

compd	init condns, CH <sub>3</sub> CN: TEAA	CH <sub>3</sub> CN gradient
T <sub>Me</sub> *T	5:95	1% min <sup>-1</sup> for 30 min
A <sub>Me</sub> *T	5:95	1% min <sup>-1</sup> for 30 min
3a	30:70	1% min <sup>-1</sup> for 10 min, then isocratic
3b	30:70	1% min <sup>-1</sup> for 10 min, then isocratic
3c	30:70	1% min <sup>-1</sup> for 10 min, then isocratic
3d	30:70	1% min <sup>-1</sup> for 10 min, then isocratic
3e	5:95	2% min <sup>-1</sup> for 10 min, then 1% min <sup>-1</sup>
3f	5:95	2% min <sup>-1</sup> for 10 min, then 1% min <sup>-1</sup>

**Nuclease P1 Catalyzed Hydrolysis of 3e and 3f.** A dry sample (ca. 0.2 OD<sub>260</sub> unit) of each diastereomer of the oligonucleotide analogue was dissolved in 100  $\mu$ L of 0.025 M Tris-HCl buffer (pH 7.0), and a buffered solution (3  $\mu$ L) of nuclease P1 from Penillium citrinum (Sigma Chem., Co., St. Louis, MO; 370 units of protein dissolved in 2 mL of buffer) was added at 37 °C. After 24 h of incubation at 37 °C, MgCl<sub>2</sub> was added (concentration = ca. 10 mM) followed by alkaline phosphatase (Sigma; 5  $\mu$ L of a solution of 44 units of alkaline phosphatase, Type III-R from *Escherichia coli*, in 2 mL of 0.01 M Tris-acetate buffer, pH 8.8). Incubation was continued at 37 °C for an additional 2 h. Aliquots were heated for 3 min at 100 °C (protein denaturation) prior to HPLC analysis as described above. Digests of 3e "fast" and 3e "slow" gave products with elution times of 22.98 and 23.87 min, respectively, which were collected, concentrated in vacuo, and hydrolyzed with formic acid as described above. The 1:1 ratio of Gua:Ade found for both products were taken as evidence for G<sub>DMT</sub>A "fast" and "slow", respectively. The digests of 3f "fast" and 3f "slow" gave products with elution times 21.01 and 21.83 min, respectively, which were collected and identified as A<sub>DMT</sub>T "fast" and A<sub>DMT</sub>T "slow", respectively, based on the 1:1 ratio of Ade:Thy given by formic acid hydrolysis.

**Removal of 5'-DMT Group.** HPLC-collected products having a 5'-DMT group were detritylated with 3% v/v HOAc-H<sub>2</sub>O (1 mL, pH 2.5-2.7) at room temperature for 5-10 min, which was followed by extraction of DMT-OH with EtOAc and then concentration to dryness using a vacuum centrifuge.

**Formic Acid Degradation.** One OD<sub>260</sub> unit of GGAATTCC<sup>17</sup> standard was dissolved in formic acid (90%, 1 mL) and the resultant solution was transferred to a vial (4 mL) for heating at 120 °C in a heat block for 12 h. The cooled solution was evaporated to dryness under reduced pressure and the resultant residue was dissolved in 0.1 M TEAA buffer, pH 7 (200  $\mu$ L) for analysis by HPLC ( $\mu$ Bondapak reverse-phase C<sub>18</sub> column, 7.8 mm  $\times$  30 cm; eluent: 0.1 M TEAA buffer, pH 7 containing 2% (v/v) of CH<sub>3</sub>CN, flow rate = 4 mL/min, isocratic). The average ratio of absorptions measured at 280 nm for quadruplicate injections of the resultant equimolar amounts of Cyt (4.76 min), Gua (8.21 min), Thy (10.18 min), and Ade (15.26 min) were used to calculate<sup>16</sup> the base composition of all of the presently reported di- and oligonucleotide phosphonates and their side products, which were treated with formic acid and analyzed as described above for GGAATTCC.

**Acknowledgment.** We thank Dr. Paul S. Miller (The Johns Hopkins University) for providing authentic samples of A<sub>Me</sub>\*T for comparison with our products. James Cone (Laboratory of Experimental Carcinogenesis, National Cancer Institute) provided assistance in obtaining the FAB-MS data, and Dr. Michael F. Summers was helpful in recording NMR spectra. The comments of a referee were useful in prompting some of the control experiments regarding the attempted benzoylation reaction described herein.

