The mother liquor was evaporated in air to *ca.* 2 ml. Yellow crystals (100 mg., 9% over-all) of 7,13-epithio-α-6-deoxytetracycline were obtained. An analytical sample was prepared by recrystallization from hot methanol, with acetone wash. It showed λ_{max}^{KBr}, no bands between 5 and 6 μ: $\lambda_{max}^{MeOH-0.01\ N\ HCl}$ 251, 337, and 420 mμ, log ϵ 4.38, 4.08, and 3.64; $\lambda_{max}^{MeOH-0.01\ N\ NaOH}$ 248 and 392 mμ, log ϵ 4.18 and 4.40.

Anal. Calcd. for $C_{22}H_{22}N_2O_7S \cdot HCl \cdot H_2O$: C, 51.5; H, 4.9; N, 5.5; S, 6.3; Cl⁻, 6.9; H_2O, 3.5. Found: C, 51.4; H, 4.9; N, 5.2; S, 6.2; Cl⁻, 7.1; H_2O, 3.4.

11a-Bromo-4-dedimethylaminotetracycline, Its 6,12-Hemiketal, and 9 - Bromo - 5a,6 - anhydro - 4 - dedimethylaminotetracycline. —Following the procedure of Green, Wilkinson, and Boothe[16] for the preparation of 11a-bromo-4-dedimethylaminotetracycline in acetic acid on a 10-g. scale, a slight excess of bromine (1.37 ml., 1.07 equiv., rather than 1.28 ml., 1.0 equiv.) was inadvertently employed. There resulted, apparently because of a slight imbalance in acidity, a direct yield of 11.6 g. (100%) of crystalline 9-bromo-5a,6-anhydro-4-dedimethylaminotetracycline.[16] On a second 10-g. scale preparation the bromine was reduced to 1.25 ml. (0.98 equiv.) and the sodium acetate increased to 2.25 g.

(rather than 2.05 g.). In this case 7.1 g. (60%) of pure 11a-bromo-4-dedimethylaminotetracycline crystallized directly from the reaction mixture—thus avoiding precipitation and crystallization steps. The product showed a strong infrared band at 5.77μ in KBr and in dioxane. Recrystallization of this material from chloroform gave 11a-bromo-4-dedimethylaminotetracycline-6,12-hemiketal (λ_{max}^{KBr} no bands 5 to 6 μ, identical with that of the material prepared by the N-bromosuccinimide–chloroform method of Green, Wilkinson, and Boothe[16]; $\lambda_{max}^{dioxane}$ 5.77μ, identical with that of material prepared by either method).

Mechanisms of Photochemical Reactions in Solution.
## XIX. Photodimerization of Methyl β-Naphthyl Ether

By Jerald S. Bradshaw[1] and George S. Hammond

Methyl β-naphthyl ether dimerizes upon irradiation with ultraviolet light in a variety of solvents. Other naphthalenes, monosubstituted in the α- or β-position by methyl, hydroxy, bromo, amino, and in the α-position by methoxy groups, do not show this phenomenon. The photodimer is probably formed by a 1,4–1,4 dimerization of the unsubstituted ring through an excited singlet state. Benzophenone efficiently quenches the reaction, probably by accepting singlet excitation from the naphthyl ether in an energy transfer process.

Unlike anthracenes,[2] naphthalene and its derivatives have not hitherto been reported to undergo photodimerization. It has now been found in these laboratories that methyl β-naphthyl ether dimerizes in a variety of solvents upon irradiation with ultraviolet light of wave lengths shorter than 3300 Å. The photodimer was almost completely insoluble in all solvents except strong acids. This insolubility probably aids in its formation. On being heated to its decomposition point (155–160°) or dissolution in strong acid, the photodimer reverts to methyl β-naphthyl ether. Related compounds such as methyl α-naphthyl ether, α- and β-methylnaphthalenes, α- and β-bromonaphthalenes, α- and β-naphthylamines, α- and β-naphthols, and naphthalene itself did not undergo dimerization under the same conditions. No product was formed on irradiation of methyl β-naphthyl ether in the presence of either maleic anhydride or dimethyl acetylenedicarboxylate.

