf.* [48]). The *trans/cis*-isomerization of phenyl-substituted cyclopropane derivatives proceed, as a rule, much cleaner in the triplet than in the singlet state (*cf.* [48]). Since the *trans/cis*-isomerization of (+)-(1′*S*,2′*S*)- and (+)-(1′*R*,2′*S*)-**7**, at short times of irradiation, took place without formation of further products, we suppose that it mainly occurs

[22]) 3-Arylcyclohexenes (aryl = 2-(*N*-methylamino)phenyl [49] or 4-formylphenyl [50]) undergo the T_1-ADPM rearrangement upon irradiation to yield the corresponding *exo*-configurated 6-arylbicyclo[3.1.0]hexanes. The energetically favoured pseudoequatorial position of the aryl substituent at the cyclohexene ring corresponds to the *t,t*-arrangement of **4**. To adopt at *t,c*-like conformation, the aryl substituent should occupy the energetically unfavourable pseudoaxial position at the cyclohexene ring. Therefore, it seems that ADPM rearrangements can easily occur in a *t,t*-like conformation of the reactant – a general experience in DPM and ODPM rearrangements (*cf.* [1–3]).

in the triplet state. The fact that the *trans/cis*-isomerization of (+)-*trans*-**7** and (+)-*cis*-**7** *(cf. Scheme 8* and *9)* is accompanied by 9% and 12% inversion of configuration, respectively, can best be explained by assuming that the triplet-excited molecules undergo ring cleavage to the corresponding 1,3-diradicals not only at the C(1′)–C(2′) bond but also at the C(1′)–C(3) bond. If we presuppose that the *trans/cis*-isomerization *via* cleavage of the C(1′)–C(2′) bond will lead to a complete loss of the optical activity, the observed remaining optical activity will be a direct measure for the extent of C(1′)–C(3′) bond cleavage *(cf. Scheme 15)*. This bond cleavage can only lead to inversion of configuration at C(1′) as observed. On the other hand, in the case of thermal stereomutations of cyclopropane derivatives, the general tendency in the corresponding 1,3-diradicals is directed to a slower rotation of the more massively substituted radical centres than the others (*cf.* [47b] [51]), in accordance with a ponderal deceleration of internal rotations (*cf.* [52] [53]). Thus, if the remaining optical activity in the *trans/cis*-isomerization of (+)-*trans*- and (+)-*cis*-**7** would be the result of different rates of rotation due to a ponderal effect in the 1,3-diradicals (generated by C(1′)–C(2′) bond cleavage), one would expect inversion of configuration at C(2′) in the resulting isomers.

Scheme 15[a])



(+)-*trans*-**7** (+)-*cis*-**7** (±)-*trans*-**12**

A = $(CH_3)_2N$

[a]) The percentages refer to bond cleavage under direct irradiation.

Our results obtained with (+)-*trans*-**7** and (+)-*cis*-**7** are in good agreement with earlier observations made by *Salisbury* [54] who found that the gas-phase photolysis of racemic *trans*-1-methyl-2-phenylcyclopropane ((±)-*trans*-**12**) yields, besides (±)-*cis*-**12**, methallylbenzene, the formation of which can only be explained by the cleavage of the C(1)–C(3) bond (*cf. Scheme 15;* for other examples, see [48]). The observed percentage of the cleavage (5%) of the C(1)–C(3) bond is in good agreement with our values observed on the corresponding anilines *(cf. Scheme 15)*[23]).

We thank Miss *A. Spiess* for experimental help, Dr. *W. Bernhard* for mass spectra, Dr. *M. Cosandey* for NMR spectra, and *F. Nydegger* for elemental analyses. Support of this work by the *Swiss National Research Foundation* is gratefully acknowledged.

[23]) The fact that electronically excited cyclopropane derivatives may undergo bond cleavage not only at the 'most substituted bond' is already known for a longer time (*cf.* [48] [55]). On the other hand, the kinetic interpretation of thermal stereomutations of cyclopropane derivatives was, for a long time, based on the 'most substituted bond hypothesis', *i.e.* the assumption that vibrationally induced bond cleavage occurs only at the bond linking the most substituted C-atoms in the cyclopropane ring. Recently, it has been recognized in several cases that also thermal bond cleavage in cyclopropane derivatives may occur at different bonds (*cf.* [33] and lit. cited therein).

Experimental Part

General. See [10]. Flash chromatography (FC) according to *Still et al.* [56] on silica gel *60 (Merck No. 9385)*.

1. (−)-(*S*)-*N*,*N*-Dimethyl-2-(1′-methylallyl)aniline ((−)-(*S*)-4) (*cf.* [11]). – A mixture of *(−)-(S)-2-(1′-methylallyl)aniline* ((−)-(*S*)-**5**; 2.66 g, 18.07 mmol; $[\alpha]_D^{25} = -30.8 \pm 1.3°$ (*c* = 2.54, cyclohexane; p = 0.788 ± 0.064)) [10] and MeI (5.13 g, 36.14 mmol) was stirred at r.t. in dried acetone (85 ml; freshly distilled over P_2O_5) in the presence of K_2CO_3 (4.99 g, 36.14 mmol) during 38 h. The acetone was evaporated, and the residue treated with 100 ml of Et_2O, filtered, and the soln. again evaporated. FC (petroleum ether/Et_2O 30:1): 2.80 g (88.4%) of pure (−)-(*S*)-**4** (bulb-to-bulb destillation at 100–125°/12 Torr). $[\alpha]_D^{25} = -57.3 \pm 1.5°$ (*c* = 2.19, cyclohexane)[24]) and −67.1 ± 1.4° (*c* = 7.13, CCl_4). UV (MeCN): 278.7 (1350, sh), 251.0 (4420). UV (EtOH): 280.7 (960, sh), 249.2 (3800). IR (film): 2838, 2735 ($(CH_3)_2N$); 1639, 1601, 1497 (Ar); 951, 916 ($CH=CH_2$); 760 (4 adj. arom. H). ^{1}H-NMR: 7.2–6.8 (*m*, 4 arom. H); 5.96 (*ddd*, H–C(1′)); 5.1–4.8 (*m*, 2 H–C(3′)); 4.3–3.9 (*dq*, H–C(1′)); 2.62 (*s*, $(CH_3)_2N$); 1.27 (*d*, CH_3–C(1′)). MS: 176 (5, $M^{+\cdot}$ + 1), 175 (29, $M^{+\cdot}$) 161 (14), 160 (100), 158 (8), 146 (33), 145 (33), 144 (22), 134 (6), 132 (14), 131 (19), 130 (11), 118 (10), 117 (8), 115 (7), 91 (7). Anal. calc. for $C_{12}H_{17}N$ (175.28): C 82.23, H 9.78, N 7.99; found: C 82.30, 9.88, N 7.99.

2. Enantioselective Synthesis of the 2-Phenylcyclopropanecarboxylic Acids (*cf.* [32]). – 2.1. *Preparation of Bis[(−)-(1R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2,3-dione-(2E,3Z)-dioximato]cobalt(II) Hydrate.* 2.1.1. *(−)-(1R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2,3-dione Dioxime.* Essentially, the procedure described by *Forster* [57] was followed. Camphorquinone monoxime (38.8 g, 0.21 mol) as a 62:38 mixture of the (*Z*)- and (*E*)-isomer (so-called *Claisen* mixture [58]; determined by ^{1}H-NMR, *cf.* [59]) was dissolved in EtOH (192 ml) and combined with a soln. of $NH_2OH \cdot HCl$ (30.9 g, 0.45 mol) and $AcONa \cdot 3\,H_2O$ (61.8 g, 0.45 mol) in H_2O (202 ml). The orange-brown crystals (29.1 g) formed after 10 d standing at r.t. were separated and washed with boiling acetone (4 × 194 ml). From the combined acetone solns., 6.35 g of the (−)-(2*E*,3*Z*)-dioxime were separated by slow cooling. The residue of the first crop of crystals (14.7 g) was again boiled in acetone (280 ml). Cooling the filtrate yielded again 3.17 g of the (−)-(2*E*,3*Z*)-dioxime crystals which were recrystallized from AcOEt (1000 ml) to yield 5.96 g (23% yield with respect to the (3*Z*)-camphorquinone monoxime) of the pure (−)-(2*E*,3*Z*)-dioxime. M.p. 191–193° (dec.; [32a]: 201°). $[\alpha]_D^{22} = -63.7 \pm 1.6°$ (*c* = 2.47, EtOH; [32a]: −61.9°).

A second run with 78.5 g of camphorquinone monoxime yielded, after standing for 40 d, 16.7 g (31.8%) of (−)-(2*E*,3*Z*)-dioxime (m.p. 185–186°; $[\alpha]_D^{22} = -64.5 \pm 1.6°$ (*c* = 2.63, EtOH)). IR (*cf.* [60]): 3190 (OH); 3130; 3060; 3000; 2975; 2940; 2880; 1665 (>C=N–); 1617; 1571; 1490 (OH); 1422; 1400; 1395; 1378; 1372; 1121; 1067; 1025; 1000; 993; 961 (=N–O–); 911; 873; 821; 657. ^{1}H-NMR: Identical with that reported in [59b].

