boxy sulfones containing *para*-deactivating groups are reported not to undergo ring closure.[6]

We have now found that diphenyl sulfone-2,4′,5-tricarboxylic acid (**3**), although inert to cyclization with sulfuric acid at 160 or 200° as expected,[6] is smoothly converted into thiaxanthone 5,5-dioxide-2,7-dicarboxylic acid (**4**) on heating in polyphosphoric acid. The yield of **4** in the PPA cyclization increased with increasing temperature. Reaction for 0.5 hr at 250, 275, and 290° gave **4** in yields of 10, 40, and 85%, respectively. It was then found that reaction of **3** in concentrated H_2SO_4 at 270° gave **4** in 85% yield. An acid medium was essential; heating **3** in Dowtherm at 260° or in a melt at 300° produced no thiaxanthone.

For qualitative comparison, diphenyl sulfone-2-carboxylic acid[7] and 4′-methyldiphenyl sulfone-2-carboxylic acid[8] were readily cyclized, as expected, by heating in PPA for 0.5 hr at 210°. The known products[9] of these sulfones, thiaxanthone 5,5-dioxide and 2-methylthiaxanthone 5,5-dioxide, respectively, were obtained in 97% yield.

Experimental Section[10]

2,4′,5-Trimethyldiphenyl Sulfone.—The Friedel–Crafts procedure (80°, 4 hr) starting with 100 g (0.526 mol) of *p*-toluenesulfonyl chloride, 150 g (1.41 mol) of *p*-xylene, and 133.3 g (1 mol) of aluminum chloride gave 203 g (78%) of the title compound after crystallization of the crude reaction product from aqueous methanol, mp 106–107°, lit.[11] mp 109°.

Diphenyl Sulfone-2,4′,5-tricarboxylic Acid (3).—Following the reported procedure for the oxidation of 2,5-dimethyldiphenyl sulfone,[12] aqueous nitric acid (580 ml, 35%) oxidation of 2,4′,5-trimethyldiphenyl sulfone (198 g) in a stainless steel pressure vessel afforded crude **3**. Purification of this product was achieved in 48% yield by crystallization from acetic acid, mp 336–339° dec.

Anal. Calcd for $C_{15}H_{10}O_8S$: C, 51.40; H, 2.87; S, 9.15; neut equiv, 116.8. Found: C, 51.10; H, 3.30; S, 9.30; neut equiv, 117.8.

Treatment of **3** with ethereal diazomethane gave 2,4′,5-tricarbomethoxydiphenyl sulfone (88%), mp 139.6–140.5°, from aqueous methanol.

Anal. Calcd for $C_{18}H_{16}O_8S$: C, 55.10; H, 4.11; sapon equiv, 130.8. Found: C, 55.10; H, 4.20; sapon equiv, 129.0.

Cyclization of 3 into Thiaxanthone 5,5-Dioxide-2,7-dicarboxylic Acid (4).—In a typical reaction, 10.0 g (0.0286 mol) of **3** was added to 150 ml of polyphosphoric acid (Victor Chemical Co.). The stirred reactants were heated in a dry atmosphere at 290° for 0.5 hr, and the cooled reaction mixture was poured into 2 l. of distilled water and allowed to digest overnight. The solid was collected by suction filtration, washed thoroughly with cold water, and extracted five times with 150-ml portions of hot methanol. The light tan solid residue was dried at 110° (2 hr) to give 8.10 g (85%) of pure **4**, mp 426–429° dec.

Anal. Calcd for $C_{15}H_8O_7S$: C, 54.22; H, 2.42; S, 9.64; neut equiv, 166.1. Found: C, 53.90; H, 2.61; S, 9.70; neut equiv, 166.1.

Dimethyl and Didecyl Esters of 4.—Normal esterification of **4** could not be achieved due to its extreme insolubility. However, treatment of **4** with ethereal diazomethane gave the diester, dimethyl thiaxanthone 5,5-dioxide-2,7-dicarboxylate, mp 200–201°, from methanol. In addition, reaction of **4** with thionyl chloride followed by treatment with excess methanol afforded the dimethyl ester.

