Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.27; H, 6.74. Found: C, 84.15; H, 6.60.

1,1-Diphenyl-4-methyl-2-pentyne-1,4-diol.—This diol was prepared by the method of Babayan,[14] yield 76%, mp 115°.

1,1-Diphenyl-4-methyl-1,4-dimethoxy-2-pentyne (XXII).—XXII was prepared by the procedure used for XX. Instead of crystallizing the residual oil from methanol, it was distilled *in vacuo*, yield 64%, bp 138–142° (0.55 mm), $n^{22}D$ 1.5495; the ir spectrum showed the methoxy absorption at 2825 cm^{-1}.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48. Found: C, 81.55; H, 7.41.

2,5-Diphenyl-3-hexyne-2,5-dicarboxylic Acid (XXIII).—2,5-Diphenyl-2,5-dimethoxy-3-hexyne (XVII) (5.88 g, 0.02 mol) was added to 200 ml of dry tetrahydrofuran, and 3.2 g (0.082 g-atom) of potassium was added under nitrogen. After stirring for 24 hr the dark solution was poured onto Dry Ice. The Dry Ice was allowed to evaporate and *tert*-butyl alcohol was added to destroy the excess potassium. The mixture was poured into water and the solution acidified with hydrochloric acid. The solution was extracted with ether and the extract was dried ($MgSO_4$). After removing the ether, the residue was recrystallized from carbon tetrachloride, yield 69%, mp 224° dec.

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.53; H, 5.59. Found: C, 74.34; H, 5.68.

Decarboxylation of XXIII to 2,5-Diphenyl-2,4-hexadiene (XXIV).—Compound XXIII (1.61 g) was heated at 225° until the evolution of carbon dioxide had ceased. The residue was recrystallized from 95% ethyl alcohol, yield 68%, mp 138°; uv ($CHCl_3$) 317 mμ (ε 34,100). These values agreed with literature values.[15]

Protonation of the Dianion XVIII Corresponding to 2,5-Diphenyl-2,3,4-hexatriene. Preparation of 2,5-Diphenyl-2,3-hexadiene (XXV).—To a dianion solution prepared from 5.88 g (0.02 mol) of 2,5-diphenyl-2,5-dimethoxyhexyne-3 (XVII) and 3.2 g (0.082 g-atom) of potassium in 200 ml of tetrahydrofuran was added an excess of methanol at −20°. The solution was poured into water, and the resulting oil was separated, taken up in ether, and dried ($MgSO_4$). After removing the ether, the viscous oil was transferred to an alumina column with the aid of a little petroleum ether (bp 70–110°). The column was eluted with 500 ml of petroleum ether. The movement of the allene band was followed by the yellow color of the band and its fluorescence when irradiated with a uv lamp. Evaporation of the solvent gave the pure allene as a yellow oil, yield 48%; the uv spectrum showed the absence of any conjugated diene.

Anal. Calcd for $C_{18}H_{18}$: C, 92.30; H, 7.70; mol wt, 234. Found: C, 92.12; H, 7.82; mol wt, 242 (Rast method).

Isomerization of 2,5-Diphenyl-2,3-hexadiene (XXV) to 2,5-Diphenyl-2,4-hexadiene (XXIV).—XXV (1 g) was refluxed with 50 g of methanol containing 1 g of concentrated sulfuric acid for 2 hr. The solution was partially evaporated and cooled. The resulting product was recrystallized from ethanol, yield 60%, mp 138°, uv ($CHCl_3$) 320 mμ (ε 34,100).

1,1,4-Triphenyl-2-pentyne-1,4-dicarboxylic acid (XXVI).—A dianion solution prepared from 7.12 g (0.02 mol) of 1,1,4-triphenyl-1,4-dimethoxy-2-pentyne (XX) and 3.2 g (0.082 g-atom) of potassium, in 200 ml of tetrahydrofuran, was poured onto Dry Ice. The resulting solution was worked up as in the preparation of the diacid XXIII. The product was recrystallized from chloroform–cyclohexane, yield 64%, mp 194° dec.

Anal. Calcd for $C_{25}H_{20}O_4$: C, 76.71; H, 5.39. Found: C, 76.90; H, 5.49.

Decarboxylation of XXVI to 1,1,4-Triphenyl-1,3-pentadiene (XXVII).—Compound XXVI (1.92 g) was heated at 200° until the evolution of carbon dioxide had ceased. The residue was recrystallized from ethanol–water, yield 42%, mp 121–122°.

Anal. Calcd for $C_{23}H_{20}$: C, 93.24; H, 6.76. Found: C, 93.05; H, 6.87.