2.1.2. *Bis[(−)-(1R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2,3-dione-(2E,3Z)-dioximato]cobalt(II) Hydrate.* 1.02 g (5.22 mmol) of the (−)-(2*E*,3*Z*)-dioxime were reacted according to the procedure in [32a] with 0.621 g (2.61 mmol) of $CoCl_2 \cdot 6\,H_2O$ under Ar to yield 1.03 g (84%) of the Co(II) catalyst. The catalyst was applied in the enantioselective cyclopropanization reaction without further purification.

Table 2. *Results of the Enantioselective Synthesis of (+)-(1S,2R)- and (+)-(1S,2S)-***9**

Run	Yield[a])		*trans/cis*-ratio	$[\alpha]_D^{25}$ (EtOH)[b])		Optical purity (p)	
	[g]	[%]		(+)-(1*S*,2*S*)-**9**	(+)-(1*S*,2*R*)-**9**	(+)-(1*S*,2*S*)-**9**	(+)-(1*S*,2*R*)-**9**
1	1.2	39	2.41	113.5 ± 2.9	10.3 ± 0.6	0.36 ± 0.05[c])	0.42 ± 0.05[c])
2	23.3	86	3.13	163.0 ± 2.9	12.9 ± 0.9	0.52 ± 0.03	0.53 ± 0.12
3	17.7	86	2.45	116.5 ± 2.0	8.9 ± 0.8	0.37 ± 0.02	0.36 ± 0.09
4	22.7	84	1.54	188.3 ± 3.4	19.1 ± 1.2	0.60 ± 0.03	0.78 ± 0.18
[32a][d])	3.0	93	0.98	...	...	0.75[e])	0.67[e])

[a]) Distilled mixture of (+)-(1*S*,2*R*)- and (+)-(1*S*,2*S*)-**9**.

[b]) *c* = 2.6 to 2.8. Anal. samples of the stereoisomers were separated by FC.

[c]) Based on the p-values of the corresponding acids (see *2.2.2* to *2.2.4*). The other p-values are calculated for the ethyl esters with $[\alpha]_D^{25} = 311.7 \pm 11.7$ ((+)-(1*S*,2*S*)-**9**) and $[\alpha]_D^{25} = 24.5 \pm 4.1$ ((+)-(1*S*,2*R*)-**9**) in EtOH for the optically pure form.

[d]) Reaction temp. 24°.

[e]) p of the corresponding acid [32a].

[24]) $[\alpha]_D^{25} = 58.3°$ in [11] is a misprint.

2.2. *(+)-(1S,2R)- and (+)-(1S,2S)-2-Phenylcyclopropanecarboxylic Acid* ((+)-(1*S*,2*R*)- and (+)-(1*S*,2*S*)-**8**). 2.2.1. *Ethyl (+)-(1S,2R)- and (+)-(1S,2S)-2-phenylcyclopropanecarboxylate* ((+)-(1*S*,2*R*)- and (+)-(1*S*,2*S*)-**9**). The reaction of styrene and $N_2CHCOOEt$ in the presence of the Co(II) catalyst was performed under Ar. All reagents and solvents had been degassed and saturated with Ar before use. In a typical run (*cf.* [32a]), a soln. of $N_2CHCOOEt$ (16.28 g, 142.6 mmol; prepared [61] and freshly distilled [62]) in styrene (18 ml) was slowly (3 h) dropped into a soln. of the Co(II) catalyst (2.00 g, 4.28 mmol) in styrene (36 ml) under stirring at 15–20°. The stirring was continued until the evolution of N_2 had ceased (about 6 h). Distillation under vacuum (0.05 Torr) yielded, after a forerun of styrene, a mixture (23.3 g, 85.9%) of (+)-(1*S*,2*R*)- (24.2%) and (+)-(1*S*,2*S*)-**9** (75.8%) at 66–67°. Two further runs yielded an additional amount (40.4 g) of the mixture (see *Table 2, Runs 2–4*).

2.2.2. *Determination of the Optical Purities.* A pilot run *(Run 1, Table 2)* led to a 2.4:1 mixture of (+)-(1*S*,2*S*)- and (+)-(1*S*,2*R*)-**9** which were separated by FC (pentane/Et_2O 5:1) and further purified by bulb-to-bulb distillation.

(+)-(1*S*,2*S*)-**9** (0.66 g, 21.5%). IR (film): 1726 (COOR); 1410; 1337; 1324; 1186 (C–O–C); 755; 697. ^{1}H-NMR: Identical with that reported in [32b].

(+)-(1*S*,2*R*)-**9** (0.23 g, 7.5%). IR (film): 1735 (COOR); 1611, 1504 (Ar); 1454; 1407; 1388; 1361; 1280; 1166; 1090; 1041; 800; 760; 729; 704. ^{1}H-NMR: Identical with that reported in [32b].

The pure samples of (+)-(1*S*,2*S*)- and (+)-(1*S*,2*R*)-**9** (0.66 g and 0.23 g, resp.) were stirred with an equimolar amount of NaOH in EtOH/H_2O (1:1) at r.t. during 24 h. Workup and bulb-to-bulb distillation yielded the pure acids.

(+)-(1*S*,2*S*)-**8** (0.494 g, 51%). After distillation (125–135°/0.05 Torr). $[\alpha]_D^{22} = +113.5 \pm 2.9°$ (*c* = 2.58, EtOH; *cf. Run 1, Table 2*), *i.e.* p = 0.36 ± 0.05 *(cf. 2.2.3)*. IR (*cf.* [19] [63]): 1693 (COOH); 1605, 1497 (Ar); 1461; 1448; 1238 (C–O); 936; 753; 698. ^{1}H-NMR: Identical with that reported in [32b].

(+)-(1*S*,2*R*)-**8** (0.146 g, 75%). After distillation (135–140°/0.04 Torr). $[\alpha]_D^{20} = 10.3 \pm 0.6°$ (*c* = 3.39, $CHCl_3$; *cf. Run 1, Table 2*), i.e. p = 0.42 ± 0.05 *(cf. 2.2.4)*. IR: 1697 (COOH): 1607, 1500 (Ar); 1449; 1430; 1354; 1301; 1237 (C–O); 1159; 1112; 1101; 1085; 959; 891; 839; 821; 790; 755; 723; 698. ^{1}H-NMR: Identical with that reported in [32b].

2.2.3. *(+)-(1S,2S)*-**8**. The mixture (63.8 g, 0.34 mol) of (+)-(1*S*,2*S*)- and (+)-(1*S*,2*R*)-**9** of *Runs 2–4* (see *Table 2*) and NaOH (10.1 g, 0.253 mol; calc. for a (+)-(1*S*,2*S*)-**9** content of 74%) were dissolved in EtOH/H_2O (82:27 ml), the soln. slowly distilled, and the amount of distillate (82 ml after 130 min) substituted in the reaction flask by H_2O (82 ml; *cf.* [18]). The cooled mixture was diluted with H_2O (103 ml) and extracted with benzene (68 ml and then 2 × 40 ml). The aq. soln. was acidified with conc. HCl (26.7 ml) and extracted 3 times with Et_2O to yield, after drying, the raw (+)-(1*S*,2*S*)-**8** (43.4 g). Crystallization from CCl_4/pentane removed some racemic acid. The mother liquor yielded (+)-(1*S*,2*S*)-**8** (26.3 g, 0.16 mol; $[\alpha]_D^{22} = 193.8°$ (*c* = 2.21, EtOH)) which was treated with dehydroabietylamine (46.6 g, 0.16 mol) in AcOEt (1.5 l). The salt was twice recrystallized from AcOEt to yield finally 6.5 g (17% with respect to the content of (+)-(1*S*,2*S*)-**9** in the mixture) of the pure acid (+)-(1*S*,2*S*)-**8**. M.p. 27–30° ([18]: 25–26°). $[\alpha]_D^{2} = 304.1 \pm 5.9°$ (*c* = 3.74, EtOH; p = 0.976 ± 0.019; [16]: 311.7 for p = 1.0[25])). IR and ^{1}H-NMR were identical with those reported (see *2.2.2*). Anal. calc. for $C_{10}H_{10}O_2$ (162.19): C 74.06, H 6.22; found: C 73.88, H 6.39.

2.2.4. *(+)-(1S,2R)*-**8**. The combined benzene extracts from *2.2.3* were treated with NaOH (5.4 g) in H_2O (54 ml) (*cf.* [18]). The benzene (128 ml) was distilled off and substituted by EtOH (103 ml). Under further boiling, the solvent mixture (103 ml) was slowly removed by distillation (130 min). The cooled residual soln. was extracted with Et_2O (2 × 30 ml), acidified, and again extracted with Et_2O (3 × 50 ml) to yield, after drying of the Et_2O extracts, the raw acid (+)-(1*S*,2*R*)-**8** (15.4 g, 93% with respect to the content of (+)-(1*S*,2*R*)-**9** in the mixture). The acid was transformed into the quinine salt and the salt twice recrystallized from MeOH/H_2O (3:1, 180 ml). The purified salt yielded (+)-(1*S*,2*R*)-**8** which was recrystallized from CCl_4/pentane; m.p. 77–79°[26]). $[\alpha]_D^{20} = 23.9 \pm 1.0°$ (*c* = 2.83, $CHCl_3$; p = 0.819 ± 0.045; [17] [65]: $[\alpha]_D^{20} = 30°$ for p = 1.0). The e-value of the methyl ester (+)-(1*S*,2*R*)-**10** is 0.848 ± 0.013 (see *4.1*), *i.e.* the maximum specific rotation of (+)-(1*S*,2*R*)-**8** should be 29.2 ± 1.2° (instead of 30°) assuming that e = p. IR and ^{1}H-NMR: identical with those reported under *2.2.2*. Anal. calc. for $C_{10}H_{10}O_2$ (162.19): C 74.06, H 6.22; found: C 74.01, H 6.27.

