56-2; XIII, 14760-97-5; XIV, 7601-87-8; XV, 14760-99-7; XVI, 14805-57-3; XXII, 14805-58-4; hydrogen peroxide, 7722-84-1.

Acknowledgments.—Research reported in this publication was supported by the Advanced Research Projects Agency under contract to the Office of Naval Research. We gratefully acknowledge our great debt to the late Dr. Robert C. Hirt who designed the spectroradiometer used in this study. The authors thank Mr. A. M. Semsel for his assistance with the kinetic measurements.

Photocyclizations of Compounds Containing Two Anthracene Rings

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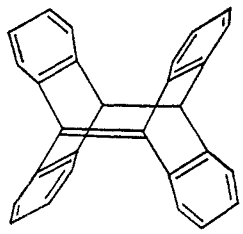
Received August 10, 1967

It has been found that di-9-anthryl carbonate, 9-anthryl-9-anthramide, and 9,9′-azoanthracene undergo photocyclizations readily to give the cyclic carbonate, β-lactam, and cyclic azo compound, respectively. The last substance proved unexpectedly stable, no nitrogen being evolved under pyrolytic or photolytic conditions. Attemps to photocyclize 1,2-bis-10′-bromo-9′-anthrylethane, bis-10-bromo-9-anthrylmethane, 10-chloro-9-anthroic anhydride, and 10-bromo-di-9-anthrylmethane all failed.

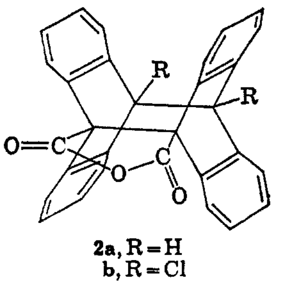
Previous work in this laboratory on the anthracene photodimers[1] has been directed toward a synthesis of the bridgehead olefin, 9,9′-dehydrodianthracene (**1**).



1

Though neither **1** nor any derivative of it has been isolated, evidence for the intermediacy of such a structure in the reaction of the photodimer of 9-chloroanthracene with phenyllithium has been offered.[1] A significant difficulty in the synthesis of olefins of type **1** is the unwillingness of most anthracene photodimerizations to give vicinal bridgehead functional groups, preferring to give the head-to-tail dimers from 9-substituted anthracenes[2] and usually no dimers from 9,10-disubstituted anthracenes.[3]

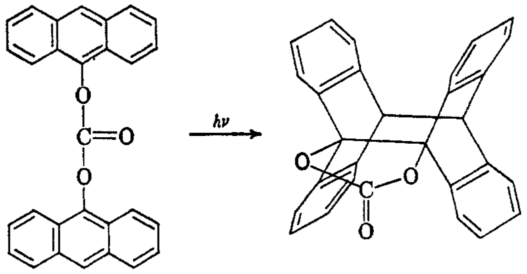
Exceptions are the photocyclization of 9-anthroic anhydride to give **2a**[4] and other similar reactions of molecules containing more than one anthracene ring.[5,6]



2a, R = H
b, R = Cl

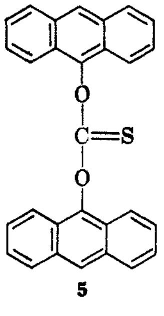
The aim of the present work was to exploit the photocyclization reaction in systems where the resulting bridgehead functionality would offer rational syntheses of the bridgehead olefin.

Di-9-anthryl carbonate (**3**) was prepared by the reaction of the enolate of anthrone with phosgene in tetrahydrofuran (85% yield) and was photocyclized in benzene to **4** (52% yield) (eq 1). The carbonyl



3 **4** (1)

absorption frequencies of **3** and **4** are at the expected values of 1770 cm^{-1} and 1815 cm^{-1}, respectively.[7] It was hoped that **4** might be converted with P_2S_5 to the thionocarbonate, which would be an ideal starting material for the Corey olefin synthesis (with trialkyl phosphite).[8,9] Alternatively, if **3** could be converted to the corresponding thionocarbonate (**5**), photo-



5

cyclization of this might give the same olefin precursor. Neither of these possibilities was realized under various conditions with P_2S_5. Direct synthesis of **5** from

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[1] D. E. Applequist, R. Searle, M.-D. Steinhardt, E. C. Friedrich, and R. L. Litle, *J. Org. Chem.*, **30**, 2126 (1965), and references cited therein.

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

[3] R. Lalande and R. Calas, *Bull. Soc. Chim. France*, 144 (1960).

[4] F. D. Greene, S. L. Misrock, and J. R. Wolfe, *J. Am. Chem. Soc.*, **77**, 3852 (1955).

[5] F. D. Greene, *Bull. Soc. Chim. France*, 1356 (1960).

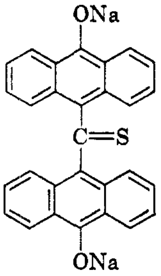
[6] I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 2695 (1952).

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 125, 127.

[8] E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965).

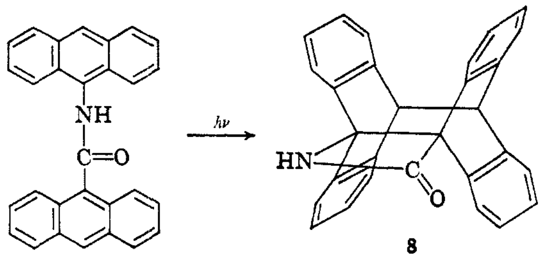
[9] E. J. Corey and R. A. E. Winter, *ibid.*, **85**, 2677 (1963).

anthrone and thiophosgene also failed, possibly owing to attack on the carbon rather than the oxygen of the enolate. A substance having a satisfactory analysis for **6** was obtained in 31% yield, along with a 58% yield of 10,10'-bianthronyl.

