Syntheses and Diels–Alder Reactions of Two Dimethyl 10-Methoxyanthryl Phosphates

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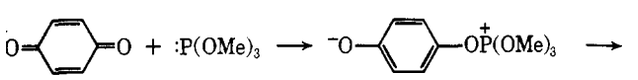
Dimethyl 10-methoxy-9-anthryl phosphate (**3**) and dimethyl 4,5-dichloro-10-methoxy-9-anthryl phosphate (**5**) were synthesized by treating anthraquinone and 1,8-dichloroanthraquinone with trimethyl phosphite. The structure of **5** was shown by its conversion into 1,8-dichloro-9-anthrone on treatment with a hydriodic acetic acid mixture and by its formation of 4,5-dichloro-10-methoxyanthrone in aqueous sodium hydroxide. The formation of **5** indicates that steric rather than electronic factors controlled the initial nucleophilic attack of phosphite on the unsymmetrical 1,8-dichloroanthroquinone. The acid cleavage showed that the ether link was cleaved more rapidly than that of an anthryl phosphate. Both **3** and **5** condensed readily with maleic anhydride to give adducts whose nmr spectra showed the phosphoryl methoxy doublet was further split by a long range action of an asymmetric environment. Reductive cleavage of these adducts with hydriodic acid gave (10-keto-9,10-dihydro-9-anthryl)succinic acid. In a similar fashion (1,8-dichloro-10-keto-9,10-dihydro-9-anthryl)succinic acid was prepared from 1,8-dichloro-9-methoxyanthracene. The condensation of acrylic acid with **5** and the condensation of acrylic acid and acrylonitrile with 1,8-dichloro-9-methoxyanthracene gave adducts in which the carboxyl or nitrile group was shown to be vicinal to the ether group.

Methyl Phosphite-Quinone Condensations.—Trimethyl phosphite has been reported[2] to react with *p*-benzoquinone and symmetrically substituted *p*-benzoquinones to yield dimethyl *p*-methoxyaryl phosphates. The pathway proposed involves nucleophilic attack of phosphite at the carbonyl center to form an intermediate quaternary phosphonium salt, **1**, which undergoes intermolecular methyl group transfer to form the product, **2**.[2a] The driving force in this reaction is due to the formation of a P–O bond and the resonance stabilization of a benzene ring.



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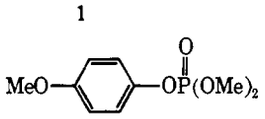
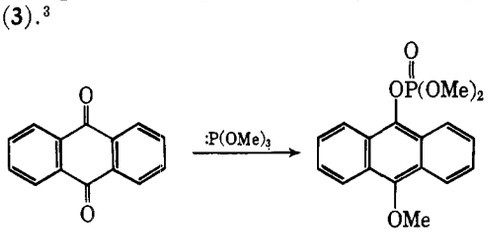


2

Since the reaction had not been reported for anthraquinones or unsymmetrically substituted quinones and the reaction with anthraquinones would lead to 9,10-disubstituted anthracenes that would be of interest to us as dienes in orientation studies in the Diels–Alder reaction, the extension of the quinone–phosphite condensation was investigated.

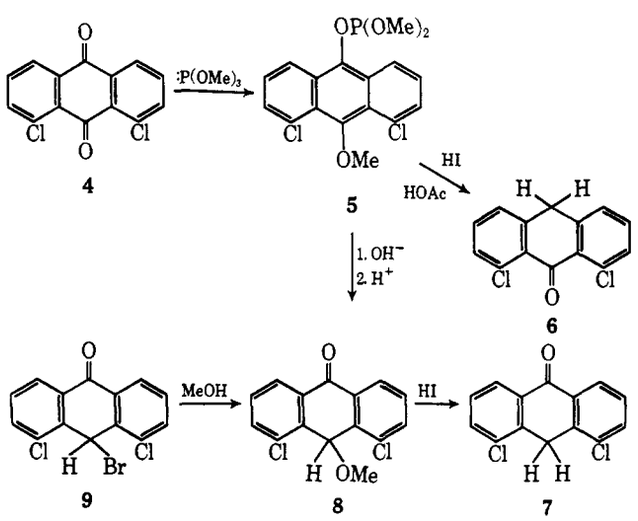
The resonance energy released in condensing anthraquinone with methyl phosphite would be less than that with a *p*-benzoquinone, but anthraquinone reacted readily to give dimethyl 10-methoxy-9-anthryl phosphate (**3**).[3]



3

1,8-Dichloroanthraquinone was chosen as an unsymmetrically substituted quinone. Theoretically it could lead to two different phosphates. Since chloranil is reported[2b] to react more vigorously than *p*-benzoquinone, one might expect attack to occur more readily on the 9-carbonyl group, but if steric factors play a significant part, then the less-hindered 10-carbonyl group would form the phosphate linkage.