Protonation of Dianion XXI. Preparation of 1,1,4-Triphenyl-1,2-pentadiene (XXVIII).—To an anion solution prepared from 1,1,4-triphenyl-1,4-dimethoxy-2-pentyne (XX), prepared in the usual manner, was added an excess of methanol at −20°. The reaction mixture was worked up by the procedure used for XXV. A yellow oil was obtained after column chromatography, yield 55%.

Anal. Calcd for $C_{23}H_{20}$: C, 93.24; H, 6.76. Found: C, 93.11; H, 6.87.

Dimerization of 1,1,4-Triphenyl-1,2-pentadiene (XXVIII) to 1,2-Bis(diphenylmethylene)-3,4-bis(1-phenylethyl)cyclobutane (XXIX).—One gram of the allene XXVIII was heated at 150° for 2 hr. The residue was dissolved in acetone and precipitated by the addition of ethanol. The product was recrystallized from chloroform–methanol, yellow crystals, yield 39%, mp 197°.

Anal. Calcd for $C_{46}H_{40}$: C, 93.24; H, 6.76; mol wt, 592. Found: C, 93.41; H, 6.92; mol wt, 576 (Rast method).

Isomerization of 1,1,4-Triphenyl-1,2-pentadiene (XXVIII) to 1,1,4-Triphenyl-1,3-pentadiene (XXVI).—XXVII (1 g) was refluxed in 50 ml of ethanol containing 5 ml of concentrated sulfuric acid for 3 hr. On cooling, an oil separated which was crystallized from methanol–water and recrystallized from methanol–water, yield 34%, mp 121–122°.

Attempted Preparation of a Dianion Corresponding to 1,1-Diphenyl-4-methyl-1,2,3-pentatriene. Ethylation of the Resulting Solution to Form 3,3,10,10-Tetraphenyl-6,6,7,7-tetramethyl-4,8-dodecadiyne (XXX).—To a solution prepared from 5.88 g (0.02 mol) of 1,1-diphenyl-4-methyl-1,4-dimethoxy-2-pentyne (XXII) and 3.2 g (0.082 g-atom) of potassium was added 15.4 g (0.1 mol) of diethyl sulfate at 0°. After 30 min, methanol was gradually added to destroy the excess potassium, and the mixture was then poured into water. The oil which separated was taken up in ether, washed with water, and dried ($MgSO_4$). After the ether was removed, the residue was recrystallized from methanol, yield 50%, mp 154°.

Anal. Calcd for $C_{40}H_{42}$: C, 91.95; H, 8.05; mol wt, 522. Found: C, 91.76; H, 8.18; mol wt, 501 (Rast method).

Registry No.—III, 31382-35-1; IV, 12537-75-6; V, 31382-36-2; VI, 31382-37-3; VII, 31382-38-4; VIII, 31382-39-5; IX, 31382-40-8; XI, 31382-41-9; *rac*-XIII, 31382-42-0; *meso*-XIII, 31382-43-1; *rac*-XIV, 31382-44-2; *meso*-XIV, 31382-45-3; XV, 31382-46-4; XVI, 6289-26-5; XVII, 31382-48-6; XVIII, 12537-72-3; XIX, 2979-97-7; XX, 31382-49-7; XXI, 12537-74-5; XXII, 31382-50-0; XXIII, 31428-89-4; XXIV, 16819-47-9; XXV, 31382-52-2; XXVI, 31382-53-3; XXVII, 31382-54-4; XXVIII, 31382-55-5; XXIX, 31382-56-6; XXX, 31382-57-7; 1,1-diphenyl-4-methyl-1,2,3-pentatriene dianion, 12537-73-4; 1,4-diphenyl-1,4-di(1-naphthyl)-1,4-dimethoxy-2-butyne, 31382-58-8.

(14) J. Salkind and V. Teterin, *Chem. Ber.*, **60B**, 32 (1927); A. T. Babayan, *J. Gen. Chem. USSR*, **10**, 1177 (1940).
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Isomerization of Fluorenone Anil *N*-Oxide to *N*-Phenylphenanthridone by Photochemical and Mass Spectral Pathways

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In an earlier note[2] it was suggested that in the isomerization of 2-phenylisatogen to 2-phenyl-4*H*-3,1-benzoxazin-4-one there was similar behavior in both the photolytic and the mass spectral pathways. The nitrone–amide rearrangement has been discussed in terms of a photochemical–mass spectral analogy.[3] A common oxaziridine intermediate was proposed for both 2-phenylisatogen and 2-phenyl-4*H*-3,1-benzoxazin-4-one in their mass spectral fragmentations.[2]

(1) Department of Chemistry, York College, Jamaica, N. Y. 11432
(2) D. R. Eckroth, *Chem. Commun.*, 465 (1970).
(3) R. G. Cooks, *Org. Mass Spectrom.*, **2**, 481 (1969).

