

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<sub>6</sub>H<sub>5</sub>).**—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<sub>3</sub> and water, dried (Na<sub>2</sub>SO<sub>4</sub>), 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<sub>6</sub>H<sub>5</sub>, 0.19 g, 29.8%) separated: mp >350° (lit.<sup>5</sup> mp >350°); the ir and uv spectra are identical with the reported<sup>5</sup> spectra.

**The Reaction of the Diol X with Methylmagnesium Iodide.**—A solution of X<sup>10</sup> (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°);  $\nu_{\text{max}}^{\text{KBr}}$  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<sup>-1</sup> (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°;  $\nu_{\text{max}}^{\text{KBr}}$  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<sup>-1</sup> (w);  $\lambda_{\text{max}}^{\text{EtOH}}$  (log  $\epsilon$ ) 237.5 (4.67), 281 (3.89), and 292 m $\mu$  (3.89); mass spectrum *m/e* 312 (molecular ion).

*Anal.* Calcd for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>: 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°);  $\nu_{\text{max}}^{\text{KBr}}$  3325 (s), 3192 (ms), 1625 (w), 1391 (w), 791 (m), 770 (s), 748 (s), 730 (m), 720 (m), and 708 cm<sup>-1</sup> (m); mass spectrum *m/e* 340 (molecular ion).

*Anal.* Calcd for C<sub>22</sub>H<sub>20</sub>N<sub>4</sub>: 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°;  $\nu_{\text{max}}^{\text{KBr}}$  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<sup>-1</sup> (w);  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{Cl}}$  (log  $\epsilon$ ) 264 (4.14), 286 (4.88), 298.5 (5.22), 334 (4.38), 364 (3.37), 283 (3.62), and 408 m $\mu$  (3.80);  $\lambda_{\text{sh}}$  (log  $\epsilon$ ) 316 m $\mu$  (4.39); mass spectrum *m/e* 396 (molecular ion).

*Anal.* Calcd for C<sub>26</sub>H<sub>20</sub>O<sub>4</sub>: 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<sub>3</sub>) 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<sub>3</sub>). 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<sub>3</sub>, 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<sub>3</sub>), 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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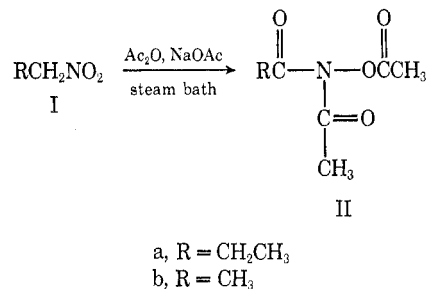
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In the course of structure proof of miserotoxin,<sup>2</sup> we discovered a new reaction of primary nitro compounds which is exemplified by the following reaction scheme.



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<sup>3</sup> chemically.

*Anal.* Calcd for C<sub>7</sub>H<sub>11</sub>NO<sub>4</sub> (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<sup>-1</sup> (strong, broad, –CONRCO–); nmr (parts per million from TMS) 1.11 (triplet, 3 H, CH<sub>3</sub>CH<sub>2</sub>), 2.68 (quartet, 2 H, CH<sub>3</sub>CH<sub>2</sub>), 2.28 (singlet, 3 H, CH<sub>3</sub>C=O), 2.38 (singlet, 3 H, CH<sub>3</sub>C=O).

(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).

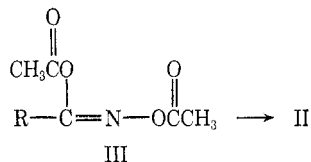
(3) T. Urbanski, *J. Chem. Soc.*, 3374 (1949).

O); mass spectrum (*m/e*, rel intensity) 173, 1 ( $M^+$ ), 57, 60 ( $CH_3CH_2CO^+$ ), 43, 100 ( $CH_3CO^+$ ), no other peaks above 2% relative intensity.

Treatment of Ib in the same manner yielded IIb, corresponding in properties to IIb prepared<sup>3</sup> by Urbanski. A similar derivative was prepared in high yield from miserotoxin.<sup>2</sup>

The key to high yield preparation of II compounds (which can be considered as *N*-acyloxymides or triacylhydroxylamines) is the use of steam-bath heat rather than reflux, as used by Urbanski.<sup>3</sup> Thus, Urbanski isolated only IIb as the main product, no matter what R was present in I. Indeed, we found that, if the reaction mixture is heated to reflux, a self-sustaining exothermic reaction takes place which results in complete conversion of all II compounds into IIb. The II derivatives are excellent for mass spectral studies since the  $RC=O^+$  fragment is readily formed and this provides a handle for interpretation.

