fact that only a few per cent of I is formed during the synthesis of II.

An independent confirmation of the structural assignment, based on nuclear magnetic resonance data, was obtained with a single-crystal structure determination. The methyl ester of the biologically active, low-melting isomer II could be crystallized and the structure was determined with the isomorphous replacement method. Crystal data and other details are summarized in the Experimental Section.

Figure 1 shows the electron-density map representing the projection of the crystal structure along the *c* axis. All atoms are resolved and it is clear that the C-2 atoms occupy the *trans* configuration with respect to the *p*-chlorophenyl ring. Also, the molecular conformation in the crystalline state, as viewed along the axis of projection, is consistent with the nmr results in solution; the plane of the *p*-chlorophenyl ring appears approximately normal to the plane of the indene ring.

Experimental Section

All nmr data reported here were obtained with a Varian Associates Model 4300B high-resolution spectrometer equipped with a superstabilizer and a phase detector and operating at 60 Mcps. All spectra were obtained with 5–10% (w/v) solutions in deuteriochloroform or deuterioacetone placed in a spinning Wilmad precision-bore tube. The resonance positions were determined relative to benzene as an external reference and scaled by the use of side bands[2] generated by a frequency counter calibrated Hewlett–Packard audio oscillator, Model 2000 CD. The chemical shifts were calculated with the equation $t = \Delta\nu/\nu^\circ + 3.50$,[3] where $\Delta\nu$ is the observed resonance displacement from benzene in cycles per second and ν° is the spectrometer frequency in megacycles. All data in Table I are converted to internal TMS as a reference.

Isolation of I from the original mother liquor solids of II was carried out as follows. Ten grams of the total mother liquor was dissolved in 100 ml of boiling absolute ethanol, and 50 ml of hot water was added until a slight turbidity occurred. When the solution was cooled slowly to 60–70°, 320 mg of crystals were separated by hot filtration. These crystals were recrystallized in 5 ml of boiling absolute ethanol, and 2 ml of hot water was added. When the solution was cooled slowly to *ca.* 50°, 190 mg of pure I was obtained. The purity of this material was determined by uv and nmr spectroscopy and by solubility analysis, which demonstrated it to be better than 99% pure.

Anal. Calcd for $C_{20}H_{17}O_3Cl$ (mol wt 340.81): C, 70.6; H, 5.0; Cl, 10.4. Found: C, 70.72; H, 5.11; Cl, 9.93.

Initial separation of the isomers I and II from a slightly impure (*ca.* 5%) sample of II was obtained by reverse-phase partition column chromatography. The column consisted of dichlorodimethylsilane (GE Dri-Film) treated silicic acid powder as carrier containing a 1:1 chloroform–isooctane stationary phase, through which flowed a mobile phase consisting of 65:35 methanol–water. The ratio of carrier to stationary phase was 0.5 ml/g. The column bed was 25 ml in diameter and *ca.* 0.5 m long. The sample was charged by dissolving 0.06 g in 2 ml of the stationary phase and letting this flow into the top of the column bed. Isomer I occurs first behind the liquid front followed by II. The effluent is easily monitored by uv spectroscopy and observation of the ratio of the 286- to 238-mμ absorptions. Although the chromatographic bands of I and II from the above column are not widely separated, fractionation of I and II is good enough for subsequent purification of the eluted material by simple crystallization from chloroform–petroleum ether. This method is slow and tedious but seems to be the only one which works with samples of II containing only small amounts (<10%) of I.

Single crystals of the methyl ester of low-melting form II, grown from methanol, are orthorhombic, with a = 22.12 Å, b = 17.36 Å, c = 4.71 Å; d_{obsd} = 1.26 g/cm³, d_{calcd} = 1.30 g/cm³; space group $P_{2_12_12_1}$ (from systematic absences), four molecules of $C_{21}H_{19}O_3Cl$ per unit cell. The structure is isomorphous with the corresponding bromo derivatives. The intensities of the hko reflections, necessary for the *c*-axis projection, were determined from Weissenberg photographs by visual estimation.