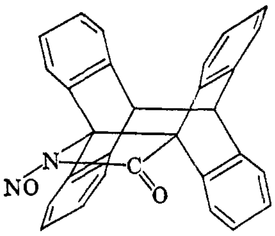


6

9-Anthryl-9-anthramide (**7**) was prepared in 98% yield from 9-anthroyl chloride and 9-aminoanthracene. Irradiation of **7** in benzene gave the β-lactam **8** in 50% yield, characterized by analysis and by the expected carbonyl absorption[10] at 1745 cm^{-1}. It was hoped that **8** could be N-nitrosated to give **9**, which might be expected to undergo rearrangement[11] to the azo ester and loss of CO_2 and N_2 to give **1**.[12] However, all attempts to nitrosate **8** gave either recovered lactam or the N-nitrolactam **10** (characterized by elemental analysis and infrared bands at 1283, 1533, and 1810 cm^{-1}). The latter was formed when N_2O_4 was used under strenuous conditions or when nitrosyl chloride was used without careful purification. Perhaps NO_2Cl serves as the nitrating agent in impure NOCl. Even the lithium salt of **8**, prepared with phenyllithium, failed to give **9** after reaction with NOCl and a normal hydrolytic isolation procedure. A possible interpretation of these failures, consistent with the unreactivity of other dianthracene bridgehead functional groups, is that the steric situation drove the nitrosating agents to the oxygen of the amide, and that the resulting iminonitrite (**11**) reverted to **8** upon contact with water.



7 **8**



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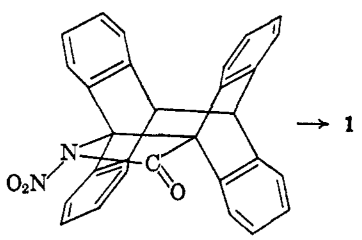

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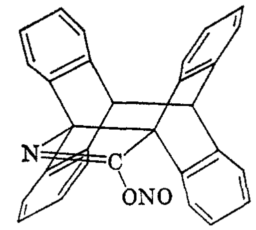
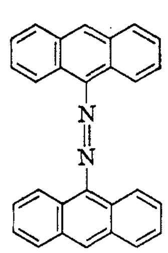


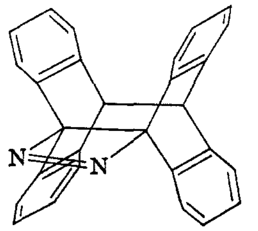
11

The thermal decomposition of **10** was investigated briefly. At 200° in furan, it failed to decompose. At 240°, without solvent, decomposition gave a 22% yield of anthraquinone and some black tar.

9,9'-Azoanthracene (**12**) was prepared from 9-anthryldiazonium fluoborate and cuprous chloride in 29% yield by the method of Rigaudy and Barcelo.[13] Irradiation of a benzene solution of **12** with a mercury-arc lamp (λ_{max} 3500 A) gave a 58% yield of an isomer assigned structure **13**. The compound showed λ_{max} 247 mμ (ε 4100) and no bands in the region 325–390 mμ characteristic of anthracenes.[14] The molecular weight was satisfactory. It was expected, although without close precedent, that **13** would readily lose nitrogen to generate **1**, but at 284–287° **13** simply reverted to **12**. Prolonged irradiation of a benzene solution of **13** at 2537 A gave no reaction. It is of interest for comparison that tetrafluoro-3,4-dihydro-1,2-diazetine (**14**) decomposes thermally above 150°, rapidly at 240°, to give nitrogen and tetrafluoroethylene, and is also cleaved photochemically.[15]



12



13

$$\begin{array}{c} N{=}N \\ | \quad\; | \\ F_2C{-}CF_2 \end{array}$$

14

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(10) Reference 7, p 214.

(11) E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1174 (1961).

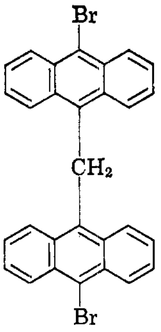
(12) M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85**, 1792 (1963).

(13) J. Rigaudy and J. Barcelo, *Compt. Rend.*, **258**, 4799 (1964).

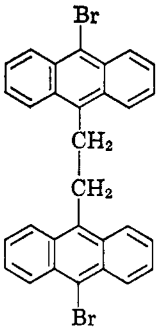
(14) H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 322.

(15) H. J. Emeleus and G. L. Hurst, *J. Chem. Soc.*, 3276 (1962).

Vicinal bridgehead halogens would provide obvious paths to bridgehead olefins of type **1**. Because the 9-haloanthracenes (F, Cl, Br, I) all give head-to-tail photodimers,[16,17] and 9,10-disubstituted anthracenes usually do not yield dimers,[3] a possible approach to vicinal halogens is a photocyclization of 10-haloanthracenes linked together at the 9 positions. Compounds **15** and **16** were synthesized to test this possibility.



15



16

Compound **15** was prepared by bromination of bis-9-anthrylmethane. The bromination was noteworthy in that the second substitution required far more drastic conditions than the first (150° with bromine and iron in carbon tetrachloride compared with bromine alone in refluxing carbon tetrachloride), even though the intermediate monobromide was soluble in the reaction medium. The structure of **15** was assigned on the basis of the expected orientation, the elemental analysis, and the nmr spectrum (τ 1.7–2.9, area 15.6; τ 7.0, area 2). The intermediate monobromide gave almost an identical multiplet in the aromatic region, so the nmr does not convincingly confirm the assigned positions of substitution.

