Photochemical Reactions of Dimethyl Acetylenedicarboxylate with Benzene and Naphthalene[1]

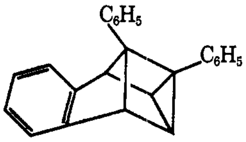
ERLING GROVENSTEIN, JR., THOMAS C. CAMPBELL, AND TOMOO SHIBATA

School of Chemistry of the Georgia Institute of Technology, Atlanta, Georigia 30332

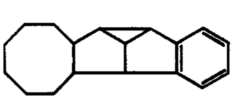
Received November 14, 1968

The photochemical reaction of dimethyl acetylenedicarboxylate with benzene gives dimethyl cycloocta-1,3,5,7-tetraene-1,8-dicarboxylate. In contrast, photoreaction of dimethyl acetylenedicarboxylate with molten naphthalene gives dimethyl 1-naphthalenefumarate (VII), dimethyl 3,4-benzotricyclo[3.3.0.0.^{2,8}]octa-3,6-diene-6,7-dicarboxylate (IX), dimethyl 2-naphthalenefumarate (X), and dimethyl *trans*-acenaphthene-1,2-dicarboxylate (XI). Adduct XI has been shown to result from photocyclization of VII and also of dimethyl 1-naphthalenemaleate. In methanol as solvent photoadduct XI is the chief 1:1 adduct. The photochemical reaction in molten naphthalene (90°) is complicated by a thermal reaction of naphthalene with dimethyl acetylenedicarboxylate which gives dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (VI); the latter undergoes photolysis to give chiefly dimethyl benzocyclooctene-7,8-dicarboxylate (VIII) on short irradiation and isomeric products on long irradiation or irradiation in acetone as solvent.

While the photochemical reactions of benzene with maleic anhydride,[2] simple olefins,[3] conjugated dienes,[4] and acetylene derivatives[3c,5] have been studied in considerable detail and the mechanisms of these reactions are now partially understood,[6] corresponding reactions of naphthalene have been little investigated. No photochemical reaction of naphthalene with maleic anhydride has been found.[7] While β-methoxynaphthalene upon irradiation with ultraviolet (uv) light has been reported to give a dimer, similar products have not been obtained from naphthalene or other simple derivatives of naphthalene; moreover, β-methoxynaphthalene has been reported not to give photoadducts with maleic anhydride or dimethyl acetylenedicarboxylate.[8] Naphthalene has been reported to form readily 1:1 photoadducts with primary and secondary aliphatic amines; although the structures of these adducts have not been revealed, they are likely analogous to the corresponding 1,4 photoadducts of benzene.[9] While the present work was in progress,[10] naphthalene was reported[11] to undergo a photochemical addition of diphenylacetylene to give an adduct of structure I; similar products were obtained from dimethylnaphthalenes. More recently, in a brief statement, naphthalene was reported to form two 1:1 photoadducts with cyclooctene; spectroscopic evidence was said to be consistent with structure II for the major isomer.[3c] We wish to report some new types of photochemical adducts from reaction of naphthalene with dimethyl acetylenedicarboxylate and to report further details upon the reaction of benzene with dimethyl acetylenedicarboxylate.[5a,b]



I

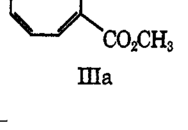


II

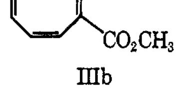
Results and Discussion

Benzene with Dimethyl Acetylenedicarboxylate.—The photochemical reaction of benzene with dimethyl acetylenedicarboxylate gives some 15% yield of dimethyl cyclooctatetraene-1,2-dicarboxylate together with unidentified products of higher molecular weight. The structure of the cyclooctatetraene derivative was deduced from physical and chemical properties which were given in a preliminary communication[5a] and were verified and extended by Bryce-Smith and Lodge.[5b] This structural assignment is now confirmed by comparisons of melting point, mixture melting point, and infrared (ir) spectrum with those of a sample of dimethyl cyclooctatetraene-1,2-dicarboxylate prepared by a copolymerization technique.[12]

In our preliminary communication[5a] we pointed out that the valence-bond structure of dimethyl cyclooctatetraene-1,2-dicarboxylate might be that of tautomer IIIa or IIIb. Shortly thereafter Anet[13] reported on the



IIIa



IIIb

---

[1] Abstracted in large part from the Ph.D. thesis of T. C. Campbell, Georgia Institute of Technology, 1967.

[2] (a) H. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 4791 (1960); (b) E. Grovenstein, Jr., D. V. Rao, and J. W. Taylor, *J. Amer. Chem. Soc.*, **83**, 1705 (1961); (c) G. O. Schenck and R. Steinmetz, *Tetrahedron Lett.*, 1 (1960).

[3] (a) R. Srinivasan and K. A. Hill, *J. Amer. Chem. Soc.*, **87**, 4653 (1965); (b) K. E. Wilzbach and L. Kaplan, *ibid.*, **88**, 2066 (1966); (c) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.*, 512 (1966); (d) N. C. Perrins and J. P. Simmons, *ibid.*, 999 (1967).

[4] G. Koltzenburg and K. Kraft, *Tetrahedron Lett.*, 389 (1966).

[5] (a) E. Grovenstein, Jr., and D. V. Rao, *ibid.*, 148 (1961); (b) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963); (c) J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Rabb, *J. Amer. Chem. Soc.*, **85**, 2257 (1963).

[6] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Comm.*, 593 (1966), and references cited therein.

[7] G. O. Schenck, J. Kuhls, S. Mannsfeld, and C. H. Krauch, *Chem. Ber.*, **96**, 813 (1963).

[8] J. S. Bradshaw and J. S. Hammond, *J. Amer. Chem. Soc.*, **85**, 3953 (1963).

[9] M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Comm.*, 862 (1967).

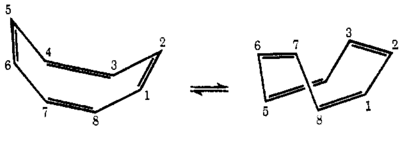
[10] We wish to thank Messrs. W. E. McGonigal, P. G. Arapakos, F. W. Walker, and G. Cohn for conducting many of the difficult preliminary phases of this investigation.

[11] W. H. F. Sasse, P. J. Collin, and G. Sugowdz, *Tetrahedron Lett.*, 3373 (1965); P. J. Collin and W. H. F. Sasse, *ibid.*, 1689 (1968).

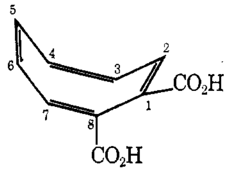
[12] This sample was kindly supplied by the late Dr. Arthur C. Cope and was prepared by a copolymerization technique given in the Ph.D. thesis of J. E. Meili, Massachusetts Institute of Technology, 1952 [*cf.* A. C. Cope and H. C. Campbell, *J. Amer. Chem. Soc.*, **73**, 3536 (1951); **74**, 179 (1952); A. C. Cope and D. S. Smith, *ibid.*, **74**, 5136 (1952)]. Reduction of this dimethyl ester with lithium aluminum hydride gave a glycol which was identical with the glycol prepared from 2-butyne-1,4-diol diacetate by a copolymerization procedure; finally all of the isomeric cyclooctatetraenedicarboxylic acids have been prepared by oxidation of the corresponding diacetyl cyclooctatetraenes (personal communication from the late Dr. A. C. Cope).

[13] F. A. L. Anet, *J. Amer. Chem. Soc.*, **84**, 671 (1962).

basis of an nmr study that there is a rapid equilibrium between the two identical, nonplanar tautomers (IVa and IVb) of cyclooctatetraene with the life time of a

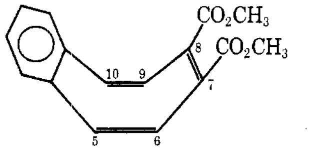


IVa IVb



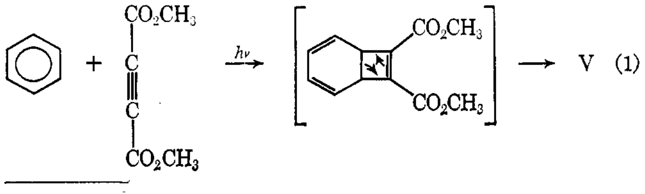
V

tautomer being only about 0.04 sec at −10°. Bryce-Smith and Lodge[5b] have noted that the failure of the dicarboxylic acid derived from dimethyl cyclooctatetraene-1,2-dicarboxylate to give an anhydride under conventional means is consistant with tautomeric structure V for the dicarboxylic acid since in this structure the carboxyl groups are oriented away from one another at a skew angle of about 70°.[14] The nmr spectrum of dimethyl cyclooctatetraene-1,2-dicarboxylate in chloroform solution (see Experimental Section) has the doublet assigned to the protons adjacent to the carboxylate groups split by only 1.9 Hz; this small coupling constant is in agreement with a structure analogous to V for the dimethyl ester since the protons on C-2 and C-7 are at a skew angle of about 70° to the adjacent protons on C-3 and C-6.[15] Some confirmation of this structure is provided by the nmr spectrum of dimethyl benzocyclooctene-7,8-dicarboxylate (see later discussion) which must, on general considerations, exist almost entirely in the tautomeric form VIII and whose corresponding acid is readily converted into an anhydride. For this compound the coupling constant between protons on C-5 and C-6 (C-9 and C-10) is 11 Hz as expected for *cis* protons on an olefinic double bond.[15] The reason why tautomeric structure V is more stable than the alternative structure (in absence of other factors which exist for VIII) appears to be that this structure minimizes repulsions between the carboxyl groups (*cf.* the greater stability of fumaric over maleic acid); also in structure V two double bonds are conjugated, one to each carboxyl group, whereas in the alternative structure only one double bond is effectively conjugated to both carboxyl groups.



VIII

In summary the photochemical reaction between benzene and dimethyl acetylenedicarboxylate can be represented by process 1. It seemed of interest to see if naphthalene can undergo a similar reaction with dimethyl acetylenedicarboxylate.



Naphthalene with Dimethyl Acetylenedicarboxylate.—Irradiation of a solution of dimethyl acetylenedicarboxylate in a 14-fold molar excess of molten naphthalene at 90° with uv light for 4 days in a quartz apparatus gave a complex mixture of products from which unreacted naphthalene was separated by distillation *in vacuo* at 100° and less soluble materials were removed by solvent precipitation from petroleum ether. The soluble product according to vapor phase chromatography (vpc) contained about an 11% yield of 1:1 adducts. These are designated, in order of increasing retention times, as VI–XI and were formed in relative proportions of 3, 34, 6, 34, 10, and 13%, respectively. The more abundant products, VII and IX, were separated by chromatography on silica gel and were purified by recrystallization. Irradiation of a solution of dimethyl acetylenedicarboxylate and a twofold molar excess of naphthalene in methanol at reflux temperature for 60 hr gave some 10% yield[16] of 1:1 photoadducts VII, IX, X, and XI in relative amounts of 8, 7, 9, and 76%, respectively. Following an isolation procedure like that for VII and IX, adduct XI was obtained in 7% over-all yield after recrystallization from methanol.

