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Sulfoxonium Ylide Chemistry. III.[1] The Photochemistry of Stable Sulfoxonium Ylides[2]

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Photochemical reaction of dimethylsufoxonium 3-ethoxycarbonyl-2-phenylallylide (I) gave diethyl *p*-terphenyl-2′,5′-dicarboxylate (II) in low yield. Irradiation of dimethylsulfoxonium 1,2-dicarbomethoxy-5-carbethoxy-4-phenyl-1,4-pentadien-3-ylide (VI) with an ultraviolet lamp afforded three products, 3-carbethoxy-1,2-dicarbomethoxy-4-methylnaphthalene (VII) (37.5% yield), dimethyl 3-oxo-1,3-dihydronaphtho[1,2-*c*]furan-4,5-dicarboxylate (VIII) (0.39% yield) and dimethyl 3-oxo-1,3,4,5-tetrahydronaphtho[1,2-*c*]-furan-4,5-dicarboxylate (IX) (0.35% yield).

Recently much attention has been focused on the chemistry of stable sulfoxonium ylides,[4] but there are few reports concerning the photochemistry of sulfur–ylides.[4b,5] Corey, *et al.*[5a] have obtained a ring opened sulfoxide derivative by ultraviolet (UV)-irradiation of a cyclic stable sulfoxonium ylide, and Trost[5b] has found a cyclopropane formation by photochemical reaction of stable dimethylsulfoxonium phenacylide. Similar type of reactions has been reported by Nozaki, *et al.*[4b] The photochemical reaction of these sulfur–ylides could be best explained in the light of a carbene intermediate,[4b,5] however, a rigorous verification of this intermediate remains to be accomplished.

We now wish to report photochemical reactions of stable sulfoxonium ylides.

Irradiation of dimethylsulfoxonium 3-carbethoxy-2-phenylallyide (I)[6] in tetrahydrofuran with an ultraviolet lamp (Hanovia, 450 W) gave a number of products from which only one compound was obtained in a pure state (0.95% yield) by silica-gel chromatography. The mass spectrum of this compound (II), mp 129—130°, showed a peak at *m/e* 374 for the molecular ion, suggesting a dimeric product. The nuclear magnetic resonance (NMR) spectrum of II showed peaks at 7.88 ppm (2H, singlet) and 7.42 ppm (10H, nearly singlet) due to aromatic hydrogens, in addition to two equivalent ethyl ester peaks. From these spectroscopic data two possible structures, diethyl *p*-terphenyl-2′,5′-dicarboxylate (II) and diethyl *p*-terphenyl-2′,3′-dicarboxylate (III) could be drawn. However, the chemical shift of two hydrogens at 7.88 ppm would favor the structure (II) for the photochemical reaction product. Both compounds (II and III) are unknown but corresponding dicarboxylic acids and dimethyl ester derivatives have been reported.[7] Therefore, *p*-terphenyl-2′,5′-dicarboxylic acid was

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[1] Part II: J. Ide and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **16**, 793 (1968).

[2] A part of this report was published in *Tetrahedron Letters*, **1968**, 1139 in a preliminary form.

[3] Location: *2-58, 1-chome, Hiromachi, Shinagawa-ku, Tokyo.*

[4] *a*) A.W. Johnson, "Ylide Chemistry," Academic Press Inc., New York and London, 1966; *b*) H. Nozaki, M. Takaku, D. Tsunemoto, Y. Yamamoto and H. Kondo, *Nippon Kagaku Zasshi*, **88**, 1 (1967), and references cited therein; *c*) A.F. Cook and J.G. Moffatt, *J. Am. Chem. Soc.*, **90**, 740 (1968), and references cited therein.

[5] *a*) E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1640 (1964); *b*) B.M. Trost, *J. Am. Chem. Soc.*, **88**, 1587 (1966); *idem*, *ibid.*, **89**, 138 (1967).

[6] *a*) J. Ide and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **16**, 784 (1968); *b*) *Idem*, *Tetrahedron Letters*, **1966**, 1787.

[7] *a*) *p*-terphenyl-2′,5′-dicarboxylic acid: F. Ebel and W. Deuschel, *Chem. Ber.*, **89**, 2794 (1956); *b*) *p*-terphenyl-2′,3′-dicarboxylic acid and its dimethyl ester: C. Weizmann, E. Bergman and L. Haskelberg, *J. Chem. Soc.*, **1939**, 391.