Anal. Calcd for $C_{17}H_{12}O_7S$: C, 56.66; H, 3.36. Found: C, 56.80; H, 3.62.

Similar reaction of **4** with thionyl chloride followed by treatment with excess *n*-decanol gave the corresponding didecyl ester mp 80–81°, from aqueous methanol.

Anal. Calcd for $C_{35}H_{48}O_7S$: C, 68.79; H, 7.90. Found: C, 68.90; H, 8.20.

Using conventional methods,[13] attempts to prepare 2,4-DNP derivatives of **4**, and its two esters, were not successful. Closely related systems, *e.g.* xanthone,[14] also fail to give a 2,4-DNP derivative.

Dimethylformamide (DMF) Adduct of 4.—When **4** was dissolved in boiling DMF, the cooled solution afforded a yellow solid adduct with composition **4·2DMF**. The theoretical amount of DMF was lost when this adduct was heated at 170°, and pure white **4** was recovered.

Anal. Calcd for $C_{21}H_{22}N_2O_9S$: C, 52.71; H, 4.64; neut equiv, 239.2. Found: C, 53.23; H, 4.88; neut equiv, 239.0.

Registry No.—**3**, 21615-52-1; trimethyl ester of **3**, 21615-53-2; **4**, 21615-54-3; dimethyl ester of **4**, 21615-55-4; didecyl ester of **4**, 21615-56-5; DMF adduct of **4**, 21615-57-6.

Acknowledgment.—We wish to thank Mr. Rudolph Goetz for the cyclization results found for diphenyl sulfone-2-carboxylic acid and for 4′-methyldiphenyl sulfone-2-carboxylic acid.

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The Structures of the Photodimers of 9-Nitroanthracene, 9-Aminoanthracene, and 9-Anthryl Isocyanate[1]

O. L. CHAPMAN AND KYUHOE LEE

Department of Chemistry,
Iowa State University, Ames, Iowa 50010

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The photodimers of 9-substituted anthracenes have posed a vexing problem in structure. Chemical methods have proved quite satisfactory for interrelating dimers[2] but have been less useful for distinguishing between the head-to-head and head-to-tail orientations. Among the physical methods which have been employed in the study of these structures, the use of dipole moments has been the most successful in distinguishing head-to-head (2) from head-to-tail (1) structures.[3–5] Our interest in the photochemistry of 9-nitroanthracene[6] and sodium 9-anthroate[7] prompted us to undertake a study of the structure of the photodimer of 9-nitroanthracene.[8]

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[1] Photochemical Transformations. XXXII.

[2] See, for example, R. Calas, R. Lalande, J. G. Faugere, and F. Moulines, *Bull. Soc. Chim. Fr.*, 119 (1965).

[3] D. E. Applequist, T. L. Brown, J. P. Kleinman, and S. T. Young, *Chem. Ind.* (London), 850 (1959).

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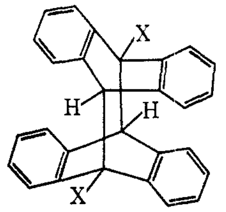
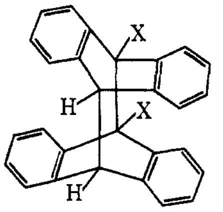
Our approach to this problem was based on the ^{13}C-side-band technique first described by Anet.[9] Measurement of the magnitude of the coupling constant of the bridgehead protons would permit a distinction between 1 and 2. In the head-to-tail orientation (1) the coupling constant should approach zero, while in the head-to-head orientation (2) a coupling constant of 6–10 Hz would be expected for the rigidly eclipsed bridgehead protons. It is not possible to obtain J_{AA} from an A_2 spectrum, but it is possible to take advantage of the 1.1% natural abundance of ^{13}C. In molecules containing ^{13}C at a bridgehead position, the bridgehead protons and the ^{13}C will constitute an AA′X system. The coupling constant between the bridgehead protons ($J_{AA'}$) can be determined by analysis of the ^{13}C side bands of the bridgehead protons. This method is, in principle, general and will be limited only by the solubility of the dimers.