Compound **16** was prepared by reaction of 10-bromo-9-chloromethylanthracene with methylmagnesium iodide.[18]

Irradiation of benzene solutions of compounds **15** and **16** with a mercury-arc lamp for 2 and 21 days, respectively, gave no detectable cyclization. Under similar conditions, bis-9-anthrylcarbinol[5,19] and 1,2-bis(9-anthryl)ethane[6,20] are readily photocyclized to the dianthracene structures. It has now been found that even one 10-bromo substituent on bis-9-anthrylmethane effectively prevents photocyclization. It has similarly been found that the anhydride of 10-chloro-9-anthroic acid fails to photocyclize to **2b** in suspension or in solution. At this time, only speculative reasons may be offered for the effect of halogen substituents in inhibiting photocyclizations.

Experimental Section[21]

Di-9-anthrylcarbinol was prepared in 92% yield by the method of Greene and Kaminski[19] from 9-anthrylmagnesium bromide and 9-anthraldehyde. The product (crystals from benzene) showed mp 198–200° dec (lit.[5,19] mp 197–199° dec).

Di-9-anthrylmethane.—A solution of 3.5 g (9.11 mmoles) of di-9-anthrylcarbinol in 335 ml of absolute ethanol was added to a suspension of prehydrogenated 5% palladium on Darco (5.7 g, 1.6 mmoles) in 50 ml of absolute ethanol.[22] The reaction was allowed to continue until hydrogen consumption had ceased. The mixture was filtered and the solid collected was extracted with benzene in a Soxhlet extractor to afford, at first 350 mg (10% recovery) of di-9-anthrylcarbinol, mp 197–199°, and then 2.75 g (82%) of di-9-anthrylmethane, mp 382–384° dec. Two recrystallizations from benzene–ethanol gave an analytical sample, mp 382–384° dec.

Anal. Calcd for $C_{29}H_{20}$: C, 94.57; H, 5.43. Found: C, 94.58; H, 5.30.

10-Bromo-9,9′-dianthrylmethane.—A mixture of 1.6 g (4.35 mmoles) of di-9-anthrylmethane, 10.7 g (48 mmoles) of anhydrous cupric bromide and 100 ml of carbon tetrachloride was stirred at reflux for 8 hr.[23] The reaction mixture was filtered and the precipitate washed with methylene chloride. The combined filtrate and washings were concentrated *in vacuo* to give a reddish oily solid which was crystallized from methylene chloride–95% ethanol to afford 1.69 g (87%) of gold solid, mp 188–191°. Two recrystallizations from 95% ethanol gave an analytical sample, mp 189–191° dec. The nmr spectrum showed a singlet at τ 6.95 (area 1) and a multiplet at τ 1.6–3.0 (area 8.5).

Anal. Calcd for $C_{29}H_{19}Br$: C, 77.86; H, 4.28; Br, 17.86. Found: C, 77.75; H, 4.41; Br, 17.59.

Attempt to Photocyclize 10-Bromo-9,9′-dianthrylmethane.—A solution of 300 mg (0.67 mmole) of 10-bromo-9,9′-dianthrylmethane in 6 ml of benzene was boiled to expel oxygen, sealed, and irradiated with a mercury-arc lamp for 11 days. No solid had formed by the end of the irradiation and the solvent was removed to give a 99% recovery of starting material, 297 mg, as identified by a comparison of their infrared spectra.

Reaction of Di-9-anthrylmethane with Iron and Bromine.—A mixture of 985 mg (2.68 mmoles) of di-9-anthrylmethane, 57 mg (1.02 mg-atoms) of iron wire and 1.19 g (7.43 mmoles) of bromine in 40 ml of carbon tetrachloride was heated in a sealed combustion tube for 7 hr at 150°. The tube was cooled and opened and the contents were removed. The reaction mixture was washed with aqueous sodium bisulfite and the organic phase withdrawn and dried over sodium sulfate. Filtration, followed by removal of solvent gave a red oil which was crystallized from 95% ethanol to give 310 mg (22%) of red solid, mp 170–172°. The product was recrystallized from 95% ethanol to give an analytical sample, mp 170–172°. The infrared spectrum was different from that of 10-bromo-9,9′-dianthrylmethane and the nmr showed a singlet (area 1) at τ 7.0 and a multiplet (area 7.8) at τ 1.7–2.9. These data, along with the elemental analysis, identified the product as 10,10′-dibromo-9,9′-dianthrylmethane (**15**).

Anal. Calcd for $C_{29}H_{18}Br_2$: C, 66.16; H, 3.42; Br, 30.42. Found: C, 66.29; H, 3.20; Br, 30.40.

The mother liquor from the first crystallization was concentrated to afford 710 mg of gold solid, mp 190–192°, identified by comparison of infrared spectra as 10-bromo-9,9′-dianthrylmethane (59%).

Attempted Photocyclization of 10,10′-Dibromo-9,9′-dianthrylmethane.—A solution of 270 mg of 10,10′-dibromo-9,9′-dianthrylmethane in 7 ml of dry benzene was boiled to expel oxygen, sealed, and irradiated with a mercury-arc lamp for 2 days. No crystals separated and the solvent was removed to give a red solid, 251 mg (92% recovery), mp 170–174° (mmp 170–174°).