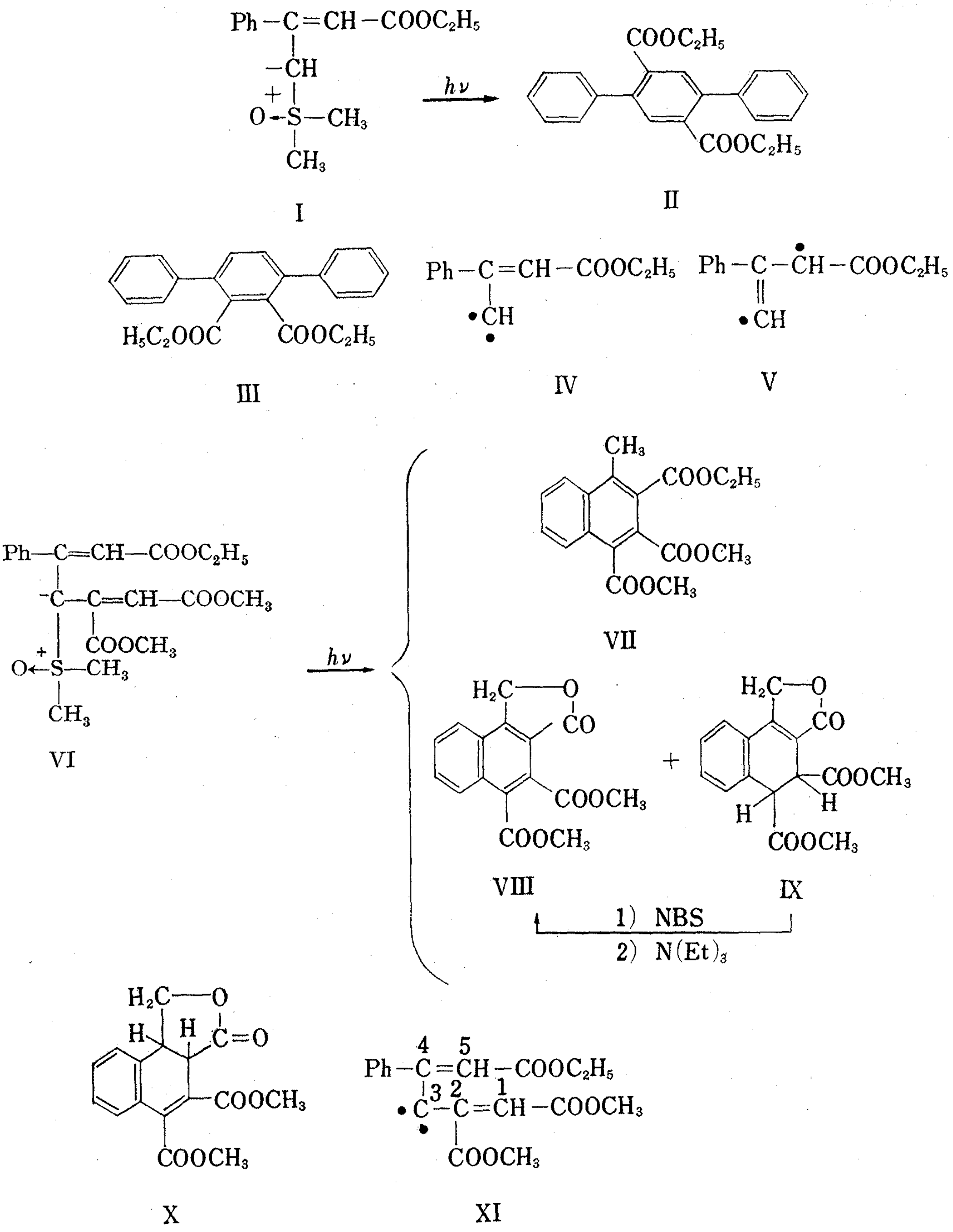

Chart 1

synthesized from *p*-xylene and cyclohexene according to Ebel's method.[7a)] This acid was converted to diethyl ester in an usual way to give diethyl *p*-terphenyl-2′,5′-dicarboxylate (II), mp 130—131°, which was identical with the photochemical reaction product from I in all respects.

A first intermediate leading to II would be a triplet carbene (IV), which dimerized and suffered from dehydrogenation to give II. It is not clear whether a diradical species (V) can participate in this process.

Irradiation of dimethylsulfoxonium 1,2-dicarbomethoxy-5-carbethoxy-4-phenyl-1,4-pentadien-3-ylide (VI)[6a)] in a mixture of EtOH–THF (1:2) with an ultraviolet lamp (Hanovia, 450 W) for 2.5 hr gave three products which were purified carefully by chromatography on silica gel. The UV spectrum of the major product (VII), $C_{18}H_{18}O_6$, mp 106—107° (37.5% yield) showed maxima at 241 mμ (log ε:4.72), 278 mμ (3.69) (shoulder), 288 mμ (3.79), 297 mμ