**Registry No.** 3a (isomer 1), 97352-74-4; 3a (isomer 2), 97414-05-6; 3b (isomer 1), 97352-75-5; 3b (isomer 2), 97414-06-7; 3c (isomer 1), 97352-76-6; 3c (isomer 2), 97414-94-3; 3d (isomer 1), 97352-77-7; 3d (isomer 2), 97414-07-8; 3e (isomer 1), 97352-78-8; 3e (isomer 2), 97414-08-9; 3f (isomer 1), 97352-79-9; 3f (isomer 2), 97414-09-0; T<sub>Me</sub>\*T (isomer 1), 97352-80-2; T<sub>Me</sub>\*T (isomer 2), 97414-10-3; "Fast" A<sub>Me</sub>\*T (Rp), 71830-18-7; "Slow" A<sub>Me</sub>\*T (Sp), 71790-90-4; [<sup>13</sup>C]CH<sub>3</sub>I, 4227-95-6; benzoyl chloride, 98-88-4.

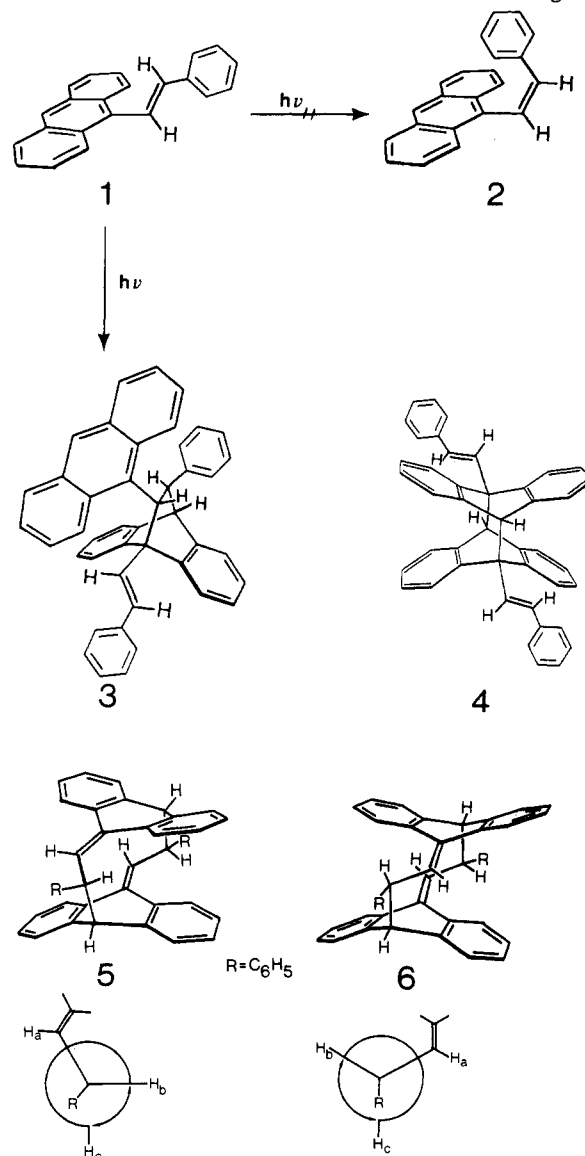
## Photochemistry of the Anthracene Chromophore: The Dimerization of *trans*-1-(9-Anthryl)-2-phenylethylene

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Most *trans*-1,2-diaryl substituted ethylenes upon photoexcitation undergo geometrical isomerization,<sup>1</sup> but all our attempts to prepare *cis*-1-(9-anthryl)-2-phenylethylene (2) by irradiation of its *trans* isomer (1) have been unsuccessful.<sup>2,3</sup> When a 10<sup>-4</sup> M solution of 1 in degassed



benzene is irradiated, a seemingly clean<sup>4</sup> unimolecular reaction proceeds with a quantum efficiency of 0.0014, but neither is the *cis* isomer 2 detectable by UV spectroscopy nor has it been possible to isolate or characterize any other

(1) Mazzucato, U. *Pure Appl. Chem.* 1982, 54, 1705 and references cited therein.

(2) Becker, H.-D.; Andersson, K. *J. Org. Chem.* 1983, 48, 4549.