10-Bromo-9-hydroxymethylanthracene.—A mixture of 19.25 g (67.6 mmoles) of 10-bromo-9-anthraldehyde, 20.4 g (100 mmoles) of aluminum isopropoxide and 430 ml of isopropyl alcohol was stirred at reflux for 12 hr. The solvent was removed at reduced pressure and the residue stirred for 1.5 hr with 600 ml of chloroform and 300 ml of 2 *N* hydrochloric acid. Filtration gave 12.75 g of orange solid, mp 200–208°. The chloroform solution was separated from the filtrate, dried over sodium sulfate, and filtered and the solvent removed to give 2.0 g of orange solid, mp 195–201°. The infrared spectra of both solids were identical. The total yield of 10-bromo-9-hydroxymethylanthracene was 14.75 g (77%). The product was recrystallized from methanol-water to give light fluffy needles, mp 203–203.5°. A sample

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[16] D. E. Applequist, E. C. Friedrich, and M. T. Rogers, *J. Am. Chem. Soc.*, **81**, 457 (1959).

[17] Unpublished work by M. A. Lintner and A. Ehret in these laboratories.

[18] F. H. C. Stewart, *Australian J. Chem.*, **14**, 177 (1961).

[19] L. A. Kaminski, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., May 1959.

[20] R. Livingston and K. S. Wei, *J. Am. Chem. Soc.*, **89**, 3098 (1967).

[21] Melting points and boiling points are uncorrected. Infrared and nmr spectra were measured in part by Mr. Dick Johnson and associates, mass spectra by Mr. J. Wrona, and elemental analyses by Mr. J. Nemeth and associates.

[22] R. Baltzly and J. S. Buck, *J. Am. Chem. Soc.*, **65**, 1984 (1943).

[23] D. C. Nonhebel, *Org. Syn.*, **43**, 15 (1963).

was recrystallized from benzene for analysis, mp 203–203.5°. The infrared spectrum had no absorptions in the region from 1650 to 1900 cm^{-1}.

Anal. Calcd for $C_{15}H_{11}BrO$: C, 62.74; H, 3.86; Br, 27.83. Found: C, 62.64; H, 3.85; Br, 27.70.

10-Bromo-9-chloromethylanthracene.—A mixture of 10.4 g (36.2 mmoles) of 10-bromo-9-hydroxymethylanthracene, 4.32 g (36.3 mmoles) of thionyl chloride and 100 ml of dioxane was stirred at reflux for 6.5 hr. The solution was allowed to cool to below room temperature (ice bath) and filtered to give a yellow solid which was washed with dioxane to afford 9.0 g of yellow needles, mp 197.5–199.5°. Removal of solvent from the filtrate gave a dark yellow solid which was crystallized from dioxane to give 0.43 g of yellow needles, mp 197–199°; the mixture melting point with the yellow solid described above was 197–199°. The combined product was recrystallized from dioxane to give an analytical sample, mp 198–199.5°. The total yield was 9.43 g (86%).

Anal. Calcd for $C_{15}H_{10}BrCl$: C, 58.95; H, 3.30; Br, 26.15; Cl, 11.60. Found: C, 59.21; H, 3.35; Br, 25.93; Cl, 11.50.

1,2-Bis-10′-bromo-9′-anthrylethane (16).—To a stirred solution of 49 ml (32.1 mmoles) of 0.655 *N* methylmagnesium bromide in ether was added a solution of 9.0 g (29.4 mmoles) of 10-bromo-9-chloromethylanthracene in 320 ml of dry benzene.[18] The stirred mixture was heated at reflux for 1.25 hr, hydrolyzed with 30 ml of dilute sulfuric acid and filtered to give 7.7 g of yellow solid, mp 236–237°. A sample was crystallized two times from benzene to give an analytical sample, mp 237–237.5°.

Anal. Calcd for $C_{30}H_{20}Br_2$: C, 66.69; H, 3.73. Found: C, 66.87; H, 3.80.

Irradiation of 1,2-Bis-10′-bromo-9′-anthrylethane.—A solution of 510 mg of 1,2-bis-10′-bromo-9′-anthrylethane in 400 ml of benzene was boiled to expel oxygen, sealed, and irradiated with a mercury-arc lamp for 21 days. The solution was evaporated to give 488 mg of greenish solid, mp 229–230° (96% recovery). The infrared spectrum of the solid was identical with that of the starting material.

10-Chloro-9-anthroic Acetic Anhydride.—Ketene, from the pyrolysis of acetone, was bubbled into a slurry of 5.00 g (0.0198 mole) of 10-chloro-9-anthroic acid[24] in 300 ml of benzene at a rate of about 0.5 mole/hr for 50 min.[4] A clear solution formed in 40 min. The solvent was evaporated to leave 5.58 g (94%) of solid, mp 152–165°. The infrared spectrum showed anhydride bands at 1750 and 1820 cm^{-1}. Recrystallization of 4.00 g from cyclohexane gave 1.70 g, mp 153–160°, without change in the infrared spectrum. A small amount was sublimed at 120° (0.1 mm) for analysis, mp 149–156° dec.

Anal. Calcd for $C_{17}H_{11}ClO_3$: C, 68.35; H, 3.71. Found: C, 69.04; H, 3.74.

10-Chloro-9-anthroic Anhydride.—10-Chloro-9-anthroic acetic anhydride, 0.89 g (0.003 mole), mp 156–160°, was heated in an oil bath under vacuum to 167°, then allowed to cool to 153° over 5 hr. The resulting 0.72 g of solid was recrystallized from benzene to yield 0.26 g (35%) of the desired anhydride, mp 238–246°. Several recrystallizations from benzene gave a fairly pure analytical sample, mp 242–245°, with infrared bands at 1740 and 1800 cm^{-1}.

Anal. Calcd for $C_{30}H_{16}Cl_2O_3$: C, 72.74; H, 3.26. Found: C, 73.78; H, 3.38.