The ultraviolet absorption spectrum of the photodimer offers very convincing evidence as to its structure. The positions and intensities for maxima in the spectra of the dimer and other pertinent compounds are listed in Table I. On the basis of the similarity of the ultraviolet spectra of dianthracene and *o*-xylene, Coulson and co-workers concluded that dianthracene has the structure formed by bonding the *meso* atoms of two anthracene molecules (I).[3] This same similarity between the spectra of the photodimer of methyl β-naphthyl ether and *o*-xylene is noted except that in the case of the dimer a distinct bathochromic shift has taken place. Similar bathochromic shifts, attributable to methoxy groups, are observed on comparison of the
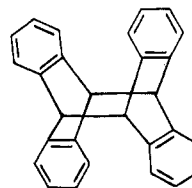
I

spectra of toluene and *m*-xylene with those of the corresponding methyl ethers (Table I). These spectral data strongly indicate that the dimer is formed by a 1,4–1,4 dimerization of the unsubstituted ring. The product II may have either of two steric configurations and may have either symmetrical or unsymmetrical disposition of the methoxyl groups with respect to each other. We have no way of further reducing the structural uncertainty at this time.
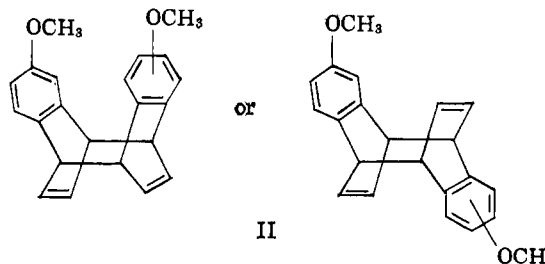
II

The infrared spectrum of the photodimer exhibits bands at 3010 and 3040 and at 1650 cm.⁻¹. Such bands have been attributed, respectively, to the C—H and C=C stretching modes of *cis*-olefins.[4]

Attempts to establish the structure more rigorously were foiled by the insolubility of the material and the fact that, in solution, it appears to revert rapidly to

(1) National Science Foundation Postdoctoral Fellow 1962–1963.

(2) See F. D. Greene, S. L. Misrock, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **77**, 3852 (1955), for a discussion and background concerning anthracene dimers.

(3) C. Coulson, L. E. Orgel, W. Taylor, and J. Weiss, *J. Chem. Soc.*, 2961 (1955).

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34.

<div align="center">TABLE I</div>

<div align="center">THE ULTRAVIOLET ABORPTION SPECTRA OF THE PHOTODIMER AND RELATED COMPOUNDS</div>

Compound	λ_{max}, Å. (ϵ)		
Methyl β-naphthyl	$2260\ (8.2 \times 10^4)$	$2615\ (5.2 \times 10^3)$	$3135\ (1.4 \times 10^3)$
ether		$2710\ (5.2 \times 10^3)$	$3280\ (1.8 \times 10^3)$
Photodimer	$2230\ (8.4 \times 10^3)$	$2750\ (1.6 \times 10^3)$	$2825\ (1.8 \times 10^3)$
o-Xylene[a]	$2120\ (7.9 \times 10^3)$	$2630\ (2.5 \times 10^2)$	$2710\ (2.5 \times 10^2)$
Dianthracene[b]	$2175\ (2 \times 10^4)$	2600–$2800\ (1 \times 10^3)$	
m-Xylene[c]		2655	2725
3,5-Dimethylanisole[d]		$2715\ (1.7 \times 10^3)$	$2795\ (1.7 \times 10^3)$
Toluene[c]		2615	2685
p-Methylanisole[d]		$2775\ (2.1 \times 10^3)$	$2845\ (1.8 \times 10^3)$

[a] Am. Petrol. Inst. Res. Project 44, ser. 55, p. 173 (see also ref. 3). [b] See ref. 3. [c] D. D. Tunnicliff, R. R. Brattain, and L. R. Zumwalt, *Anal. Chem.*, 21, 890 (1949). [d] A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 2310 (1952).

monomer. Attempts were made to effect hydrolysis in the presence of sulfuric or trifluoroacetic acids, to effect oxidation with aqueous alkaline permanganate, to ozonize suspensions of the material in methanol or ethyl acetate, and to hydrogenate a suspension of the substance in methanol over platinum. Starting material, monomer, or low molecular weight materials were all that could be recovered. The analyst[11] reported that no solvent could be found in which the molecular weight could be measured by cryoscopic methods.