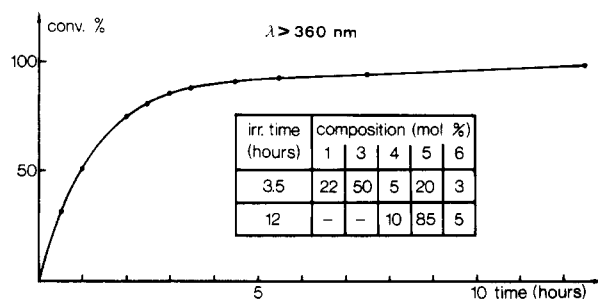
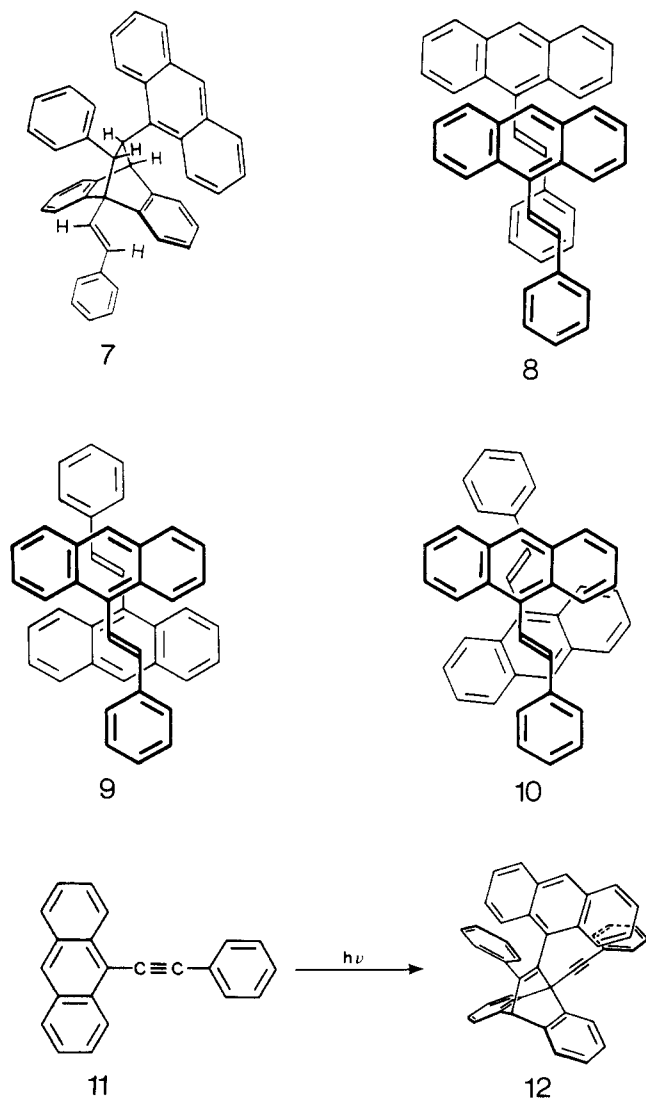
(3) For other examples of one-way photoisomerizations, see: Arai, T.; Karatsu, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* 1983, 24, 2873. Cf. also: Lewis, F. D.; Petisce, J. R.; Oxman, J. D.; Nepras, M. J. *J. Am. Chem. Soc.* 1985, 107, 203.

(4) The absorption spectral changes during the disappearance of 1 give rise to an isosbestic point at 328 nm.

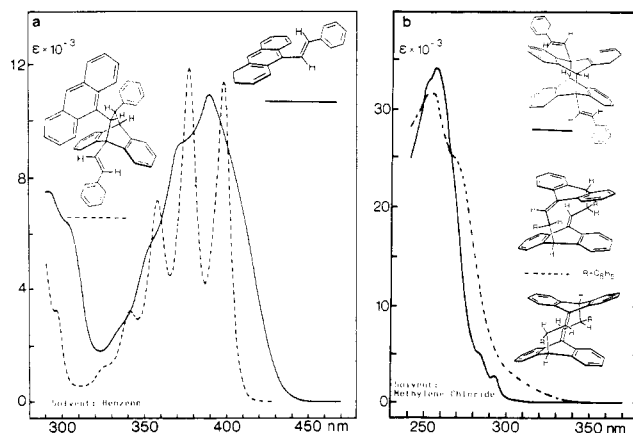
product from this reaction. We have now found that the photochemistry of *trans*-1-(9-anthryl)-2-phenylethylene in benzene solution is concentration dependent, and its major mode of reaction at high concentration is by way of various dimerizations.