TABLE I
MASS SPECTRAL DATA

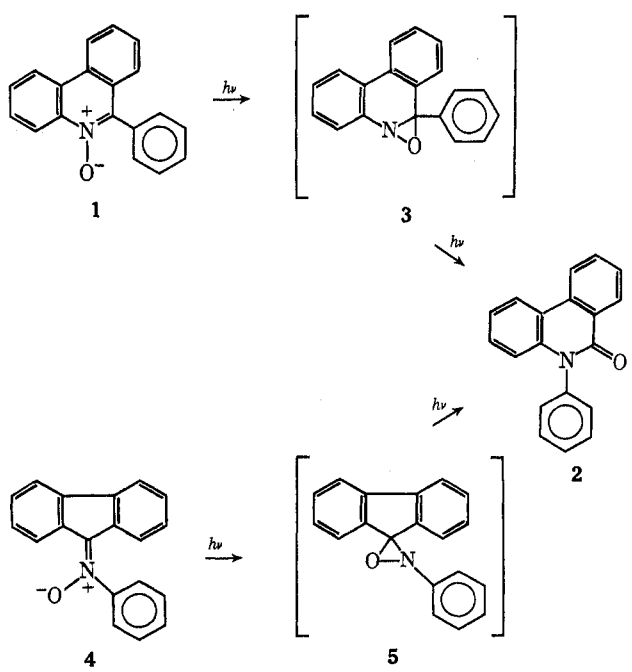
m/e in 1, 2, and 4	Rel intensity 1, 70 eV	Rel intensity 2, 70 eV	Rel intensity 4, 20 eV	Rel intensity 4, 70 eV	m/e in 4*[a]	Rel intensity 4*, 20 eV	Rel intensity 4*, 70 eV
272	17.3	21.7	21.0	20.0	^{13}C M$^+$	100.0	71.2
271 M$^+$	90.2	100.0	100.0	100.0	^{13}C M − H	97.5	100.0
270 M − H	100.0	33.9	34.5	75.0		27.0	46.1
256	7.8	0.7	2.2	2.8	^{13}C M − O	4.0	9.8
255 M − O	41.0	3.2	7.5	12.5	^{13}C M − OH	14.0	17.2
254 M − OH	89.6	7.4	2.0	15.8		13.5	14.5
244				1.5	^{13}C M − CO		3.5
243 M − CO	7.1	14.0	3.5	6.0	^{13}C M − ^{13}CO or ^{13}C M − CHO	8.0	10.5
242 M − CHO	21.2	9.5	3.2	19.2	^{13}C M − ^{13}CHO or ^{13}C M − NO	17.0	10.5
241 M − (CHO + H) or M − NO	14.7	10.2	0.5	4.8	^{13}C M − (^{13}CHO + H) or ^{13}C M − NOH	9.0	6.5
240 M − (CHO + 2H) or M − NOH	5.4	3.3		2.2			4.0
181			1.2	5.0	^{13}C M − C_6H_5N	18.0	21.8
180 M − C_6H_5N			7.1	32.5		11.0	18.8
179				2.1	^{13}C M − (C_6H_5 + O)		7.0
178 M − (C_6H_5 + O)	2.8	2.5		8.0			10.0
169	1.4	8.4		1.1		5.0	5.0
168 M − C_6H_5CN	9.2	54.2		7.0		4.0	5.0
164 M − (C_6H_5 + NO)				5.8			11.0
163 M − (C_6H_5 + NOH)				10.5			8.8
153				2.2			4.0
152 M − (C_6H_5N + CO)	2.3	0.8		2.1			16.5
151 M − (C_6H_5N + CHO)	5.3	2.3		13.1			14.0
139 M − (C_6H_5CN + CHO)	7.2	36.6		1.9			3.5
105	6.2	23.5					
91			13.1	84.0			85.0
77	5.0	10.6		5.3			6.5

[a] 4* contains 52.6:47.4 ^{13}C–^{12}C at C-9 calculated at 20 eV.

Taylor, *et al.*,[4] have described the photoisomerization of 10-phenylphenanthridine *N*-oxide (**1**) to *N*-phenylphenanthridone (**2**) for which they proposed the intermediate oxaziridine **3**.[5] The mass spectra[6] of **1** and **2** at 70 eV show similar fragmentation patterns; they appear to undergo skeletal rearrangement involving the oxaziridine intermediate **3**.