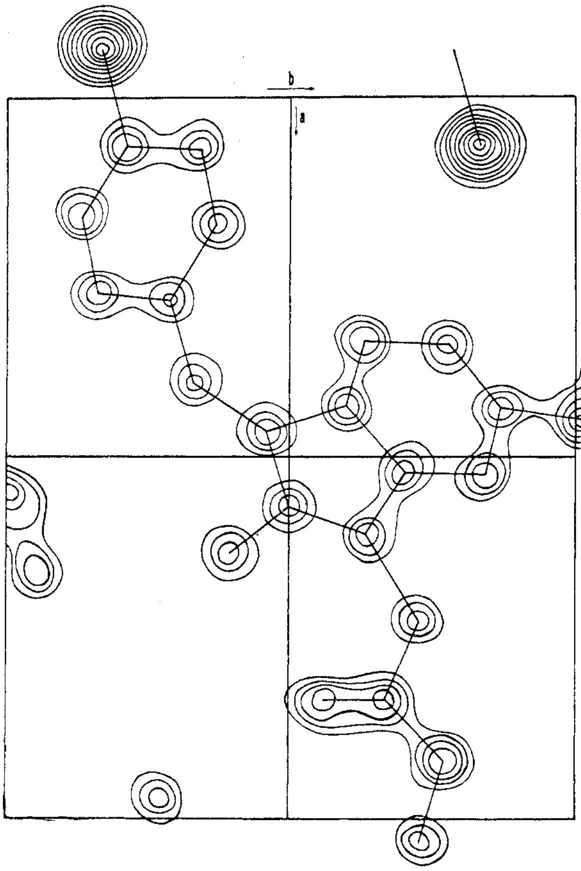

Figure 1.—Fourier synthesis of the electron-density projection along the direction of the *c* axis.

After the positions of the heavy atoms were determined with Patterson syntheses, the structure was solved in the usual way and refined by difference Fourier syntheses. The final Fourier synthesis is shown in Figure 1, and the final *R* factor is 0.145. A list of coordinates and structure factors is available from the authors on request.

Registry No.—I, 22287-03-2; II, 20754-69-2.

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[2] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

[3] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

A New Synthetic Route to Dibenzo[*b*,*h*]biphenylene and Its 5,6,11,12-Tetramethyl and -Tetraphenyl Derivatives

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Since the first[1] successful synthesis of I (R = H) was achieved, several alternative routes[2-4] to I (R = H) and

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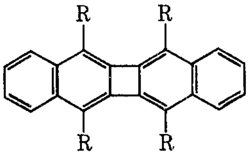
[1] R. F. Curtiss and G. Viswanath, *Chem. Ind.* (London), 1174 (1954); *J. Chem. Soc.*, 1670 (1959).

[2] E. R. Ward and B. D. Pearson, *ibid.*, 1676 (1959).

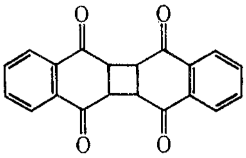
[3] E. R. Ward and B. D. Pearson, *ibid.*, 515 (1961).

[4] J. W. Barton and S. A. Jones, *ibid.*, 1276 (1967).

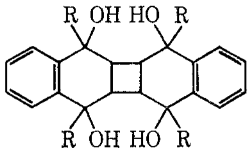
some of its derivatives[5,6] have been developed. These methods are, however, fairly laborious and mostly characterized by low overall yields.[1-3] The *syn* and *anti* photodimers[7] of 1,4-naphthoquinone, namely II and III, which are readily available and easily converted[6,7] into *lin*-binaphthylene derivatives I (R = OH, OCH_3, or $OCOCH_3$), contain carbon skeletons identical with that of I. Reduction with suitable reagents should furnish tetrahydroxy derivatives (IV, R = H, alkyl, or aryl), which should be convertible into I (R = H, alkyl, or aryl).



I



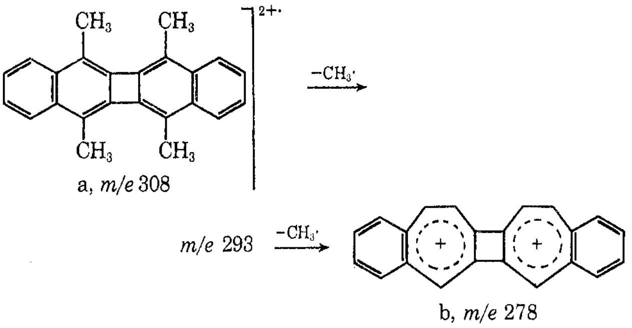
II, *syn*
III, *anti*



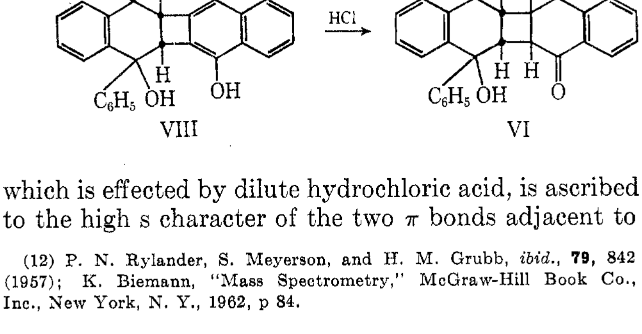
IV

The reaction of III with lithium aluminum hydride in tetrahydrofuran led in high yield to an amorphous, colorless product (IV, R = H) which contains no carbonilic groups and shows typical hydroxylic absorption in its infrared spectrum. Dehydration of IV (R = H), however, proceeded only under drastic conditions, leading mainly to undesired and unidentified products. Thus, with phosphoryl chloride in pyridine, the optimum yield of I (R = H) was 5%.