The mechanism of this reaction is obviously complex and must involve several steps. The clearest step of the reaction is likely to be the last one, which is probably a 1,3-acyl migration from III. At the present



there is no way of choosing between several ways<sup>3</sup> of arriving at III. However, elucidation of the mechanism may well have a bearing on a known rearrangement<sup>4</sup> of cyclic nitro ketones.

**Registry No.**—IIa, 22427-07-2.

(4) H. O. Larson and E. K. W. Wat, *J. Amer. Chem. Soc.*, **85**, 827 (1963); A. Hassner and J. Larkin, *ibid.*, **85**, 2181 (1963).

## Photochemical Synthesis of Aromatic Chloro Compounds from Aromatic Iodo Compounds<sup>1</sup>

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The photodecomposition of aromatic iodo compounds has long been known, but only recently has this process been used for synthetic purposes. Thus, photolysis of aromatic iodides has led to syntheses of biphenyls, phenanthrenes, and organophosphorus and organoboron compounds, all in acceptable yields.<sup>3</sup>

Aromatic iodo compounds are now readily accessible from a wide variety of aromatic hydrocarbons through initial thallation with thallic trifluoroacetate followed by treatment with aqueous potassium iodide,<sup>4</sup> and we

(1) We gratefully acknowledge partial financial support of this work by the Smith Kline and French Laboratories, Philadelphia, Pa.

(2) NRCC Postdoctoral Fellow, 1968-1970.

(3) For a review, see R. K. Sharma and N. Kharasch, *Angew. Chem.*, **80**, 69 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 36 (1968).

(4) A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor, and G. McGillivray, *Tetrahedron Lett.*, 2427 (1969).

were therefore interested in exploring further their potential as synthetic intermediates.

We have found that irradiation of dilute solutions of aromatic iodo compounds in carbon tetrachloride with 3000-Å light leads to formation of the corresponding chloro compounds. Replacement of an iodo substituent by chlorine using iodine monochloride as the chlorine donor is known to take place on irradiation with visible light,<sup>5</sup> but the only reported use of carbon tetrachloride as a chlorine donor is in the formation of 4-chlorobiphenyl from 4-iodobiphenyl.<sup>6</sup> Exchange of chlorine for iodine takes place cleanly without contamination by positional isomers. In most cases irradiation for 5 hr was sufficient to effect a 70-75% conversion into the chloro compound, although actual yields were higher because of recovery of unchanged starting material. Longer reaction times were avoided because of possible complications involving reactions with the iodine liberated in the course of the photolysis. Within a given period of time, percentage conversion of the aromatic iodide into the corresponding chloride was (compared with iodobenzene) greater for compounds with electron-donating substituents; the electron-withdrawing carboxyl group, for example, considerably slowed the reaction<sup>7</sup> and substantial amounts of unreacted *o*-iodobenzoic acid could be recovered.

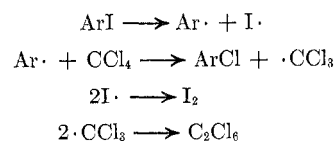
Representative results are summarized in Table I.

TABLE I  
PHOTOLYSIS OF AROMATIC IODO COMPOUNDS IN  
CARBON TETRACHLORIDE

Substrate	% yield of corresponding chloro compound <sup>a</sup>
Iodobenzene	76 <sup>b</sup>
2-Iodotoluene	60
2-Iodoanisole	78
4-Iodoanisole	96
2-Iodophenol	80
1,4-Dimethyl-2-iodobenzene	75
2-Iodophenylacetic acid	81
3-(4-Iodophenyl)butanoic acid	78
4-(4-Iodophenyl)butanoic acid	87
3-(4-Iodophenyl)propanoic acid	76
2-Iodobenzoic acid	51

<sup>a</sup> Based on recovered starting material and determined by glpc. Identity of products was confirmed by melting point, spectral analysis, and/or chromatographic means. <sup>b</sup> Irradiated for 8 hr.

In accordance with the generally accepted mechanism for photodecomposition of iodo compounds, we suggest the following reaction scheme to account for our results.



Hexachloroethane could be isolated from the photolyses in yields up to 5%, in agreement with the above suggested reaction pathway.

Irradiation of 2-iodotoluene and 1,4-dimethyl-2-iodobenzene gave, in addition to the product of halogen

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(6) N. Kharasch, R. K. Sharma, and M. Hussain, unpublished results; see ref 60 in ref 3.

(7) W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).