Adduct VI, which was not formed in appreciable quantity in the photochemical reaction at lower temperature, was found to be identical in vpc retention time on two columns (Apiezon L and silicone gum rubber) with the 1:1 adduct formed by thermal reaction of dimethyl acetylenedicarboxylate with excess naphthalene (25% yield of crystalline adduct after 3 days at 170–180° or 2.9% yield after 7 days at steam-bath temperature). According to its mode of formation,[17] analysis, molecular weight, and spectral properties, this previously unknown adduct, mp 76.5–77.0°, should have the structure of dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate (dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate) expected for a normal Diels–Alder addition. This structure was confirmed by hydrogenation in ethyl acetate over a palladium catalyst which proceeded with absorption of 2 molar equiv of hydrogen to give a product of mp 90.5–91.0°, with melting point and nmr spectrum identical with the reported values for *exo*-dimethyl 2,3-benzobicyclo[2.2.2]octa-2-ene-5,6-dicarboxylate.[18]

Irradiation of dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate in methanol solution with uv light through a Pyrex filter gave an 80% yield of a white crystalline product, mp 77.0–77.5°, which was identical in vpc retention time on two columns with the adduct VIII above. This compound has an analysis and a molecular weight corresponding to $C_{16}H_{14}O_4$.

---

[14] A similar conclusion was relayed to us in a personal communication in 1961 by the late Dr. A. C. Cope who also reported unsuccessful attempts to resolve the dicarboxylic acid with two optically active bases and noted "failure to resolve the acid if it has that structure (V) can be explained by spontaneous racemization through a planar structure, but of course an unsuccessful resolution is not definitive."

(15) *Cf.* J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J. 1965, pp 114–18.

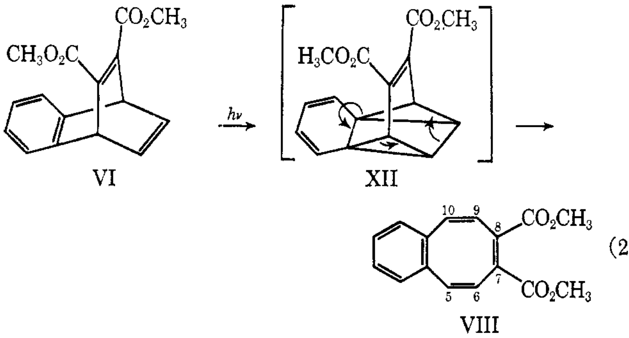
(16) The reaction in methanol is complicated by photochemical addition of methanol to dimethyl acetylenedicarboxylate. *Cf.* the photochemical addition of 2-propanol to acetylenedicarboxylic acid [G. O. Schenck and R. Steinmetz, *Naturwissenschaften*, **47**, 514 (1960); M. Pfau, R. Dulou, and M. Vilkas, *Compt. Rend.*, **251**, 2188 (1960)].

(17) (a) *Cf.* the thermal addition of dicyanoacetylene to naphthalene[17b] and to 1,4-diphenylnaphthalene[17c] and of benzyne to naphthalene.[17d] (b) R. C. Cookson and J. Dance, *Tetrahedron Lett.*, 879 (1962); (c) C. Dufraisse, J. Rigaudy, and M. Ricard, *Tetrahedron*, 491 (1966); (d) R. G. Miller, and M. Stiles, *J. Amer. Chem. Soc.*, **85**, 1798 (1963).

(18) K. Takeda, K. Kitahonoki, M. Sugiura, and Y. Takano, *Chem. Ber.*, **95**, 2344 (1962); K. Tori, Y. Takano, and K. Kitahonoki, *ibid.*, **97**, 2798 (1964).

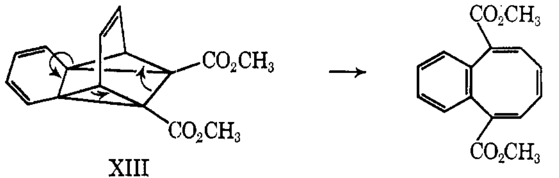
The nmr spectrum (in CCl_4) shows four aromatic protons centered at τ 2.9 (symmetrical multiplet), two vinyl protons in a doublet at 3.29 (J = 11.3 Hz), two more vinyl protons in a doublet at 3.89 (J = 11.3 Hz), and six methoxyl protons in a singlet at 6.35. The coupling constant between the vinyl protons is consistent[15] with the protons on the double bond being *cis*. The methoxyl singlet indicates that the carbomethoxyl groups are equivalent and together with the simplicity of the remainder of the spectrum gives evidence that the molecule has a plane of symmetry. The uv absorption [$\lambda_{max}^{C_2H_5OH}$ 200 mμ (ϵ 30,500), shoulders at 230 (20,500) and 290 (1800)] is similar to that of benzocyclooctatetraene[19] and dimethyl cyclooctatetraene-1,2-dicarboxylate.[5a,b] In agreement with expectations for a benzocyclooctatetraene derivative, hydrogenation over a palladium catalyst in ethyl acetate solution gave an uptake of 3 molar equiv of hydrogen. Finally saponification of the ester and vacuum sublimation of the resulting carboxylic acid at 180° gave a yellow cyclic anhydride, $C_{14}H_8O_3$; this result demonstrates that the carboxyl groups of VIII are on adjacent carbon atoms. The sum of the available evidence requires that compound VIII have the structure of dimethyl benzocyclooctene-7,8-dicarboxylate.

The photolysis of dimethyl 2,3-benzobicyclo[2.2.2]-octatriene-5,6-dicarboxylate to give dimethyl benzocyclooctene-7,8-dicarboxylate can be rationalized by process 2 which proceeds by the vinyl–benzo cycloadduct XII analogous to that recently reported[20] for 2,3-benzobicyclo[2.2.2]octatriene ("benzobarrelene") itself. A second vinyl–benzo cycloadduct XIII could also be visualized in the present case; however, this should give dimethyl benzocyclooctene-5,10-dicarboxylate (XIV). Also the vinyl–vinyl cycloadduct XV could be formed and this should give appreciable amounts of both dimethyl benzocyclooctene-7,8-dicarboxylate (VIII) and 6,9-dicarboxylate XVI. No evidence for the formation of XIV and XVI has been found; however, prolonged irradiation of VI resulted in disappearance of initially formed VIII and appearance of unidentified products, chiefly a product of slightly longer retention time than photoadduct IX. The formation of VIII as the initial major product of photolysis confirms the elegant deuterium tracer studies of Zimmerman and coworkers[20] which demonstrated that vinyl–benzo cycloaddition is preferred over vinyl–vinyl cycloaddition in the direct photolysis of "benzobarrelene." The present work also demonstrates that intermediate XII is preferred over XIII. The direct photolysis likely involves singlet excitation of VI. If the photolysis is run in acetone solution (Pyrex filter), three isomeric products result, of which one is likely dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-5,6-dicarboxylate (IX) (see later discussion). These products evidently result from a triplet excited state *via* acetone sensitization; analogous results have been obtained in the simpler case of "benzobarrelene." [20]

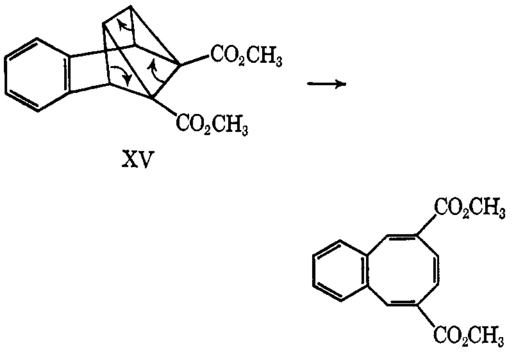


VI XII VIII

(2)



XIII XIV



XV XVI

The pale yellow photoadduct VII, mp 62.0–63.0°, which is a major product from the photochemical reaction of dimethyl acetylenedicarboxylate with molten naphthalene, is assigned the structure of dimethyl 1-naphthalenefumarate. This compound has the correct elemental analysis and molecular weight for a 1:1 adduct, $C_{16}H_{14}O_4$, and has uv absorption somewhat similar to that of a 1-vinylnaphthalene.[21a] The nmr spectrum showed two nonequivalent methoxyl singlets and eight protons in the region τ 2.2–3.0. That the vinyl proton of VII absorbs in the normal aromatic region is to be expected since the vinyl protons of diethyl fumarate absorb at τ 3.17.[21b] Hydrogenation of VII resulted in uptake of 1 molar equiv of hydrogen and gave a colorless compound of mp 60.0–60.5°. This compound was found to be identical with a synthetic sample of dimethyl 1-naphthalenesuccinate prepared from the known compound 1-naphthalenemaleic anhydride[22] by esterification and hydrogenation. Since the dimethyl ester of 1-naphthalenemaleic anhydride is an oil of different vpc retention time from that of VII, the crystalline photoadduct VII is evidently the *trans* isomer, dimethyl 1-naphthalenefumarate.

The colorless photoadduct IX, mp 86.5–87.0°, is another of the major products from the photochemical reaction of dimethyl acetylenedicarboxylate with molten naphthalene. This compound has the correct

---

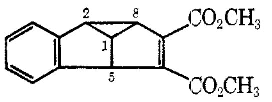
(19) G. Wittig, H. Eggers, and P. Duffner, *Ann. Chem.*, **619**, 10 (1958).

(20) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 4191 (1968); *cf.* G. R. Ziegler and G. S. Hammond, *ibid.*, **90**, 513 (1968); P. W. Rabideau, J. B. Hamilton, and L. B. Friedman, *ibid.*, **90**, 4465 (1968); J. P. N. Brewer and H. Heaney, *Chem. Comm.*, 811 (1967).

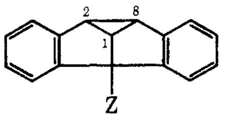
(21) (a) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1951, spectra no. 232 and 233. (b) N. S. Bhacca, L. F. Johnson and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Vol. 1, Varian Associates, Palo Alto, Calif., 1962, spectrum no. 213.

(22) L. Denivelle and D. Razavi, *Compt. Rend.*, **237**, 570 (1953).