When the irradiation of **1** (100 mg) with light of lengths  $>440$  nm in degassed benzene (4 mL) is monitored by  $^1\text{H}$  NMR spectroscopy, the formation of four different and previously unknown dimerization products, i.e., **3**, **4**, **5**, and **6**, is distinguishable. The rate of conversion decreases with decreasing concentration of **1**, and, significantly, throughout the irradiation dimers **3**–**6** are formed in a constant ratio of about 20:2:2:1. Consequently, all four dimers apparently are formed directly from photoexcited **1** rather than by consecutive photochemical reactions. A rather different product ratio is obtained when the irradiation of **1** is carried out with wavelengths  $>360$  nm, so that consecutive photoreactions become possible (see Figure 1).

The structural assignments of dimers **3**–**6** are based on their spectroscopic properties. Thus, the structure of the major product **3**, derived by photochemical Diels–Alder dimerization of **1** involving the addition of the styryl group to the anthracene moiety, is supported by its electronic absorption spectrum (Figure 2a), its  $^1\text{H}$  NMR spectrum (see Experimental Section), and by its photochemical isomerization discussed below. We have no  $^1\text{H}$  NMR spectroscopic evidence for the presence of regioisomer **7**.



**Figure 1.** Photochemical conversion of **1** into dimers **3**, **4**, **5**, and **6** as a function of time. The inserted table refers to the composition the reaction mixture as analyzed by  $^1\text{H}$  NMR.



**Figure 2.** (a) Electronic absorption spectra of **1** and dimer **3** in benzene. (b) Electronic absorption spectra in methylene chloride of dimer **4** and of **5** containing about 5% dimer **6**.

Apparently, the formation of the orientation complexes **9/10** is favored over that of **8**. The formation of **3** from photoexcited **1** thus parallels the photochemical Diels–Alder dimerization of 9-(phenylethynyl)anthracene (**11**), which was found to give **12**.<sup>5</sup>

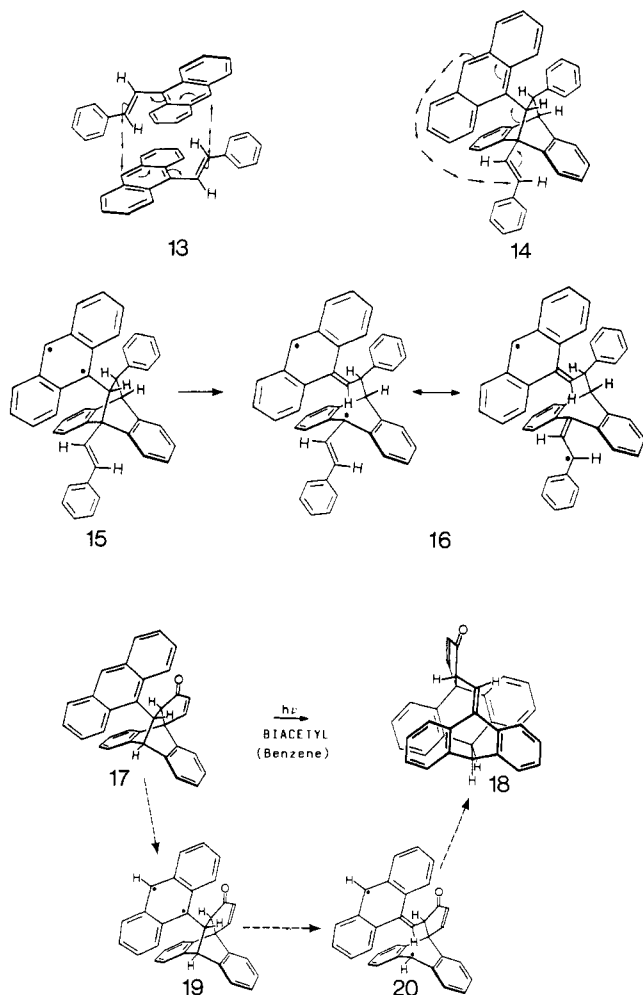
Dimer **4** is the  $4\pi + 4\pi$  cycloaddition product of **1** and its photolysis ( $\lambda$  290 nm) in methylene chloride smoothly regenerates **1**. The structure of **4** is supported by its  $^1\text{H}$  NMR spectrum and its electronic absorption spectrum (see Figure 2b). The head-to-tail rather than the head-to-head geometry is assigned to **4** in analogy with numerous other head-to-tail photodimers of 9-substituted anthracenes.<sup>6,7</sup>