(3.75) (shoulder), and 334 mμ (3.15) which were characteristic of a naphthalene derivative. The NMR spectrum of VII exhibited signals at 2.71 ppm (3H, singlet) ascribable to a methyl group attached to an aromatic ring, 3.91 ppm (3H, singlet) and 4.01 ppm (3H, singlet) due to two kinds of methyl ester groups, 1.38 ppm (triplet, 3H, J=7.5 cps) and 4.42 ppm (2H, quartet, J=7.5 cps) assignable to an ethyl ester group, and in addition, the complex multiplet at 7.53—8.25 ppm due to aromatic hydrogens (4H). Since the starting material had no methyl group, the above UV and NMR data which showed the presence of a methylnaphthalene moiety, suggested that a complex rearrangement had occurred. The mass spectrum of this compound (VII) showed a peak at *m/e* 330 for the molecular ion, and peaks at *m/e* 141 and 115 which were assignable to benzotropylium and benzocyclopentadienyl cation, respectively, also indicating the methylnaphthalene derivative structure. In order to establish the structure of VII the following chemical transformations were made. Reduction of VII with lithium aluminum hydride afforded a triol (XII), mp 168—169°, which was brominated with phosphorous tribromide to give a tribromide (XIII), mp 193—194°. Treatment of this tribromide with lithium aluminum hydride in tetrahydrofuran gave 1,2,3,4-tetramethylnaphthalene (XIV), mp 106—107°, which was identical in all respects with an authentic sample prepared from 2,3-dimethylnaphthalene according to Hewett's method.[8] Hydrolysis of VII with sodium hydroxide solution, followed by treatment with hydrochloric acid, afforded a mixture of two kinds of carboxylic acid anhydrides. The mixture was decarboxylated, without purification, by heating in quinoline in the presence of copper powder

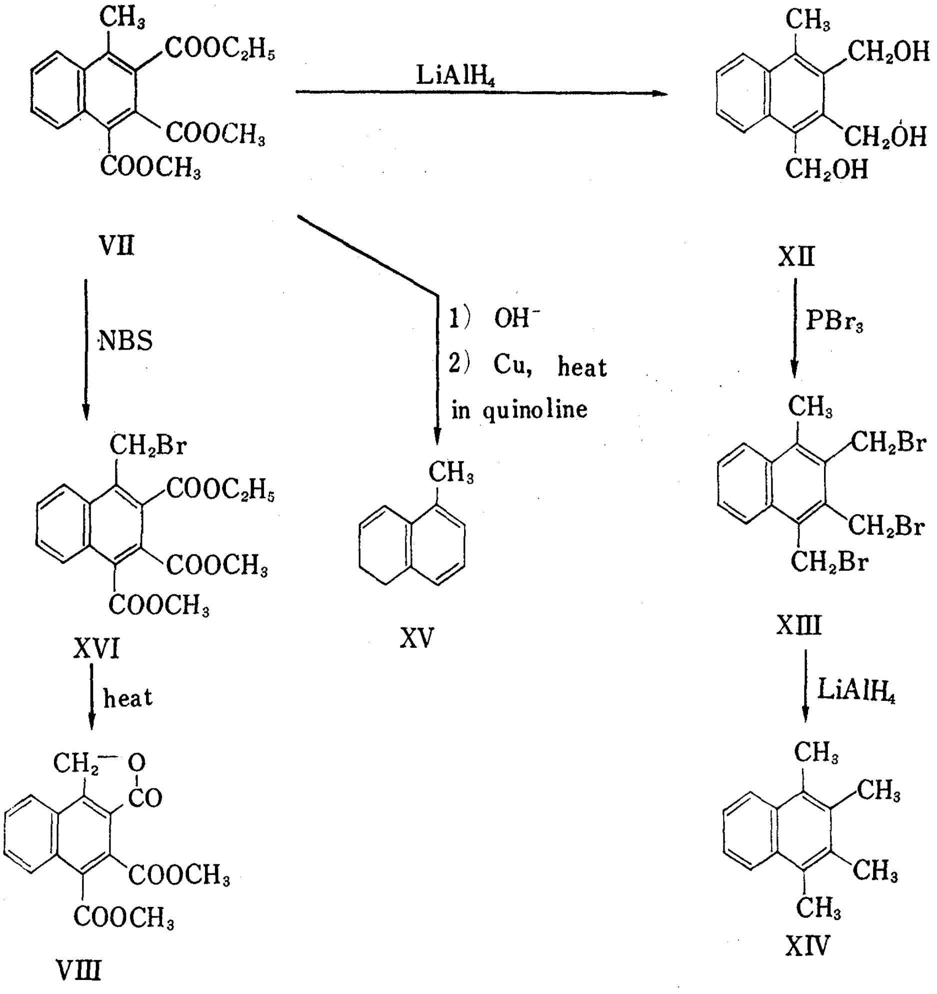

Chart 2

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[8] C.L. Hewett, *J. Chem. Soc.*, **1940**, 293.

to give 1-methylnaphthalene (XV) which was identified by gas chromatography using three different columns. From these data and a lactonization reaction, which will be described later, the structure of VII was concluded to be 3-carbethoxy-1,2-dicarbomethoxy-4-methylnaphthalene (VII).

The second photochemical product was separated from the third by chromatography using silica gel impregnated with silver nitrate. Compound (VIII) thus obtained (0.39% yield) had a molecular formula, $C_{16}H_{12}O_6$, and melted at 180.5—182°. The UV spectrum were again characteristic of a naphthalene nucleus. The NMR spectrum of VIII gave signals at 4.00 ppm (3H, singlet) and 4.15 ppm (3H, singlet) due to two kinds of methyl ester groups, 5.60 ppm (2H, singlet), and 7.67—8.45 ppm (4H, multiplet) ascribable to aromatic hydrogens. The infrared (IR) spectrum of VIII showed an unsaturated γ-lactone absorption at 1772 cm^{-1} (in $CHCl_3$). Therefore, compound (VIII) would have a lactone moiety, structurally derived from the methyl and the carbethoxy group of VII. This deduction was confirmed by the following reactions. Bromination of VII with NBS in carbon tetrachloride afforded a monobrominated compound (XVI), mp 109—111°, which was heated at 200° according to Hirshberg's method⁹⁾ to give the same lactone (VIII). Thus the structure of VIII was established as dimethyl 3-oxo-1,3-dihydronaphtho[1,2-*c*]furan-4,5-dicarboxylate.