Fluorenone anil *N*-oxide (**4**) can be photoisomerized to **2** by irradiation for 3 hr in cyclohexane or absolute ethanol solutions of 10^{-3} or 10^{-4} *M* with Rayonet 2537-Å lamps. Johnson[7] irradiated 4.15×10^{-2} *M* **4** in acetonitrile with no observable reaction. We find irradiation of 10^{-2} *M* **4** in cyclohexane or absolute ethanol with a 450-W medium-pressure lamp exhibits no isomerization. A reaction dependence upon concentration is implied.[8] The oxaziridine **5** is proposed as an intermediate in the photoisomerization.

Earlier studies of mass spectral fragmentations of α-phenylnitrones have shown the oxaziridine intermediate to be unimportant in the metastable loss of CO.[9] In order to determine whether **5** is taking part in the fragmentation pattern of **4**, ^{13}C-labeled fluorenone anil *N*-oxide (**4***) was studied. That **5** is operative in the skeletal rearrangement of **4** is obvious since 80% of the CO lost in the spectrum of **4*** contained ^{13}C, while only approximately 20% of the fragmentation of **4*** to give CO involves loss of a carbon from one of the fused benzene rings. The metastable OH loss occurs by a H abstraction mechanism. All rearrangement processes are of the general type $[ABC]^+ \rightarrow [AC]^+ + B$.



1 3 2 4 5

(4) E. C. Taylor and G. G. Spence, *Chem. Commun.*, 767 (1966); 1037 (1968).
(5) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970).
(6) Mass spectra were determined by Mrs. Willa Jones with an Atlas CH-4 mass spectrometer at 20 and 70 eV using a direct probe with source temperature of 175–225°.
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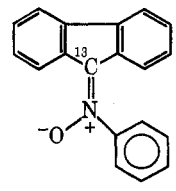
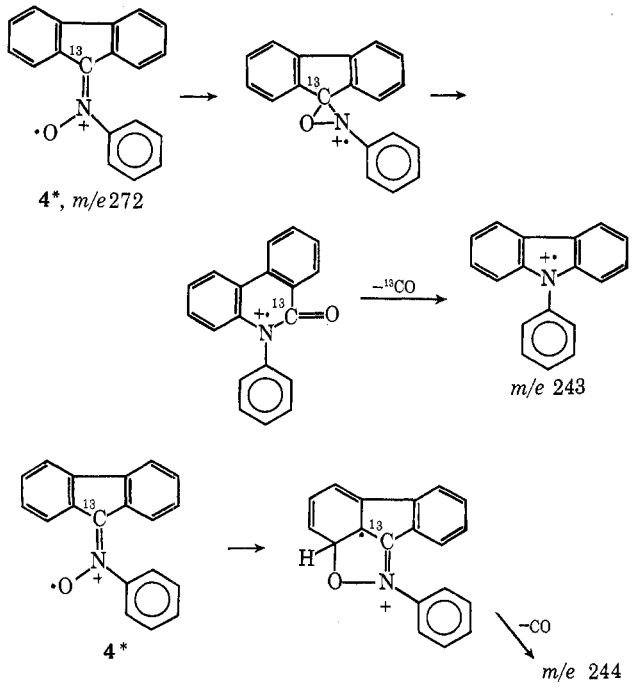
(8) Concentration dependence of photoisomerization has been observed before; see D. R. Eckroth and R. H. Squire, *ibid.*, **36**, 224 (1971).
(9) T. H. Kinstle and J. G. Stam, *Chem. Commun.*, 185 (1968).



4*

While the mass spectra of **1** and **4** are quite normal and in accord with results reported in an earlier study,[2] the mass spectral fragmentation of **2** is remarkably similar to that of **1** but significantly unlike that of **4** (see Table I).



Experimental Section

Fluorenone anil was prepared according to the procedure described by Reddelien.[10]

Fluorenone Anil *N*-Oxide (4).—To a solution of 5.0 g of fluorenone anil in 200 ml of chloroform was added 7.2 g of *m*-chloroperoxybenzoic acid (85% pure). The yellow solution, which turned pale yellow after 45 min, was kept at room temperature for 3 days. The solution was poured through a column of neutral alumina and then evaporated on the Rotovac. The resulting material was crystallized from 95% ethanol affording yellowish needles of **4**, 3.4 g (64%), mp 189–190° (lit.[7] mp 191–193°).