1



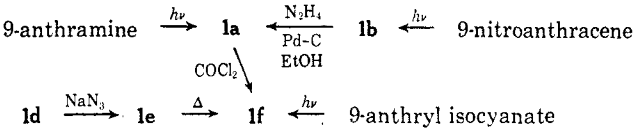
2

a, X = NH_2
b, X = NO_2
c, X = CO_2H
d, X = COCl
e, X = CON_3
f, X = N=C=O

The photodimer of 9-nitroanthracene proved too insoluble for satisfactory nmr spectra; so it was reduced to the corresponding diamine. Irradiation of 9-aminoanthracene gave the same diamine. The photodimer of 9-aminoanthracene was sufficiently soluble in formic acid to obtain satisfactory ^{13}C-side-band spectra using spectrum accumulation techniques. The proton spectrum of the photodimer of 9-aminoanthracene showed a singlet (2 H) at δ 4.96 (bridgehead protons) and a multiplet (16 H) at 7.29 (aromatic protons). This spectrum, together with the infrared and ultraviolet spectra, establishes the useful fact that the photodimer is formed by coupling at the 9,10 positions, but it does not distinguish between the head-to-tail (**1a**) and head-to-head (**2a**) orientations. The ^{13}C side bands of the bridgehead protons gave $J_{AA'} \approx 0$ and $J_{^{13}C-H} = 136$ Hz. The value of $J_{AA'}$ shows that 9-aminoanthracene photodimer has the head-to-tail orientation (**1a**) and establishes the head-to-tail orientation (**1b**) for 9-nitroanthracene photodimer.

As a cross check on the nmr method, we sought to interrelate the photodimer of 9-aminoanthracene (**1a**) and the photodimer of 9-anthroic acid (**1c**) which had been assigned the head-to-tail orientation.[3] Our plan was to convert the diacid (**1c**) to the diamine (**1a**) *via* the diacid chloride, (**1d**) the diacyl azide, (**1e**) and the diisocyanate (**1f**). In the end, it proved easier to convert the diamine (**1a**) to the diisocyanate for comparison (**1f**). Treatment of (**1a**) with phosgene gave the diisocyanate (**1f**) in low yield and the bishydrochloride of 9-aminoanthracene photodimer. Irradiation of 9-anthryl isocyanate (prepared from 9-anthroic acid) gave a photodimer which was identical with the diisocyanate **1f** (Scheme I).

SCHEME I



Experimental Section

Preparation of the Photodimer of 9-Aminoanthracene.—A solution of 9-aminoanthracene (500 mg) in toluene (25 ml) was degassed with argon for 10 min and irradiated externally with a Pyrex filtered Hanovia Type A mercury arc lamp. Filtration and tituration of the residue in boiling chloroform and benzene until the infrared spectrum showed no change gave 9-aminoanthracene photodimer (450 mg, 90%): mp 155–160° dec; 6.27, 6.81 and 6.90 μ (KBr); $\lambda_{max}^{CHCl_3}$ 241 mμ (ϵ 5060), $\lambda_{max}^{CHCl_3}$ 271 mμ (ϵ 1500), $\lambda_{max}^{CHCl_3}$ 281 mμ (ϵ 895); nmr (90% formic acid) δ 4.96 singlet (2 H), 7.29 multiplet (16 H). The accumulated nmr spectrum showed a singlet ^{13}C side band of the bridgehead protons ($J_{^{13}C-H}$ 136 cps). The mass spectrum showed base peak at 193 (*m/e*) and did not show a molecular ion peak at 386 (*m/e*).

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.00; H, 5.75; N, 7.25. Found: C, 86.94; H, 5.76; N, 7.05.