Dimers **5** and **6** are structural isomers that merely differ in symmetry. Dimer **5** is characterized by a twofold axis of symmetry, and dimer **6** has a center of symmetry. Their structures are supported by their  $^1\text{H}$  NMR spectra in which the nonaromatic protons in **5** and **6**, summarized in Table I, give rise to characteristically different spectral patterns. Inspection of Dreiding molecular models reveals that the dihedral angle between the bridgehead proton  $\text{H}_c$  and its vicinal proton  $\text{H}_b$  in the  $\text{C}_2$  isomer **5** is about  $90^\circ$ , so that  $\text{H}_c$  gives rise to a singlet. In the *i*-isomer **6**, the corresponding angle is about  $120^\circ$ , as is borne out in the coupling constant of 3 Hz associated with  $\text{H}_b$  and  $\text{H}_c$ . Moreover, in the *i*-isomer **6**,  $\text{H}_b$  is shifted upfield due to shielding by the aryl moieties. We rationalize the formation of dimers **5** and **6** from photoexcited **1** by a  $6\pi + 6\pi$  cycloaddition (cf. **13**), in which the orientation complex with parallel-aligned ethylene bonds (**9**) gives rise to **6**,

(5) Becker, H.-D.; Andersson, K. *J. Photochem.* 1984, 26, 75.

(6) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P. *Pure Appl. Chem.* 1980, 52, 2633.

(7) Cowan, D. O.; Drisko, R. L. "Elements of Organic Photochemistry"; Plenum Press: New York and London, 1976; pp 19–74.



while the  $C_2$  isomer **5** will be formed from an orientation complex (**10**) in which the ethylene bonds are in an angular arrangement with respect to each other. It should be kept in mind, however, that *trans*-1-(9-anthryl)-2-phenylethylene in its electronic ground state is not planar. Rotation about the 9-anthryl ethylene single bond is hindered, and its molecular geometry as revealed by X-ray diffraction is such as to have the plane of the ethylene twisted out of the plane of the anthracene by  $65.5^\circ$ , and the angle between the plane of the ethylene and that of the phenyl group is  $6.8^\circ$ .<sup>8</sup>

Dimer **3** upon photoexcitation ( $\lambda > 360$  nm) undergoes cycloreversion with low quantum efficiency (0.03) to give **1**. Interestingly, however, **3** isomerizes upon irradiation to give **5** with a quantum yield of 0.10. According to  $^1\text{H}$  NMR analysis, there is no centrosymmetric isomer **6** formed from **3** by direct photoexcitation. By contrast, isomer **6** rather than **5** is formed with a quantum yield of 0.01 in the triplet (biacetyl)-sensitized reaction of **3**, though cycloreversion to give **1** is the major chemical deactivation pathway of triplet state **3** ( $\varphi = 0.3$ ). We explain the formation of **5** from directly excited **3** by a singlet state  $4\pi + 2\sigma + 2\pi$  cycloaddition as shown in **14**. The other conceivable route from photoexcited **3** to **5** involving an intramolecular Diels-Alder addition of the styryl double bond to the anthracene moiety, followed by electrocyclic opening of the resulting cyclobutane, appears unlikely for geometrical reasons. The formation of **6** in the biacetyl-sensitized reaction suggests the centrosymmetrical dimer

Table I.  $^1\text{H}$  NMR Spectral Data of Dimers **5** and **6**<sup>a</sup>

H	<b>5</b>	<b>6</b>
H <sub>a</sub>	5.79 (d, $J = 11.5$ Hz)	5.78 (d, $J = 12$ Hz)
H <sub>b</sub>	5.25 (d, $J = 11.5$ Hz)	4.31 (dd, $J = 12, 3$ Hz)
H <sub>c</sub>	4.15 (s)	4.16 (d, $J = 3$ Hz)
H <sub>Ar</sub>	6.84–7.61	6.84–7.61