The third substance (IX), $C_{16}H_{14}O_6$, obtained in 0.35% yield from VI, melted at 165—167°. The UV spectrum of IX showed maxima at 223 mμ (plateau) (log ε: 4.21), 229 mμ (4.23), and 287 mμ (4.19), which were similar to that of *trans*-cinnamic acid. The NMR spectrum showed peaks at 3.64 ppm (3H, singlet) and 3.65 ppm (3H, singlet) assignable to two kinds of methyl esters, 4.28 ppm (1H, multiplet), 4.55 ppm (1H, doublet, $J=2$ cps), 5.08 ppm (1H, quartet, $J_1=2$ cps, $J_2=17$ cps), 5.26 ppm (1H, quartet, $J_3=1$ cps, $J_2=17$ cps), and 7.20—7.55 ppm (4H, multiplet). Double irradiation at 4.28 ppm changed the peak at 4.55 ppm into a singlet, and the signals at 5.08 and 5.26 ppm into a doublet ($J=17$ cps), respectively (Fig. 1). In the IR spectrum IX showed a lactone absorption at 1762 cm^{-1} (in $CHCl_3$) and in the mass spectrum a molecular ion peak at *m/e* 302 was observed. As in the case of VII, benzotropylium and benzocyclopentadienyl cation at *m/e* 141 and 115, respectively, were also recognized in the mass spectrum. These spectroscopic data suggested that IX was a dihydro derivative of VIII. Attempted dehydrogenation of IX with DDQ or powdered sulfur was not successful and only the starting material was recovered. Therefore, compound (IX) was brominated with NBS in chloroform and the resulting brominated substance, without purification, was dehydrobrominated with triethylamine to yield the second photochemical reaction product, VIII, whose structure had already been determined by the correlation with VII. Thus, photochemical reaction products obtained from VI were intercorrelated by

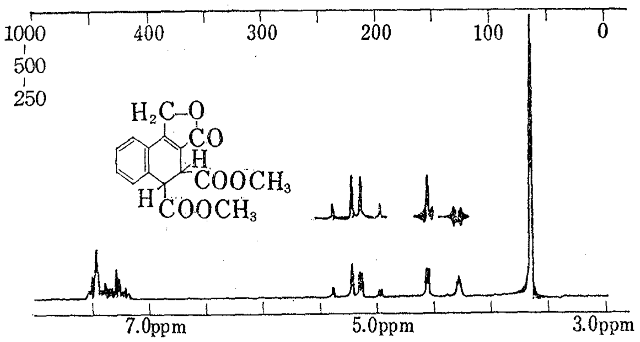

Fig. 1

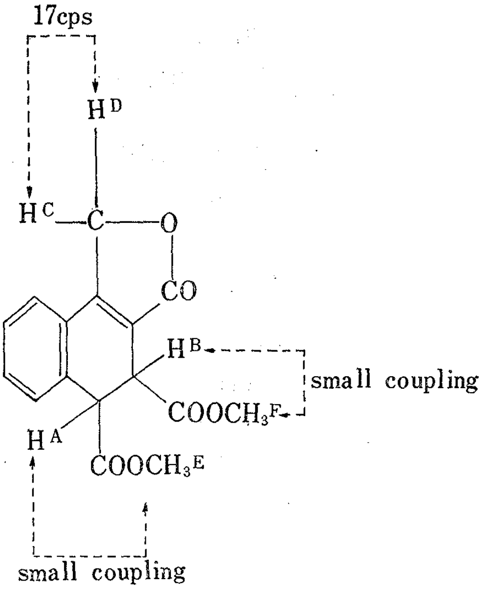

Fig. 2

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9) Y. Hirshberg, D. Lavie and E.D. Bergmann, *J. Chem. Soc.*, **1951**, 1030.

the chemical reactions. From these reactions only two possible structures, IX, *i.e.* dimethyl 3-oxo-1,3,4,5-tetrahydronaphtho[1,2-*c*]furan-4,5-dicarboxylate and a double bond isomer (X) remained for the third photochemical reaction product. However, X was definitely excluded from the following decoupling experiments using 100 Mc NMR: Both HA and HB weakly coupled with methyl ester hydrogens $CH_3{}^E$ and $CH_3{}^F$, respectively. Moreover, there was noticed a Nuclear Overhauser Effect (NOE)10) between H^A and an aromatic hydrogen.

In addition to these facts, the observed coupling constant (17 cps) between H^C and H^D preferred to X, since in the structure (X) the coupling constant of methylene hydrogens adjacent to oxygen should not exceed over 12 cps.11) Thus the structure of the third photochemical reaction product from VI can be concluded as dimethyl 3-oxo-1,3,4,5-tetrahydronaphtho-[1,2-*c*]furan-4,5-dicarboxylate (IX).