3. Synthesis of (+)-(1′*S*,2′*S*)-*N*,*N*-Dimethyl-2-(2′-methylcyclopropyl)aniline ((+)-(1′*S*,2′*S*)-7). – 3.1. *Methyl (+)-(1S,2S)-2-Phenylcyclopropanecarboxylate* ((+)-(1*S*,2*S*)-**10**). According to [35], (+)-(1*S*,2*S*)-**8** (6.49 g, 40.0 mmol; p = 0.976 ± 0.019) was esterified with CH_2N_2 at −5 to −10° (*cf.* [66]). Bulb-to-bulb distillation (80–85°/0.01

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[25]) *Baldwin et al.* [64] reported $[\alpha]_D^{22} = 314°$ for the pure acid.

[26]) For $[\alpha]_D^{23} = 20°$, a m.p. 51–52° has been reported [21].

Torr; [19]: 65–75°/0.15 Torr) yielded pure (+)-(1*S*,2*S*)-**10** (6.68 g, 94.8%). $[\alpha]_D^{20} = 329.5 \pm 4.0°$ (*c* = 5.75, $CHCl_3$)[27]). The ^{1}H-NMR-spectroscopic determination of the enantiomeric purity with $Eu(hfc)_3$ in 1,1,1-trichloro-2,2-trifluoroethane yielded e = 1.0 with an uncertainty of 2%. IR (film): 2860 (CH_3O); 1726 ($COOCH_3$); 1608, 1499 (Ar); 1462; 1445; 1404; 1346; 1332; 1274; 1224; 1202; 1175; 1082; 1045; 939; 909; 845; 759; 700. ^{1}H-NMR: Identical with that reported in [32b].

3.2. *(+)-(1S,2S)-(2-Phenylcyclopropyl)methanol* ((+)-(1*S*,2*S*)-**11**). Ester (+)-(1*S*,2*S*)-**10** (6.68 g, 41.2 mmol), dissolved in Et_2O (100 ml), was reduced with $LiAlH_4$ (1.15 g, 30.3 mmol) [35]. Bulb-to-bulb distillation (95–100°/0.01 Torr) yielded (+)-(1*S*,2*S*)-**11** (5.54 g, 90.8%) with a purity (GC) of 98.2%. $[\alpha]_D^{12} = 89.2 \pm 1.4°$ (*c* = 5.64, EtOH, calc. for 100% chemical purity; [35]: $[\alpha]_D^{12} = -46.6°$ for p = 0.513, *i.e.* p = 0.98 ± 0.02 for (+)-(1*S*,2*S*)-**11**). IR (film): 3350 (OH); 1608, 1501 (Ar); 1095; 1037, 1028 (CH_2OH); 757; 747, 701 (5 adj. arom. H). ^{1}H-NMR: 7.3–6.8 (*m*, 5 arom. H); 3.44 (*m*, CH_2OH); 2.6 (br. *s*, OH); 1.67 (*m*, 1 H); 1.5–1.0 (*m*, 1 H); 0.76 (*t*-like, 2 H). MS: 149 (0.5, $M^{+\cdot}$ + 1), 148 (0.3, $M^{+\cdot}$), 88 (9), 86 (55), 84 (99), 58 (10), 51 (37), 49 (100). Anal. calc. for $C_{10}H_{12}O$ (148.21): C 81.04, H 8.16; found: C 80.81, H 8.33.

3.3. *(+)-(1S,2S)-1-Methyl-2-phenylcyclopropane* ((+)-(1*S*,2*S*)-**12**). The alcohol (+)-(1*S*,2*S*)-**11** (5.54 g, 37.4 mmol) was dissolved in 2,6-lutidine (21.6 g, freshly distilled over BaO), and freshly distilled MsCl (5.71 g, 49.8 mmol) was added (*cf.* [35]). The formed methanesulfonate was reduced at −10 to 0° with $LiAlH_4$ (3.97 g, 104.7 mmol) without further purification. The workup *via* FC (pentane/Et_2O 10:1) yielded a hydrocarbon fraction, and unreacted (+)-(1*S*,2*S*)-**11**, which was again subjected to reduction. In this way, a hydrocarbon fraction (3.78 g; b.p. (bulb-to-bulb distillation) 105–110°/50 Torr) was obtained with a content of (+)-(1*S*,2*S*)-**12** of 80.8% (GC)[28]). IR (film): 1609, 1599 (Ar); 747, 700 (5 adj. arom. H). ^{1}H-NMR (*cf.* [67]): 7.3–6.8 (*m*, 5 arom. H); 1.43 (*m*, H–C(2)); 1.01 (*d* with f.s., CH_3–C(1)); 1.2–0.4 (*m*, 2 H–C(3), H–C(1)).

3.4. *(1'S,2'S)-1-(2'-Methylcyclopropyl)-2-nitrobenzene* ((1'*S*,2'*S*)-**13**). Compound (+)-(1*S*,2*S*)-**12** (3.78 g, 23.1 mmol) was added dropwise under stirring at −60 to −55° to a mixture of Ac_2O (14.3 ml) and fuming HNO_3 (4 ml) (*cf.* [36–38]). The mixture was then added, in small portions, to hot H_2O (50 ml) and extracted, after cooling, with Et_2O. The combined Et_2O extracts were washed with 2N Na_2CO_3 soln. and H_2O. Bulb-to-bulb distillation of the residue (65–77°/0.02 Torr) yielded 4.39 g of a mixture of 82% of *o*- and 11% of *p*/*m*-nitrated (mainly *p*-isomer) (1'*S*,2'*S*)-**13**. IR (film): 1612 (Ar); 1527, 1346 (arom. NO_2).

3.5. *(+)-(1'S,2'S)-2-(2'-Methylcyclopropyl)aniline* ((+)-(1'*S*,2'*S*)-**14**). The mixture of *3.4* (4.39 g, with 76.5% of the *o*-nitro compound) was suspended in H_2O (18 ml)/conc. HCl (7.8 ml) and $CaCl_2$ (3.88 g), and Fe turnings (3.88 g) were added (*cf.* [36] [37]). After 1 h at 100°, additional Fe turnings (3.88 g) and conc. HCl (7.8 ml) were added and the mixture kept at 100° for further 0.7 h. After cooling, the mixture was basified with 35% KOH and the anilines steam-distilled. The mixture of anilines was separated by FC (hexane/Et_2O/MeOH 20:8:1). Distillation (117–118°/30 Torr) of the faster-moving compound yielded pure (+)-(1'*S*,2'*S*)-**14** (2.35 g, 84.2%). $[\alpha]_D^{25} = 85.6 \pm 0.8°$ (*c* = 5.38, CCl_4; p = 0.976 ± 0.021 based on (+)-(1*S*,2*S*)-**8**). IR (film): 3473, 3382 (NH_2); 3200 (arom. NH_2; *cf.* [68]); 1619, 1582, 1501 (Ar); 1459; 1302; 1274; 752 (4 adj. arom. H). ^{1}H-NMR: 7.0–6.3 (*m*, 4 arom. H); 3.84 (br. *s*, NH_2); 1.4–1.1 (*m*, H–C(1')); 1.21 (*d*, *J* = 5.3, CH_3–C(2')); 1.1–0.4 (*m*, 2 H–C(3'), H–C(2')). MS: 148 (12, $M^{+\cdot}$ + 1), 147 (100, $M^{+\cdot}$), 146 (15), 144 (5), 133 (9), 132 (79), 131 (14), 130 (15), 118 (24), 117 (24), 115 (13), 105 (8), 104 (5), 93 (6), 91 (10), 77 (7). Anal. calc. for $C_{10}H_{13}N$ (147.22): C 81.59, H 8.90, N 9.51; found: C 81.52, H 9.04, N 9.69.

trans-*4-(2'-Methylcyclopropyl)aniline*[29]). *Slower-Moving Isomer.* IR (film): 3440, 3334 (NH_2); 3217 (arom. NH_2; *cf.* [68]); 1629, 1524 (Ar); 1459; 1280; 831, 783 (2 adj. arom. H). ^{1}H-NMR: 6.8–6.2 (*m*, *AA'BB'*, 4 arom. H); 3.17 (*s*, NH_2); 1.39 (*m*, H–C(1')); 1.14 (*d*, *J* = 5.2, CH_3–C(2')); 1.1–0.4 (*m*, 2 H–C(3'), H–C(2')). MS: 148 (12, $M^{+\cdot}$ + 1), 147 (100, $M^{+\cdot}$), 146 (18), 133 (9), 132 (92), 131 (17), 130 (16), 120 (12), 119 (6), 118 (17), 117 (17), 115 (14), 106 (35), 105 (19), 104 (6), 93 (5), 91 (9), 86 (10), 84 (19), 77 (7). Anal. calc. for $C_{10}H_{13}N$ (147.22): C 81.59, H 8.90, N 9.51; found: C 81.70, H 9.01, N 9.60.