<sup>a</sup> 270-MHz spectra in deuterated chloroform. Chemical shifts in  $\delta$  downfield from  $\text{Me}_4\text{Si}$ .

to be thermodynamically favored over the  $C_2$  isomer **5**. Conceivably, the triplet-state conversion of **3** into **6** involves biradical intermediates **15** and **16**. Support for a biradical mechanism may be seen in the photochemical isomerization of anthracene **17**, which is structurally related to **3**. Both upon direct excitation and in a biacetyl-sensitized reaction, **17** isomerizes to give **18**, whose formation may be explicable by biradical intermediates **19** and **20**.<sup>9</sup>

From a graphic presentation of quantum yield data as a function of the concentration of **1** in degassed benzene, we obtained

$$1/\varphi = 4.2 + 0.27(1/[1])$$

and the limiting quantum yield for the disappearance of **1** was calculated to be 0.24. Based on the fluorescence lifetime of **1** of 3.62 ns as measured by single photon counting, the rate constant for the dimerization of **1** was calculated to be  $5.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . For unsubstituted anthracene, the rate constant for the dimerization in benzene was found to be  $10 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>10</sup> The sum of rate constants for dimerization and self-quenching of **1** ( $4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) is close to the value expected for a diffusion-controlled process. From the concentration dependence of the fluorescence quantum yield of **1**, a similar rate constant of  $4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was obtained, suggesting the dimerization to occur from the excited singlet state.

### Experimental Section

All photoreactions were carried out in an optical bench arrangement by irradiating degassed solutions in cylindrical quartz cells through appropriate cutoff filters with a 1000-W xenon-mercury lamp. Degassing was accomplished by four freeze-thaw cycles.

**Dimerization of 1 To Give 3.** A solution of **1** (100 mg) in benzene (4 mL) was irradiated for 5 h at 10–15 °C with wavelengths  $>440$  nm (cutoff filter). The reaction mixture was refluxed in benzene for 20 min in order to convert dimer **4** into **1**. Vacuum evaporation of solvent gave an oily residue that was dissolved in methylene chloride and treated with activated charcoal in order to remove **1** by adsorption. Addition of methanol to the filtrate followed by slow evaporation of solvent gave 15 mg of **3**: pale greenish yellow crystals; mp 178–179 °C. Anal. Calcd for  $\text{C}_{44}\text{H}_{32}$ : C, 94.25; H, 5.75. Found: C, 93.70; H, 5.74.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.27 (s, 1), 7.96–6.42 (m, 26), 6.63 (d,  $J = 17$  Hz, 1), 6.41 (d,  $J = 17$  Hz, 1), 4.92 (d,  $J = 9$  Hz, 1), 4.57 (d,  $J = 1$  Hz, 1), 4.25 (dd,  $J = 9, 1$  Hz, 1).

**Dimerization of 1 To Give 4, 5, and 6.** A solution of **1** (100 mg) in benzene (4 mL) was irradiated for 12 h with wavelengths  $>360$  nm (cutoff filter). According to NMR analysis, the reaction mixture contained **4**, **5**, and **6** in a ratio of 10:85:5, and there was no dimer **3** detectable. The residue obtained on vacuum evaporation of solvent was dissolved in methylene chloride (1 mL) to give 1.5 mg of **4** as colorless crystalline precipitate: mp 171–175 °C dec;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.74–6.78 (m, 30), 5.04 (s, 2). Vacuum evaporation of solvent gave a residue, which was dissolved in benzene, and the solution was refluxed for 20 min in order to dissociate residual dimer **4**. Charcoal treatment as described above

(8) Becker, H.-D.; Patrick, V. A.; White, A. H. *Aust. J. Chem.* 1984, 37, 2215.

(9) The structure of **18** has been established by X-ray diffraction (Becker, H.-D.; White, A. H., to be published).

(10) Cf.: Cowan, D. O.; Schmiegel, W. W. *J. Am. Chem. Soc.* 1972, 94, 6779.

followed by slow crystallization from methylene chloride and methanol gave colorless crystals (48 mg, mp 188–192 °C dec) which, according to  $^1\text{H}$  NMR analysis (cf. Table I), consisted of 5 and 6 in a ratio of 20:1. Dimers 5 and 6 crystallize together, and we have not been able to separate the two isomers.