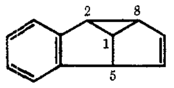
elementary analysis and molecular weight for a 1:1 adduct, $C_{16}H_{14}O_4$, and has the following spectral properties: $\lambda_{\max}^{\mathrm{EtOH}}$ 200 mμ (ϵ 42,500), 220 (shoulder, 19,650), 265 (4770); nmr ($CDCl_3$) at τ 2.4–3.1 (4 H, complex multiplet), 5.81 (1 H, doublet, J = 5.9 Hz), 6.37 (3 H, singlet), 6.42 (3 H, singlet), 6.5–6.9 (2 H, complex multiplet), 6.9–7.3 (1 H, complex multiplet). Hydrogenation with a palladium catalyst in acetic acid resulted in uptake of 2 molar equiv of hydrogen. No deuterium exchange was observed after refluxing in 3.5 *M* $NaOCH_3$ in CH_3OD for 48 hr. Oxidation by $KMnO_4$ in aqueous acetone containing a little acetic acid and esterification of the acidic products with diazomethane gave 55% yield of dimethyl phthalate. It is believed that these data are best explained on the basis of the structure dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate for adduct IX. This structure accounts for the four aromatic protons in the nmr spectrum and the oxidation to phthalic acid. The nonaromatic portion of the nmr spectrum of IX may be interpreted as follows: the six protons, three each at τ 6.37 and 6.42, correspond to two carbomethoxyl groups which are in nonequivalent locations as given in the proposed structure; the single proton (doublet) at τ 5.81 corresponds to the proton on C-5 (*cf.* the proton on C-5 in XVII which absorbs as a doublet at 5.68[23] and the corresponding proton in XIX which absorbs at 6.1–6.3 with J_{15} = 6.0 Hz[20]); the proton at τ 6.9–7.3 corresponds to that on C-2 (*cf.* the proton on C-2 in XVII which absorbs at 7.10,[23] that in XVIII at 6.92,[24] and that in XIX at 7.0–7.3[20]); the two protons at τ 6.5–6.9 correspond to those on C-1 and C-8 (*cf.* the proton on C-1 in XVII which absorbs at 6.47,[23] and the protons on C-1 and C-8 of XIX which absorb at 6.7–7.0 and 7.3–7.6, respectively[20]). Hydrogenation of IX resulted in absorption of 2 molar equiv of hydrogen, corresponding to reduction of the double bond and the cyclopropane ring. Reduction of the double bond first followed by reduction of the cyclopropane ring would lead to at least two compounds since two bonds of the cyclopropane ring of IX are benzylic and nearly equally likely to be reduced; in fact, hydrogenation of IX afforded two products according to vpc analysis.



IX



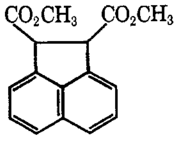
XVII, Z = H
XVIII, Z = CO_2CH_3



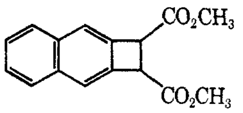
XIX

Photoadduct X, which was not isolated in a pure state, was found to be identical in vpc retention time on two columns with a sample of dimethyl 2-naphthalenefumarate, mp 51.8–52.5°, prepared from the known compound 2-naphthalenemaleic anhydride[22] by esterification and photoisomerization. The structure of dimethyl 2-naphthalenefumarate was confirmed both by its spectral properties and by hydrogenation to dimethyl 2-naphthalenesuccinate.

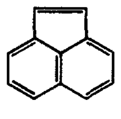
The photoadduct XI, mp 84.5–85.0°, is the major 1:1 adduct from photochemical reaction of dimethyl acetylenedicarboxylate with naphthalene in hot methanol and is also formed from the same reaction in molten naphthalene. This colorless adduct, of analysis and molecular weight corresponding to $C_{16}H_{14}O_4$, has uv absorption similar to that of acenaphthene.[25] The nmr spectrum shows six aromatic protons at τ 2.3–2.9, two benzyl protons in a singlet at 4.95, and six methoxyl protons in a singlet at 6.33. The two benzylic protons are readily exchanged for deuterium using sodium methoxide in CH_3OD. This ready exchange implies that both protons are on carbon atoms adjacent to carbomethoxyl groups. Adduct XI failed to absorb any hydrogen over a palladium-on-charcoal catalyst under general conditions which were successful with the other adducts reported here. On the basis of the evidence presented so far, XI might have either structure XX or XXI. A distinction between these possibilities was obtained by the following degradation. Saponification of the adduct with alcoholic KOH gave the corresponding dicarboxylic acid (as shown by reaction with diazomethane to regenerate XI). Oxidation of this acid with lead tetraacetate[2b] in pyridine for 5 min at 70° gave acenaphthylene XXII which was identified by comparison with an authentic sample; hence adduct XI must have the structure XX. The more stable *trans* structure is assigned to XI in view of failure to detect any appreciable isomerism of XI with sodium methoxide under conditions which exchanged the hydrogen atoms α to the carbomethoxy groups, failure to obtain a volatile anhydride upon refluxing the acid with acetic anhydride, and failure of the corresponding di-N-benzylamide to give a cyclic imide in trifluoroacetic acid under conditions wherein the di-N-benzylamide of naphthalene-2,3-dicarboxylic acid gave an imide in good yield. In conclusion adduct XI is assigned the structure of dimethyl *trans*-acenaphthene-1,2-dicarboxylate.[26]



XX



XXI



XXII

While photoadducts IX, X, and XI appear to be stable under the usual conditions of irradiation, dimethyl 1-naphthalenefumarate (VII) in methanol solution upon irradiation through a Pyrex filter gave a 59% yield of dimethyl *trans*-acenaphthene-1,2-dicarboxylate (XI). Irradiation of dimethyl 1-naphthalenemaleate under similar conditions gave as high as 92.5% yield of XI; in the early stages of the photolysis much of the dimethyl 1-naphthalenemaleate was transformed to dimethyl 1-naphthalenefumarate before cyclization to XI.

---

(23) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965).

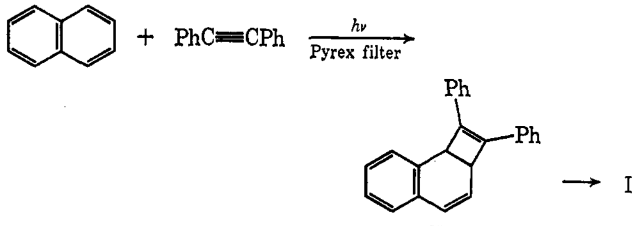
(24) E. Ciganek, *ibid.*, **88**, 2882 (1966).

(25) See ref 21a, spectrum no. 212.

(26) We are indebted to Dr. Charles L. Liotta for first suggesting to us this possible structure.

Conclusions

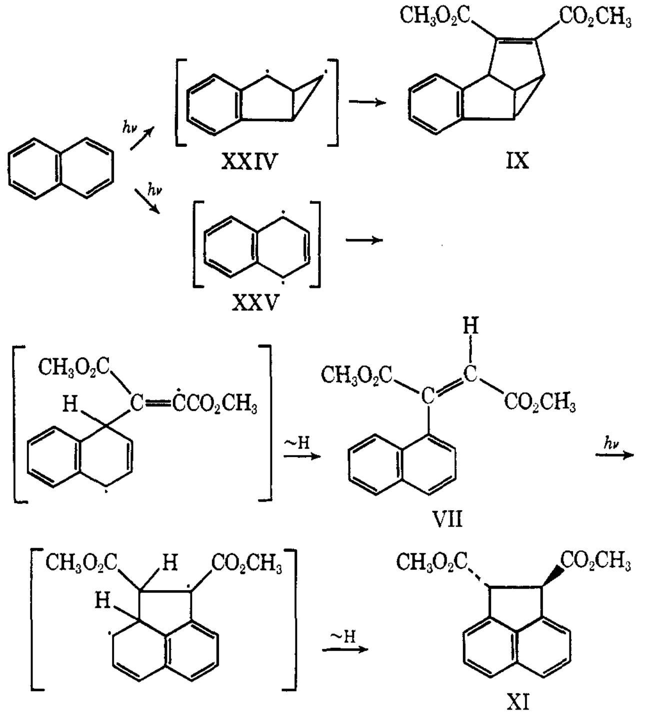
Whereas the photochemical reaction of benzene with dimethyl acetylenedicarboxylate proceeds by 1,2–1,2 addition[5a,b] to give finally dimethyl cycloocta-1,3,5,7-tetraene-1,8-dicarboxylate, the corresponding reaction of naphthalene follows a diverse course. This is surprising since the photochemical reaction[11] of naphthalene with diphenylacetylene follows a path analogous to that of benzene except that the intermediate XXIII undergoes an intramolecular 1,2–1,2 addition to give I rather than tautomerism to a benzocyclooctatetraene. A reasonable explanation begins with the postulate that the photochemical reaction of naphthalene with diphenylacetylene (with use of Pyrex filter[11]) involves photochemical activation of diphenylacetylene rather than naphthalene in accord with likely activation[6] of dimethyl acetylenedicarboxylate rather than benzene in the reaction leading to dimethyl cycloocta-1,3,5,7-tetraene-1,8-dicarboxylate. This postulate appears reasonable since diphenylacetylene has a strong absorption maximum at 298 mμ (ε 25,000) while naphthalene has comparatively weak absorption in this area [298 mμ (ε 320)].[27] The photoreaction of molten naphthalene with dimethyl acetylenedicarboxylate gives about the same mixture of 1:1 adducts (though in reduced yield) with use of a Pyrex filter as without a filter. Since dimethyl acetylenedicarboxylate has only negligible absorption[5b] at wavelengths longer than 300 mμ, while naphthalene has weak but appreciable absorption [at 300 mμ (ε 280), 311 (250)] and was in large excess, we believe that the present photochemical reactions are initiated by photoexcitation of naphthalene which then combines with the acetylenic ester.



XXIII

The photoadducts VII, IX, and XI are conveniently rationalized by the scheme shown (see Scheme I). Intermediates XXIV and XXV could be in singlet and triplet states, respectively, in analogy with suggestions for the corresponding biradicals from photoexcitation of benzene;[6] however, at present, we think that the question of the multiplicity of these intermediates should be left open. Dimethyl 2-naphthalenefumarate X is likely formed by a path analogous to that for VII. The formation of IX is similar to the photoreaction of naphthalene with cyclooctene to give II.[3c] The formation of dimethyl 1- and 2-naphthalenefumarates in fair yield (8.3% VII and of its photoproduct XI and 0.9% X in methanol) appears to be without good precedent,[28] although trace amounts (<0.5%) of cyclooctylbenzene are reported in the photoreaction of benzene with cyclooctene.[3c]

SCHEME I



The photocyclization of dimethyl 1-naphthalenefumarate (VII) and dimethyl 1-naphthalenemaleate to give good yields of dimethyl *trans*-acenaphthene-1,2-dicarboxylate also seems to be without good precedent for a homocyclic system. The photocyclization of *trans*-1,3-diphenylpropene to 1-phenylindan (5% yield) appears at first hand to be a similar process; however, this reaction was interpreted as a 1,2 migration of either phenyl or hydrogen to give a 1,3 diradical XXVI or XXVII which then underwent cyclization followed by

$Ph\dot{C}HCH_2\dot{C}HPh$
XXVI

$Ph\dot{C}HCHPh\dot{C}H_2$
XXVII

rearomatization to give 1-phenylindan or cyclization in an alternative way to give *cis*- and *trans*-1,2-diphenylcyclopropanes (each in 6% yield).[29] A more analogous cyclization, but to a heterocyclic system, is the photocyclization of alkyl-substituted arylic acid anilides to dihydrocarbostyrils,[30] which has been suggested to proceed by a mechanism like that for the conversion of VII into XI in Scheme I.