Irradiation of 10-Chloro-9-anthroic Anhydride.—A solution of 350 mg of 10-chloro-9-anthroic anhydride in 300 ml of benzene was boiled to expel oxygen, sealed and irradiated with a mercury-arc lamp for 7 days. Removal of solvent gave 341 mg of yellow solid, identified as starting material by a comparison of their infrared spectra (97% recovery).

Another attempt was made with a suspension of 1.00 g of anhydride in about 50 ml of chloroform. The irradiation was with 57 days of July and August sunlight (through Pyrex). Only starting anhydride and some of the free acid were found in the reaction mixture.

Attempted Synthesis of Di-9-anthrylthionocarbonate.—To a stirred mixture of 1.94 g (10 mmoles) of anthrone and 240 mg (10 mmoles) of powdered sodium hydride was added 50 ml of dry tetrahydrofuran. Immediate evolution of gas was evident and a deep orange solution resulted. The solution was stirred at reflux for 1 hr and a solution of 575 mg (5 mmoles) of freshly distilled thiophosgene in 10 ml of dry tetrahydrofuran was added. An immediate reaction occurred and an orange solid was formed. The mixture was stirred at reflux for 2.5 hr, cooled, and filtered to give an orange solid and a gold solution. The filtrate was evaporated to give 786 mg (42%) of 10,10′-bianthronyl as a pale yellow solid, mp 243–244°, identified by a comparison of its infrared spectrum with that of an authentic sample. The solid from the filtration was washed with water until the washings were chloride free. A sodium fusion indicated the presence of sulfur and the absence of halogens. The product was crystallized from chloroform to give an orange solid, mp >370°. The product (possibly 6) exhibited strong infrared absorptions at 1640, 1590, 1520, 1300, 770, and 680 and medium absorptions at 1575, 1470, 1270, 1170, 930, 710, and 648 cm^{-1}.

Anal. Calcd for $C_{29}H_{16}SO_2Na_2$: C, 73.63; H, 3.37. Found: C, 73.89; H, 3.38.

Di-9-anthryl Carbonate (3).—To a stirred mixture of 1.94 g (10 mmoles) of anthrone and 240 mg (10 mmoles) of powdered sodium hydride was added 50 ml of dry tetrahydrofuran. Gas evolution occurred and a deep orange solution resulted. To this solution at −80° was added a solution of 495 mg (5 mmoles) of phosgene in 15 ml of dry tetrahydrofuran. After addition was complete, the resulting yellow solution was allowed to warm up and stirred for 3 hr. Filtration gave a colorless solid which was washed with water until the washings were chloride free. The solid was dried to afford 777 mg of colorless solid, mp 292–296°. The filtrate was evaporated to give 891 mg of yellow solid, mp 292–296°. The infrared spectra of the two solids were identical. The combined product was crystallized from benzene to give 1.644 g (79.5%) of pale yellow solid, mp 294–295°. A sample was recrystallized twice from benzene to give an analytical sample. The infrared spectrum had a strong peak at 1770 cm^{-1}. The reaction was scaled up tenfold to give an 85.3% yield of the carbonate.

Anal. Calcd for $C_{29}H_{18}O_3$: C, 84.04; H, 4.38. Found: C, 84.32; H, 4.50.

2,4-Dioxa-3-oxo-6(7),10(11),12(13),14(15)-tetrabenzotetracyclo[6.2.2.2.^{5,8}.0^{1,5}]tetradeca-6,10,12,14-tetraene (4).—A solution of 6.0 g of dianthrylcarbonate in 1600 ml of benzene was boiled to expel oxygen, sealed, and irradiated for 3 days with a mercury-arc lamp (λ_{max} 3500 A). Filtration gave 3.12 g (52%) of colorless solid, mp 293–295°. The infrared spectrum exhibited absorption at 1815 cm^{-1}.

Anal. Calcd for $C_{29}H_{18}O_3$: C, 84.04; H, 4.38. Found: C, 84.16; H, 4.41.

Reaction of Cyclic Carbonate (4) **with Phosphorus Pentasulfide.**—A mixture of 1.0 g (2.44 mmoles) of **4** and 1.084 g (4.88 mmoles) of phosphorus pentasulfide in 90 ml of dry toluene was stirred at reflux for 7.5 hr. The reaction mixture was cooled and 25 ml of water was added. The mixture was filtered and the toluene phase removed, dried over sodium sulfate, and filtered. Evaporation of the solvent gave 910 mg (91% recovery) of white solid, mp 291–295° dec. It was identified as starting material by a comparison of their infrared spectra. When a trace of anhydrous aluminum chloride was added and the reaction carried out at 150°, the starting material was recovered in 99.1% yield. However, at 200° for 6.5 hr in the presence of a trace of anhydrous aluminum chloride, considerable ring opening occurred as evidenced by infrared absorption at 1770 cm^{-1}, due to **3**.

A mixture of 1.0 g (2.44 mmoles) of **4**, 1.084 g (4.88 mmoles) of phosphorus pentasulfide and 30 ml of dry pyridine was heated at 150° for 47 hr. The reaction mixture was poured into a mixture of dilute hyrochloric acid and benzene. The mixture was stirred at reflux for 1 hr, the organic layer removed and washed with dilute hydrochloric acid. The organic phase was dried over sodium sulfate and filtered, and the solvent removed to give 975 mg (97.5% recovery) of tan solid, mp 292–295°. The infrared spectrum of the product was identical with that of starting material.