3.6. *(+)-(1'S,2'S)-N-N-Dimethyl-2-(2'-methylcyclopropyl)aniline* ((+)-(1'*S*,2'*S*)-**7**). A mixture of (+)-(1'*S*,2'*S*)-**14** (1.40 g, 9.51 mmol), MeI (2.70 g, 19.02 mmol), and Na_2CO_3 (2.02 g, 19.02 mmol) was stirred during 15 h at r.t. in acetone (25 ml). FC (pentane/Et_2O 100:3) of the aniline mixture yielded, as the fastest-moving form, (+)-(1'*S*,2'*S*)-7 (1.12 g, 65.5%; purity 97.5% (GC), followed by the monomethylated aniline. Starting material

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[27]) From [35] follows for p = 1.0 $[\alpha]_D^{12} = 335°$, and from [19] $[\alpha]_D^{20} = 333.4°$, *i.e.* p = 0.988 for (+)-(1*S*,2*S*)-**10**, in perfect agreement with p = 0.976 ± 0.019 for the acid.

[28]) The main by-product was presumably 4-phenyl-1-butene (^{1}H-NMR; *cf.* [27] [35]).

[29]) Data of a racemic sample. The optically active form could not be obtained pure enough for a reliable $[\alpha]_D$ measurement.

(9%) was recovered as the slowest-moving form. Pure (+)-(1′*S*,2′*S*)-**7** was obtained by FC on silica gel charged with 10% $AgNO_3$ (pentane/Et_2O 100:3) followed by distillation (68–73°/0.035 Torr). The aniline was purified in the same manner to yield, after bulb-to-bulb distillation (75–80°/0.035 Torr), 88.3 mg (5.8%).

(+)-(1′*S*,2′*S*)-**7**. $[\alpha]_D^{25} = 41.0 \pm 0.4°$ ($c = 3.68$, CCl_4; p = 0.976 ± 0.028 based on (+)-(1*S*,2*S*)-**8**; *i.e.* optically pure (+)-(1′*S*,2′*S*)-**7** should have $[\alpha]_D^{25} = 42.0 \pm 0.4°$). UV (EtOH): 280.6 (1660, sh), 249.1 (5840). IR (film): 2780 ($(CH_3)_2N$); 1600, 1578, 1497 (Ar); 1454; 1312; 1192; 1158; 1097; 1050; 950; 761, 753 (4 adj. arom. H). ^{1}H-NMR: 7.1–6.4 (*m*, 4 arom. H); 2.73 (*s*, $(CH_3)_2N$); 1.97 (*m*, H–C(1′)); 1.24 (*d*, *J* = 5.0, CH_3–C(2′)); 1,2–0.5 (*m*, 2 H–C(3′), H–C(2′)). MS: 176 (16, $M^{+\cdot}$ + 1), 175 (100, $M^{+\cdot}$), 174 (23), 161 (9), 160 (71), 158 (6), 146 (12), 145 (16), 144 (24), 134 (14), 133 (8), 132 (55), 131 (45), 130 (16), 118 (7), 117 (7), 91 (14), 77 (7). Anal. calc. for $C_{12}H_{17}N$ (175.28): C 82.23, H 9.78, N 7.99; found: C 82.29, H 9.50, N 8.28.

(+)-(1′S,2′S)-N-Methyl-2-(2′-methylcyclopropyl)aniline. $[\alpha]_D^{25} = 93.5 \pm 1.5°$ ($c = 1.82$, CCl_4; p = 0.976 ± 0.035 based on (+)-(1*S*,2*S*)-**8**; *i.e.* the optically pure compound should have $[\alpha]_D^{25} = 95.8 \pm 1.5°$). IR (film): 3444 (NH); 2820 (CH_3N); 1609, 1585, 1516 (Ar); 1463; 1325; 1307; 1264; 1169; 749 (4 adj. arom. H). ^{1}H-NMR: 7.1–6.3 (*m*, 4 arom. H); 3.94 (br. *s*, NH); 2.89 (*s*, CH_3N); 1.28 (*d*, *J* = 5.2, CH_3–C(2′)); 1.3–1.1 (*m*, H–C(1′)); 1.1–0.4 (*m*, 2 H–C(3′), H–C(2′)). MS: 162 (34, $M^{+\cdot}$ + 1), 161 (100, $M^{+\cdot}$), 160 (11), 147 (11), 146 (79), 144 (11), 132 (15), 131 (20), 130 (21), 120 (10), 119 (5), 118 (29), 117 (11). Anal. calc. for $C_{11}H_{15}N$ (161.25): C 81.94, H 9.38, N 8.69; found: C 81.72, H 9.44, N 8.71.

4. Synthesis of (+)-(1′*R*,2′*S*)-*N*,*N*-Dimethyl-2-(2′-methylcyclopropyl)aniline ((+)-1′*R*,2′*S*)-7). – 4.1. *Methyl (+)-(1S,2R)-2-Phenylcyclopropanecarboxylate* ((+)-(1*S*,2*R*)-**10**). The acid (+)-(1*S*,2*R*)-**8** (7.1 g, 43.8 mmol; $[\alpha]_D^{20} = 23.9 \pm 1.0°$, see *2.2.4*) was esterified with CH_2N_2 as described in *3.1*. Bulb-to-bulb distillation of the ester 68–73°/0.02 Torr yielded pure (+)-(1′*R*,2′*S*)-**10** (7.71 g, 100%). $[\alpha]_D^{20} = 34.7 \pm 1.3°$ ($c = 1.68$, $CHCl_3$), $[\alpha]_D^{20} = 48.3 \pm 1.3°$ ($c = 2.51$, EtOH). By ^{1}H-NMR with $Eu(hfc)_3$ in 1,1,2-trichloro-1,2,2-trifluoroethane, e was determined as 0.848 ± 0.013. Three independent measurements of e yielded, for enantiomerically pure (+)-(1′*R*,2′*S*)-**10**, $[\alpha]_D^{20} = 40.9 \pm 0.9$ ($CHCl_3$; *cf. Footnote 9*). IR (film): 2861 (CH_3O); 1737 ($COOCH_3$); 1607, 1501 (Ar); 1446; 1390; 1287; 1202; 1180; 1165; 1089; 927; 796; 756; 728; 700. ^{1}H-NMR: 7.14 (*s*, 5 arom. H); 3.30 (*s*, CH_3OCC); 2.40 (*ddd*, *J*(2,1) = 8.4, *J*(2,3 (*cis*)) = 7.8, *J*(2,3 (*trans*)) = 6.4, H–C(2)); 1.93 (*ddd*, *J*(1,2) = 8.4, *J*(1,3 (*cis*)) = 6.9, *J*(1,3 (*trans*)) = 5.3, H–C(1)); 1,56 (*ddd*, *J*(3,3) = 3.8, *J*(3,1 (*trans*)) = 5.3, *J*(3,2 (*trans*)) = 6.4, H–C(3)); 1.15 (*ddd*, *J*(3,3) = 3.8, *J*(3,1 (*cis*)) = 6.9, *J*(3,2 (*cis*)) = 7.8, H–C(3)). Anal. calc. for $C_{11}H_{12}O_2$ (176.22): C 74.98, H 6.86; found: C 75.05, H 6.88.

4.2. *(+)-(1S,2R)-(2-Phenylcyclopropyl)methanol* ((+)-(1*S*,2*R*)-**11**). The ester (+)-(1*S*,2*R*)-**10** (7.70 g, 43.7 mmol) was added at 0° to a soln. of $LiAlH_4$ (1.21 g, 31.92 mmol) in Et_2O (100 ml) and the mixture boiled during 1.25 h under reflux. Workup and bulb-to-bulb distillation (69–73°/0.02 Torr) yielded pure (+)-(1*S*,2*R*)-**11** (6.33 g, 98%). $[\alpha]_D^{20} = 44.1 \pm 1.0°$ ($c = 5.0$, $CHCl_3$; e = 0.848 ± 0.032, based on (+)-(1*S*,2*R*)-**10**, yields $[\alpha]_D^{20} = 52.0 \pm 1.2°$ for the enantiomerically pure compound[30]). IR (film): 3250 (OH); 2881 (C–O); 1500; 1030; 774, 739, 702 (5 adj. arom. H), 602. ^{1}H-NMR: 7.13 (*s*, 5 arom. H); 3.11 (*d*, *J* = 8.7, CH_2OH); 2.25 (br. *s*, OH); 2.10 (*m*, H–C(2)); 1.25 (*m*, H–C(1)); 1.0–0.5 (*m*, 2 H–C(3)). MS: 149 (9, $M^{+\cdot}$ + 1), 148 (74, $M^{+\cdot}$), 132 (10), 131 (100), 130 (43), 129 (16), 128 (5), 118 (27), 117 (86), 116 (10), 115 (35), 107 (9), 104 (27), 103 (10), 92 (6), 91 (24), 78 (9), 77 (7). Anal. calc. for $C_{10}H_{12}O$ (148.21): C 81.04, H 8.16; found: C 80.88, H 8.12.

4.3. *(+)-(1S,2R)-1-Methyl-2-phenylcyclopropane* ((+)-(1*S*,2*R*)-**12**). The alcohol (+)-(1*S*,2*R*)-**11** (5.7 g, 38.5 mmol) was mesylated in 2,6-lutidine (22 g) with MsCl (5.88 g, 51.3 mmol) as described in *3.3*. The following reduction with $LiAlH_4$ yielded, after bulb-to-bulb distillation (110–115°/50 Torr), a mixture of hydrocarbons (4.26 g) with a content of 80.1%[28]) (GC) of (+)-(1*S*,2*R*)-**12**. IR (film): 1609, 1503 (Ar); 1456; 762, 704 (5 adj. arom. H). ^{1}H-NMR (*cf.* [67]): 7.11 (*s* with f.s., 5 arom. H); 1.95 (*m*, H–C(2)); 1.3–0.3 (*m*, H–C(1), 2 H–C(3), CH_3–C(1)).