The reaction of III with methylmagnesium iodide, which was carried out according to a recently developed method[8] for highly insoluble substrates, proceeded smoothly, yielding crystalline IV (R = CH_3) practically quantitatively. The dehydration of IV (R = CH_3) is facilitated by the tertiary nature of the hydroxylic groups. Only one product, I (R = CH_3), which crystallized as golden yellow needles from benzene and analyzed for $C_{24}H_{20}$, was isolated in 40% yield from the reaction mixture. The relatively simple infrared spectrum displays the presence of methyl groups (2985, 2910,[9] and 1443 cm^{-1}). The characteristic olefinic absorption at 1612 cm^{-1} is probably due to the C=C stretching vibration of the localized double bonds, adjacent to the strained four-membered ring.[10,11] The ultraviolet spectrum of I (R = CH_3) corresponds to that of I (R = H),[1,2] differing only in position of the maxima, owing to a bathocromic shift caused by the methyl substituents. The mass spectrum of I (R = CH_3) is quite simple and shows, apart from the molecular ion (a, *m/e* 308), which is also the base peak, two prominent peaks at *m/e* 293 and 278, accompanied by two corresponding metastable peaks at *m/e* 279 and 264. The consecutive loss of two methyl radicals in the mass spectrometer most probably results in the formation of the dipositive ion b. To show[12] that the *m/e* 278 ion was probable dipositive ion b, the mass spectra of 1,2-, 2,3-, and 1,4-dimethylnaphthalene were investigated. In all cases a stable benzotropilium ion (*m/e* 141) was formed, confirming the correctness of the proposed fragmentation a → b. Treatment of I (R = CH_3) with 2,4,7-trinitro-9-fluorenone led to a deep red 1:2 adduct (V), which, when chromatographed in benzene solution over alumina, afforded I (R = CH_3).



When III was treated with an excess of phenylmagnesium bromide and the reaction mixture was treated with dilute hydrochloric acid, a colorless, crystalline product, which appeared to be VI, was obtained in 61% yield, showing that two carbonyl groups of III were retained. Compound VI was recovered after further treatment with phenylmagnesium bromide. Since steric shielding of the two "unchanged" carbonyl groups in the intermediate adduct VII seemed doubtful, the above reaction was repeated, and the reaction mixture was carefully decomposed with a quantity of hydrochloric acid equivalent to the amount of Grignard reagent used. In this case a tetrahydroxylated compound, VIII, was isolated, showing that enolization of VII, followed by proton exchange, probably led to the formation of IX. The ketonization of VIII to VI, which is effected by dilute hydrochloric acid, is ascribed to the high s character of the two π bonds adjacent to



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(5) C. D. Nenitzescu, M. Avram, I. G. Dinulescu, and G. Mateescu, *Ann.*, **653**, 79 (1962).

(6) J. M. Bruce, *J. Chem. Soc.*, 2782 (1962).

(7) J. Dekker, P. J. van Vuuren, and D. P. Venter, *J. Org. Chem.*, **33**, 464 (1968).

(8) J. Dekker and T. G. Dekker, *ibid.*, **33**, 2604 (1968).

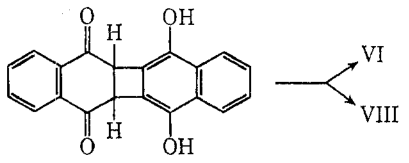
(9) The relatively high frequency of the C–H stretching vibration is ascribed to the high s character of the adjacent π bonds. This phenomenon is also encountered in the case of XV.

(10) D. P. Venter and J. Dekker, *J. Org. Chem.*, **34**, 2224 (1969).

(11) A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, **90**, 1357 (1968).

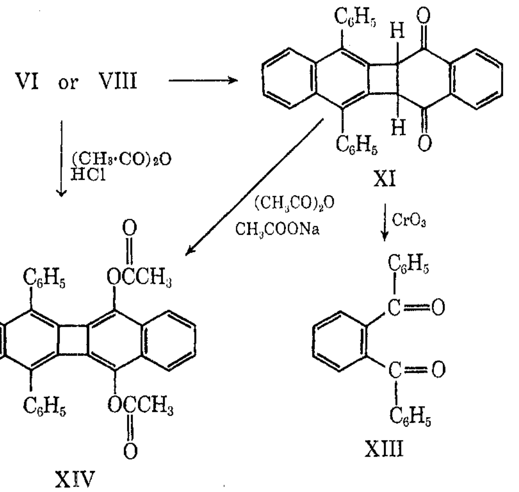
(12) P. N. Rylander, S. Meyerson, and H. M. Grubb, *ibid.*, **79**, 842 (1957); K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 84.

the strained four-membered ring.[10,11] Compounds VI and VIII were additionally synthesized by treatment of X,[10] the partially enolized derivative of II and III, with phenylmagnesium bromide.