**Irradiation of 3 To Give 1 and 5.** A solution of 3 (3 mg) in benzene (4 mL) was irradiated for 2 h with light of  $378 \pm 8$  nm (monochromator).  $^1\text{H}$  NMR analysis of the residue obtained on vacuum evaporation revealed the presence of starting material (28 mol %), the formation of 1 (27 mol %), and the formation of 5 (45 mol %). There was no dimer 6 detectable.

**Triplet-Sensitized Reaction of 3.** A solution of 3 (10 mg) and biacetyl (90 mg) in benzene (4 mL) was irradiated for 20 min with wavelengths  $>440$  nm (cutoff filter). The reaction mixture was analyzed by  $^1\text{H}$  NMR spectroscopy and found to consist of unchanged starting material (46 mol %), styrylanthracene 1 (52 mol %), and dimer 6 (2 mol %). There was no dimer 5 detectable. (Styrylanthracene 1 was found to be stable in the presence of photoexcited biacetyl.)

**Triplet-Sensitized Isomerization of 17 To Give 18.** A degassed solution of 17 (6.5 mg) and biacetyl (150 mg) in benzene (12 mL) was irradiated with wavelengths  $>440$  nm for 81 min. Vacuum evaporation of solvent and biacetyl gave a residue, which according to  $^1\text{H}$  NMR analysis consisted of 18:  $^1\text{H}$  NMR  $\delta$  7.57 (d,  $J = 7.3$  Hz, 1), 7.41 (d,  $J = 5.7$  Hz, 1), 6.70–7.25 (m, 15), 6.68 (d,  $J = 5.7$  Hz, 1), 5.18 (d,  $J = 10.7$  Hz, 1), 5.0 (d,  $J = 10.7$  Hz, 1), 4.27 (d,  $J = 10$  Hz, 1), 4.00 (d,  $J = 10$  Hz, 1). In the photochemical isomerization of 17 (100 mg) by direct excitation in benzene (120 mL;  $\lambda > 340$  nm; 125-W mercury lamp; immersion-well apparatus; argon), 18 was isolated in 90% yield [colorless crystals, which turn yellow upon heating around 90 °C, melting around 135 °C, followed by resolidification; the final melting point is around 290 °C, which is that of *trans,trans*-1,5-bis(9-anthryl)penta-1,4-dien-3-one (cf. ref 2)].

**Quantum Yield Measurements.** The dimerization quantum yields are based on the potassium ferrioxalate actinometer, and they refer to measurements conducted at 20 °C in the concentration range between 0.01 and 0.1 M. However, for some unknown reason and independent of the initial concentration, at conversions below 0.05 the disappearance of 1 was found to proceed faster than is in accordance with the concentration-dependent change of quantum yield. Therefore, the measurements were evaluated iteratively for conversions ranging from 0.05 to 0.25.

The fluorescence quantum yields were determined with an Aminco Bowman SPF 500 spectrofluorometer modified for frontal illumination. The quantum yields and the fluorescence life time in dilute benzene solution were measured at 20 °C.

**Registry No.** 1, 42196-97-4; 3, 97635-20-6; 4, 97635-19-3; 5, 97635-21-7; 6, 97673-32-0; 17, 84599-82-6; 18, 97635-22-8; *trans,trans*-1,5-bis(9-anthryl)penta-1,4-dien-3-one, 84599-83-7.

### Asymmetric Nucleophilic Acylation via Metalated $\alpha$ -Amino Nitriles Possessing an Axially Disymmetric Tertiary Amino Group