When the naphthyl ether was irradiated in the presence of benzophenone, no product was observed either with unfiltered light or when only light of wave lengths greater than 3300 Å. was used. The transfer of the excited triplet energy from benzophenone, which absorbs light of about 3450 Å., to other molecules has been extensively studied.[5] The triplet energy of benzophenone is about 70 kcal.[5] and that of methyl β-naphthyl ether is about 62 kcal. Therefore, the triplet energy transfer from benzophenone to methyl β-naphthyl ether should be a diffusion-controlled process. Since no dimer was formed in the presence of benzophenone, we infer that *dimerization involves excited singlet states of the naphthyl ether*.[6]

In the experiment in which a solution containing both the naphthyl ether and benzophenone was irradiated with unfiltered light, no dimer was produced despite the fact that some light must have been absorbed by the naphthalene derivative. The experiment implies that there is a transfer of singlet excitation from methyl β-naphthyl ether to benzophenone. The intramolecular analog of this process has recently been observed[9]; however, no intermolecular transfer of singlet excitation from a naphthalene derivative to benzophenone has been reported. In order to test the explanation of the quenching action, emission spectra of the naphthyl ether and benzophenone at room temperature were measured in cyclohexane. Solutions of the ether alone showed strong fluorescence as a broad, structureless band. No phosphorescence was observed. Only about 10% of the fluorescence of the ether was observed when a solution containing the ether (0.05 M) and a small amount of benzophenone (0.01 M) was irradiated. No emission of any kind was observed when a solution containing both compounds in 0.5 M concentration in benzene was irradiated. Thus under the conditions of the dimerization reaction, benzophenone effectively

quenches the excited singlet state of methyl β-naphthyl ether.

The apparent preference shown for dimerization involving the unsubstituted ring is interesting but must be interpreted with caution. Since the dimer produced is very labile, related dimers should also be unstable. Perhaps others are formed but revert to monomers at a rate sufficient to prevent their build-up to the saturation level in solution. On the other hand, the result may show that one particular kind of dimeric intermediate, perhaps a biradical,[2] is formed preferentially. Consideration of the structures of such intermediates reveals no very obvious reason for such a preference.

Experimental

Materials.—Methyl β-naphthyl ether (m.p. 71–72°) was purchased from C.A.F. Kahlbaum G.m.b.H. (pre-World War II product) and used without further purification. Methyl α-naphthyl ether was prepared from α-naphthol and methyl iodide by the method of Musser and Adkins.[10] All other naphthalenic compounds as well as maleic anhydride were purchased from Eastman Kodak Co. and used without further purification. Dimethyl acetylenedicarboxylate was purchased from Aldrich Chemical Co. and distilled prior to use. Reagent grade benzene (Baker and Adamson) and isopropyl alcohol (Matheson Coleman and Bell) were used without further purification. Dioxane (General Chemical Co., technical grade) was partially purified by absorption of alumina and distillation of the eluent. Furan (Harshaw Chemical Co.) was washed with a solution of dilute ferrous sulfate in aqueous hydrochloric acid and distilled.

Apparatus.—Irradiation was carried out using a Hanovia quartz immersion reactor. All reactions were conducted in Pyrex tubes placed around the quartz water-jacket. When necessary, a uranium glass sleeve was used to cut off all radiation below 3300 Å. Infrared spectra were taken with a Beckman IR-7 spectrophotometer. Ultraviolet spectra were taken by means of a Cary recording spectrophotometer Model 11M. Emission spectra were obtained using a photoelectric spectrophosphorimeter consisting of a Jarrell–Ash Ebert scanning monochrometer (f/9), an EMI 9558 photomultiplier tube, a "rotating can" phosphoroscope, and appropriate recording electronics. For excitation a General Electric AH4 mercury lamp was employed along with appropriate Corning glass filters or interference filters to isolate the groups of mercury lines at 3130 and 3660 Å. For fluorescence studies the phosphoroscope was removed. The phosphorescence spectrum of methyl β-naphthyl ether was measured in a 5:1 methylcyclohexane–isopentane glass at 77°K.