X

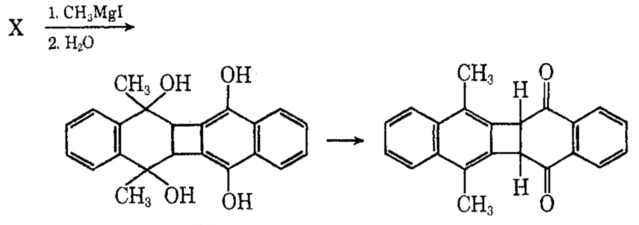
Both VI and VIII are readily dehydrated to XI. The infrared spectrum of XI illustrates typical, carbonilic absorption at 1685 cm^{-1}. The presence and position of the two carbonilic groups in XI was evidenced by the formation of the corresponding dihydrazone (XII) and oxidative degradation to *o*-dibenzoylbenzene (XIII). Acetylation of XI led to 1,4-diacetoxy-5,8-diphenyldibenzo[*b,h*]biphenylene (XIV). On the other hand, XIV was obtained directly simply by refluxing either VI or VIII in acetic anhydride containing a small amount of concentrated hydrochloric acid. The infrared spectrum of XIV shows strong absorption at 1205 and 1177 cm^{-1}, which is typical for phenolic acetates.[13] The spectral data obtained were consistent with the structure.



The reaction of III with phenyllithium led to an amorphous product. The latter was refluxed with acetic anhydride, whereupon three crystalline compounds, namely XIV (47% yield), 2,2′-di-1,4-naphthoquinonyl (5% yield), and an unidentified product, were obtained.

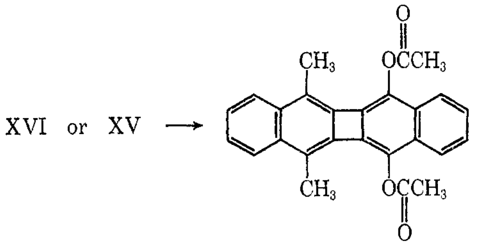
In order to obtain I (R = C_6H_5), the diketone XI was treated with excess phenylmagnesium bromide. The reaction mixture was decomposed with dilute hydrochloric acid and extracted with ether. The ether-soluble product was subsequently refluxed in a mixture of acetic anhydride and acetyl chloride, whereby orange-yellow needles of I (R = C_6H_5) were obtained in 28% yield.

The synthesis of the diketone XV was accomplished simply by treating X with methylmagnesium iodide, whereby a colorless crystalline product—which, by virtue of its typical hydroxylic absorption and the absence of carbonilic absorption in its infrared spectrum, was characterized as XVI—was obtained in 70% yield. Dehydration of XVI produced XV in 66% yield. The spectral data obtained were consistent with the structure. The ultraviolet spectrum closely resembles that of XI, showing broad maxima at 230 and 305 mμ. Further characterization was done by conversion of XV into its dihydrazone (XVII).



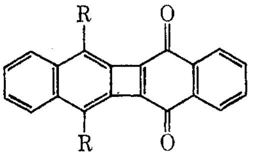
XVI XV

Acetylation of XV led to the formation of golden yellow needles of XVIII. The ultraviolet spectrum of XVIII resembles that of XIV, showing a small hypsochromic effect. Compound XVIII was additionally obtained by refluxing XVI in acetic anhydride containing hydrochloric acid. Furthermore, the reaction of XV with methylmagnesium iodide, followed by dehydration, led in good yield (35%) to the formation of I (R = CH_3).

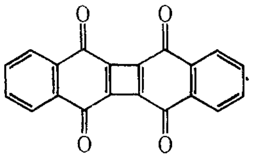


XVIII

The conversion of the diketones XI and XV into the naphtho[*b*]cyclobutadiene derivatives XIX (R = CH_3 or C_6H_5) is presently being investigated in order to obtain information regarding the stabilization of the cyclobutadiene derivative XX, which we aim to synthesize eventually.



XIX, R = CH_3 or C_6H_5



XX

Experimental Section

The following instruments were used for the recording of physical properties: a Perkin-Elmer Model 221 spectrophotometer, an Unicam SP 800 spectrophotometer, a M.S.9 mass spectrometer, and a Gallenkamp (design no. 889339) melting point apparatus. Melting points are uncorrected. Owing to the low solubilities of the various compounds, no nmr spectra could be obtained.[14]

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(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1959, p 152.

(14) After 400 scans on a saturated DMSO-d_6 solution of I (R = CH_3), weak aromatic signals (τ 2.62) were observed. The methyl bands could not be recorded because of the H_2O and d_5 impurity in the solvent. The CH_3 absorption was, however, recorded as a singlet (τ 7.38) in a single scan with CS_2 as solvent. This indicates that the methyl protons are benzylic. These spectra were recorded on a Varian HA-100 spectrometer and interpreted by Dr. Jim Feeney (Varian A. G., Klausstrasse 43, Zürich 8, Switzerland).

Dibenzo[*b*,*h*]biphenylene (I, R = H).—A suspension of III[7] (0.24 g) and $LiAlH_4$ (0.6 g) in sodium-dried THF (45 ml) was refluxed for 24 hr. The reaction mixture was concentrated to 15 ml and decomposed with 0.5 *N* hydrochloric acid. The insoluble product (IV, R = H) was filtered off and washed with water. A solution of the crude IV (R = H, 0.187 g) in pyridine (4 ml) and phosphoryl chloride (2 ml) was refluxed for 3 hr. The reaction mixture was treated carefully with water and extracted with hot benzene. The extract was washed with water, dried (Na_2SO_4), and chromatographed (alumina). Evaporation of the solvent yielded crystalline I (R = H, 0.01 g, 5%) as yellow plates, which sublimed at 342–345° (lit.[1] 340–345°); the infrared and ultraviolet spectra of I (R = H) were identical with the reported[1,2] spectra.