H^B would be pseudo axial because of the observed homoallylic coupling12) ($J_{BC}=2$ cps, $J_{BD}=1$ cps) and H^A and H^B might be *cis* oriented which was deductive from the coupling constants ($J=2$ cps).

By an analogy to IV, a first intermediate of this photochemical reaction of VI would be a carbene (XI), which is probably in a triplet state. In order to prove this, an attempt to trap this intermediary in a solid state (77° K) in 2-methyltetrahydrofuran by electron spin resonance was made. However, only absorptions due to a radical were observed ($g=2$). These signals are frequently detected by UV-irradiation of an organic compound.

The intermediates from XI to VII, VIII and IX are not clear at present and there remains a problem, "which carbon of XI corresponds to the methyl group of VII". A tracer experiment using ^{14}C can be useful for clarifying this problem. Although a scientific proof is not available now, there is a possibility, darely saying, that the C-3 carbon of XI would correspond to the methyl group of VII from a mechanistic point of view.

Experimental13)

Diethyl *p*-Terphenyl-2′,5′-dicarboxylate (II)——Dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (I)6) (3.0 g) was dissolved in anhyd. tetrahydrofuran and irradiated with an ultraviolet lamp (Hanovia, 450 W) for 10 hr. After evaporation of the solvent, the oily residue was chromatographed on silica gel (120 g). Elution with *n*-hexane–benzene (3:2) and evaporation gave a mixture of an oil and a crystalline substance (81 mg), which was washed with a small amount of EtOH to give practically pure diethyl *p*-terphenyl-2′,5′-dicarboxylate (II) (40 mg: 0.95% yield). Recrystallization from EtOH gave a sample of mp 129—130° as colorless needles. *Anal.* Calcd for $C_{24}H_{22}O_4$: C, 76.98; H, 5.92. Found: C, 76.93; H, 5.99. UV $\lambda_{\text{max}}^{\text{EtOH}}$ mμ (log ε): 232.5 (4.47), 303 (3.72). IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 1723 (CO). NMR (10% solution in $CDCl_3$) δ ppm: 1.01 (6H, triplet, $J=7$ cps, $-COOCH_2C\underline{H}_3$), 4.13 (4H, quartet, $J=7$ cps, $-COOC\underline{H}_2CH_3$), 7.42 (10H, nearly singlet, aromatic hydrogens), 7.88 (2H, singlet, hydrogens *ortho* to carbethoxy group).

Diethyl *p*-Terphenyl-2′,5′-dicarboxylate (II) from Terphenyl-2′,5′-dicarboxylic Acid——A mixture of *p*-terphenyl-2′,5′-dicarboxylic acid7*a*) (4.0 g) , abs. EtOH (100 ml), anhyd. benzene (80 ml) and conc. H_2SO_4 (3 g) was refluxed with concomitant separation of water for 20 hr. About three fourths of the solvents were evaporated under reduced pressure. The residue was taken up into ether (100 ml) and washed successively with H_2O, $NaHCO_3$ solution and H_2O. After drying over Na_2SO_4 the solvent was evaporated to give a crystalline substance (1.1 g). Recrystallization from EtOH gave diethyl *p*-terphenyl-2′,5′-dicarboxylate (II) as colourless needles, mp 129—131° (690 mg). An analytical sample melted at 130—131°. *Anal.* Calcd. for $C_{24}H_{22}O_4$: C, 76.98; H, 5.92. Found: C, 76.76; H, 5.93.

Photoreaction of Dimethylsulfoxonium 1,2-Dicarbomethoxy-5-carbethoxy-4-phenyl-1,4-pentadien-3-ylide (VI)——A solution of dimethylsulfoxonium 1,2-dicarbomethoxy-5-carbethoxy-4-phenyl-1,4-pentadien-3-

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10) J.G. Colson, P.T. Lansburg and F.D. Saeva, *J. Am. Chem. Soc.*, **89**, 4987 (1967). M.C. Woods, H.C. Chiang, Y. Nakadaira and K. Nakanishi, *J. Am. Chem. Soc.*, **90**, 522 (1968) and references cited therein.

11) R.C. Cookson, T.A. Crabb, J.J. Frankel and J. Hudec, *Tetrahedron*, Supplement No. 7, **1966**, 355.

12) N.S. Bhacca and D.H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry. Illustrations from the Steroid Fleld," Holden-Day, Inc. San Francisco, London, Amsterdam, **1964**, p. 110.