The phosphite reaction appeared to proceed more readily with quinone **4** than with anthraquinone as judged by the more rapid development of a red color,[4] but this may be due to the greater solubility of **4** in trimethyl phosphite, since it is the lower melting of the two quinones. A crystalline dimethyl dichloro-10-methoxy-9-anthryl phosphate (**5**) was isolated. Only traces of a second isomer were detected in an nmr spectrum of the mother liquor. In order to prove conclusively the position of the chlorine atoms, compound **5** was hydrolyzed under acidic and basic conditions. When the phosphate was refluxed in a hydriodic–acetic acid mixture, 1,8-dichloro-9-anthrone (**6**) was formed.



4 **5** **6** **9** **8** **7**

This anthrone was obtained by Barnett and Matthews from the reduction of quinone **4** by aluminum powder in concentrated sulfuric acid.[5] Since chlorine atoms *ortho* to a carbonyl group should protect it from

(1) National Institutes of Health, Predoctoral Fellow, 1965–1967.

(2) (a) F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.*, **81**, 587 (1959); (b) F. Ramirez, E. H. Chen, and S. Dershowitz, *ibid.*, 4338 (1959).

(3) After this paper was submitted the preparation of **3** was reported by F. Ramirez, S. B. Bhatia, A. V. Patwardhan, E. H. Chen, and C. P. Smith [*J. Org. Chem.*, **33**, 20 (1968)].

(4) A transient red color was noted previously in this sort of reaction and was ascribed to a charge transfer complex.[2b] Later work indicates phosphonium substituted semiquinones may be involved: E. A. C. Leuchen, *J. Chem. Soc.*, 5123 (1963). For a discussion of the subject see R. F. Hudson, "Structure and Mechanisms in Organophosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, p 188.

(5) E. B. Barnett and M. A. Matthews, *J. Chem. Soc.*, 123, 2549 (1923).

reduction, they felt that isomer **6** was the more likely structure. Later, they and Cook[6] prepared the isomeric anthrone **7** from 1,8-dichloroanthracene by a six-step synthesis where the structure assigned the key intermediate was logical but not rigorously proven.

However, their assignments of structures for the two isomers are correct and **6** and **7** can be distinguished by nmr spectroscopy since *peri* protons on anthracene and naphthalene derivatives are deshielded by substituents *peri* to them.[7] An nmr spectrum ($CDCl_3$) of 4,5-dichloro-9-anthrone (**7**) exhibited a quartet at 8.15–8.3, a complex multiplet at 7.25–8.00 and a sharp singlet at 4.12 ppm for the two *peri*-aromatic protons, the remaining aromatic protons, and the two methylene protons, respectively. The downfield quartet is characteristic of anthrone derivatives having protons *peri* to a carbonyl group and are absent in derivatives having halo substituents in these positions. The quartet results from coupling of the *peri*-hydrogen nuclei with aromatic protons *ortho* and *meta* to them.

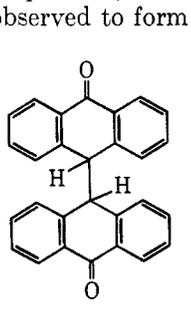
An nmr spectrum of 1,8-dichloro-9-anthrone (**6**) showed only a narrow multiplet at 7.2–7.45 ppm for the six aromatic hydrogen nuclei and a singlet at 4.16 ppm for the two methylene hydrogen nuclei.

Compound **5**, after heating in 20% aqueous sodium hydroxide solution gave, after acidification, a nearly quantitative yield of 4,5-dichloro-10-methoxyanthrone (**8**) previously prepared by methanolysis of 4,5-dichloro-10-bromoanthrone (**9**).[8] An nmr spectrum of compound **8** ($CDCl_3$) exhibited the quartet characteristic of *peri*-deshielded aromatic hydrogen nuclei.

This basic cleavage establishes the structure of phosphate **5** and shows that the hydriodic acid cleaves the methyl ether group faster than it hydrolyzes the phosphate anthryl linkage. If the reverse were true or the rates were equivalent, then anthrone **7** would have been formed.

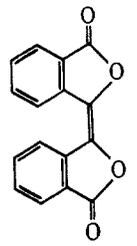
Treatment of compound **8** with hydriodic acid provides a ready route to **7** and the phosphite addition appears to open routes for the selective reduction of either carbonyl group in a 1,8-disubstituted anthraquinone.

In addition to phosphate **4**, a small amount of bianthronyl, **10**, was observed to form in the reaction of



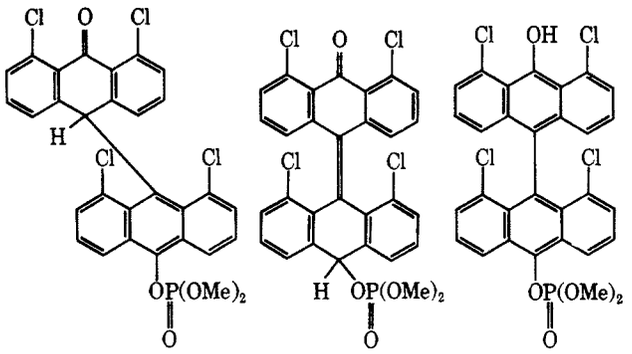
10

anthraquinone with trimethyl phosphite. The only other product observed was trimethyl phosphate. Although nmr analysis of the trimethyl phosphite used showed the presence of only a small amount of trimethyl phosphate as an impurity, it is felt that the large amount observed in the crude product mixture could have formed from air oxidation as well as oxygen abstraction during the reductive coupling of anthraquinone to bianthronyl in the presence of some moisture. A reductive coupling of dibenzoylethylene in ethanolic triethyl phosphite is known to give *meso*-1,2,3,4-tetrabenzoylbutane,[3c,9] and phthalic anhydride is known to be converted into biphthalyl (**11**) by trimethyl phosphite.[10]