Adducts VI and VIII are *not* formed in appreciable amount under the present conditions by photochemical reaction of naphthalene with dimethyl acetylenedicarboxylate, but instead dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (VI) is formed by a thermal reaction of naphthalene with dimethyl acetylenedicarboxylate at 90° as confirmed by a test experiment in absence of light. Moreover, when the photochemical reaction is run at room temperature in benzene, methanol, or cyclohexane as solvent, no appreciable quantity of VI or VIII is detectable. Finally

---

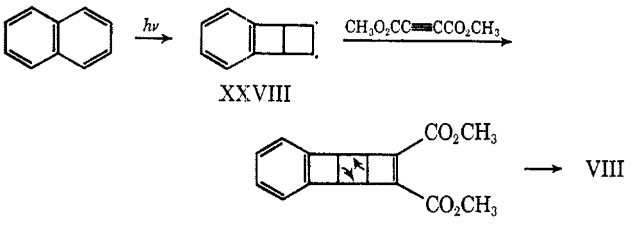
[27] See ref 21a, spectra no. 131 and 195; however, for a recent contrary conclusion, see R. J. McDonald and B. K. Selinger, *Tetrahedron Lett.*, 4791 (1968).

[28] Recently the photochemical reaction of naphthalene with acrylonitrile has been reported to give 8-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (*cf.* XXIII) and substituted naphthalenes, evidently 2-(1-naphthyl)- and 2-(2-naphthyl)propionitrile [J. J. McCullough, C. Calvo, and C. W. Huang, *Chem. Comm.*, 1176 (1968)].

[29] G. W. Griffin J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, **87**, 1410 (1965); G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965); *cf.* H. Kristinsson and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 5968 (1967).

[30] P. G. Cleveland and O. L. Chapman, *Chem. Comm.*, 1964 (1967).

dimethyl benzocyclooctene-7,8-dicarboxylate (VIII) results from photochemical isomerism of VI. These conclusions are of interest since concerted 1,4 addition of dimethyl acetylenedicarboxylate to naphthalene is not allowed according to orbital symmetry rules[31] as a photochemical reaction but is allowed as a thermal reaction (Diels–Alder reaction). The path shown below, which at first hand might appear attractive by analogy with similar additions of olefins to benzene[6] is evidently not a favored path for naphthalene. A likely reason is that the presumed intermediate XXVIII is destabilized by steric strain resulting from fusion of the benzene ring to the bicyclic biradical; this additional strain is, of course, absent in the case of photolysis of benzene itself. The greater rigidity of the naphthalene nucleus may also be a factor in explaining why 1,2-dimethylnaphthalene does not isomerize to 1,3-dimethylnaphthalene upon irradiation (mercury lamp, quartz apparatus)[32] while photorearrangements of alkyl groups upon the benzene nucleus are now well known, *e.g.*, *o*-xylene to *m*-xylene.[33]



Finally, the variation of product composition with solvent in the photoreaction of naphthalene with dimethyl acetylenedicarboxylate is worthy of comment. In molten naphthalene as solvent the ratio of adducts (VII plus XI)/IX is 1.4 and drops to about half this value in cold benzene; however, in cold or hot methanol this ratio is about 12 and is only slightly less in cold cyclohexane. The relative yield of X/IX follows a similar trend with solvent composition. The explanation of these apparent solvent effects must await a more detailed study of reaction mechanism, but practical advantage was afforded by these large variations in facilitating isolation of products in the present work.

Experimental Section[34]

Photochemical reactions were run in a cylindrical quartz cell which had an inner jacket for water cooling (or heating) and an outer jacket of 350-ml capacity for the reaction mixture. Nitrogen could be bubbled through the reaction solution and a Pyrex filter could be inserted between the lamp and the cell to eliminate nearly all irradiation below 3000 Å if desired. Radiant energy was supplied by a medium-pressure mercury lamp (type LL) of 30-cm arc length made by the Hanovia Chemical and Manufacturing Co., Newark, N. J.; this lamp operated on about 1000 W at a current of 3.8 to 4.2 A.

Irradiation of Dimethyl Acetylenedicarboxylate in Benzene.—Dimethyl acetylenedicarboxylate (20 ml) dissolved in 300 ml of thiophene-free benzene was placed in the water-cooled quartz cell and irradiated for 24 hr. The benzene and unreacted dimethyl acetylenedicarboxylate (some 14 g recoverable) were removed *in vacuo* on a rotating evaporator with heat supplied as required by a steam bath. The residue was distilled in a modified Hickman still[35] at 50 μ and a bath temperature of 90–150° and gave, after washing with a little alcohol, 0.7–0.8 g of crude yellow crystals. A dark red glassy residue remained undistilled; this residue is soluble in benzene and in acetone but has not been further investigated. The crude yellow crystals were combined with crystals from a similar run and upon sublimation at 102° (30 μ) gave 1.4 g of crystals of mp 107.2–108.6°. After two recrystallizations from methanol and resublimation, 0.8 g of pale yellow crystals of mp 109.4–110.4° was obtained. On the basis of previously reported physical and chemical properties[5a,b] this compound was assigned the structure of dimethyl cyclooctatetraene-1,2-carboxylate. This structure is supported by the nmr absorption ($CDCl_3$) at τ 2.84 (2 H, doublet, J = 1.9 Hz), 4.02 (4 H, unsymmetrical multiplet), and 6.30 (6 H, singlet) which are assigned, respectively, to ring protons adjacent to carbomethoxyl groups, other ring protons, and methoxyl protons. A sample of dimethyl cyclooctatetraene-1,2-dicarboxylate[12] kindly supplied by the late Dr. Arthur C. Cope had mp 109.0–110.9°, gave no mixture melting point depression, and had an ir spectrum (KBr disk) identical with that of the photochemical adduct.

Similar photochemical preparations of dimethyl cyclooctatetraene-1,2-dicarboxylate from 5.0 ml of dimethyl acetylenedicarboxylate rather than 20 ml gave 0.5–0.7 g of isolable crude crystalline product after 26 hr or irradiation; increasing the irradiation time to 96 hr gave 0.8 g of product. Photolysis of 5.0 ml of dimethyl acetylenedicarboxylate in 325 ml of benzene for 20 hr under a nitrogen atmosphere gave, according to product analysis by vpc on the silicon gum rubber column, 1.33 g (15% yield) of dimethyl cyclooctatetraene-1,2-dicarboxylate. The present photolyses are accompanied by the formation of a yellow-orange film on the inner wall of the quartz cell next to the light source. This film is derived at least in part from the acetylenic ester since it can be removed from the cell wall by treatment with alcoholic KOH (no appreciable solution but immediate dark red coloration of the film) followed by solution in water.

When dimethyl cyclooctatetraene-1,2-dicarboxylate (1.5 g) dissolved in a minimum quantity of absolute ethanol was treated with 2 g of potassium hydroxide dissolved in 20 ml of hot ethanol, there was an immediate dark red coloration which nearly disappeared within 1 min as tan-yellow crystals of the potassium salt of cyclooctatetraene-1,2-dicarboxylic acid appeared. These crystals after some 15 min were separated by filtration, washed with a little absolute ethanol, and acidified with hydrochloric acid to yield cyclooctatetraene-1,2-dicarboxylic acid. This acid after two recrystallizations from water gave canary yellow crystals, mp 206–208° dec, of satisfactory analysis[5a] for $C_{10}H_8O_4$. This acid (0.1 g) could be sublimed at 40 μ at a bath temperature of 180–200° without detectable decomposition into the corresponding anhydride (melting point, analysis, and ir spectral comparison); however, when the acid was heated in a sublimation apparatus at a bath temperature of 235–240° (20 mm), the sublimate which is obtained is of ill-defined melting point and, in large part, will not resublime 200° (5 μ).

Irradiation of Dimethyl Acetylenedicarboxylate with Naphthalene. A. In Molten Naphthalene.—A solution of 307 g (2.40 mol) of molten naphthalene (Baker reagent grade) and 20 ml (0.160 mol) of dimethyl acetylenedicarboxylate (redistilled *in vacuo*) was placed in the quartz cell and kept at 90 ± 3° by passing hot water through the inner compartment during irradiation for 4 days. The unreacted starting materials were removed from the deep red solution with the aid of a rotating evaporator, equipped with a Dry Ice condenser, at a final pressure of 0.1 mm on a steam bath. The nonvolatile residue weighed 20 g. This was dissolved in 50 ml of chloroform and the solution was poured slowly into 3 l. of 30–60° petroleum ether. A

---

[31] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

[32] Unpublished experiments with T. Shibata.

[33] R. B. Cundall and A. J. R. Voss, *Chem. Comm.*, 902 (1968); H. R. Ward, *J. Amer. Chem. Soc.*, **89**, 2367 (1967).

[34] Melting points were determined on a Mel-Temp apparatus and are corrected. Proton magnetic resonance (pmr) spectra were obtained at 60 MHz on a Varian A-60A spectrometer relative to tetramethylsilane as an internal standard. Ultraviolet spectra were determined on a Cary Model 14 spectrophotometer. Infrared spectra were measured on a Perkin-Elmer Model 237 Infracord. Vapor phase chromatographs were obtained on an F & M Scientific Co. Model 810 research chromatograph equipped with dual flame ionization and thermal conductivity detectors with use of either 12 ft × 0.25 in. stainless steel columns packed with 10% SE-30 silicone gum rubber on 80–100 mesh Diatoport S (acid washed, treated with dimethyldichlorosilane) or 5 ft × 0.25 in. stainless steel columns packed with 10% Apiezon L on 60–80 mesh Chromosorb P (acid washed, silanized with dimethyldichlorosilane). Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

[35] K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 66.

flocculent precipitate formed immediately; this (7 g) was re-removed by filtration and discarded. The solvent was removed from the filtrate *in vacuo*. Analysis of the petroleum ether soluble residue (12.9 g) on the Apiezon L column at 260° gave dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (VI, 6.2 min, 0.13 g, 0.30%), dimethyl 1-naphthalenefumarate (VII, 7.0 min, 1.6 g, 3.6%), dimethyl benzocyclooctene-7,8-dicarboxylate (VIII, 7.5 min, 0.28 g, 0.64%), dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate (IX, 8.5 min, 1.6 g, 3.6%), dimethyl 2-naphthalenefumarate (X, 9.5 min, 0.50 g, 1.2%), and dimethyl *trans*-acenaphthene-1,2-dicarboxylate (XI, 10.5 min, 0.59 g, 1.4%). The indicated per cent yields are based upon the starting quantity of dimethyl acetylenedicarboxylate in the reaction mixture. A similar photochemical reaction but with an irradiation time of only 24 hr gave 4.5 g of petroleum ether soluble product, and another run with an irradiation time of 6 hr gave 1.6 g of such product. The combined crude product (19 g) from these three runs was chromatographed on a column (5.5 × 108 cm) packed with 1140 g of Brinkman Instruments Co. No. 7734 silica gel wet with petroleum ether. Elution with 4 l. of benzene gave 2.4 g of naphthalene and unknown substances; elution with 2 l. of 3% (by volume) ethyl ether in benzene gave 0.3 g of unknown; elution with 3 l. of 5% ethyl ether in benzene gave 7.4 g of 1:1 photoadducts; and prolonged elution (finally with 50:50 benzene–acetone) gave 8.3 g of unknown products. The middle fraction (6.5 g) of the 1:1 photoadducts was rechromatographed on silica gel wet with petroleum ether (column 4.1 × 85 cm). Elution with 1% ethyl ether in benzene gave 0.03 g of unknown after 3 l. of eluent and then 1.2 g (fraction A) in the next 0.5 l. of eluent; continued elution with 0.5 l. of the same solvent and then 1.2 l. of 5% ethyl ether in benzene gave 2.2 g of complex mixtures of adducts; and final elution with 0.5 l. of 5% acetone in benzene gave 2.6 g (fraction B). Fraction A according to vpc analysis consisted of eight parts VII, one part X, and two and one-half parts XI. Fraction A dissolved in 5 ml of methanol, was cooled to −78° to initiate crystallization and stored in a freezer for 2 days. After separation by filtration 0.17 g of cream-colored crystals, mp 61–63°, were obtained; these were about 95% pure VII according to vpc analysis and, after two recrystallizations from methanol, consisted of pale yellow crystals of mp 62.0–63.0°. Fraction B according to vpc analysis consisted of seven and one-half parts IX and one part VIII. This fraction upon crystallization from 1:2 mixture of methylene chloride and petroleum ether at −78° yielded 1.1 g of crystals of mp 84–86° and, after recrystallization from the same solvent, 0.25 g of white crystals (pure IX) of mp 86.5–87.0°.