13) All melting points were uncorrected. NMR spectra were taken using Varian Associates A-60 and HA-100 spectrometers with tetramethylsilane as internal standard.

ylide (VI)[6] (2.5 g) in anhyd. tetrahydrofuran (100 ml) and abs. EtOH (50 ml) was irradiated with an UV-lamp (Hanovia, 450 W) using a pyrex filter for 2.5 hr. This process was repeated 12 times and total 30.0 g of VI was submitted to the photoreaction. Then all reaction mixtures were combined and the solvents were evaporated under reduced pressure to give an oil. The oil was dissolved in a small amount of benzene and chromatographed on silica gel (600 g). Elution with benzene–$CHCl_3$ (3:1) and evaporation gave crystalline 3-carbethoxy-1,2-dicarbomethoxy-4-methylnaphthalene (VII) (10.1 g: 37.5% yield). Recrystallization from EtOH afforded pure VII of mp 106—107° as prisms (6.4 g). *Anal.* Calcd. for $C_{18}H_{18}O_6$: C, 65.45; H, 5.49. Found: C, 65.42; H, 5.72. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 241 (4.72), 278 (3.69) (shoulder), 288 (3.79), 297 (3.75) (shoulder), 334 (3.15). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1736 (ester). NMR (10% solution in $CDCl_3$) δ ppm: 2.71 (3H, singlet, $-CH_3$), 3.91 (3H, singelt, $-COOCH_3$), 4.01 (3H, singlet, $-COOCH_3$), 1.38 (3H, triplet, $J=7.5$ cps, $-COOCH_2C\underline{H}_3$), 4.42 (2H, quartet, $J=7.5$ cps, $-COOC\underline{H}_2CH_3$), 7.53—8.25 (4H, multiplet, aromatic hydrogens).

Elution with benzene–$CHCl_3$ (1:1) gave a crystalline substance (170 mg), which was found to be a mixture of 2 substances by analyzing its NMR spectrum. The mixture was dissolved in benzene and rechromatographed on silica gel (30 g) impregnated with 5% $AgNO_3$. Elution with benzene gave crystalline dimethyl 3-oxo-1,3-dihydronaphtho[1,2-*c*]furan-4,5-dicarboxylate (VIII) (94 mg: 0.39% yield). Recrystallization from MeOH gave prisms of mp 180—181° (72 mg). An analytical sample of VIII melted at 180.5—182°. *Anal.* Calcd. for $C_{16}H_{12}O_6$: C, 63.99; H, 4.03. Found: C, 64.04; H, 4.08. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 243 (4.79), 288 (3.73), 299 (3.70) (shoulder), 320 (3.35) (shoulder), 334 (3.25). IR $\nu_{\max}^{\text{CHCl}_3}$ cm^{-1}: 1772 (lactone), 1736 (ester). NMR (10% solution in $CDCl_3$) δ ppm: 4.00 (3H, singlet, $-COOCH_3$), 4.15 (3H, singlet, $-COOCH_3$), 5.60 (2H, singlet, $-CH_2-O-$), 7.67—8.45 (4H, multiplet, aromatic hydrogens).

Further elution with benzene gave crystalline dimethyl 3-oxo-1,3,4,5-tetrahydronaphtho[1,2-*c*]furan-4,5-dicarboxylate (IX) (78 mg: 0.35% yield). Recrystallization from MeOH afforded prisms of mp 163.5—165.5° (55 mg). One more recrystallization from MeOH gave pure IX, mp 165—167°. *Anal.* Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.72; H, 4.90. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 223 (4.21) (plateau), 229 (4.23), 287 (4.19). IR $\nu_{\max}^{\text{CHCl}_3}$ cm^{-1}: 1762 (lactone), 1736 (ester). NMR (10% solution in $CDCl_3$) (100 Mc) δ ppm: 3.64 (3H, singlet, $-COOCH_3$), 3.65 (3H, singlet, $-COOCH_3$), 4.28 (1H, multiplet, $-CH-COO-$), 4.55 (1H, doublet, $J=2$ cps, $-CH-COO-$), 5.08 (1H, quartet, $J_1=2$ cps, $J_2=17$ cps, $-CH-O-$), 5.26 (1H, quartet, $J_3=1$ cps, $J_2=17$ cps, $-HC-O-$), 7.20—7.55 (4H, multiplet, aromatic hydrogens).

4-Methyl-1,2,3-trihydroxymethylnaphthalene (XII)——To a mixture of $LiAlH_4$ (0.207 g: 1.823×3 mmole) and anhyd. tetrahydrofuran (10 ml) was added dropwise 3-carbethoxy-1,2-dicarbomethoxy-4-methylnaphthalene (VII) (0.60 g:1.82 mmole) in anhyd. tetrahydrofuran (20 ml) at 30°. The reaction mixture was stirred at room temperature for 3 hr. Ethyl acetate (0.9 g), wet ether and finally 5% H_2SO_4 (12 ml) were added, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate and the combined organic solvents were washed with $NaHCO_3$ solution and H_2O until neutral to litmus, dried over Na_2SO_4 and evaporated to give an oil, which crystallized on addition of benzene. Recrystallization from benzene afforded 4-methyl-1,2,3-trihydroxymethylnaphthalene (XII) of mp 162—166° (0.109 g). An analytical sample melted at 168—169°. *Anal.* Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.43; H, 7.07. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 229 (4.84) (shoulder), 235 (5.01), 279 (3.79) (shoulder), 289 (3.85), 299 (3.73) (shoulder). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3330 (–OH). NMR (10% solution in CD_3SOCD_3) ppm: 2.70 (3H, singlet, $-CH_3$), 4.82 (2H, singlet, $-CH_2-O-$), 4.86 (2H, singlet, $-CH_2-O-$), 5.00 (2H, singlet, $-CH_2-O-$), about 4.85 (broad, –OH), 7.40—8.41 (4H, multiplet, aromatic hydrogens).