***N*-Phenylphenanthridone (2).** **A.**—A 4×10^{-3} *M* solution of **4** (500 ml) in cyclohexane was irradiated for 8 hr in a water-cooled chamber with a 450-W medium-pressure total immersion lamp (quartz filter). After irradiation, examination of the solution by thin layer chromatography gave evidence that most of the starting material had been unaffected by the irradiation. Evaporation of solvent gave an oil which was passed through a column of silica gel with chloroform. The first eluted fraction, after removal of solvent, was an oil which had an infrared spectrum similar to that of an authentic sample of *N*-phenylphenanthridone.

B.—A 10^{-4} *M* solution of **4** (500 ml) in 95% ethanol was irradiated for 3 hr in a Rayonet reaction chamber with 2537-Å lamps and then the solvent was evaporated. The solid residue (8.5 mg, mp 218°) was recrystallized from 95% ethanol to give colorless crystals of **2**, 2.8 mg (21%), mp 227° (lit.[11] mp 225°). The infrared spectrum, identical with that of an authentic sample of **2**, exhibited characteristic peaks at 2920, 1650, 1450, 1370, and 745 cm^{-1}.

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(11) D. H. Hey and T. M. Moynehan, *J. Chem. Soc.*, 1563 (1959).

Biphenyl-2-carboxylic Acid-α-^{13}C.—2-Iodobiphenyl was converted to the Grignard reagent which was carbonated using the vacuum line technique at −20° with 100 ml of $^{13}CO_2$[12] (54% enrichment, Bio-Rad Laboratories). Crystallization yielded 574.3 mg of colorless crystals (81.2% based on CO_2), mp 113.5–114°. The infrared spectrum exhibited a carbonyl peak at 1680 cm^{-1}; nmr (in CCl_4) showed peaks at δ 11.6 (s, H of acid) and 7.2–8.0 (m, 9 H).

Fluorenone-9-^{13}C.—Ring closure was carried out with 574.3 mg (2.92 mmol) of biphenyl-2-carboxylic acid-α-^{13}C dissolved in 2.6 ml of 80% sulfuric acid.[13] The mixture was heated at 85° for 0.5 hr and poured onto crushed ice. The greenish-yellow product was extracted with ether and the ether extract was washed with 3 *N* sodium hydroxide. Ether was removed and crystallization from water yielded 419.9 mg (2.32 mmol, 79.5%) of yellow-green product, mp 82° (lit.[13] 84–86°). Ir and nmr spectra were identical with those of unlabeled fluorenone.

9-Fluorenone hydrazone-α-^{13}C was prepared according to the procedure described by Wieland and Roseau.[14]

9-Diazofluorene-α-^{13}C was prepared by following the procedure of Closs, *et al.*[15]

Fluorenone anil *N*-oxide-α-^{13}C (4*) was prepared according to the procedure for the synthesis of **4** as described by Johnson.[16] A slurry of 383.2 mg of 9-diazofluorene-α-^{13}C (1.98 mmol) and 212 mg (1.98 mmol) of nitrosobenzene in 10 ml of dry ether was stirred for 1 hr. The mixture was filtered and the yellow crystals were recrystallized from 95% ethanol, mp 198–199° (lit.[16] mp 200°). Ir (CCl_4) exhibited a peak at 1270 cm^{-1} (N→O). The mass spectrum at 20 eV showed 52.6% excess ^{13}C.

Registry No.—**1**, 15263-58-8; **2**, 13355-65-2; **4**, 4535-09-5; biphenyl-2-carboxylic acid-α-^{13}C, 31504-46-8.

Acknowledgment.—We are grateful to Professor Edward C. Taylor for generous supplies of compounds **1** and **2**.

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(16) A. W. Johnson, *J. Org. Chem.*, **28**, 2153 (1963).

Nitration of Antibiotic X-537A and Facile Conversion to 6-Hydroxy-2,7-dimethyl-5-nitroquinoline

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The structure[1] and biosynthesis[2] of antibiotic X-537A (**1a**) have been reported recently. As part of a chemical study on this antibiotic, we have investigated the nitration of **1a** in glacial acetic acid. Treatment with 5 molar equiv of concentrated nitric acid gave the expected 5-nitro derivative **1b**. However, the major product was shown by base degradation to be dinitrophenol **1c**. This result was consistent with the observation[3] that nitration of highly substituted benzene

(1) (a) J. W. Westley, R. H. Evans, Jr., T. Williams, and A. Stempel, *Chem. Commun.*, 71 (1970); (b) S. M. Johnson, J. Herrin, S. J. Liu, and I. C. Paul, *ibid.*, 72 (1970).
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(3) H. Barbier, *Helv. Chim. Acta*, **11**, 157 (1928).