Irradiation of 20 ml of dimethyl acetylenedicarboxylate in 307 g of naphthalene at 90° for 7 days in the quartz cell equipped with Pyrex filter gave after the usual work-up 8.0 g of petroleum ether insoluble residue and 2.7 g of petroleum ether soluble product. The latter on approximate vpc analysis on the SE-30 column indicated the following relative amounts—1:3:3:3:1:5—for adducts VI–XI, respectively.

Irradiation of a similar mixture of dimethyl acetylenedicarboxylate and naphthalene containing 5.0 g of benzophenone for 24 hr in the quartz cell at 90° gave according to vpc analysis 0.45 g (1.0%) of VII, 0.44 g (1.0%) of IX, 0.12 g (0.28%) of X, 0.34 g (0.8%) of XI, and only traces of VI and VIII.

B. In Methanol.—A solution of 60 g (0.47 mol) of naphthalene and 20 ml (0.160 mol) of dimethyl acetylenedicarboxylate in 275 ml of hot methanol was placed in the quartz cell which was heated by hot water which was passed through the inner jacket of the cell at such a rate that the solution was kept at gentle reflux through the 60-hr period of irradiation. A duplicate run was made and the combined reaction mixtures were worked up according to the procedure for runs in molten naphthalene. There was obtained 29 g of petroleum ether insoluble residue and 24 g of petroleum ether soluble product. The latter according to analysis by vpc contained 0.68 g (0.79%) of VII, 0.61 g (0.71%) of IX, 0.75 g (0.81%) of X, 6.5 g (7.5%) of XI, and less than 0.05 g of other 1:1 adducts (yields based upon starting dimethyl acetylenedicarboxylate). Chromatography of the petroleum ether soluble product on silica gel after the manner previously described gave 8.5 g of 1:1 adducts. These were dissolved in 25 ml of hot methanol and allowed to crystallize overnight at about 5°. White crystals of XI, 6.13 g (7.1% yield), mp 84.0–85.0°, were isolated by filtration.

In another preparation 20 g of naphthalene and 5.0 ml of dimethyl acetylenedicarboxylate in 300 ml of methanol were irradiated in the quartz cell for 24 hr at 15° while a slow stream of nitrogen bubbled through the solution. The starting materials were removed on a rotary evaporator at 100° (0.1 mm). From ten such runs 14.9 g of nonvolatile residue was obtained. Analysis of the residue by vpc gave 0.38 g (0.32%) of VII, 0.11 g (0.10%) of IX, 0.30 g (0.29%) of X, 0.96 g (0.89%) of XI, and 2.0 g (2.9%) of dimethyl 2-hydroxymethylfumarate. The last compound came prior to adduct VII during vpc analysis. It could be isolated by liquid chromatography on silica gel and was eluted after the adducts VII–XI by 25% acetone in benzene. After a second chromatography on silica gel it was obtained in greater than 99% purity (vpc analysis).

Dimethyl Hydroxymethylfumarate.—This compound was isolated (see above) as a colorless oil from photochemical reactions of dimethyl acetylenedicarboxylate with naphthalene in methanol solution. Irradiation of 5.0 ml of dimethyl acetylenedicarboxylate in 325 ml of methanol in the quartz cell at room temperature for 24 hr under a nitrogen atmosphere gave, according to analysis by vpc, 0.45 g (6.5% yield) of dimethyl hydroxymethylfumarate. This compound was identified by its spectral properties: nmr ($CDCl_3$) τ 3.78 (1.0 H, triplet, J = 1.8 Hz, CH=), 5.70 (2.0 H, doublet, J = 1.8 Hz, CH_2), 6.22 (3.1 H, singlet, CH_3O), 6.30 (3.1 H, singlet, CH_3O). The coupling between the vinyl hydrogen and the methylene group is that expected for a *trans* relationship between these groups.[15] The ir spectrum (neat) had broad OH absorption at 2.75–3.2, broad strong C=O absorption centered at 5.78, and medium C=C absorption at 6.00 μ. This compound arose from the photochemical addition of methanol to dimethyl acetylenedicarboxylate analogous to the photochemical addition of 2-propanol to acetylenedicarboxylic acid.[16]

C. In Cyclohexane.—A solution of 20.0 g (0.0156 mol) of naphthalene and 5.0 ml (0.040 mol) of dimethyl acetylenedicarboxylate was irradiated in the quartz cell under nitrogen for 24 hr at room temperature. The solvent and starting materials were removed *in vacuo* to give 1.33 g of residue which vpc analysis indicated to contain 0.033 g (0.36%) of cyclohexane adducts of dimethyl acetylenedicarboxylate (see below) and <0.07 g of 1:1 adducts of naphthalene and dimethyl acetylenedicarboxylate. These latter were formed in the ratio for VII/IX/X/XI of about 6:1:4:4.

Cyclohexane Adducts of Dimethyl Acetylenedicarboxylate.—A solution of 8.0 ml (0.064 mol) of dimethyl acetylenedicarboxylate in 300 ml of cyclohexane (which had been purified by distillation from concentrated sulfuric acid and then passage through a column packed with activated alumina) was irradiated for 24 hr under nitrogen in the quartz cell. An insoluble product was formed in the cell during irradiation; this (3.6 g) was removed by filtration. The solvent was removed on a rotating evaporator and the yellow viscous residue (7.9 g) was distilled through a modified Hickman still.[35] The first fraction (1.0 g) was mostly unreacted dimethyl acetylenedicarboxylate (vpc analysis) and the second fraction [1.5 g which distilled at a bath temperature of 150–160° (20 mm)] was mostly cyclohexane adducts of dimethyl acetylenedicarboxylate (containing about a 5:1 ratio of the two major components). The second fraction was purified by preparative vpc at 200° on a 6 ft × 0.5 in. column containing 10% polyphenyl ether on Chromosorb. There was obtained 0.76 g of product which by vpc analysis (silicone gum rubber column) consisted of 95% a compound of retention time of 10.5 min with the remainder being a 3:1 mixture of compounds of retention times of 9.7 and 10.0 min: nmr (CCl_4) τ 4.70 (0.84 H, CH=), 6.56 (3.0 H, CO_2CH_3), 6.67 (3.0 H, CO_2CH_3), 7.5–9.2 (11.5 H, C_6H_{11}). The major product is assumed to be dimethyl cyclohexylfumarate and the major impurity dimethyl cyclohexylmaleate.

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02; mol wt, 226. Found: C, 63.00, 63.18; H, 7.85, 7.96; mol wt, 241, 242.

D. In Benzene.—A solution of 20.0 g of naphthalene and 5.0 ml of dimethyl acetylenedicarboxylate in 325 ml of benzene was irradiated under nitrogen for 22 hr in the quartz cell at room temperature. After removal of solvents and reactants, finally at 100° (0.1 mm), there remained 1.01 g of residue which contained no more than 0.1 g of 1:1 adducts of naphthalene and dimethyl acetylenedicarboxylate. According to vpc analysis these adducts were formed in the ratio for VII/IX/X/XI of about 0.8:2.7:0.7:1.0. Only a small amount of dimethyl cyclooctatetraene-1,2-dicarboxylate was formed; other experiments showed that as little as 0.52 g of naphthalene in a similar experiment (20-hr irradiation) reduced the yield of this benzene adduct from 15 to 9.8%.

Thermal Reaction of Dimethyl Acetylenedicarboxylate with Naphthalene.—A mixture of 40.0 g (0.310 mol) of naphthalene and 20.0 ml (0.161 mol) of dimethyl acetylenedicarboxylate was sealed in a heavy-walled Pyrex tube and heated in an oil bath at 180–185° for 48 hr. After removal of starting materials on a rotating evaporator at 100° (0.1 mm), 31 g of residue was obtained. The residue was dissolved in 80 ml of chloroform and the solution was poured into 3.5 l. of petroleum ether to give, after filtration and removal of the solvent, 17.6 g of soluble product. The petroleum ether soluble product was chromatographed on 1300 g of Brinkman No. 7734 silica gel. Elution with benzene containing 1–3% ethyl ether gave 7.3 g (17% yield) of crude dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (VI), which after one recrystallization from methanol gave 6.1 g of white crystals, mp 75–76°. Further elution with 5% ethyl ether in benzene gave 1.9 g of another substance which after recrystallization from methanol gave white crystals (1.2 g) of mp 118.5–119.0°. This compound had $\lambda_{\max}^{\text{EtOH}}$ 277 mμ (ϵ 14,600), shoulder 250 (9400); nmr ($CDCl_3$) four peaks of equal area at τ 5.73, 6.03, 6.15, and 6.18 attributable to OCH_3. These properties are similar to those reported recently for trimethyl 5-methoxyfuran-2,3,4-tricarboxylate[36] and this structure is confirmed by the following analysis.

Anal. Calcd for $C_{11}H_{12}O_8$: C, 48.5; H, 4.44; mol wt, 272. Found: C, 48.5; H, 4.54; mol wt, 262 (in $CHCl_3$).

Repetition of the above reaction with 35 g of naphthalene, 20.0 ml of dimethyl acetylenedicarboxylate, and 0.25 g of hydroquinone in a sealed tube at 170–180° for 3 days gave, after a similar work-up, 10.7 g (25% yield) of crude VI.

In a reaction which was run to simulate conditions (but in absence of light) of a photochemical reaction with molten naphthalene, 154 g of naphthalene and 10.0 ml of dimethyl acetylenedicarboxylate were heated in a stoppered flask covered with aluminum foil for 7 days in a steam bath. Analysis of the product by vpc indicated the formation of 0.63 g (2.9% yield) of VI.

Dimethyl 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (VI).—This compound was prepared as above from thermal reaction of dimethyl acetylenedicarboxylate with naphthalene. After two recrystallizations from methanol the compound had mp 77.0–77.5°; $\lambda_{\max}^{\text{EtOH}}$ 204 mμ (ϵ 25,600), 208 (25,300), 238 (16,900), 274 (2160), 283 (2010), 318 (482), 334 (444); nmr ($CDCl_3$) τ 2.7–3.2 (6.1 H, complex multiplet), 4.78 (1.9 H, doublet of doublets, J = 3 and 5 Hz), 6.27 (6.0 H, singlet).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; mol wt, 270. Found: C, 71.47, 71.49; H, 5.38, 5.14; mol wt, 269, 260 (in chloroform).