5,6,11,12-Tetramethyldibenzo[*b*,*h*]biphenylene (I, R = CH_3). A.—A solution of III[7] (0.5 g) in an excess of methylmagnesium iodide in ether (4.1 *M*, 16 ml) was stirred magnetically in a stoppered flask for 36 hr. The clear solution was carefully treated with excess 0.5 *N* hydrochloric acid. The reaction product (IV, R = CH_3) was filtered and washed with ether. A solution of IV (R = CH_3) in a mixture of acetic anhydride (15 ml) and acetyl chloride (2 ml) was refluxed for 5 hr and cooled. Compound I (R = CH_3) separated as yellow needles. A solution of I (R = CH_3) in hot benzene was chromatographed over alumina. Golden yellow needles of I (R = CH_3, 0.198 g, 40%) crystallized from the eluate, which sublimed at 333–340°: ν_{max}^{KBr} 3060 (w), 2986 (w), 2910 (w), 1611 (w), 1590 (w), 1512 (w), 1443 (w), 945 (w), 761 (s), and 750 cm^{-1} (s); $\lambda_{max}^{CH_2Cl\cdot CH_2Cl}$ ($\log \epsilon$) 286.5 (4.93), 299.5 (5.24), 335 (4.36), 364 (3.36), 370 (3.36), 383 (3.78), and 408 mμ (3.96); λ_{sh} ($\log \epsilon$) 315 (4.42) and 344 mμ (3.99); mass spectrum *m/e* 308 (molecular ion).

Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.70; H, 6.55.

A dilute solution in benzene exhibits a strong blue fluorescence.

B. The 2,4,7-Trinitro-9-fluorenone Complex (V) of I (R = CH_3).—A hot suspension of I (R = CH_3, 0.31 g) in benzene (350 ml) was treated with a solution of 2,4,7-trinitro-9-fluorenone (0.7 g) in benzene (100 ml), and the clear, deep red solution was concentrated to 75 ml and cooled. Deep red needles separated, and recrystallization from benzene yielded V (0.53 g, 54.7%), mp 250–252° dec.

Anal. Calcd for $C_{50}H_{30}O_{14}N_6$: C, 63.97; H, 3.22; N, 8.95. Found: C, 63.75; H, 3.11; N, 9.01.

A solution of V (0.2 g) in benzene was chromatographed over alumina. The yellow eluate was concentrated and cooled, and yellow needles (0.045 g, 69.2%) of I (R = CH_3) separated.

5b,6,11,11a-Tetrahydro-5,6,11,12-tetrahydroxy-6,11-diphenyldibenzo[*b*,*h*]biphenylene (VIII). A. From the *anti* Dimer III.—A solution of III[7] (4 g) in an excess of phenylmagnesium bromide in ether (2.5 *M*, 80 ml) was stirred magnetically in a stoppered flask for 36 hr. The reaction mixture was treated with 0.05 *N* hydrochloric acid (100 ml). The amorphous product was filtered off, washed with ether, and recrystallized from acetone, yielding colorless crystals (VIII, 4.18 g, 70%): mp 289–291°; ν_{max}^{KBr} 3540 (s), 3380–3350 (broad, s), 1382 (m), 1310 (s), 1170 (w), 1150 (w), 1110 (ms), 1001 (ms), 998 (ms), 863 (s), 769 (sh), 760 (s), 743 (w), 729 (ms), and 708 cm^{-1} (w); mass spectrum *m/e* 472 (molecular ion).

Anal. Calcd for $C_{32}H_{24}O_4$: C, 81.33; H, 5.11. Found: C, 81.14; H, 5.03.

B. From the Diol X.—A solution of X[10] (2 g) in sodium-dried THF (200 ml) was introduced dropwise (2 hr) to a solution of phenylmagnesium bromide in ether (2.5 *M*, 40 ml). The reaction mixture was refluxed (24 hr), concentrated (50 ml), and treated with ether (20 ml) and 0.06 *N* hydrochloric acid (50 ml). The water layer was separated and extracted twice with ether (100 ml). The combined organic extract was washed successively with 5% $NaHCO_3$ and 5% $Na_2S_2O_3$ and dried (Na_2SO_4). Evaporation to dryness afforded a solid, which was triturated with ether (10 ml) and filtered off. Recrystallization from acetone yielded VIII (1.79 g, 60%), and the product was identified by ir spectroscopy and melting point.