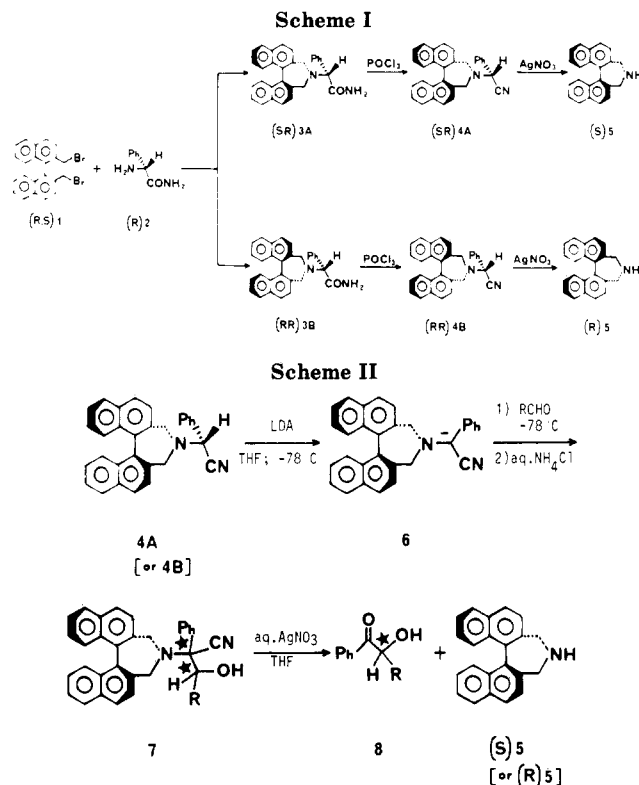
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GR No. 12, C.N.R.S., 94320 Thiais, France

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Asymmetric versions of nucleophilic acylation reactions, using metalated chiral  $\alpha$ -amino nitriles as acyl anion equivalents in nucleophilic addition to aldehydes, have been recently developed.<sup>1</sup> In these reactions, the chirality information, easily introduced via the amino function, originated from secondary amines derived from natural (S)-proline and contained one or several asymmetric carbon atoms.

<sup>†</sup> Deceased April 21, 1984.



Considering the high interest raised for the past few years by axially disymmetric compounds in asymmetric synthesis,<sup>2</sup> we have been inclined to apply the known preparation of binaphthyl tertiary amines<sup>2d,3</sup> to the synthesis of  $\alpha$ -amino nitriles bearing a binaphthyl unit, in order to investigate the relative efficiency of such a  $C_2$ -symmetric chiral auxiliary in asymmetric nucleophilic acylation reactions.

In the present paper, we report the synthesis of the diastereoisomerically pure  $\alpha$ -amino nitriles 4A and 4B from racemic 2,2'-bis(bromomethyl)-1,1'-binaphthyl [(RS)-1] and their use as chiral acyl anion equivalents in nucleophilic addition to aldehydes.

Furthermore, compounds 4A and 4B are direct precursors of the secondary amines (S)-5 and (R)-5, which are interesting key substances for the development of new binaphthyl derivatives and are obtained by this method in an optically pure state or nearly so from the racemic dibromide (RS)-1.<sup>4</sup>

Treatment of 2,2'-bis(bromomethyl)-1,1'-binaphthyl [(RS)-1]<sup>6</sup> with an excess of D-(-)- $\alpha$ -aminophenylacetamide

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(2) (a) Nishizawa, N.; Yamada, M.; Noyori, R. *Tetrahedron Lett.* 1981, 247. (b) Ishiguro, M.; Koizumi, N.; Yasuda, M.; Ikekawa, N. *J. Chem. Soc. Chem. Commun.* 1981, 115. (c) Olivero, A. G.; Weidmann, B.; Seebach, D. *Helv. Chim. Acta* 1981, 64, 2585. (d) Mazaleyrat, J. P.; Cram, D. J. *J. Am. Chem. Soc.* 1981, 103, 4585. (e) Cram, D. J.; Sogah, G. D. *J. Chem. Soc. Chem. Commun.* 1981, 625. (f) Miyashita, A.; Yasuda, A.; Takaya, A.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* 1980, 102, 7932. (g) Mazaleyrat, J. P. *Tetrahedron Lett.* 1983, 24, 1243. (h) Sakane, S.; Fujiwara, J.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* 1983, 105, 6155. (i) Amano, M.; Watanabe, M.; Baba, N.; Oda, J.; Inouye, Y. *Bull. Chem. Soc. Jpn.* 1983, 56, 3672.

(3) Cottineau, F.; Maigrot, N.; Mazaleyrat, J. P. *Tetrahedron Lett.* 1985, 26, 421.

(4) Synthesis of the amine 5 by direct reaction of ammonia with the dibromide 1 is unsatisfactory because of the occurrence of a further bis alkylation reaction which is difficult to control and leads to a quaternary ammonium salt.<sup>5</sup>

(5) Unpublished results from our laboratory and: Wittig, G.; Koenig, G.; Clauss, K. *Justus Liebigs Ann. Chem.* 1955, 593, 127.