Reduction of the Photodimer of 9-Nitroanthracene.—A suspension of 9-nitroanthracene photodimer[8] (250 mg) in 95% ethanol (13 ml) was treated with hydrazine hydrate (2 ml of 99–100%) with stirring and then with palladium on charcoal (10%, 40 mg) in small portions. The solution was refluxed for 24 hr, cooled, and filtered. The residue was washed three times with 5-ml portions of hot 95% ethanol, dissolved in 5 ml of 90% formic acid, and left overnight. This solution was filtered through Celite, diluted with water, and made basic with concentrated ammonium hydroxide while cooling externally with ice water. Filtration and trituration of the residue in boiling benzene gave 9-aminoanthracene photodimer (90 mg, 41%), mp 155–160° dec. The infrared absorption spectrum (KBr) was superimposable on that of the photodimer of 9-aminoanthracene.

Preparation of 9-Anthroyl Azide Dimer.—A stirred acetone (20 ml) suspension of 9-anthroyl chloride dimer[3] (420 mg, 0.88 mmol) at 0° was treated dropwise with a solution of sodium azide (140 mg) in water (0.8 ml). After 1 hr the mixture was poured into water (60 ml), filtered, and dried over phosphorus pentoxide overnight. The resulting solid was triturated in boiling hexane giving 9-anthroyl azide dimer (400 mg, 92.2%, mp 185–186° dec). The infrared spectrum of this compound showed bands at 4.65 and 5.89 μ. This material was used without further purification for the preparation of 9-anthryl isocyanate dimer.

Preparation of 9-Anthryl Isocyanate Dimer.—9-Anthroyl azide dimer (300 mg) was heated (refluxing water) in a drying pistol for 48 hr. The resulting compound was 9-anthryl isocyanate dimer (266 mg, 100% yield, mp 188–189° dec). The same compound was prepared by refluxing the azide for 25 hr in benzene and recrystallizing from carbon tetrachloride. The infrared spectrum showed the isocyanate band at 4.47 μ and the dimer bands at 6.79 and 6.88 μ and was superimposable on that of the photodimer of 9-anthryl isocyanate and that of the 9-anthryl isocyanate dimer prepared from the photodimer of 9-aminoanthracene (see below). The mass spectrum showed the base peak at 219 (*m/e*) and did not show a molecular ion peak at 438 (*m/e*).

Anal. Calcd for $C_{30}H_{18}N_2O_2$: C, 82.30; H, 4.10; N, 6.40. Found: C, 82.27; H, 4.26; N, 6.38.

Preparation of the Photodimer of 9-Anthryl Isocyanate.—A solution of 9-anthryl isocyanate (30 mg) in hexane (3 ml) was degassed with argon for 5 min, irradiated externally with a Hanovia Type A mercury arc lamp in a cooling water jacket (Pyrex) for 6 hr. Suction filtration gave white crystals which were triturated in boiling hexane giving the photodimer of 9-anthryl isocyanate (22 mg, 73% yield, mp 188–189°, dec). The infrared spectrum showed the isocyanate peak at 4.47 μ and the dimer peaks at 6.79 and 6.88 μ and was superimposable on that of 9-anthryl isocyanate dimer prepared from the 9-anthroic acid photodimer and from 9-aminoanthracene photodimer.

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Preparation of 9-Anthryl Isocyanate Dimer from 9-Aminoanthracene Photodimer.—Phosgene (500 mg) was passed into a stirred solution of 9-aminoanthracene photodimer (300 mg) in 50 ml of dry toluene (distilled from phosphorus pentoxide) and left at room temperature for 23 hr. The solution was then refluxed under reduced pressure for 1 hr to remove unreacted phosgene. The white solid was collected by suction filtration. This compound was the 9-aminoanthracene dimer hydrochloride salt (300 mg, 85% yield, mp >250° dec). The infrared spectrum showed peaks at 3.6, 6.2, and 6.6 μ (1516 cm^{-1}). A small amount of this compound was made basic with aqueous ammonia, and the resulting white precipitate was collected by suction filtration and dried under reduced pressure. The infrared spectrum of the product was superimposable on that of the photodimer of 9-aminoanthracene.

Evaporation of the filtrate from the toluene solution under reduced pressure and trituration of the residue in boiling hexane gave 9-anthryl isocyanate dimer (30 mg, 8.9% yield, mp 188–189° dec). The infrared spectrum was superimposable on that of the photodimer of 9-anthryl isocyanate and that of 9-anthryl isocyanate dimer prepared from the photodimer of 9-anthroic acid.