Procedure for Dimerization.—Two grams of methyl β-naphthyl ether was dissolved in a mixture of 10 ml. of benzene and 10 ml. of isopropyl alcohol. The mixture was placed in a Pyrex tube, degassed, sealed *in vacuo*, and irradiated. The progress of the reaction was followed by observing a slow separation of a white solid. After 2 weeks of continuous irradiation, 900 mg. (45%) of solid, m.p. 155–160° dec., was isolated. After about 2 months of irradiation, a high yield (>90%) was realized. The dimer was insoluble in most organic solvents. The product reverted to starting material (m.p. 71–72°, m.m.p. 71–72°) on heating above the decomposition point. Starting material (m.p. 71–72°, m.m.p. 71–72°) was also recovered by dissolving the photodimer in trifluoroacetic acid and slowly adding water. When the uranium glass sleeve was used, no dimerization took place. The same photodimer was produced by irradiation of 2 g. of methyl β-naphthyl ether in 20 ml. of benzene, a mixture of 10 ml. of water and 10 ml. of dioxane, or 20 ml. of tetrahydrofuran. An infrared spectrum was obtained from a solid potassium bromide

(5) See G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, 66, 1144 (1962), and subsequent papers of that series.

(6) Evidence for singlet mechanism in the photodimerization of anthracene has been presented.[7,8]

(7) E. J. Bowen and D. W. Tanner, *Trans. Faraday Soc.*, 51, 475 (1955).

(8) R. Livingston, "Photochemistry in the Liquid and Solid States," L. J. Heidt, *et al.*, Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 76.

(9) P. A. Leermakers, G. W. Byers, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, 25, 2670 (1963).

(10) D. M. Musser and H. Adkins, *ibid.*, 60, 664 (1938).

pellet. The ultraviolet spectrum was measured with a dilute solution of the dimer ($1.6 \times 10^{-5} M$) in spectral grade methanol (Eastman Kodak Co.). The molecular weight could not be determined due to the insolubility of the dimer.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.34; H, 6.29.[11]

Quenching Experiment and Emission Spectra.—A mixture of 0.5 g. of benzophenone and 0.5 g. of methyl β-naphthyl ether in 5 ml. of the benzene–isopropyl alcohol mixture was divided into two portions. One part (degassed) was irradiated using the uranium glass filter and the other without. No product was observed in either case. The emission spectrum of this solution exhibited no fluorescence or phosphorescence. The emission spectrum of the naphthyl ether at 77°K. exhibited a weak 0–0 band at 4595 Å. ($21,700$ cm.$^{-1}$, 62 kcal.). At room temperature the emission spectrum in cyclohexane showed a broad fluorescence band with the maximum at 3530 Å. ($28,300$ cm.$^{-1}$) and no phosphorescence. A mixture of methyl β-naphthyl ether ($0.05 \ M$) and benzophenone ($0.01 \ M$) in cyclohexane gave the same emission spectrum as that reported above for the naphthyl ether in cyclohexane except the intensity was reduced by about 90%.

(11) Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

Attempted Preparation of Other Naphthalenic Dimers.—Solutions, each containing 2 g. of substrate in a mixture of 10 ml. of benzene and 10 ml. of isopropyl alcohol, were prepared and irradiated as before. The naphthalene derivatives used in this study were: naphthalene, methyl α-naphthyl ether, α- and β-methylnaphthalenes, α- and β-bromonaphthalenes, α- and β-naphthylamines, and α- and β-naphthols. No products were formed in any of these experiments. Comparisons of the ultraviolet absorption spectra of the solutions after at least 1 week of irradiation with that of the starting material indicated that no reaction had taken place.