Hydrogenation of 0.340 g (1.26 mmol) of VI over a 5% palladium-on-charcoal catalyst in ethyl acetate resulted in absorption of 2.05 mol of hydrogen/mol of VI. From the hydrogenation mixture 0.25 g of compound, mp 90.5–91.0° (twice recrystallized from methanol), was recovered: nmr (CCl_4) τ 2.84 (4.2 H, singlet), 6.34 (6.0 H, singlet), 6.70 (2.2 H, multiplet), 7.3 (2.3 H, broad singlet), 7.8 (1.8 H, multiplet), 8.7 (1.8 H, multiplet). These values agree with those reported for *exo*-dimethyl 2,3-benzobicyclo[2.2.2]octane-5,6-dicarboxylate.[18]

Irradiation of Dimethyl 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (VI).—A solution of 3.00 g (0.011 mol) of VI in 325 ml of methanol was irradiated for 11 hr under a nitrogen atmosphere in the quartz cell equipped with a Pyrex filter between the lamp and cell. Analysis of the product by vpc indicated that 2.4 g (80% yield) of dimethyl benzocyclooctene-7,8-dicarboxylate (VIII) had been formed and the remainder of the volatile product consisted of about an equal mixture of starting material VI and of another product of retention time slightly longer than that of IX. The solvent was removed *in vacuo* and the residue was taken up in 15 ml of hot methanol. A white precipitate (0.13 g) was removed by filtration, washed with methanol, and discarded. The methanol solution and wash liquors were concentrated to 10 ml and kept at 5° overnight. White crystals of VIII, 2.2 g (72% yield), were isolated by filtration and had mp 76.0–77.0°.

In the above run the conversion of VI into VIII was followed by periodic vpc analysis of small portions of the reaction mixture and was terminated when the yield of VIII was near a maximum. Continued irradiation of a similar solution under the same conditions gave increasing amounts of a compound of retention time slightly longer than that of IX, such that after 42 hr this compound made up some 88% of the total volatile product, which also contained small quantities of VI, VIII, and two unknown products of longer retention time. Irradiations in absence of a Pyrex filter appear to be qualitatively similar but proceed much more rapidly.

A solution of 0.54 g of VI in 300 ml of acetone was irradiated for 2.5 hr under a nitrogen atmosphere in the quartz cell equipped with a Pyrex filter. Analysis of the product by vpc gave three compounds in relative amounts of about 5:3:2. The first of these had a retention time near that of VII but was clearly different from this compound (peak broadening on admixture with VII), the second was identical in retention time to IX, while the third component had a retention time intermediate between IX and X.

Dimethyl Benzocyclooctene-7,8-dicarboxylate (VIII).—The synthesis of this compound by irradiation of VI is given above. A product of identical vpc retention time on two columns (silicone gum rubber and Apiezon L) was obtained from irradiation of dimethyl acetylenedicarboxylate in molten naphthalene. The white compound isolated from the former source had mp 77.0–77.5° after a total of three recrystallizations from methanol.

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; mol wt, 270. Found: C, 70.96, 71.24; H, 5.27, 5.44; mol wt, 262, 274 (in chloroform).

Hydrogenation of VIII (0.0627 g, 0.232 mmol) in ethyl acetate over a 5% palladium-on-charcoal catalyst resulted in the uptake of 2.9 molar equiv of hydrogen. The recovered hydrogenated liquid ester gave $\lambda_{\max}^{\text{EtOH}}$ 209 mμ (ϵ 9940), 211 (9900), 263 (460), 271 (400); nmr (CCl_4) τ 2.92 (4.0 H, singlet), 6.38 (6.4 H, singlet), 6.7–8.5 (9.2 H, complex multiplets).

Saponification of VIII (1.13 g, 4.2 mmol) with 1.3 g of potassium hydroxide in 20 ml of 95% ethanol at reflux for 15 min gave a lustrous precipitate. The mixture was cooled and the precipitate was separated by filtration. The precipitate was washed with absolute ethanol, dissolved in water, and acidified to pH 2. The bright yellow precipitate was separated by filtration, washed, and dried to give 0.64 g (60% yield) of acid of mp 200–202° dec. A portion (0.10 g) of this acid upon treatment with an ethereal solution of diazomethane regenerated the starting ester VIII (according to melting point and mixture melting point). The remainder upon vacuum sublimation at 20 μ and a bath temperature of 180° for some 24 hr gave 0.51 g of orange-yellow crystals of mp 196.0–197.0°. Treatment of a portion of these with acetic anhydride (reflux temperature, 6 hr) and recrystallization of the dark brown residue from benzene–petroleum ether gave yellow crystals, mp 196.0–197.0° which were indistinguishable (mixture melting point and ir spectral comparisons) from the crystals from vacuum sublimation. The ir spectrum (CCl_4) showed characteristic absorption at 5.42 (s), 5.65 (vs), and 6.07 μ (m) as expected for an unsaturated cyclic anhydride. The compound gave the correct analysis for benzocyclooctene-7,8-dicarboxylic anhydride.

Anal. Calcd for $C_{14}H_8O_3$: C, 75.00; H, 3.60. Found: C, 75.05, 74.94; H, 3.91, 3.86.

Dimethyl 1-Naphthalenefumarate (VII).—This pale yellow compound of mp 62.0–63.0° was separated from the photochemical reaction products of dimethyl acetylenedicarboxylate and molten naphthalene by the procedure already given. The compound had $\lambda_{\max}^{\text{EtOH}}$ 223 mμ (ϵ *ca.* 70,000), 264 (shoulder, 4400), 272 (5430), 281 (5780), and 288 (shoulder, 4670); nmr (CCl_4) at τ 2.2–3.0 (7.8 H, complex multiplet), 6.52 (3.0 H, singlet), and 6.80 (3.0 H, singlet).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; mol wt, 270. Found: C, 71.02, 71.14; H, 5.30, 5.21; mol wt, 272, 268 (in acetone).

Dimethyl 1-Naphthalenesuccinate from VII.—A 0.813-g (3.01 mmol) sample of VII (95% pure *via* vpc analysis, remainder XI) upon hydrogenation in ethyl acetate over 1.8 g of 5% palladium-on-charcoal catalyst absorbed 0.96 molar equiv of hydrogen. After filtration and removal of solvent 0.73 g of crude hydrogenation product was recovered; this was combined with 0.60 g of similar material from another hydrogenation. Chromatography on silica gel with elution with benzene gave a main fraction (1.01 g) which upon recrystallization from methanol amounted to 0.58 g of white crystals of mp 60.0–60.5°; nmr (CCl_4) τ 1.8–2.7 (6.8 H, complex multiplet), 5.12 (0.97 H, doublet of doublets, J = 5.4 and 10.0 Hz), 6.45 (3.0 H, singlet), 6.47 (3.0 H, singlet), 6.70 (0.9 H, doublet of doublets, J = 10.0

---

(36) E. Winterfeldt and G. Giesler, *Angew. Chem.*, **78**, 588 (1966); C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Lett.*, 1185 (1966).

and 17.0 Hz), and 7.42 (1.1 H, doublet of doublets, J = 5.4 and 17.0 Hz).

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.54, 70.31; H, 5.80, 5.83.

Dimethyl 1-Naphthalenesuccinate from Dimethyl 1-Naphthalenemaleate.—Arylation of maleic acid with diazotized 1-aminonaphthalene gave according to the procedure of Denivello and Razavi[22] an 11% yield of 1-naphthalenemaleic anhydride, which after recrystallization from benzene–petroleum ether consisted of yellow crystals of mp 115.0–116.0° (lit.[22] mp 116°). Solution of the anhydride in 10% aqueous KOH, acidification to pH 2 with hydrochloric acid, and extraction with ether gave a solution of 1-naphthylmaleic acid which upon reaction with ethereal diazomethane yielded, upon removal of solvent, oily dimethyl 1-naphthalenemaleate. A portion of this material upon hydrogenation in ethyl acetate over a 5% palladium-on-charcoal catalyst gave, after recrystallization from methanol, white crystals of mp 59.0–60.0°. The ir spectrum, mixture melting point, and vpc retention time of this sample of dimethyl 1-naphthalenesuccinate indicated that it was identical with the compound prepared above from hydrogenation of VII. On the other hand, compound VII (dimethyl 1-naphthalenefumarate) had a higher melting point than dimethyl 1-naphthalenemaleate and a shorter vpc retention time (8.7 *vs.* 13.8 min on Apiezon L column at 280°).

Dimethyl 2-Naphthalenemaleate and Dimethyl 2-Naphthalenesuccinate.—These compounds were prepared for comparison with VII and dihydro VII since dimethyl 2-naphthalenesuccinate has a reported[37] melting point of 65°, near that found for dihydro VII. 2-Naphthalenemaleic anhydride was prepared in 20% yield by reaction of diazotized 2-aminonaphthalene with maleic acid according to the procedure of Denivello and Razavi.[22] The bright yellow anhydride (2.0 g), mp 168.0–169.0° (lit.[22] mp 168°), after hydrolysis with aqueous KOH, acidification, extraction with ether, and reaction of the extract with ethereal diazomethane gave 2.1 g of crude dimethyl 2-naphthalenemaleate (mp 78–80°). Recrystallization from methanol gave crystals of mp 80.0–80.5°.

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.80, 70.70; H, 5.14, 5.19.

Hydrogenation of dimethyl 2-naphthalenemaleate over 5% palladium on charcoal in ethyl acetate gave, after two recrystallizations from methanol, dimethyl 2-naphthalenesuccinate, mp 63.5–64.0° (lit.[37] mp 65°).

Not only is the melting point of dimethyl 2-naphthalenemaleate much different from that of VII but also the vpc retention time of dimethyl 2-naphthylsuccinate (9.6 min) is longer than that of dihydro VII (dimethyl 1-naphthalenesuccinate, 7.8 min on Apiezon L column at 280°).