Registry No.—1a, 22037-98-5; 1a hydrochloride, 22003-71-0; 1b, 22003-72-1; 1e, 22003-73-2; 1f, 22003-74-3.

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Reactions of Phthalic Anhydride with Biphenyl at 700°

Ellis K. Fields

Research and Development Department,
Amoco Chemicals Corporation,
Whiting, Indiana 46394

Seymour Meyerson

Research and Development Department,
American Oil Company,
Whiting, Indiana 46394

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Phthalic anhydride at 700° loses carbon dioxide and carbon monoxide to give benzyne; in the presence of benzene it yields biphenyl by insertion and naphthalene by 1,2 and 1,4 addition and subsequent loss of acetylene.[1] With biphenyl, phthalic anhydride should give 1- and 2-phenylnaphthalene and the three terphenyls as the major products (Scheme I).

To test this prediction and to determine the relative yields of the insertion and addition products as well as isomer distribution, we allowed a mixture of phthalic anhydride and biphenyl to react at 700° and obtained the products shown in Table I.

Phenylnaphthalene and terphenyls were indeed formed as major products. Gas chromatographic analysis gave the yields and isomer distributions shown in Table II.

Scheme I

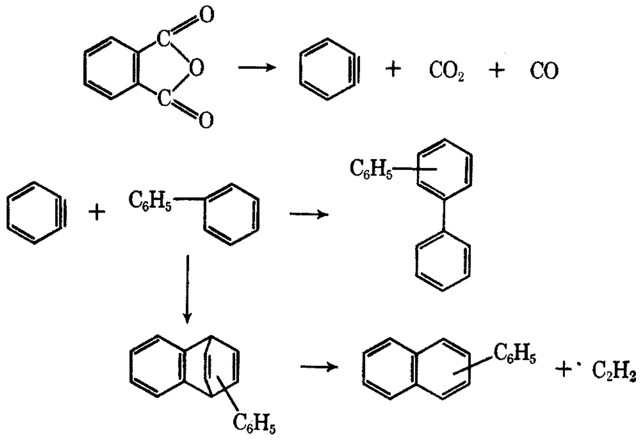

Table I

Products from the Reaction of Phthalic Anhydride with Biphenyl[a]

Product	Relative concentration[b]
Anthracene, phenanthrene	24
Phenylnaphthalene	36
Terphenyl	100
Binaphthyl	20
Naphthylbiphenyl	18
Quaterphenyl	73
Quinquephenyl	14
Sexiphenyl	4

[a] Conditions: 0.02 mol of phthalic anhydride, 0.1 mol of biphenyl; 700°; contact time, 35 sec; N_2, 10 cc/min; total weight of products, 4.55 g. [b] Relative intensity in the low-voltage (7.5 V uncorrected) mass spectrum on the basis terphenyl = 100.

Table II

Product	Yield, mol %	Isomer, %
Phenylnaphthalene	16.7	1, 27
		2, 73
Terphenyl	40.6	*ortho*, 8
		meta, 57
		para, 35

On the basis of other studies,[2] we had assumed that little or no terphenyl would arise from biphenyl alone,[3] and, for confirmation, we pyrolyzed biphenyl at 700° with the results shown in Table III. Evidently biphenyl gives terphenyl at high temperatures, and about as much as quaterphenyl, contrary to previous

Table III

Products from Biphenyl[a]

Products	Relative concentrations[b]	
Benzene[c]	28	25
Terphenyl	116	71
Quaterphenyl	100	100
Quinquephenyl	2	3
Sexiphenyl		0.5

[a] Conditions: 0.1 mol biphenyl; 700°; N_2, 10 cc/min; contact time, 7.5 sec (1.2% conversion) and 37 sec (6.6% conversion), respectively. [b] Relative intensity in the low-voltage mass spectrum normalized to quaterphenyl = 100. [c] Owing to work-up procedure, most benzene was lost before analysis. The figures merely serve to indicate that benzene was a product of the reaction.

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[3] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 21 (1966).