4.4. *(1′R,2′S)-1-(2′-Methylcyclopropyl)-2-nitrobenzene* ((1′*R*,2′*S*)-**13**). Compound (+)-(1*S*,2*R*)-**12** (4.21 g, 22.46 mmol; purity 80.1%) was nitrated as described in *3.4*. Bulb-to-bulb distillation (70–75°/0.02 Torr) yielded a mixture (4.38 g) of the *o*- (73.2%) and *p*-nitrated (13.7%) compounds. IR (film): 1609, 1599 (Ar); 1522, 1344 (arom. NO_2).

4.5. *(+)-(1′R,2′S)-2-(2′-Methylcyclopropyl)aniline* ((+)-(1′*R*,2′*S*)-**14**). The mixture from *4.4* (4.28 g) was reduced with Fe turnings as described in *3.5*. Workup by steam distillation, FC, and consecutive bulb-to-bulb distillation (69–74°/0.015 Torr) yielded pure (+)-(1′*R*,2′*S*)-**14** (1.53 g, 57.3%). $[\alpha]_D^{25} = 120.3 \pm 1.2°$ ($c = 5.48$, CCl_4; e = 0.848 ± 0.021 based on (+)-(1*S*,2*R*)-**10**, *i.e.* $[\alpha]_D^{25} = 141.9 \pm 1.4°$ for the enantiomerically pure material). IR (film): 3472, 3382 (NH_2); 3200 (arom. NH_2; *cf.* [68]); 1619, 1582, 1501 (Ar); 1458; 1304; 1272; 751 (4 adj. arom H).

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[30]) In [17], an $[\alpha]_D^{20}$-value of 39.2° ($CHCl_3$) for p = 0.5 is reported. This value seems to be too high in the light of our findings.

^{1}H-NMR: 7.1–6.4 (*m*, 4 arom. H); 3.68 (br. *s*, NH_2); 1.70 (*m*, H–C(1')); 1.4–0.9 (*m*, H–C(2'), H–C(3')); 0.79 (*d*, *J* = 5.2, CH_3–C(2')); 0.50 (*m*, H–C(3')). MS: 148 (15, $M^{+\cdot}$ + 1), 147 (100, $M^{+\cdot}$), 146 (15), 133 (7), 132 (95), 131 (18), 130 (18), 129 (5), 128 (6), 120 (27), 119 (22), 117 (22), 106 (51), 105 (5), 104 (5), 77 (8). Anal. calc. for $C_{10}H_{13}N$ (147.22): C 81.59, H 8.90, N 9.51; found: C 81.31, H 8.97, N 9.60.

4.6. *(+)-(1'R,2'S)-N,N-Dimethyl-2-(2'-methylcyclopropyl)aniline* ((+)-(1'*R*,2'*S*)-**7**). Compound (+)-(1'*R*,2'*S*)-**14** (1.0 g, 6.97 mmol) was methylated with MeI (2.41 g, 17.0 mmol) in acetone (35 ml) in the presence of Na_2CO_3 (1.8 g, 17.0 mmol) at r.t. during 19 h. Then, an additional amount of MeI (0.48 g, 3.4 mmol) was added and stirred again at r.t. for further 12 h. Workup and FC (pentane/Et_2O 100:3) yielded (+)-(1'*R*,2'*S*)-**7** (0.82 g, 63.8%; purity (GC) 92.6%) and the monomethylated form. Both products were further purified by FC on silica gel, charged with 10% $AgNO_3$ (pentane/Et_2O 100:3 and hexane/Et_2O 5:1, resp.). The monomethylated form (bulb-to-bulb distillation; 65–70°/0.02 Torr) was obtained in 17.3% (0.189 g) yield.

(+)-(1'*R*,2'*S*)-**7**. $[\alpha]_D^{25}$ = 155.2 ± 2.1° (*c* = 4.04, CCl_4; e = 0.848 ± 0.024 based on (+)-(1*S*,2*R*)-**10**, *i.e.* $[\alpha]_D^{25}$ = 183.0 ± 2.5° for the enantiomerically pure material). UV (EtOH): 281.9 (1630, sh), 251.6 (6210). IR (film): 2780 ($(CH_3)_2N$); 1599, 1575, 1495 (Ar); 1454; 1314; 1195; 1160; 1148; 1099; 1052; 949; 762, 748 (4 adj. arom. H). ^{1}H-NMR: 7.2–6.7 (*m*, 4 arom. H); 2.76 (*s*, $(CH_3)_2N$); 2.27 (*ddd*, *J* = 8.7, 8.7, 6.5, H–C(1')); 1.4–0.5 (*m*, H–C(2'), 2 H–C(3')); 0.82 (*d*, *J* = 6.5, CH_3–C(2')). MS: 176 (11, $M^{+\cdot}$ + 1), 175 (75, $M^{+\cdot}$), 174 (37), 161 (12), 160 (100), 159 (7), 158 (6), 146 (25), 145 (29), 144 (47), 143 (5), 134 (9), 133 (11), 132 (99), 131 (75), 130 (47), 129 (7), 128 (7), 120 (8), 119 (6), 118 (40), 117 (53), 116 (11), 115 (12), 103 (12), 91 (37), 77 (15), 69 (25). Anal. calc. for $C_{12}H_{17}N$ (175.28): C 82.23, H 9.78, N 7.99; found: C 81.97, H 9.88, N 7.86.

(+)-(1'R,2'S)-N-Methyl-2-(2'-methylcyclopropyl)aniline. $[\alpha]_D^{25}$ = 136.9 ± 1.2° (*c* = 5.24, CCl_4; e = 0.848 ± 0.020 based on (+)-(1*S*,2*R*)-**10**, *i.e.* $[\alpha]_D^{25}$ = 161.4 ± 1.4° for the enantiomerically pure material). IR: 3444 (NH); 2822 (CH_3N); 1608, 1584, 1516 (Ar); 1464; 1449; 1432; 1322; 1305; 1265; 1176; 1035; 751 (4 adj. arom. H). ^{1}H-NMR: 7.2–6.3 (*m*, 4 arom. H); 4.00 (br. *s*, NH); 2.90 (*s*, CH_3N); 1.63 (*m*, H–C(1')); 1.4–0.4 (*m*, H–C(2'), 2 H–C(3')); 0.75 (*d*, *J* = 5.4, CH_3–C(2')). MS: 162 (31, $M^{+\cdot}$ + 1), 161 (100, $M^{+\cdot}$), 160 (10), 147 (12), 146 (95), 145 (7), 144 (11), 132 (21), 131 (23), 130 (26), 120 (16), 119 (6), 118 (38), 117 (14), 115 (5), 91 (11), 77 (7). Anal. calc. for $C_{11}H_{15}N$ (161.25): C 81.94, H 9.38, N 8.69; found: C 81.81, H 9.45, N 8.70.

5. Synthesis of 2-([1',1'-$^2H_2$]Allyl)-*N*,*N*-dimethylaniline (17) (*cf.* [3a]). – 5.1. *2-([1',1'-$^2H_2$]Allyl)aniline. N*-(2'-Propinyl)aniline [69] was deuterated at C(3') with *N*-methylpyrrolidine/D_2O 1:1 (*cf.* [70]), reduced with $LiAlH_4$ in dry THF by boiling under reflux, and the mixture deuterolyzed with D_2O to yield a mixture of 81% of *N*-([3',3'-$^2H_2$]allyl)aniline and 17.6% of *N*-([3',3',3'-$^2H_3$]propyl)aniline. This mixture was heated in 1-g quantities in 0.2N aq. H_2SO_4 at 185° (2 h) in sealed *Pyrex* bombs. The formed 2-allylaniline was purified by CC on silica gel (hexane/Et_2O 10:1 and $CHCl_3$) and by bulb-to-bulb distillation. ^{1}H-NMR: 7.1–6.4 (4 arom. H); 6.2–5.7 (*m*, 0.68 H, H–C(2')); 5.2–4.8 (*m*, 2.00 H, H–C(3')); 3.42 (*s*, NH_2); 3.22 (*m*, 0.41 H, H–C(1')); reference for integration: 4 arom. H. MS: 137 (1), 136 (16), 135 (100, $M^{+\cdot}$), 134 (40), 133 (9), 132 (6).

5.2. *Dimethylation of 2-([1',1'-$^2H_2$]Allyl)aniline* was performed at r.t. (117 h) in acetone with MeI in the presence of K_2CO_3. Workup and CC yielded 58.6% of **17** after bulb-to-bulb distillation (95–100°/12 Torr). IR: 2845, 2830, 2785 ($(CH_3)_2N$); 2240, 2195, 2140, 2100 (C–D); 1605, 1498 (Ar); 1459; 1320; 1199; 1168; 1060; 956; 921; 772. ^{1}H-NMR: 7.2–6.7 (*m*, 4 arom. H); 6.2–5.7 (*m*, 0.67 H, H–C(2')); 5.2–4.8 (*m*, 2.00 H, H–C(3')); 3.45 (*m*, 0.41 H, H–C(1')); 2.65 (*s*, $(CH_3)_2N$); reference for integration: 4 arom. H. ^{2}H-NMR (15.4 MHz; CCl_4): 6.03 (*s*, ^{2}H–C(2')); 3.49 (*s*, ^{2}H–C(1')); ratio ^{2}H–C(1')/^{2}H–C(2') = 0.82: 0.18 (calc. form the ^{1}H-NMR: 0.83: 0.17). MS: 164 (13), 163 (100, $M^{+\cdot}$), 162 (53), 149 (6), 148 (40), 147 (13), 146 (15), 145 (12).