Reaction of Di-9-anthrylcarbonate with Phosphorus Pentasulfide in the Presence of Aluminum Chloride.—A mixture of 1.0 g (2.44 mmoles) of di-9-anthryl carbonate, 1.084 g (4.88 mmoles) of phosphorus pentasulfide, a trace of anhydrous aluminum chloride and 50 ml of dry benzene was heated in a sealed tube for 24 hr at 100°. The mixture was cooled, the tube opened and the contents poured into benzene–water and stirred at reflux for 1 hr. The resulting mixture was filtered, the organic phase removed from the filtrate and dried over sodium sulfate. Filtration was followed by evaporation of the solvent and afforded 980

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[24] B. M. Mikhailov and V. P. Bronovitskaya, *J. Gen. Chem. USSR*, **22**, 195 (1952).

mg (98% recovery) of white solid, mp 292–296°; the mixture melting point with starting material was 292–295°. When this reaction was repeated at 200°, a 97.1% recovery of starting material was obtained.

9-Anthryl-9-anthramide (7).—A mixture of 8.3 g (43 mmoles) of 9-aminoanthracene, 10.3 g (43 mmoles) of 9-anthroyl chloride,[19] 15 ml of dry pyridine, and 500 ml of dry toluene was stirred at reflux for 20 hr. The reaction mixture was cooled and filtered to give 10.6 g of tan solid, mp 302–304°. The filtrate was washed with dilute hydrochloric acid until pyridine free, dried over sodium sulfate and filtered, and the solvent removed to give 6.2 g of tan solid, mp 302–305°; a mixture melting point with the solid collected by filtration was 302–304°. The total yield of 9-anthryl-9-anthramide was 16.8 g (98.5%). Two recrystallizations from benzene gave an analytical sample as colorless crystals, mp 302–304°. The product exhibited infrared absorptions at 1655, 3090, and 3280 cm^{-1}.

Anal. Calcd for $C_{29}H_{19}NO$: C, 87.63; H, 4.82; N, 3.52. Found: C, 87.41; H, 4.84; N, 3.41.

2-Aza-3-oxo-5(6),9(10),11(12),13(14)-tetrabenzotetracyclo-[6.2.2.2.^{4,7}0^{1,4}]tetradeca-5,9,11,13-tetraene (8).—A solution of 800 mg of 9-anthryl-9-anthramide in 650 ml of benzene was boiled to expel oxygen, sealed, and irradiated for 14 days with a mercury-arc lamp (λ_{max} 3500 A). The resulting solution was concentrated, cooled, and filtered to give 400 mg (50%) of tan solid, mp 300–304°, remelt 300–304°. Two recrystallizations from benzene gave an analytical sample as colorless crystals, mp 302–304°. The product exhibited infrared absorption at 1745 and 3390 cm^{-1}.

Anal. Calcd for $C_{29}H_{19}NO$: C, 87.63; H, 4.82; N, 3.52. Found: C, 87.69; H, 4.77; N, 3.43.

Attempted Syntheses of N-Nitrosolactam 9. Method A.—To a stirred mixture of 435 mg (5.3 mmoles) of anhydrous sodium acetate, 324 mg (3.6 mmoles of dinitrogen tetroxide and 50 ml of methylene chloride cooled in an ice–salt bath at −4° was added a solution of 393 mg (1 mmole) of **8** in 300 ml of methylene chloride.[11] Once the addition was complete, the mixture was stirred for 1 hr, and then poured into cold water. The organic phase was separated, washed with aqueous sodium bicarbonate and dried over sodium sulfate. Filtration, followed by removal of solvent left a red oil which was triturated with methylene chloride to leave 389 mg (99% recovery) of light tan solid, mp 306.5–307.5°, identified as starting material by a comparison of their infrared spectra.

Method B.—A mixture of 500 mg (1.26 mmoles) of **8**, 260 mg (2.565 mmoles) of potassium acetate, 21 mg (1.38 mmoles) of phosphorus pentoxide, 14.27 g (215 mmoles) of carefully distilled nitrosyl chloride (bp −6 to −5°) and 40 ml of acetic anhydride was heated at 60° for 30 min in a sealed tube. The tube was cooled, opened, and the contents poured into ice water. Filtration gave 492 mg (98.4% recovery) of pale tan solid, mp 301–305° dec. The infrared spectrum of the product was identical to that of starting material. When the reaction was repeated at 115°, a 98.2% recovery of starting material was obtained, while at 200°, 9-anthryl-9-anthramide, produced by thermal ring opening of **8** was obtained along with some unreacted **8**. The presence of 9-anthryl-9-anthramide was shown by infrared spectroscopy.

When unpurified nitrosyl chloride was used at 60° for 30 min, an 82% yield of nitrolactam **10** (below) was obtained.

Method C.—A mixture of 300 mg (0.755 mmole) of **8**, 4 ml (0.84 mmole) of 0.21 N-phenyllithium in 7:3 benzene–ether, and 100 ml of dry benzene was stirred for 2 hr at room temperature in an argon atmosphere. To the resulting mixture was added 54 mg (0.825 mmole) of nitrosyl chloride, and the mixture stirred for 30 min. The reaction mixture became lighter and was hydrolyzed by the addition of 50 ml of water. The resulting mixture was extracted with two 250-ml portions of methylene chloride, dried over sodium sulfate and filtered and the solvent removed to give a dark oil, which was crystallized from methylene chloride–low petroleum ether (30–60°) to give a greenish solid, mp 300–304° dec, identified as starting material by a comparison of their infrared spectra.