Dimethyl 2-Naphthalenefumarate from Dimethyl 2-Naphthalenemaleate.—Irradiation of 1.50 g of dimethyl 2-naphthalenemaleate dissolved in 400 ml of dioxane in a Pyrex cell under nitrogen gave after 1.0 hr 90% isomerization (vpc analysis) to a new product (8.2-min retention time *vs.* 11.4 min for the starting compound on Apiezon L column at 250°). Longer periods of irradiation up to 8 hr did not alter the yield of the photoproduct. The reaction product, after removal of dioxane, was recrystallized from methanol to give 1.2 g of crude crystals. These were combined with 0.5 g of crystals from a similar reaction and the mixture was chromatographed on silica gel with elution by benzene to give, after one recrystallization from methanol, 1.0 g of pale yellow crystals of mp 51.8–52.5°. This product has the expected spectral properties for dimethyl 2-naphthalenefumarate: $\lambda_{\max}^{\mathrm{EtOH}}$ 223 mμ (ϵ 82,700), 267.5 (13,300), 305 (shoulder, 5200), 338 (shoulder, 1700); nmr (CCl_4) τ 2.1–2.8 (6.7 H, multiplet), 3.01 (1.0 H, singlet), 6.26 (3.0 H, singlet), 6.53 (3.0 H, singlet). Hydrogenation of the product (0.49 g, 1.8 mmol) in ethyl acetate over a 5% palladium-on-charcoal catalyst resulted in uptake of 1.8 mmol of hydrogen and gave, after two recrystallizations from methanol, white needles of mp 63.0–63.5°; nmr (CCl_4) τ 2.2–2.8 (7.1 H, complex multiplet), 5.83 (1.0 H, quartet, J = 6 and 10 Hz), 6.39 (6.0 H, singlet), 6.78 (1.0 H, quartet, J = 10 and 16 Hz), 7.38 (1.0 H, quartet, J = 6 and 16 Hz). The hydrogenated photoproduct has identical melting point and ir, nmr, and vpc properties with those of the sample of dimethyl 2-naphthalenesuccinate prepared above by hydrogenation of dimethyl 2-naphthalenemaleate. The photoproduct from dimethyl 2-naphthalenemaleate is accordingly dimethyl 2-naphthalenefumarate. Photoadduct X from naphthalene and dimethyl acetylenedicarboxylate was found to be identical in vpc retention time on the two columns[34] with this sample of dimethyl 2-naphthalenefumarate; also the mixture of crude photoadducts from naphthalene likely contained minor amounts of dimethyl 2-naphthalenemaleate.

Dimethyl 3,4-Benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate (IX).—This compound was isolated from the photochemical reaction of dimethyl acetylenedicarboxylate with molten naphthalene as described earlier and consisted of colorless crystals of mp 86.5–87.0°.

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; mol wt, 270. Found: C, 71.10, 70.97; H, 5.07, 5.20; mol wt, 271, 274 (in benzene).

Hydrogenation of IX (0.156 g, 0.577 mmol) in glacial acetic acid in presence of 1.0 g of 5% palladium on charcoal resulted in uptake of 2.03 molar equiv of hydrogen. Analysis of the hydrogenated product by vpc on the Apiezon L column at 260° indicated that a 1:3 mixture of two compounds were formed having retention times of 8.9 and 9.4 min, respectively, compared with 8.5 min for IX.

Saponification of IX (0.40 g) by heating with 0.70 g of potassium hydroxide in 15 ml of methanol at reflux for 30 min, evaporation of most of the solvent on the steam bath, acidification to pH 2 with 6 N HCl, and extraction with ether gave an ethereal extract which yielded a viscous liquid hardening to a glass. Attempts to recrystallize the acidic product from common solvents were unsuccessful. A portion was esterified with ethereal diazomethane and analysis by vpc (Apiezon L column at 260°) indicated that a 3:1 mixture of IX and an unknown ester (of retention times 8.5 and 9.0 min, respectively) were present.

An attempted deuterium exchange upon IX (0.31 g, 1.6 mmol) with 1.7 mmol of $NaOCH_3$ in 5 ml of CH_3OD at reflux temperature for 48 hr gave upon work-up a product of unchanged nmr spectrum from starting IX (therefore, absence of hydrogens α to the carbomethoxyl groups is implied; *cf.* adduct XI).

Irradiation of 0.225 g of IX in 325 ml of methanol in the quartz cell under nitrogen for 1 hr gave, after recrystallization from methanol, 0.217 g of colorless crystals which were identical in melting point, mixture melting point, and vpc retention time with starting IX.

Oxidation of 0.318 g (1.18 mmol) of IX was effected with 1.09 g (0.69 mmol) of $KMnO_4$ in 20 ml of purified acetone, 10 ml of water, and 0.10 ml of glacial acetic acid overnight at room temperature. After addition of a little sodium bisulfite, manganese dioxide was removed by filtration and the precipitate was washed well with water and acetone. The combined filtrate and wash liquors were evaporated to dryness *in vacuo*. The residue was taken up in a little water, filtered to remove a trace of precipitate, acidified to pH 2, and extracted with ether. The ether extract after drying over anhydrous Na_2SO_4 and removal of ether gave 0.150 g of residue. This was esterified with excess diazomethane and vpc analysis (Apiezon L column) of the ester indicated the presence of 0.125 g (55% yield) of dimethyl phthalate and small amounts of three unknown products of retention times 5.6, 9.8, and 11.0 min (retention time of IX, 8.5 min).

Dimethyl *trans*-Acenaphthene-1,2-dicarboxylate (XI).—This compound is the major adduct from photolysis of dimethyl acetylenedicarboxylate with naphthalene in methanol at 65° and was isolated from this reaction in the manner previously described. After a total of three recrystallizations from methanol, white crystals of mp 84.5–85.0° were obtained. This compound was identical in vpc retention time on two columns (Apiezon L and silicone gum rubber) with one of the adducts from the photochemical reaction of dimethyl acetylenedicarboxylate with molten naphthalene. The compound has $\lambda_{\max}^{\mathrm{EtOH}}$ 226 mμ (ϵ 84,800), 267 (3840), 277 (6480), 287 (7690), 291 (5690), 298 (5150), 304 (1790), 315 (663), 319 (431).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; mol wt, 270. Found: C, 71.02, 71.18; H, 5.36, 5.43; mol wt, 270, 266 (in acetone).

An attempted hydrogenation of XI (0.0711 g, 0.26 mmol) in 5 ml of glacial acetic acid over 0.52 g of 5% palladium on charcoal resulted in absorption of less than 0.06 mmol of hydrogen in the normal time (1 hr) for complete hydrogenation of the other adducts.

Compound XI (0.27 g, 1.0 mmol) was dissolved in 1 ml of $CDCl_3$ and 0.5 ml of CH_3OD in an nmr tube. The region at τ 4.95 was swept through immediately and again after 10 min with

---

(37) W. H. Linnel, D. W. Matheson, and D. T. Modi, *J. Chem. Soc.*, 3257 (1953).

no change in the spectrum. A 0.05-ml portion of a solution of 0.25 g of CH_3ONa in 0.50 ml of CH_3OD was added to the nmr tube and the spectrum was swept through at intervals. There was a rapid decrease in the peak at τ 4.95; after 20 min this peak was reduced to 8% of its original area. The other nmr peaks of XI were unchanged. In another experiment 0.615 g (2.28 mmol) of XI was dissolved in 8 ml of CH_3OD containing 0.39 g (7.2 mmol) of $NaOCH_3$ and the solution was heated at reflux for 48 hr with exclusion of moisture. The solvent was removed *in vacuo*, the residue was dissolved in 5 ml of deuterium oxide, and the solution was made acidic with 2 ml of 25% D_2SO_4. The solution was extracted with ether and the ethereal extract dried over anhydrous Na_2SO_4 and then treated with diazomethane (to esterify any saponified ester). From the ethereal solution was isolated 0.555 g of residue which was at least 98% XI according to vpc analysis. Recrystallization of the residue from methanol gave 0.37 g of crystals of the same melting point and mixture melting point as those of the starting ester. The nmr spectrum showed that the absorption at τ 4.95 had been reduced to 11% of its starting peak area.

Adduct XI (1.20 g, 4.45 mmol) was saponified in 15 ml of 95% ethanol containing 2.0 g of potassium hydroxide on a steam bath for 5 min. The potassium salt which precipitated was separated by filtration and washed with 95% ethanol. The salt was dissolved in 10 ml of hot water and the cooled solution was acidified to pH 2 with 6 *N* hydrochloric acid. The acid was separated by filtration, washed with water, and dried overnight at 115° to give 1.05 g of acid of mp 205–208° dec. A small portion of this acid was treated with excess diazomethane in ether and the product was analyzed by vpc. Only the starting ester XI was found.

A 0.968 g (4.00 mmol) sample of the above acid from XI was dissolved in 25 ml of dry pyridine and heated to 70° in a hot-water bath. To this solution was added 2.00 g (4.4 mmol) of lead tetraacetate; there was an immediate evolution of gas for about 30 sec. The solution was heated for 5 min at 70° and then solvent was removed *in vacuo* on a rotary evaporator at a bath temperature at or below 70°. The residue was treated with 20 ml of 2.5 *N* hydrochloric acid. The lead salts were removed by filtration and washed with ether. The aqueous solution was extracted with ether and combined with the ether wash solution. The ethereal solution was washed three times with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. The ether was removed on a rotary evaporator to give 0.239 g of residue. Analysis of the residue on the Apiezon L column indicated that 0.126 g (21% yield) of acenaphthylene had been formed. The residue was chromatographed on 100 g of Brinkman No. 7734 silica gel with elution by petroleum ether which removed a yellow band in the first fraction. The solvent was removed and the yellow residue (0.097 g) was recrystallized from 95% ethanol to give 0.047 g of yellow crystals of mp 90.0–91.0°. A mixture melting point with an authentic sample of Aldrich Chemical Co. acenaphthylene (mp 90.5–91.3°) showed no depression and the ir spectra of the two samples were identical.

A 0.35-g sample of the acid from ester XI was heated at reflux for 48 hr with 10 ml of acetic anhydride. After removal of the solvent *in vacuo*, a black tarry residue remained. Analysis of this residue by vpc using the Apiezon L column at 290° gave no volatile product within 25 min; under these conditions 1-naphthalenemaleic anhydride has a retention time of 8.1 min.

Di-N-benzylamide of *trans*-Acenaphthene-1,2-dicarboxylic Acid.—A 0.54-g (2.00 mmol) sample of ester XI was dissolved in 5 ml of benzylamine and the solution was heated at 175° for 2 hr. The mixture was cooled to room temperature and filtered. The filter cake was washed with cold acetone to give 0.33 g of white needles, mp 257–259°; recrystallization from acetonitrile gave 0.25 g of needles of mp 259.0–260.0°. In early phases of the present work the same crystalline di-N-benzylamide was isolated by reaction of benzylamine upon crude oily photoadducts from the reaction of naphthalene and dimethyl acetylenedicarboxylate in methanol. The compound had λ_{max}^{EtOH} 227 mμ (ϵ 76,000), 269 (shoulder, 5400), 278.5 (8300), 288.5 (10,200), 292.5 (shoulder, 8000), 300 (6200), 306 (3120), 316.5 (980), 320 (830); nmr (CF_3CO_2H) τ 1.9–2.7 (16.2 H, complex multiplet with some 10 H at 2.63), 4.94 (2.1 H, singlet), 5.38 (4.0 H, doublet, J = 5 Hz). In CF_3CO_2D the hydrogens at τ 5.38 became a singlet; these hydrogens are benzylic hydrogens which in trifluoroacetic acid are split by the adjacent amide hydrogens.

Anal. Calcd for $C_{28}H_{24}N_2O_2$: C, 79.98; H, 5.75; N, 6.66. Found: C, 79.62, 79.79; H, 5.39, 5.48; N, 6.73, 6.57.

The nmr spectrum of this N-benzylamide was unchanged on standing for 8 months at room temperature in trifluoroacetic acid solution. The solution was evaporated to dryness at room temperature and on recrystallization of the residue from acetonitrile gave some 50% recovery of crystals of mp 260.4–261.3°.