6. Irradiations. – The prep. irradiations were performed with a high-pressure Hg lamp (125 W, type *125 HPK, Philips*) through a filter (*Jena*-glass, wall thickness 1.25 mm; T (at 303 nm): 10%) in *Pyrex* apparatus (150- and 250-ml working volume; *H. Mangels*, Roisdorf/Bonn). The compounds were dissolved in MeCN and degassed with N_2 during 30 min before irradiations and also during the irradiations. The photoreactions (performed at 16–20°) were followed by GC (all values are the average of 5 measurements) with dodecane or tridecane as internal reference. Anal. irradiations were performed in a merry-go-round apparatus (type *DEMA 125; H. Mangels*, Roisdorf/Bonn) with the same lamp as applied in the prep. irradiations.

6.1. (–)-(*S*)-**4**. 6.1.1. *Run 1* (*Table 3*). Aniline (–)-(*S*)-**4** (0.250 g, 1.43 mmol; $[\alpha]_D^{25}$ = –67.1 ± 1.4° (CCl_4, see *1*)) and tridecane (103.5 mg) as internal GC reference were dissolved in MeCN (150 ml, *c* = 9.51 · 10^{-3} mol/l). After 30 min of irradiation, the soln. was evaporated, the residue taken up in Et_2O and extracted with 1N aq. HCl (2×). The acidic extracts were basified with 1N NaOH and again extracted with Et_2O. The anilines were further purified by bulb-to-bulb distillation (70°/0.015 Torr). Unreacted (–)-(*S*)-**4** was separated by FC on silica gel (pentane/Et_2O 50:1). The remaining mixture of (–)-*trans*- and (+)-*cis*-**7** was separated by FC on silica gel, impregnated with 10% of $AgNO_3$ (pentane/Et_2O 50:1). The faster-moving fraction contained pure (–)-*trans*-**7** and the slower-moving one

Table 3. *Results of the Irradiations of* (−)-(S)-**4**[a]) *in MeCN*

Run	Time of Irradiation [min]	Recovered (−)-(*S*)-**4**		(−)-(1′*S*,2′*S*)-**7**		(+)-(1′*R*,2′*S*)	
		[%]	$[\alpha]_D^{25}$ [°][b])	[%]	$[\alpha]_D^{25}$ [°]	[%]	$[\alpha]_D^{25}$ [°]
1	30	85.0	− 62.5 ± 0.6 (0.734 ± 0.039)	12.0	− 4.9 ± 0.2 (0.116 ± 0.007)	2.8	[c])
2	40[d])	83.3	− 66.1 ± 2.2 (0.776 ± 0.060)	8.0	− 6.5 ± 0.4 (0.155 ± 0.014)	1.8	(5.6)[e]) (0.031)
3	40[d])	82.9	− 62.8 ± 0.7 (0.737 ± 0.041)	7.6	− 6.7 ± 0.5 (0.159 ± 0.015)	1.9	[c])
4	50	66.7	− 64.8 ± 1.7 (0.760 ± 0.053)	15.1	− 2.9 ± 0.2 (0.070 ± 0.005)	3.8	6.46 ± 0.6 (0.035 ± 0.004)
5	70	55.3	− 65.4 ± 1.5 (0.768 ± 0.051)	20.2	− 2.0 ± 0.1 (0.048 ± 0.003)	4.8	2.5 ± 0.3 (0.014 ± 0.002)

[a]) $[\alpha]_D^{25} = -67.1 \pm 1.4°$ (p = 0.788 ± 0.051). All $[\alpha]_D^{25}$-values refer to CCl_4 as solvent.
[b]) In brackets, p-values determined with $[\alpha]_D^{25} = -85.2 \pm 1.8°$ ((−)-(*S*)-**4**), 42.0 ± 0.4° ((+)-(1′*S*,2′*S*)-**7**), and 183.2 ± 2.5° ((+)-(1′*R*,2′*S*)-**7**) for the optically pure materials.
[c]) $[\alpha]_D^{25}$ could not be measured.
[d]) Irradiation was performed in the 250-ml apparatus (all other irradiations in the 150-ml apparatus).
[e]) Sign of rotation secured: $[\alpha]_D^{25}$-value unsecured.

a mixture of (−)-*trans*- and (+)-*cis*-**7**, enriched in the latter one. The $[\alpha]_D$-values of pure (+)-(1′*R*,2′*S*)-**7** were determined on the base of the GC analysis of the slower-moving fraction and the $[\alpha]_D$ for the pure (−)-*trans*-**7** of the faster-moving fraction.

The reaction data of 5 different photoreactions are collected in *Table 3*.

The spectroscopic data (IR, ^{1}H-NMR) of (−)-*trans*-**7** and (±)-*cis*-**7** (isolated from an analogous photoreaction with (±)-**4**) were identical with those reported for the independently prepared isomers (see *3* and *4*).

6.2. (+)-(1′*S*,2′*S*)-**7**. 6.2.1. *Run 4* (*Table 4*). Compound (+)-(1′*S*,2′*S*)-**7** (0.102 g, 0.58 mmol; $[\alpha]_D^{25}$ = 41.0 ± 0.4°, p = 0.976 ± 0.024; *cf. 3.6*) and tridecane (0.100 g) as internal GC reference were dissolved in MeCN (150 ml, $c = 3.87 \cdot 10^{-3}$ mol/l) and irradiated during 18 min. Workup as described in *6.1.1* yielded the mixture of (+)-(1′*S*,2′*S*)-**7** (80.2%) and (+)-(1′*R*,2′*S*)-**7** (18.0%) which was separated by FC on silica gel, impregnated with 10% $AgNO_3$ (pentane/Et_2O 50:1). *Fraction 1* (faster-moving) yielded pure (+)-(1′*S*,2′*S*)-**7** (0.0634 g, 62.3%) and *Fraction 2* (slower-moving) a mixture (0.0112 g) of (+)-(1′*R*,2′*S*)-**7** (85.0%) and (+)-(1′*S*,2′*S*)-**7** (15.0%). $[\alpha]_D^{25}$ for the pure (+)-(1′*R*,2′*S*)-**7** was determined as described in *6.1.1*. The results of 4 independent runs are collected in *Table 4*.

Table 4. *Results of the Irradiations of* (+)-(1′S,2′S)-**7**[a]) *in MeCN*

Run	Time of Irradiation [min]	Recovered (+)-(1′*S*,2′*S*)-**7**		(+)-(1′*R*,2′*S*)-**7**	
		[%]	$[\alpha]_D^{25}$ [°][b])[c])	[%]	$[\alpha]_D^{25}$ [°]
1	6	91.0	33.0 ± 0.8 (0.786 ± 0.043)	9.0	10.4 ± 1.3 (0.057 ± 0.008)
2	10	85.6	20.5 ± 0.2 (0.488 ± 0.016)	14.4	5.0 ± 0.5 (0.027 ± 0.004)
3	12	84.0	21.8 ± 0.3 (0.519 ± 0.017)	16.0	6.6 ± 0.7 (0.036 ± 0.004)
4	18	80.2	14.2 ± 0.2 (0.337 ± 0.010)	18.0	4.9 ± 0.7 (0.027 ± 0.004)

[a]) $[\alpha]_D^{25}$ = 41.0 ± 0.4° (p = 0.976 ± 0.024). All $[\alpha]_D^{25}$-values refer to CCl_4 as solvent.
[b]) See *Footnote b* in *Table 3*.
[c]) Calculated $[\alpha]_0$-value for recovered (+)-(1′*S*,2′*S*)-**7**: 50.5 ± 7.8° (r = 0.968).

The spectroscopic data (IR and ^{1}H-NMR) of recovered (+)-(1′*S*,2′*S*)-**7** and (+)-(1′*R*,2′*S*)-**7** were identical with those of authentic probes (*cf. 3.6* and *4.6*).

6.3. (+)-(1′*R*,2′*S*)-**7**. 6.3.1. *Run 4* (*Table 5*). Compound (+)-(1′*R*,2′*S*)-**7** (0.0851 g, 0.49 mmol; $[\alpha]_D^{25}$ = 155.2 ± 2.1°, p = 0.848 ± 0.024; *cf. 4.6*) and tridecane (0.080 g) as internal GC reference were dissolved in

Table 5. *Results of the Irradiations of* (+)-(1′R,2′S)-**7**[a]) *in MeCN*

Run	Time of Irradiation [min]	Recovered (+)-(1′*R*,2′*S*)-**7**		(+)-(1′*S*,2′*S*)-**7**[b])	
		[%]	$[\alpha]_D^{25}$ [°][b])[c])	[%]	$[\alpha]_D^{25}$ [°]
1	2.2	91.1	144.5 ± 4.0 (0.789 ± 0.034)	8.9	[c])
2	3.0	76.0	126.5 ± 4.6 (0.691 ± 0.035)	20.6	3.2 ± 0.8 (0.077 ± 0.019)
3	6.5	55.2	99.4 ± 8.8 (0.543 ± 0.056)	44.8	0.94 ± 0.41 (0.022 ± 0.010)
4	11.5	36.0	55.1 ± 4.9 (0.301 ± 0.031)	63.3	0.52 ± 0.09 (0.012 ± 0.002)

[a]) $[\alpha]_D^{25} = 155.2 \pm 2.1°$ (p = 0.848 ± 0.024). All $[\alpha]_D^{25}$-values refer to CCl_4 as solvent.
[b]) See *Footnote b* in *Table 3*.
[c]) Calculated $[\alpha]_0$-value for recovered (+)-(1′*R*,2′*S*)-**7**: 160 ± 39° (r = 0.986).