2-Nitro-2-aza-3-oxo-5(6),9(10),11(12),13(14)-tetrabenzotetracyclo[6.2.2.2.^{4,7}0^{1,4}]tetradeca-5,9,11,13-tetraene (10).—A mixture of 3.0 g (7.62 mmoles) of β-lactam **8**, 149.1 g (1.658 mmoles) of dinitrogen tetroxide, 11.3 g (138 mmoles) of anhydrous sodium acetate, and 500 ml of methylene chloride was stirred at room temperature for 27.5 hr. The reaction mixture was washed with aqueous sodium bicarbonate until the washings were basic. The organic layer was dried over sodium sulfate, filtered and the solvent removed to give a red oil. The oil was chromatographed on neutral, washed alumina with methylene chloride as the eluent to give 2.8 g (83%) of yellow solid, mp 224–225° dec. The product exhibited infrared absorption at 1283, 1533, and 1810 cm^{-1}.

Anal. Calcd for $C_{29}H_{18}N_2O_3$: C, 78.72; H, 4.10; N, 6.33. Found: C, 78.65; H, 4.03; N, 6.48.

When the reaction was repeated with 1.0 g (2.54 mmoles) of **8**, 7.455 g (82.9 mmoles) of dinitrogen tetroxide, and 250 ml of methylene chloride at room temperature for 20 hr, a red oil was obtained. Addition of 95% ethanol to the oil gave a gold solid. The solid was identified by infrared as a mixture of N-nitro-β-lactam and β-lactam with no extraneous peaks.

Decomposition of N-Nitrolactam 10.—A mixture of 600 mg (1.4 mmoles) of the nitrolactam **10**, 25 ml of furan and 30 ml of benzene was degassed while in a combustion tube. The mixture was sealed under oxygen-free argon (cleaned of oxygen by passing it through a tower of manganese(II) oxide) and heated for 3 hr at 150°. The solvent was removed to afford 595 mg (99.2% recovery) of starting material, identified by a comparison of the infrared spectrum of the product with that of authentic **10**. When the reaction was repeated at 200°, a 99.6% recovery of starting material was obtained.

The nitrolactam, 500 mg (1.17 mmoles) was finally decomposed in an oxygen-free argon-flushed and filled sublimator at 240° to give 107 mg (22%) of anthraquinone, identified by a comparison of their infrared spectra, and 337 mg of a black carbonaceous material.

9-Anthryldiazonium Fluoborate.[13]—A solution of 30.5 g (158.1 mmoles) in 1.922 l. of anhydrous ether was flushed with dry argon and placed in an ice bath. Nitric oxide was passed into the solution for 60 min after which dry air, along with the nitric oxide, was passed into the cooled solution while it was stirred gently for 120 min. To the resulting reaction mixture was added 273 g (1.06 mmoles) of 34% aqueous fluoboric acid and the reaction mixture stirred vigorously for 15 min. The orange precipitate which formed was collected by suction filtration, washed with 60 ml of 4:1 methanol–ether and dried overnight in a vacuum desiccator, yield 42.05 g (91%), mp 135–137°. The infrared spectrum exhibited absorption at 2200 and a broad peak from 1020 to 1090 cm^{-1} in agreement with that observed by Rigaudy and Barcelo.[13]

9,9′-Azoanthracene (12).[13]—A mixture of 3.10 g (11 mmoles) of 9-anthryldiazonium fluoborate and 6.2 g (62.7 mmoles) of freshly prepared cuprous chloride in 60 ml of water (pH 7–7.5) was stirred at high speed for 2 hr and then allowed to sit for 2 hr under an argon atmosphere. The resulting mixture was extracted with benzene–20% aqueous hydrochloric acid, the aqueous layer removed, and the organic phase washed with water. The organic phase was dried over sodium sulfate and filtered and the solvent removed to give a purple-green solid. The residue was washed with seven 150-ml portions of ether and the resulting insoluble solid was continuously extracted with ether for 2 days. The resulting purple solid (600 mg, 28.6%) had mp 304–307° dec (lit.[13] mp 347–348° dec).[25]

2,3-Diaza-5(6),9(10),11(12),13(14)-tetrabenzotetracyclo-[6.2.2.2.^{4,7}0^{1,4}]tetradeca-2,5,9,11,13-pentaene (13).—A solution of 100 mg of 9,9′-azoanthracene in 100 ml of benzene was boiled to expel oxygen, sealed, and irradiated for 7 days in a Griffin-Srinivasan Photoreactor for 7 days with mercury-arc lamps (λ_{max} 3500 A). The solvent was removed to give 94 mg of a pale yellow-green solid. The product was crystallized from benzene to give 58 mg (58%) of pale yellow solid which melted with decomposition at 284–287° to give a purple solid whose infrared spectrum was identical with that of 9,9′-azoanthracene. The product exhibited infrared absorption at 1250, 1082, and 790 cm^{-1}. The ultraviolet spectrum had λ_{max} at 247 mμ (ε 4100) and had $\epsilon_{253.7}$ 3100. Osmometric determination of the molecular weight was done in benzene at 60°.

Anal. Calcd for $C_{28}H_{18}N_2$: C, 87.96; H, 4.71; mol wt, 382. Found: C, 87.84; H, 4.93; mol wt, 372.

Irradiation of the Cyclic Azo Compound 13.—A solution of 50 mg of **13** in 200 ml of argon-flushed benzene in a quartz flask was irradiated for 2 days under an argon atmosphere in a Griffin-

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(25) A sample kindly supplied by Professor Rigaudy decomposed at 304–306° in our hands. The infrared spectra of the two materials were also the same, including absorptions at 1440, 885, and 727 cm^{-1}.

Srinivasan Photoreactor with ultraviolet lamps (λ_{max} 2537 A). The solvent was removed from the resulting solution to give a yellow solid, 48 mg (96% recovery), mp 284–288° dec, whose infrared spectrum was identical with that of the starting material.