5,12-Diketo-5,5a,5b,6,11,11a,11b,12-octahydro-6,11-dihydroxy-6,11-diphenyldibenzo[*b*,*h*]biphenylene (VI). A. From the *anti* Dimer III.—A solution of III[7] (0.3 g) in an excess of phenylmagnesium bromide in ether (2.5 *M*, 9 ml) was stirred magnetically in a stoppered flask for 24 hr. The reaction mixture was decomposed as in procedure A for I (R = CH_3). The amorphous product was recrystallized from acetone, yielding colorless crystals of VI (0.34 g, 7.54%): mp 301.5–303° (blackening commencing at 247°); ν_{max}^{KBr} 3430–3400 (broad, s), 1678 (s), 1665 (s), 1599 (s), 1443 (ms), 1325 (s), 1298 (ms), 1262 (s), 1077 (m), 1061 (ms), 1031 (ms), 800 (w), 764 (s), 752 (ms), 746 (ms), and 722 cm^{-1} (ms).

Anal. Calcd for $C_{32}H_{24}O_4$: C, 81.33; H, 5.11. Found: C, 81.74; H, 5.06.

B. From the Diol X.[10]—The reaction was carried out as in procedure B for VIII. The reaction mixture was decomposed with 0.5 *N* hydrochloric acid instead of 0.06 *N* hydrochloric acid. Recrystallization of the crude product from acetone yielded VI (2.75 g, 75.3%). The product was identified by ir spectroscopy and melting point.

C. From the Adduct VIII.—A suspension of VIII (2 g) in ether (45 ml) was treated with 0.5 *N* hydrochloric acid (40 ml), and the mixture was shaken for 20 min. The insoluble product was filtered off and recrystallized from acetone, yielding VI (1.63 g, 81.5%), and the product was identified by ir spectroscopy and melting point.

5,12-Diketo-5,5a-11b,12-tetrahydro-6,11-diphenyldibenzo[*b*,*h*]-biphenylene (XI).—Concentrated hydrochloric acid (10 ml) was added to a boiling suspension of VI or VIII (0.5 g) in ethanol (70 ml). The reaction mixture was refluxed in the dark for 5 hr and cooled. Colorless needles of XI (0.14 g, 30.5%), which was recrystallized from ethanol, separated: mp 238.5–239.5°; ν_{max}^{KBr} 1685 (s), 1593 (m), 1291 (s), 798 (w), 788 (w), 774 (s), 770 (sh), 751 (s), 731 (m), and 697 cm^{-1} (s); λ_{max}^{EtOH} ($\log \epsilon$) 229 (4.75), 236 (4.75), and 305 mμ (4.13); λ_{sh} ($\log \epsilon$) 378 mμ (2.91); mass spectrum *m/e* 436 (molecular ion).

Anal. Calcd for $C_{32}H_{20}O_2$: C, 88.05; H, 4.62. Found: C, 88.15; H, 4.66.

5,12-Diketo-5,5a,11b,12-tetrahydro-6,11-diphenyldibenzo[*b*,*h*]-biphenylenedihydrazone (XII).—A boiling solution of XI (0.2 g) in ethanol (40 ml) was treated with 80% hydrazine hydrate (2 ml). After 1 hr, colorless needles of the dihydrazone (XII, 0.178 g, 83.6%) separated. The product was filtered off and recrystallized from ethanol: mp 252–254° dec (darkening commencing at 225°); ν_{max}^{KBr} 3380 (m), 3215 (m), 1625 (w), 1584 (m), 1488 (w), 760 (sh), 750 (s), and 697 cm^{-1} (s); mass spectrum *m/e* 464 (molecular ion).

Anal. Calcd for $C_{32}H_{24}N_4$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.87; H, 5.24; N, 12.02.

Oxidative Degradation of XI to *o*-Dibenzoylbenzene (XIII).—A solution of chromium trioxide (0.5 g) in 50% acetic acid (3 ml) was added to a solution of XI (0.2 g) in acetic acid (3 ml). The reaction mixture was refluxed (5 hr), cooled, and treated with excess water (200 ml). The precipitate was filtered off, washed with water, and recrystallized from ether, yielding XIII (0.11 g, 90%): mp 148° (lit.[15] mp 148°). The infrared spectrum was identical with that of an authentic sample of XIII.

5,12-Diacetoxy-6,11-diphenyldibenzo[*b*,*h*]biphenylene (XIV). A. From the Adducts VI and VIII.—A solution of VI or VIII (0.234 g) in acetic anhydride (5 ml) and concentrated hydrochloric acid (0.5 ml) was refluxed for 3 hr. The solution was concentrated (2 ml), whereupon yellow needles separated. Recrystallization from benzene yielded bright yellow needles of XIV (0.18 g, 83.3%): mp 318.5–321° (darkening commencing at 270°); ν_{max}^{KBr} 1784 (s), 1628 (w), 1514 (m), 1491 (m), 1382 (m), 1355 (s), 1205 (s), 1175 (s), 1100 (m), 783 (sh), 773 (s), 761 (sh), 751 (s), 748 (sh), and 717 cm^{-1} (m); $\lambda_{max}^{CH_2Cl\cdot CH_2Cl}$ ($\log \epsilon$) 302.5 (5.06), 338 (4.28), 385 (3.60), and 409 mμ (3.75); λ_{sh} ($\log \epsilon$) 290 (4.79), 364 (3.49), 370 (3.35), and 400 mμ (2.95); mass spectrum *m/e* 520 (molecular ion).