MeCN ($c = 3.74 \cdot 10^{-3}$ mol/l) and irradiated during 11.5 min. The mixture of (+)-(1′*R*,2′*S*)-**7** (36.0%) and (+)-(1′*S*,2′*S*)-**7** (63.3%) was separated as described to yield pure (+)-(1′*S*,2′*S*)-**7** (0.0359 g, 42.2%) and enriched (+)-(1′*R*,2′*S*)-**7** (0.015 g) with 82.2% of (+)-(1′*R*,2′*S*)-**7** and 16.2% of (+)-(1′*S*,2′*S*)-**7** (from runs with smaller conversion rates pure (+)-(1′*R*,2′*S*)-**7** could be recovered). The results of 4 independent runs are collected in *Table 5*. The spectroscopic data (IR and ^{1}H-NMR) of (+)-(1′*S*,2′*S*)-**7** and recovered (+)-(1′*R*,2′*S*)-**7** were identical with those of authentic probes (*cf. 3.6* and *4.6*).

6.4. *2-([1′,1′-$^2H_2$]Allyl)-*N,N*-dimethylaniline* (**17**). The aniline (0.130 g, 0.80 mmol) was irradiated through quartz during 50 min in MeOH (90 ml, $c = 8.85 \cdot 10^{-3}$ mol/l). The raw aniline fraction (0.127 g, 97.8%) consisted of starting material (44.5%) and *2-([2′,2′-$^2H_2$]cyclopropyl)aniline* (**19**; 53.9%). The separation was accomplished by prep. GC on *Carbowax 20M* and yielded 24.7 mg (19.4%) of pure starting material and 45.8 mg of pure product.

17. IR: Identical with that described in *5.2*. ^{1}H-NMR: 7.2–6.7 (*m*, 4 arom. H); 6.2–5.7 (*m*, 0.68 H, H–C(2′)); 5.2–4.8 (*m*, 2.00 H, H–C(3′)); 3.39 (*m*, 0.40 H, H–C(1′)); 2.64 (*s*, $(CH_3)_2N$); reference for integration: 4 arom. H. ^{2}H-NMR (15.4 MHz; CCl_4): 6.01 (*s*, ^{2}H–C(2′)); 3.47 (*s*, ^{2}H–C(1′)); ratio ^{2}H–C(1′)/^{2}H–C(2′) = 0.83:0.17 (calc. from ^{1}H-NMR: 80:20).

19. IR (film): 2862, 2826, 2782 ($(CH_3)_2N$); 1597, 1493 (Ar); 1451 (CH in cyclopropane [17]); 1310; 1191; 1158; 1098; 1049; 948; 761, 747 (4 adj. arom. H). ^{1}H-NMR: 7.1–6.5 (*m*, 4 arom. H); 2.74 (*s*, $(CH_3)_2N$); 2.26 (*t*-like, 0.65 H, H–C(1′)); 0.93, 0.65 (2*m*, 2.43 H, H–C(2′), H–C(3′)); reference for integration: 4 arom. H. ^{2}H-NMR (15.4 MHz, $CHCl_3$): 2.28 (*s*, ^{2}H–C(1′)); 0.99, 0.71 (2*s*, ^{2}H–C(2′), ^{2}H–C(3′)); ratio ^{2}H–C(2′,3′)/^{2}H–C(1′) = 79:21 (calc. from ^{1}H-NMR: 82:18).

6.5. *Control Experiments*. 6.5.1. *Irradiation of (±)-*N,N*-Dimethyl-2-(1′-methylallyl)aniline* ((±)-**4**) *in MeOH*. Compound (±)-**4** (0.1048 g, 0.60 mmol) [11] was irradiated through quartz in MeOH (90 ml, $c = 6.62 \cdot 10^{-3}$ mol/l) during 45 min. Workup and GC analysis yielded 45.3% of starting material, 43.3% of (±)-*trans*-**7**, and 10.3% of (±)-*cis*-**7**.

6.5.2. *Irradiation of* (±)-**4** *in MeOH in the Presence of Isoprene*. Compound (±)-**4** (0.050 g) was dissolved in MeOH (50 ml, $c = 5.71 \cdot 10^{-3}$ mol/l) and the soln. distributed in 4-ml portions in 5 quartz cuvettes. Different mol-equiv. of isoprene were added (see *Table 6*) and the samples irradiated through a *Corex* filter during 60 min in the merry-go-round apparatus. Results of GC analyses are collected in *Table 6*.

Table 6. *Results of Irradiations of* (±)-**4** *in MeOH in the Presence of Isoprene*

Run	Molar Ratio Isoprene/(±)-**4**	(±)-**4** [%]	(±)-*trans*-**7** [%]	(±)-*cis*-**7** [%]	By-products[a])	
					[n]	[%]
1	–	77.0	17.3	4.6	3	1.1
2	5	86.6	10.9	1.5	8	1.0
3	10	91.7	6.2	0.3	7	1.8
4	15	94.6	2.9	0.6	8	1.9
5	20	94.9	2.5	0.3	6	2.3

[a]) Not identified; n = number of peaks in GC.

6.5.3. *Irradiation of (–)-(*S*)-**4** in MeCN for the Determination of the Initial* trans-**7**/cis-**7** *Ratio*. The aniline (0.500 g, 2.85 mmol; p = 0.788 ± 0.064) and dodecane (0.200 mg) as GC reference were dissolved in 300 ml MeCN and irradiated through the glass *(Jena)* filter. Samples were analyzed by GC in intervals of 5 min. The results are collected in *Table 7*. The linear regression yielded for t = 0 *trans*-**7**/*cis*-**7** = 4.71 ± 0.14.

Table 7. *Results of* (−)-(S)-**4** *in MeCN*

Time of Irradiation [min]	Reference/ Products	(−)-(*S*)-**4** [%]	*trans*-**7** [%]	*cis*-**7** [%]	*trans*-**7**/*cis*-**7**
0	0.222	100	–	–	–
5[a])	0.228	95.2	1.67	0.45	3.70
10	0.201	96.4	3.12	0.66	4.73
15	0.231	90.8	4.58	1.04	4.40
20	0.221	93.7	5.53	1.20	4.63
25	0.224	91.5	6.77	1.47	4.59
30	0.241	84.2	7.61	1.76	4.33
35	0.242	82.9	8.64	1.96	4.40
40	0.238	83.3	9.60	2.16	4.45

[a]) Measurement not taken into account.

REFERENCES

[1] a) S.S. Hixson, P.S. Mariano, H.E. Zimmerman, *Chem. Rev.* **1973,** *73,* 531; b) H.E. Zimmerman, in 'Rearrangements in Ground and Excited States', Ed. P. de Mayo, Academic Press, Inc., New York, 1980, Vol. 3, p. 131.

[2] a) K.N. Houk, *Chem. Rev.* **1976,** *76,* 1; b) D.I. Schuster, in 'Rearrangements in Ground and Excited States', Ed. P. de Mayo, Academic Press, Inc., New York, 1980, Vol. 3, p. 232.

[3] a) U. Koch-Pomeranz, H.-J. Hansen, H. Schmid, *Helv. Chim. Acta* **1975,** *58,* 178; U. Koch-Pomeranz, H. Schmid, H.-J. Hansen, *ibid.* **1977,** *60,* 768; b) R. Tachikawa, A. Terada, K. Tomita, T. Iwaoka, *Heterocycles* **1977,** *8,* 695; c) J.-P. Fasel, H.-J. Hansen, *Chimia* **1981,** *35,* 9; *ibid.* **1982,** *36,* 193; d) S. Jolidon, H.-J. Hansen, *ibid.* **1981,** *35,* 49; e) K. Dietliker, H.-J. Hansen, *ibid.* **1981,** *35,* 52; f) H.E. Zimmerman, J.R. Blinn, *Tetrahedron* **1981,** *37,* 3237; H.E. Zimmerman, G.-S. Wu, *Can. J. Chem.* **1983,** *61,* 866; H.E. Zimmerman, R.L. Swafford, *J. Org. Chem.* **1984,** *49,* 3069; g) H. Hemetsberger, W. Holstein, F. Werres, *Tetrahedron* **1983,** *39,* 1151; h) L.A. Paquette, M.J. Coghlan, C.E. Cottrell, T. Irie, H. Tanida, *J. Org. Chem.* **1986,** *51,* 696.

[4] a) M. Demuth, K. Schaffner, *Angew. Chem.* **1982,** *94,* 809; *ibid. Int. Ed.* **1982,** *21,* 820; b) R. Viskin, J. Oren, B. Fuchs, *Tetrahedron Lett.* **1985,** *26,* 2365; c) K. Schaffner, M. Demuth, in 'Modern Synthetic Methods 1986', Ed. R. Scheffold, Springer-Verlag, Berlin–Heidelberg, 1986, p. 61.