Registry No.—**3**, 15156-53-3; **4**, 15156-58-8; **6**, 15084-03-4; **7**, 15080-10-1; **8**, 15134-48-2; **10**, 15084-00-1; **12**, 15180-31-1; **13**, 15080-11-2; **15**, 15080-12-3; **16**, 15156-59-9; di-9-anthrylcarbinol, 15080-13-4; di-9-anthrylmethane, 15080-14-5; 10-bromo-9,9-dianthrylmethane, 15156-60-2; 10-bromo-9-hydroxymethylanthracene, 2606-53-3; 10-bromo-9-chloromethylanthracene, 15080-16-7; 10-chloro-9-anthroic acetic anhydride, 15156-61-3; 10-chloro-9-anthroic anhydride, 15084-01-2; 10,10′-bianthronyl, 434-84-4; 9-anthryldiazonium fluoborate, 15084-02-3.

Acknowledgment.—This work was supported in part by the National Science Foundation and in part by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund.

Photochemistry of Alkyl-β-naphthyl Ethers. Steric Inhibition in the Dimerization Reaction[1]

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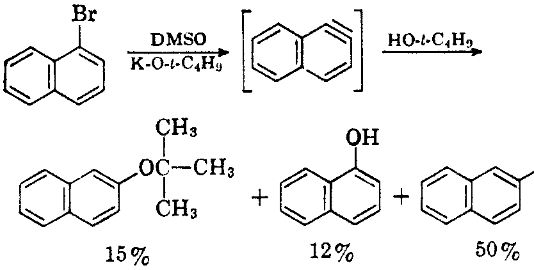
Received August 14, 1967

A series of alkyl-β-naphthyl ethers have been prepared and irradiated with ultraviolet light. Straight-chain ethers dimerized while the branched ethers did not. This coupled with the fact that no excimer fluorescence was observed for the branched alkyl ethers suggests that the photodimers have head-to-head structure I. It is proposed that an excited dimer (excimer III) is involved in photodimer formation.

We have previously reported that methyl-β-naphthyl ether undergoes photodimerization when irradiated by ultraviolet light.[2] The α-ether and other substituted naphthalene compounds did not dimerize.[2] The gross structure of the photodimer was believed to be similiar to that for the photodimer of anthracene.[3] The stereochemistry, however, could not be determined due to its instability to heat and its insolubility.[2] In an attempt to learn more about the structure of the photodimer, we have prepared and irradiated a series of alkyl-β-naphthyl ethers where the alkyl group varies from allyl to *t*-butyl. The straight chain alkyl ethers readily dimerized while branched chain materials failed to dimerize even after prolonged irradiation.

The starting ethers with exception to the *t*-butyl ether, were prepared by reacting the alkyl halide with β-naphthol in the presence of base.[4] The *t*-butyl ether could not be prepared by this method. The Sahyun–Cram procedure to prepare phenyl *t*-butyl ether was used for this synthesis.[5] This procedure involves an aryne generated from an aryl bromide in a solution of potassium *t*-butoxide in dimethyl sulfoxide (DMSO).[6] The more abundant α-bromonaphthalene was used in this reaction. A yield of only 15% *t*-butyl-β-naphthyl ether was isolated. No α-ether could be detected although it must be present. The major product (63%) of this reaction was a mixture of α- and β-naphthol at a ratio of about 18% α to 82% β[7] (see eq 1). This apparent ratio of α to β products (1:4) from a 1-naphthalyne reaction is considerably different than that (1:2) found when 1-naphthalyne was prepared by a different procedure.[8] The details of this reaction and its use to prepare other naphthyl ethers and naphthols will be reported in a future communication.



(1)

Both allyl- and *n*-butyl-β-naphthyl ethers dimerized readily when irradiated with ultraviolet light through pyrex, while the isopropyl- and *t*-butyl ethers did not. No dimerization took place in the presence of benzophenone. The dimers were very similar to the methyl-β-naphthyl ether dimer.[2] The infrared spectra of all three compounds (methyl-, allyl-, and *n*-butyl ether dimers) contained similar major bands in the following spectral regions: 2900–3100, 1625–1635, 1420–1470, 1330–1340, 1270, 1170–1200, 1140–1150, 775–780, 750–755, and 720 cm^{-1}. The major differences in the spectra can be attributed to the different alkyl (alkenyl) groups. The ultraviolet spectra were also very similar with bands at 2835, 2740, and 2315 A at about the same intensity as those reported for the methyl-β-naphthyl ether dimer.[2] Small monomer bands were observed at 3100–3300 A for both dimers. These bands greatly increased in intensity when the solution was allowed to stand for a few hours. The typical three naphthalene bands at 2600–2850 A also appeared. Both dimers also reverted to the starting ethers when heated above the melting point.

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[1] Supported by the Research Division, Brigham Young University, Provo, Utah.

[2] J. S. Bradshaw and G. S. Hammong, *J. Am. Chem. Soc.*, **85**, 3953 (1963).

[3] F. D. Greene, S. L. Misrock, and J. R. Wolfe, *ibid.*, **77**, 3852 (1955).

[4] D. S. Tarbell, *Org. Reactions*, **2**, 1 (1944).

[5] M. R. V. Sahyun and D. J. Cram, *Org. Syn.*, **45**, 89 (1965).

[6] See also D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).

[7] These products were probably prepared on the work-up. A considerable amount of phenol (29%) was isolated during the preparation of phenyl-*t*-butyl ether.[5]

[8] See J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, **23**, 904 (1958).