Anal. Calcd for $C_{36}H_{24}O_4$: C, 83.06; H, 4.65. Found: C, 83.15; H, 4.69.

B. From the Diketone XI.—A mixture of XI (0.3 g), acetic anhydride (15 ml), and anhydrous sodium acetate (0.3 g) was refluxed for 8 hr and cooled. The crystalline product was filtered off, washed successively with acetic acid and water, dried, and recrystallized from benzene, yielding XIV (0.29 g, 81.3%), and the product was identified by ir spectroscopy and melting point.

The Reaction of the *anti* Dimer III with Phenyllithium.—A solution of III[7] (0.5 g) in an excess of phenyllithium in ether (1.7 *M*, 18 ml) was stirred magnetically in a stoppered flask for 36 hr. The reaction mixture was carefully treated with 0.5 *N* hydrochloric acid (40 ml), and the precipitate was filtered off and washed with water. A solution of the crude product (0.33 g) in acetic anhydride (15 ml) was refluxed for 3 hr and cooled. From the cooled solution two crystalline products, namely 2,2′-

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(15) H. Simonis and P. Remmert, *Chem. Ber.*, **48**, 208 (1915).

di-1,4-naphthoquinonyl (0.025 g, 5%) and an unidentified, colorless product (0.026 g, mp >350°), which was separated by fractional crystallization from benzene, were obtained. The mother liquor was concentrated to 5 ml, whereupon yellow needles of XIV (0.163 g, 47.2%) were obtained. Products were identified by ir spectroscopy and melting point.

5,6,11,12-Tetraphenyldibenzo[*b*,*h*]**biphenylene (I, R = C_6H_5).**—A solution of XI (0.5 g) in an excess of phenylmagnesium bromide in ether (2.5 *M*, 20 ml) was stirred magnetically in a stoppered flask for 24 hr. The reaction mixture was decomposed with 0.5 *N* hydrochloric acid (60 ml) and extracted with ether (50 ml). The extract was washed successively with 5% $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated to 2 ml. Acetic anhydride was added and the solution was concentrated to 5 ml. Phosphoryl chloride (0.5 ml) was added and the reaction mixture was refluxed for 4 hr and cooled. Orange-yellow crystals of I (R = C_6H_5, 0.19 g, 29.8%) separated: mp >350° (lit.[5] mp >350°); the ir and uv spectra are identical with the reported[5] spectra.

The Reaction of the Diol X with Methylmagnesium Iodide.—A solution of X[10] (2.047 g) in sodium-dried THF (200 ml) was added over a period of 2 hr to a solution of methylmagnesium iodide in ether (4.1 *M*, 40 ml). The reaction mixture was treated as in procedure B for VIII. Recrystallization of the crude product from ether yielded XVI (1.58 g, 70.1%): mp 298–301° (darkening commencing at 260°); ν_{max}^{KBr} 3450–3350 (s), 1654 (m), 1646 (m), 1387 (ms), 1310 (s), 1173 (s), 1090 (ms), 1049 (ms), 1025 (ms), 993 (s), 950 (ms), 765 (s), 760 (s), 755 (s), 740 (ms), and 702 cm^{-1} (m).

5,12-Diketo-5,5a,11b,12-tetrahydro-6,11-dimethyldibenzo[*b*,*h*]**biphenylene (XV).**—Concentrated hydrochloric acid (15 ml) was added to a boiling solution of XVI (1.05 g) in ethanol (100 ml). The reaction mixture was refluxed for 3 hr. Yellow crystals started separating after 20 min. Recrystallization from ethanol yielded XV (0.63 g, 66.6%): mp 221–223°; ν_{max}^{KBr} 1685 (sh), 1679 (s), 1625 (w), 1590 (m), 1292 (s), 1230 (s), 920 (s), 790 (ms), 768 (sh), 753 (s), 722 (s), and 705 cm^{-1} (w); λ_{max}^{EtOH} (log ϵ) 237.5 (4.67), 281 (3.89), and 292 mμ (3.89); mass spectrum *m/e* 312 (molecular ion).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.75; H, 5.13.

5,12-Diketo-5,5a,11b,12-tetrahydro-6,11-dimethyldibenzo[*b*,*h*]**biphenylenedihydrazone (XVII).**—A mixture of XV (0.066 g), ethanol (70 ml), and 80% hydrazine hydrate (1 ml) was treated as in the procedure for XII. The colorless product was recrystallized from ethanol, yielding XVII (0.066 g, 92.3%): mp 286–287° (darkening commencing at 275°); ν_{max}^{KBr} 3325 (s), 3192 (ms), 1625 (w), 1391 (w), 791 (m), 770 (s), 748 (s), 730 (m), 720 (m), and 708 cm^{-1} (m); mass spectrum *m/e* 340 (molecular ion).