4-Methyl-1,2,3-tribromomethylnaphthalene (XIII)——To a mixture of 4-methyl-1,2,3-trihydroxymethylnaphthalene (XII) (0.096 g:0.413 mmole), pyridine (0.018 ml) and anhyd. tetrahydrofuran (5 ml) was added dropwise phosphorous tribromide (0.168 g: 1.5 mole equivalence) in anhyd. tetrahydrofuran (1 ml) at room temperature. The reaction mixture was stirred at 40° for 2.5 hr. To the cold mixture was added H_2O (20 ml) and extracted with $CHCl_3$. The combined extracts were washed with H_2O, dried over Na_2SO_4 and evaporated to give a crystalline substance. Recrystallization from benzene gave 4-methyl-1,2,3-tribromomethylnaphthalene (XIII) as prisms of mp 189—191° (0.082 g) (47.1% yield). An analytical sample melted at 193—194°. *Anal.* Calcd. for $C_{14}H_{13}Br_3$: C, 39.94; H, 3.11; Br, 56.95. Found: C, 40.15; H, 3.13; Br, 56.69. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 235 (4.66), 247 (4.57), 295 (3.85).

1,2,3,4-Tetramethylnaphthalene (XIV)——To a mixture of $LiAlH_4$ (0.018 g: 5 mole equivalence) and dehyd. tetrahydrofuran (3 ml) was added dropwise 4-methyl-1,2,3-tribromomethylnaphthalene (XIII) (0.040 g: 0.095 mmole) in dehyd. tetrahydrofuran (2 ml) at room temperature. The mixture was heated under reflux for 4 hr. The excess $LiAlH_4$ was decomposed by addition of ethyl acetate, wet ether and finally 5% H_2SO_4 solution. The organic layer was separated and the aqueous phase was extracted with ether. The combined organic solvents were washed with $NaHCO_3$ solution and H_2O, dried over Na_2SO_4 and evaporated to give a crystalline substance. Recrystallization from EtOH afforded 1,2,3,4-tetramethylnaphthalene (XIV) as needles, mp 106—107° (4.4 mg), which on admixture with an authentic sample[8] showed no depression in melting point. *Anal.* Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.34; H, 9.09. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 233.5 (4.89), 284 (3.74) (shoulder), 293 (3.79). NMR (10% solution in $CDCl_3$) δ ppm: 2.37 (6H, singlet, $2\times-CH_3$), 2.58 (6H, singlet, $2\times-CH_3$), 7.32—8.15 (4H, multiplet, aromatic hydrogens).

1-Methylnaphthalene (XV) from 1,2-Dicarbomethoxy-3-carbethoxy-4-methylnaphthalene (VII)——A mixture of 1,2-dicarbomethoxy-3-carbethoxy-4-methylnaphthalene (VII) (1.0 g), dioxane (40 ml), H_2O (20 ml) and conc. HCl (20 ml) was heated on a water bath (70—73°) for 7 hr. The solution was evaporated under reduced pressure to dryness to give an oil which was identified as the starting material by NMR. Then to this oil was added AcOH (14 ml), H_2O (2 ml) and conc. HCl (10 ml) and the reaction mixture was heated on a water bath (85°) for 28 hr. The solution was evaporated under reduced pressure to dryness to afford a solid substance (1.0 g), which was a mixture of the starting material and carboxylic anhydrides by IR. The substance obtained above was dissolved in dioxane (5 ml) and to this solution was added NaOH (2 g) in H_2O (5 ml) and dioxane (5 ml). The mixture was heated on a water bath(85—90°) for 4 hr. Then, in order to dissolve a solid substance appeared, H_2O (10 ml) and dioxane (10 ml) were added. The solution was further heated on a water bath (85—90°) with continuous mechanical stirring for 5 hr. The cold solution was acidified with 10% HCl solution and extracted five times with AcOEt. The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure to give a mixture of a solid and an oil (769 mg), which was submitted to the next decarboxylation reaction without purification. Four hundred miligrams of the substance obtained above was dissolved in quinoline (2 ml) and heated on an oil bath (235—240°) with powdered copper (200 mg) for 1.5 hr. The cold reaction mixture was diluted with ether and filtered. The solid substance was washed well with ether. The combined filtrate was washed three times with 10% HCl solution to remove quinoline and with $NaHCO_3$ solution, then with H_2O until neutral to litmus. After drying over Na_2SO_4 the solvent was evaporated to give an oil (320 mg). This oil was examined by gas chromatography using three different columns and identifications with 1-methylnaphthalene were done using the reference compound in all cases. None of 2-methylnaphthalene was detected. Gas chromatography: equipment; Barber Colman Model 10 (i) 1% DEGS on chromosorb W 80/100, 6 mm i.d. × 2 m, column temperature: 122.5°, retention time of 1-methylnaphthalene: 4.0 min (*cf.* that of 2-methylnaphthalene: 3.4 min) (ii) 3% carbowax 6000 on chromosorb W 60/80, 6 mm i.d. × 2 m, column temperature: 125°, retention time of 1-methylnaphthalene: 0.88 min (*cf.* that of 2-methylnaphthalene: 0.76 min (iii) 1% XE-60 on chromosorb W 60/80, 6 mm i.d. × 2 m, column temperature: 115°, retention time of 1-methylnaphthalene: 2.4 min (*cf.* that of 2-methylnaphthalene: 2.1 min).