Attempted Preparation of Cross Photoadducts.—Mixtures of 0.5 g. of methyl β-naphthyl ether and, in one case, 0.5 g. of maleic anhydride and, in a second experiment, with 0.5 g. of dimethyl acetylenedicarboxylate, in 5 ml. of the benzene–isopropyl alcohol mixture were prepared and irradiated as before. No products were formed. Comparison of the ultraviolet absorption spectra of the solutions after at least 1 week of irradiation with those of solutions before irradiation indicated that no reaction had taken place.

Organo–Iron Complexes. II.[1]   π-Pentadienyl- and π-1,5-Dimethylpentadienyliron Tricarbonyl Cations

BY J. E. MAHLER AND R. PETTIT

Stable salts of π-pentadienyl- and π-1,5-dimethylpentadienyliron tricarbonyl cations have been prepared by reaction of *trans*-dienol–iron tricarbonyl complexes with strong acids. Evidence favoring a completely cissoid disposition of the five sp² hybridized carbon atoms of the pentadienyl ligand in these cationic complexes is presented. A mechanism is proposed to account for the stereochemistry observed in the reaction of the hydrolysis of the cations and their formation from *trans*-dienol–iron tricarbonyl complexes.

Introduction

Several cationic complexes in which an iron tricarbonyl residue is π-bonded to a pentadienyl grouping have recently been reported. Stable salts of the cyclohexadienyliron tricarbonyl cation (I) were first reported in 1960 by Fischer and Fischer[2]; this cation was formed, together with triphenylmethane, upon reaction of cyclohexadieneiron tricarbonyl with triphenylmethyl fluoroborate. A similar hydride ion abstraction reaction utilizing the triphenylmethyl cation had previously been employed by Dauben and Honnen[3] for the conversion of cycloheptatrienemolybdenum tricarbonyl to salts of the tropyliummolybdenum tricarbonyl cation.

More recently, salts of the cycloheptadienyliron tricarbonyl cation have been prepared by means of a similar reaction involving hydride ion abstraction from cycloheptadiene iron tricarbonyl[4]; this same cation is also formed upon protonation of the free double bond in cycloheptatrieneiron tricarbonyl.[4,5] Addition of strong acids to cyclooctatetraeneiron tricarbonyl also gives rise to stable salts[6,7] which have recently been shown to contain the bicyclooctadienyliron tricarbonyl cation.[7]

The type of reaction employed in these preparations typically gives rise to carbonium ions and, from one extreme viewpoint, the cationic complexes just described might formally be considered as being derived

from an iron atom having, as ligands, three carbonyl groups and a substituted pentadienyl carbonium ion. Viewed in this way, the stability of the cation I is then of particular interest for its mode of formation suggests that it is more stable (less electrophilic) than the triphenylmethyl cation; this is also evident from the fact that salts of I can be recrystallized from water. The reverse order of stability holds for the cyclohexadienyl cation when it is not complexed to a metal.

Although no X-ray data for these dienyl–iron tricarbonyl complex cations are available, it seems most probable that in each case the iron atom would lie below a plane defined by the five carbon atoms of the dienyl system and, as in the case of the diene–iron tricarbonyl complexes,[8] would be situated approximately equidistant from these five carbon atoms. In common then with other organometallic systems, the two factors involved in the union of the dienyl moiety to the iron atom will be the forward coordination arising from interaction of bonding orbitals of the pentadienyl ligand with vacant iron orbitals and the back donation of electrons from iron to the ligand *via* interaction of filled orbitals on iron with low-lying, vacant molecular orbitals of the dienyl system. In these particular systems the back donation would be of special significance, for not only would it increase the ligand–metal bonding and decrease the electron density on iron, but it would also result in a decrease in the electrophilicity of the carbonium ion ligand.

Now, in each of the cationic complexes mentioned before, the dienyl ligand is part of a cyclic system and necessarily possesses a completely cissoid arrangement of sp² hybridized carbon atoms. This geometrical restriction need not necessarily be imposed upon an

(1) Part I: R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).
(2) E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960).
(3) H. J. Dauben and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958).
(4) H. J. Dauben and D. J. Bertelli, *ibid.*, **83**, 497 (1961).
(5) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961).
(6) G. N. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961).
(7) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962), and references therein.
(8) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 241 (1960).