Anal. Calcd for $C_{22}H_{20}N_4$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.32; H, 5.85; N, 16.36.

5,12-Diacetoxy-6,11-dimethyldibenzo[*b*,*h*]**biphenylene (XVIII). A. From the Diketone XV.**—A mixture of XV (0.5 g), acetic anhydride (15 ml), and anhydrous sodium acetate (0.2 g) was treated as in procedure B for XIV. The golden yellow needles were recrystallized from benzene, yielding XVIII (0.51 g, 81.5%): sublimed with melting at 302–305°; ν_{max}^{KBr} 1755 (s), 1383 (m), 1346 (m), 1215 (s), 1188 (m), 1159 (ms), 1090 (m), 1059 (m), 792 (w), 760 (s), 755 (s), and 727 cm^{-1} (w); $\lambda_{max}^{CH_2Cl \cdot CH_2Cl}$ (log ϵ) 264 (4.14), 286 (4.88), 298.5 (5.22), 334 (4.38), 364 (3.37), 283 (3.62), and 408 mμ (3.80); λ_{sh} (log ϵ) 316 mμ (4.39); mass spectrum *m/e* 396 (molecular ion).

Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.86; H, 5.16.

B. From the Adduct XVI.—A solution of XVI (0.5 g) in acetic anhydride (15 ml) and concentrated hydrochloric acid (2 ml) was treated as in procedure A for XIV. The golden yellow crystals were recrystallized from benzene, yielding XVIII (0.21 g, 36.6%), and the product was identified by ir spectroscopy and melting point.

5,6,11,12-Tetramethyldibenzo[*b*,*h*]**biphenylene (I, R = CH_3) from the Diketone XV.**—A solution of XV (0.5 g) in an excess of methylmagnesium iodide in ether (4.1 *M*, 12 ml) was treated as in procedure A for I (R = CH_3). A solution of the resulting product in acetic anhydride (5 ml) and acetyl chloride (0.5 ml) was refluxed for 5 hr and cooled. Compound I (R = CH_3, 0.173 g, 35%) separated as yellow needles, and the product was identified by ir spectroscopy and melting point.

Registry No.—I (R = H), 258-47-9; I (R = CH_3), 22286-70-0; V, 22319-39-7; VI, 22286-71-1; VIII, 22286-72-2; XI, 22286-73-3; XII, 22286-65-3; XIV, 22319-40-0; XV, 22319-41-1; XVI, 22286-66-4; XVII, 22286-67-5; XVIII, 22286-68-6.

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Oxidative Acylation. A New Reaction of Primary Nitro Compounds

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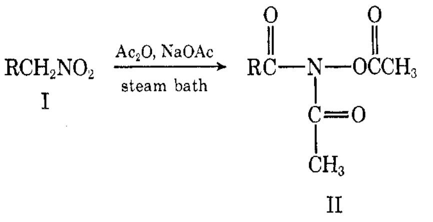
In the course of structure proof of miserotoxin,[2] we discovered a new reaction of primary nitro compounds which is exemplified by the following reaction scheme.



$$RCH_2NO_2 \xrightarrow[\text{steam bath}]{Ac_2O,\ NaOAc} RC(=O)-N(C(=O)CH_3)-OC(=O)CH_3$$

a, R = CH_2CH_3
b, R = CH_3

Thus, to 100 ml of acetic anhydride was added 22.3 g of Ia and 10.0 g of fused sodium acetate. The mixture was heated on a steam bath for 8 hr, during which time it became emerald green in color. The solution was then shaken with a chloroform–water mixture, sodium carbonate was carefully added to the aqueous layer, the mixture was again shaken, and the layers were separated. The chloroform layer was washed with water and dried over sodium sulfate, and the chloroform was removed by distillation. The remaining oil was distilled *in vacuo* and 29.8 g (70%) of IIa (bp 64–65° at 1 mm) was collected. The structure of IIa was chiefly assigned by the data below and also in analogy with the preparation of IIb, a previously known compound whose structure was proven[3] chemically.

Anal. Calcd for $C_7H_{11}NO_4$ (IIa): C, 48.55; H, 6.36; N, 8.08. Found: C, 48.53; H, 6.63; N, 7.90. The following spectral data were obtained: ir 1800 (strong, -CONOCO-), 1720–1710 cm^{-1} (strong, broad, -CONRCO-); nmr (parts per million from TMS) 1.11 (triplet, 3 H, CH_3CH_2), 2.68 (quartet, 2 H, CH_3CH_2), 2.28 (singlet, 3 H, $CH_3C{=}O$), 2.38 (singlet, 3 H, $CH_3C{=}$

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[1] National Aeronautics and Space Administration Predoctoral Fellow.

[2] F. R. Stermitz, F. A. Norris, and M. C. Williams, *J. Amer. Chem. Soc.*, **91**, 4599 (1969).

[3] T. Urbanski, *J. Chem. Soc.*, 3374 (1949).