Di-N-benzylamide of Naphthalene-2,3-dicarboxylic Acid.—The dimethyl ester of naphthalene-2,3-dicarboxylic acid of mp 47–49° (1.0 g) upon reaction with 6 ml of benzylamine containing 0.2 g of NH_4Cl at 178° for 2.7 hr gave, following the usual work-up and recrystallization from aqueous ethanol and then acetonitrile, 1.1 g of white crystals of mp 203°; λ_{max}^{EtOH} 233 mμ (ϵ 78,000), 268 (shoulder, 8770), 278 (shoulder, 7000), 316 (730), 329 (820); nmr (CF_3CO_2H) τ 1.25 (2.0 H, broad peak which disappeared in CF_3CO_2D), 1.7–2.6 (16.5 H complex multiplet, ~10 H at 2.57), 5.26 (3.9 H, singlet).

N-Benzylimide of Naphthalene-2,3-dicarboxylic Acid.—The di-N-benzylamide of naphthalene-2,3-dicarboxylic acid upon standing overnight at room temperature in CF_3CO_2D showed the appearance of new nmr absorption at τ 1.52, 1.88, 4.87, 5.06, and 5.56. A solution of 0.30 g of the di-N-benzylamide which had stood for 8 months in 1.2 ml of CF_3CO_2D was evaporated to dryness at room temperature and the residue recrystallized from aqueous ethanol to give 0.11 g of white crystals; after another recrystallization from ethanol, these had mp 211.0–212.0°. Whereas the starting di-N-benzylamide had λ_{max}^{KBr} 3.09 (NH), 6.15 and 6.54 μ (C=O), the present compound lacks NH absorption and has carbonyl absorption at 5.67 and 5.90 μ as expected for a cyclic N-benzylimide.

Anal. Calcd for $C_{19}H_{13}O_2N$: C, 79.43; H, 4.56; N, 4.87. Found: C, 79.69, 79.50; H, 4.39, 4.50; N, 5.01, 4.96.

Dimethyl *trans*-Acenaphthene-1,2-dicarboxylate (XI) from Photolysis of Dimethyl 1-Naphthalenefumarate (VII).—A solution of 0.800 g of dimethyl 1-naphthalenefumarate (VII) in 200 ml of methanol was irradiated at room temperature in the quartz cell with use of a Pyrex filter under a nitrogen atmosphere for 11 hr. Removal of the solvent *in vacuo* gave 0.794 g of residue which according to analysis by vpc (Apiezon L column) contained 0.025 g of unreacted VII and 0.47 g (59% yield) of dimethyl *trans*-acenaphthene-1,2-dicarboxylate; no other compounds of comparable volatility were detected in the vpc trace. The residue was recrystallized from methanol to give 0.38 g of white crystals of mp 83.5–84.0° (mixture melting point with dimethyl *trans*-acenaphthene-1,2-dicarboxylate XI from irradiation of naphthalene with dimethyl acetylenedicarboxylate in methanol showed no depression).

Dimethyl *trans*-Acenaphthene-1,2-dicarboxylate (XI) from Photolysis of Dimethyl 1-Naphthalenemaleate.—Crude dimethyl 1-naphthalenemaleate (2.1 g, prepared by esterification of 1-naphthalenemaleic anhydride[22] with methanol–sulfuric acid, but which according to vpc analysis was 75% pure and contained some 20% unreacted anhydride) was dissolved in 265 ml of methanol and irradiated for 8 hr in the quartz cell. Removal of solvent *in vacuo* gave a dark residue which was chromatographed on 100 g of Brinkman No. 7734 silica gel. The first fraction (elution with 300 ml of 2% ether in benzene) after removal of solvent amounted to 0.85 g and after crystallization from methanol gave 0.55 g of crystals, mp 75–77°. After two more recrystallizations from methanol, white crystals (mp 82.5–83.0°) were obtained which were identical in ir, uv, and nmr spectral comparisons and gave no mixture melting point depression with dimethyl *trans*-acenaphthene-1,2-dicarboxylate (XI) obtained from photochemical reaction of naphthalene with dimethyl acetylenedicarboxylate. A repetition of this experiment with a pure sample of dimethyl 1-naphthalenemaleate (0.900 g) in 200 ml of methanol with irradiation for 13 hr through a Pyrex filter under a nitrogen atmosphere gave 0.67 g (74% yield) of dimethyl *trans*-acenaphthene-1,2-dicarboxylate according to vpc analysis (Apiezon L column).

Irradiation of 0.456 g of dimethyl 1-naphthalenemaleate (97.4% pure *via* vpc analysis) in 150 ml of anhydrous dioxane in the quartz cell with a Pyrex filter under a nitrogen atmosphere gave after 8 hr of irradiation a 92.5% yield (vpc analysis of dimethyl *trans*-acenaphthene-1,2-dicarboxylate). This reaction was followed throughout the irradiation by withdrawal of small samples for vpc analysis. After 10 min of irradiation, 42% dimethyl 1-naphthalenefumarate, 15% dimethyl 1-naphthalenemaleate, and 39% dimethyl *trans*-acenaphthene-1,2-dicarboxylate were present; after 60 min these yields were respectively 10, 1.2, and 75%.

Registry No.—Dimethyl acetylenedicarboxylate, 762-42-5; benzene, 71-43-2; naphthalene, 91-20-3; VI, 19981-73-8; VII, 19988-65-9; VIII, 19988-66-0; VIII (hydrogenated), 19981-74-9; IX, 19981-75-0; XI, 19988-67-1; dimethyl cyclooctatetraene-1,2-carboxylate, 15956-91-9; cyclooctatetraene-1,2-dicarboxylic acid, 13753-01-0; dimethyl hydroxymethylfumarate, 19988-68-2; dimethyl cyclohexylfumarate, 19988-69-3; benzocyclooctene-7,8-dicarboxylic anhydride, 19981-78-3; dimethyl 1-naphthalenesuccinate, 19981-79-4; dimethyl 2-naphthalenemaleate, 19988-70-6; dimethyl 2-naphthalenefumarate, 19988-71-7; *trans*-acenaphthene-1,2-dicarboxylic acid (di-N-benzylamide), 19988-72-8; naphthalene-2,3-dicarboxylic acid (di-N-benzylamide), 19981-80-7; naphthalene-2,3-dicarboxylic acid (N-benzylimide), 20013-26-7.

Acknowledgment.—The support of this work by the U. S. Army Research Office (Durham) under Grant No. DA-ARO(D)-31-124-G258, by the National Aeronautics and Space Administration Grant NsG-657, and by the National Science Foundation (GP-8309) is gratefully acknowledged.

The Synthesis and Properties of Germanium Peroxides and Hydroperoxides[1]

RALPH L. DANNLEY AND GEORGE C. FARRANT

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received July 8, 1968

Triphenylgermyl, diphenyl-*p*-trifluoromethylphenylgermyl, diphenyl-*p*-methoxyphenylgermyl, and tricyclohexylgermyl hydroperoxides and bis(diphenyl-*p*-trifluoromethylphenylgermyl) peroxide have been sythesized from the corresponding organogermanium halides, hydroxides, oxides, methoxides, or amines. The infrared, pmr, and mass spectra are consistent with the proposed structures. Treatment of all of the germyl hydroperoxides or peroxides except *p*-methoxyphenyldiphenylgermyl hydroperoxide with hydrogen chloride yielded the corresponding chlorides in essentially quantitative yields. The *p*-methoxyphenyl group was partially cleaved from germanium upon treatment with hydrogen chloride to produce diphenylgermanium dichloride and anisole.

As a continuation of the studies of the hydroperoxides and peroxides of the group IVb elements,[2-5] representative germanium derivatives of this type have now been synthesized and their chemical and physical properties investigated.

Although several unsymmetrical peroxides containing the GeOOC structure[6,7] and three bisgermyl peroxides have been described,[7-9] the corresponding hydroperoxides had not been synthesized until the preliminary announcement of the preparation of triphenylgermyl hydroperoxide.[5] The present work was undertaken to synthesize a series of germanium hydroperoxides, add to the list of known bisgermyl peroxides, and to determine the physical and chemical properties of these compounds.

Results

The hydroperoxides were synthesized by either a direct nucleophilic displacement of a hydroxy or methoxy group by 98% hydrogen peroxide (method I)

$$R_3GeY + H_2O_2 \longrightarrow R_3GeOOH + HY \qquad (I)$$
$$Y = OH,\ OCH_3,\ OGe(C_6H_5)_3$$

or by displacement of a halide by hydrogen peroxide in the presence of anhydrous ammonia (method IIa).

$$R_3GeX + H_2O_2 \xrightarrow{NH_3} R_3GeOOH + NH_4X \qquad (IIa)$$

The bisgermyl peroxides were synthesized by the reaction of a stoichiometric amount of hydrogen peroxide with a triarylhalogermane in the presence of ammonia (method IIb). The yields, methods of synthesis, and analyses are given in Table I.

$$2R_3GeX + H_2O_2 \xrightarrow{NH_3} R_3GeOOGeR_3 + 2NH_4X \qquad (IIb)$$
$$X = Cl,\ Br$$

The structures of the peroxidic compounds were confirmed by physical methods as well as by elemental and active oxygen analyses. The infrared spectra of the hydroperoxides show a strong absorption in the 3570–3200-cm^{-1} region, indicative of the OH structure. The exchangeable proton in the pmr absorption spectra of the hydroperoxides in deuteriochloroform, listed in Table II, absorbs at very low-field strength, *ca.* δ 7.50. This is similar to the δ 7.8 value for the hydroperoxy proton of *t*-butyl hydroperoxide. Since the hydroxy proton of triphenylgermanol absorbs at δ 1.43 in deuteriochloroform, the low downfield absorptions of the triphenylgermyl hydroperoxide indicates that its exchangeable proton must be attached to the highly electronegative peroxy unit.

The molecular weight of triphenylgermyl hydroperoxide determined by vapor phase osmometry, employing benzene as solvent, was found to be 359 ± 12 for a 0.054 *M* solution, 325 ± 12 for a 0.017 *M* solution, and 323 ± 13 for a 0.0060 *M* solution. Since the molecular formula requires 336, these results indicate that there is a slight degree of association of the hydroperoxide in this solvent as the concentration is increased.

---

[1] (a) Supported by the U. S. Army Research Office (Durham) through Grant No. DA-ARO (D)-31-124-G720. (b) Taken in part from the dissertation of G. C. Farrant submitted in Jan. 1968 to the Graduate School of Case Western Reserve University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) Presented in part at the first Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 10, 1968.

[2] R. L. Dannley and G. Jalics, *J. Org. Chem.*, **30**, 2417 (1965).

[3] R. L. Dannley and G. Jalics, *ibid.*, **30**, 3848 (1965).

[4] R. L. Dannley and W. A. Aue, *ibid.*, **30**, 3845 (1965).

[5] R. L. Dannley and G. Farrant, *J. Amer. Chem. Soc.*, **88**, 627 (1966).

[6] A. G. Davies and C. D. Hall, *J. Chem. Soc.*, 3835 (1959).

[7] A. G. Davies and C. D. Hall, *Chem. Ind.* (London), 1695 (1958).

[8] A. Rieche and J. Dahlmann, *Angew. Chem.*, **73**, 494 (1961).

[9] A. Rieche and J. Dahlmann, *Ann.*, **675**, 19 (1964).