[5] H.E. Zimmerman, J.D. Robbins, R.D. McKelvey, C.J. Samuel, L.R. Sousa, *J. Am. Chem. Soc.* **1974,** *96,* 4630.

[6] a) P.S. Mariano, J.-K. Ko, *J. Am. Chem. Soc.* **1973,** *95,* 8670; b) P.S. Mariano, R.B. Steitle, D.G. Watson, M.J. Peters, E. Bay, *ibid.* **1976,** *98,* 5899.

[7] H.E. Zimmerman, T.P. Gannett, G.E. Keck, *J. Org. Chem.* **1979,** *44,* 1982.

[8] a) G.W. Griffin, J. Covell, R.C. Peterson, R.M. Dodson, G. Klose, *J. Am. Chem. Soc.* **1965,** *87,* 1410; b) G.W. Griffin, A.F. Marcantonio, H. Kristinsson, *Tetrahedron Lett.* **1965,** 2951.

[9] D. Kumari, S.K. Mukerjee, *Tetrahedron Lett.* **1967,** 4169.

[10] B. Scholl, H.-J. Hansen, *Helv. Chim. Acta* **1980,** *63,* 1823.

[11] B. Scholl, S. Jolidon, H.-J. Hansen, *Helv. Chim. Acta* **1986,** *69,* 184.

[12] a) V.L. Ermolaev, *Opt. Spectry (USSR), Engl. Transl.* **1961,** *11,* 266; b) C.M. Previtali, *J. Photochem.* **1985,** *31,* 233.

[13] M.W. Schmidt, E.K.C. Lee, *J. Am. Chem. Soc.* **1970,** *92,* 3579.

[14] G.P. Semeluk, R.D.S. Stevens, *Can. J. Chem.* **1971,** *49,* 2452.

[15] M. Comtet, *J. Am. Chem. Soc.* **1969,** *91,* 7761; *ibid.* **1970,** *92,* 5308.

[16] Y. Inouye, T. Sugita, H.M. Walborsky, *Tetrahedron* **1964,** *20,* 1695.

[17] T. Aratani, N. Nakanishi, H. Nozaki, *Tetrahedron* **1970,** *26,* 1675.

[18] C. Kaiser, J. Weinstock, M.P. Olmstead, *Org. Synth.* **1970,** *50,* 94.

[19] P.E. Krieger, J.A. Landgrebe, *J. Org. Chem.* **1978,** *43,* 4447.

[20] J.A. Berson, L.D. Pedersen, B.K. Carpenter, *J. Am. Chem. Soc.* **1976,** *98,* 122.

[21] H.M. Walborsky, L. Plonsker, *J. Am. Chem. Soc.* **1961,** *83,* 2138.

[22] C.R. Johnson, C.W. Schroeck, *J. Am. Chem. Soc.* **1968,** *90,* 6852.

[23] a) S. Sawada, K. Takehana, Y. Inouye, *J. Org. Chem.* **1968,** *33,* 1767; b) S. Sawada, J. Oda, Y. Inouye, *ibid.* **1968,** *33,* 2141.

[24] H. Nozaki, H. Takaya, S. Moriuti, R. Moyori, *Tetrahedron* **1968,** *24,* 3655.
[25] W.R. Moser, *J. Am. Chem. Soc.* **1969,** *91,* 1135 and 1141.
[26] T. Aratani, Y. Yoneyoshi, T. Nogase, *Tetrahedron Lett.* **1975,** 1707.
[27] T. Aratani, Y. Yoneyoshi, T. Nogase, *Tetrahedron Lett.* **1977,** 2599.
[28] J.E. Baldwin, G.E. Chung Chang, *Tetrahedron* **1982,** *38,* 825.
[29] H. Abdallah, R. Grée, R. Carrié, *Tetrahedron Lett.* **1982,** *23,* 503.
[30] A. Monpert, J. Martelli, R. Grée, R. Carrié, *Tetrahedron Lett.* **1981,** *22,* 1961.
[31] I. Arai, A. Mori, H. Yamamoto, *J. Am. Chem. Soc.* **1985,** *107,* 8254.
[32] a) A. Nakamura, A. Konishi, Y. Tatsuno, S. Otsuka, *J. Am. Chem. Soc.* **1978,** *100,* 3443, 6544; b) A. Nakamura, A. Konishi, R. Tsujitani, M. Kuda, S. Otsuka, *ibid.* **1978,** *100,* 3449.
[33] J.E. Baldwin, C.G. Carter, *J. Am. Chem. Soc.* **1982,** *104,* 1362.
[34] T. Aratani, *Yuki Gosei Kagaku Kyokai Shi* **1985,** *43,* 1134.
[35] T. Sugita, Y. Inouye, *Bull. Soc. Chem. Jpn.* **1966,** *39,* 1075.
[36] Y.S. Shabarov, R.Y. Levina, V.K. Potapov, A.M. Osipov, E.G. Treshova, *Zh. Obshch. Khim.* **1960,** *30,* 3874.
[37] R. Palmberg, Diploma Work, University of Fribourg, 1976.
[38] V.V. Karpova, S.S. Mochalov, Y.S. Shabarov, *Zh. Org. Khim.* **1982,** *18,* 310.
[39] F. Dick, Thesis No. 867, University of Fribourg, 1984; F. Dick, H.-J. Hansen, in preparation.
[40] H.J.C. Jacobs, E. Havinga, *Adv. Photochem.* **1979,** *11,* 305.
[41] E.J. Land, J.T. Richards, J.K. Thomas, *J. Phys. Chem.* **1972,** *76,* 3805.
[42] B. Testa, 'Principles of Organic Stereochemistry', Marcel Dekker, Inc., New York–Basel, 1979.
[43] M. von Büren, M. Cosandey, H.-J. Hansen, *Helv. Chim. Acta* **1980,** *63,* 738; P. Bischofberger, H.-J. Hansen, *ibid.* **1982,** *65,* 721; M. Cosandey, M. von Büren, H.-J. Hansen, *ibid.* **1983,** *66,* 1.
[44] W. Adam, N. Carballeira, O. De Lucchi, *J. Am. Chem. Soc.* **1980,** *102,* 2107.
[45] H. Morrison, *Org. Photochem.* **1979,** *4,* 143.
[46] W. Adam, O. De Lucchi, *Angew. Chem.* **1981,** *903,* 408; *ibid. Int. Ed.* **1981,** *20,* 400.
[47] a) R.G. Bergman, in 'Free Radicals', Ed. J.K. Kochi, J. Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 191; b) J.A. Berson, *Ann. Rev. Phys. Chem.* **1977,** *28,* 111.
[48] S.S. Hixson, *Org. Photochem.* **1979,** *4,* 191.
[49] S. Jolidon, H.-J. Hansen, *Helv. Chim. Acta* **1979,** *62,* 2581.
[50] K. Dietliker, H.-J. Hansen, unpublished results.
[51] W. von E. Doering, K. Sachdev, *J. Am. Chem. Soc.* **1974,** *96,* 1168.
[52] R.J. Crawford, D.M. Cameron, *J. Am. Chem. Soc.* **1966,** *88,* 2589.
[53] H.E. O'Neal, S.W. Benson, *J. Phys. Chem.* **1968,** *72,* 1866.
[54] K. Salisbury, *J. Am. Chem. Soc.* **1972,** *94,* 3707.
[55] J.A. Bell, *J. Am. Chem. Soc.* **1965,** *87,* 4966.
[56] W.C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978,** *43,* 2923.
[57] M.O. Forster, *J. Chem. Soc.* **1903,** *83,* 514; *ibid.* **1913,** *103,* 662.
[58] L. Claisen, O. Manasse, *Liebigs Ann. Chem.* **1893,** *274,* 71.
[59] a) A. Daniel, A.-A. Pavia, *C. R. Acad. Sci.* **1966,** *263,* 643; b) *Tetrahedron Lett.* **1967,** 1145.
[60] H. Saito, K. Nukada, M. Ohno, *Tetrahedron Lett.* **1964,** 2124.
[61] N.E. Searle, *Org. Synth.* **1956,** *36,* 25.
[62] V. Dave, E.W. Warnhoff, *Org. React.* **1970,** *18,* 217.
[63] Q.D. Chieu, E.G. Treshova, I.G. Bolesow, R.Y. Levina, *Zh. Org. Khim.* **1967,** *3,* 1144; *Vestn. Mosk. Univ. Ser. II* **1967,** *22,* 104.
[64] J.E. Baldwin, J. Löliger, W. Rastetter, N. Neuss, L.L. Huckstep, N. De La Higuera, *J. Am. Chem. Soc.* **1973,** *95,* 3796.
[65] T. Aratani, N. Nakanishi, H. Nozaki, *Tetrahedron Lett.* **1969,** 1809.
[66] Th.J. De Boer, H.J. Backer, *Org. Synth. Coll. Vol. IV* **1963,** 250.
[67] W.L. Dilling, *J. Org. Chem.* **1964,** *29,* 960.
[68] E. Pretsch, T. Clerc, J. Seibl, W. Simon, 'Strukturaufklärung organischer Verbindungen', Springer Verlag, Berlin, 1976.
[69] V. Wolf, D. Ramini, *Liebigs Ann. Chem.* **1959,** *626,* 47.
[70] J. Kramis, H.-J. Hansen, *Helv. Chim. Acta* **1977,** *60,* 1478.
[71] H.J. Hediger, 'Infrarotspektroskopie', Akad. Verlagsgesell., Frankfurt a.M., 1971, p. 35.