4-Bromomethyl-3-carbethoxy-1,2-dicarbomethoxynaphthalene (XVI)——A mixture of 3-carbethoxy-1,2-dicarbomethoxy-4-methylnaphthalene (VII) (1.0 g: 3.34 mmole,) NBS (0.595 g: 3.34 mmole), azobis(*iso*-butyro)nitril (2 mg), benzoyl peroxide (2 mg) and carbon tetrachloride (5 ml) was heated under reflux with mechanical stirring and UV-irradiation for 15 hr. The solid substance was filtered off, washed with carbon tetrachloride. The combined filtrate was washed with $NaHCO_3$ solution and with H_2O, dried over Na_2SO_4 and evaporated to afford a crystalline substance. Recrystallization from EtOH gave 3-carbethoxy-1,2-dicarbomethoxy-4-bromomethylnaphthalene (XVI) as prisms of mp 108—110° (0.480 g) (39.0% yield). An analytical sample melted at 109—111°. *Anal.* Calcd. for $C_{18}H_{17}O_6Br$: C, 52.58; H, 4.19; Br, 19.53. Found: C, 52.72, H, 4.24; Br, 20.09. UV λ_{max}^{EtOH} mμ (log ε): 246 (4.78), 297 (3.81) (shoulder), 304 (3.82). IR ν_{max}^{Nujol} cm^{-1}: 1732 (ester). NMR (10% solution in $CDCl_3$) δ ppm: 1.42 (3H, triplet, $J=7$ cps, $-COOCH_2C\underline{H}_3$), 4.46 (2H, quartet, $J=7$ cps, $-COOC\underline{H}_2CH_3$), 3.91 (3H, singlet, $-COOCH_3$), 4.02 (3H, singlet, $-COOCH_3$), 5.02 (2H, singlet, $-CH_2Br$), 7.58—8.37 (4H, multiplet, aromatic hydrogens).

Dimethyl 3-Oxo-1,3-dihydronaphtho[1,2-*c*]furan-4,5-dicarboxylate (VIII) from 4-Bromomethyl-3-carbethoxy-1,2-dicarbomethoxynaphthalene(XVI)——4-Bromomethyl-3-carbethoxy-1,2-dicarbomethoxynaphthalene (XVI) (307 mg) was heated on an oil bath (200°) for 1 hr. The resulting oil was dissolved in a small amount of benzene and chromatographed on silica gel (25 g). Elution with beznene gave the starting material, 4-bromomethyl-3-carbethoxy-1,2-dicarbomethoxynaphthalene (XVI) (53 mg). Further elution with benzene–$CHCl_3$ (2:1) afforded dimethyl 3-oxo-1,3-dihydronaphtho[1,2-*c*]furan-4,5-dicarboxylate (VIII)(137 mg) (60.9% yield). Recrystallization from MeOH gave pure VIII as prism, mp 180.5—182° (50 mg), which on admixture with the sample obtained from photoreaction of VI showed no depression in melting point. *Anal.* Calcd. for $C_{16}H_{12}O_6$: C, 63.99; H, 4.03. Found: C, 63.84; H, 4.12.

Dimethyl 3-Oxo-1,3-dihydronaphtho[1,2-*c*]furan-4,5-dicarboxylate (VIII) from Dimethyl 3-Oxo-1,3,4,5-tetrahydronaphtho[1,2-*c*]furan-4,5-dicarboxylate (IX)——A solution of dimethyl 3-oxo-1,3,4,5-tetrahydronaphtho[1,2-*c*]furan-4,5-dicarboxylate (IX) (175 mg, 0.58 mmole), NBS (103 mg, 0.58 mmole) and $\alpha\alpha'$-azobis(*iso*-butylnitrile) (2 mg) in $CHCl_3$ (1 ml) was heated under reflux with UV-irradiation for 6 hr. The solvent was evaporated under reduced pressure and anhyd. tetrahydrofuran (10 ml) and triethylamine (120 mg) were added to the resulting reaction mixture and heated under reflux for 2 hr. After the evaporation of the solvent, the residue was chromatographed on silica-gel impregnated with 5% $AgNO_3$. Elution with benzene gave crystalline dimethyl-3-oxo-1,3-dihydronaphtho[1,2-*c*]furan-4,5-dicarboxylate (VIII) (134 mg, 77.0% yield). Recrystallization from MeOH gave prisms of mp 180—181° (75 mg). *Anal.* Calcd. for $C_{16}H_{12}O_6$: C, 63.99; H, 4.03. Found: C, 63.77; H, 4.16.

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