11

In the reaction of 1,8-dichloroanthraquinone with trimethyl phosphite to give compound **5**, a high melting phosphate, **12**, was found which was hard to separate from still another by-product, which was probably a tetrachlorobianthronyl. The analysis of the phosphate was consistent with structures **12**, **12a**, and **12b**. The infrared spectrum revealed a carbonyl group which ruled out structure **12b**. The nmr spectrum showed a singlet at 5.12 ppm not split by a ^{31}P nucleus which is consistent with structure **12** and not **12a**. The positions of the chlorine atoms were assigned in part on the basis that the nmr spectrum did not show *peri* protons deshielded by a carbonyl group and in part on the basis that trimethyl phosphite attacked an unhindered carbonyl group in the formation of **5**.



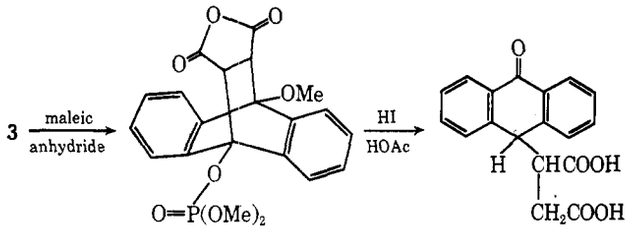
12 **12a** **12b**

Diels–Alder Reactions.—Maleic anhydride condensed readily with phosphates **3** and **5** to give adducts whose nmr spectra indicated normal addition at the 9,10 positions of the anthracene had occurred, since no bridgehead protons could be found. The spectra of the adducts revealed that the methyl groups in the phosphate ester moiety were not equivalent and they appeared as two doublets in contrast to the single doublet of the starting phosphates. This is an example of diasteromeric methyl groups and examples have been reported before.[11] It is due to ring currents of the aromatic rings and carbonyl groups having an asymmetric effect on the methyl protons rather than being

(6) E. B. Barnett, J. Cook, and M. A. Matthews, *Rec. Trav. Chim. Pays-Bas*, **45**, 68 (1926).
(7) V. Balasubramaniyan, *Chem. Rev.*, **66**, 578 (1966).
(8) E. B. Barnett, N. F. Goodway, and J. Wiltshire, *Ber.*, **63B**, 1690 (1930).
(9) R. H. Harvey and E. V. Jensen, *Tetrahedron Lett.*, 1801 (1963).
(10) F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Amer. Chem. Soc.*, **83**, 173 (1961).
(11) T. H. Siddall, III, and C. A. Prohaska, *ibid.*, **84**, 3467 (1962).

due to restricted rotation in the dimethylphosphato group.

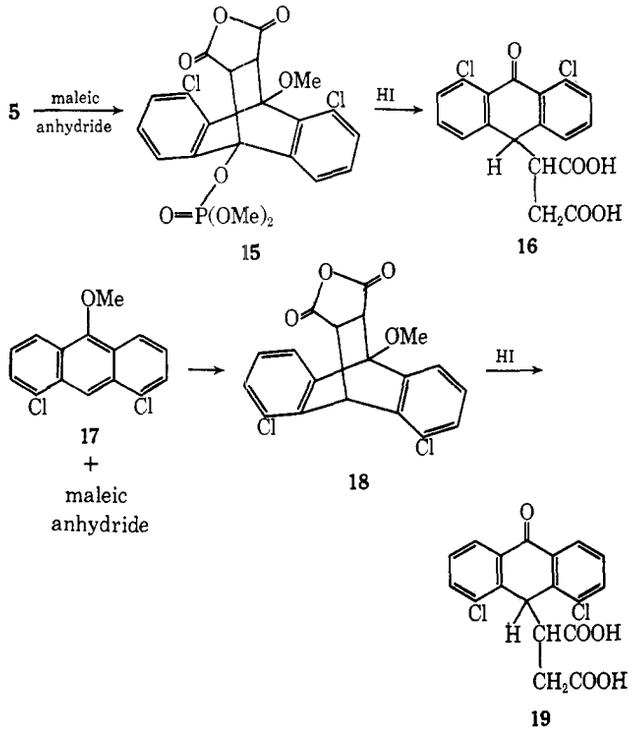
Treatment of the adduct **13** with hydriodic acid in acetic acid gave the succinic acid **14**.[12] This type of



13 **14**

reaction has been discussed previously[12] and a related ring opening has been reported by Sauer and Schroeder.[13] So far, this ring opening has been found only for compounds having a negative group on the bridge vicinal to an ether, ester or amine group on a bridgehead.

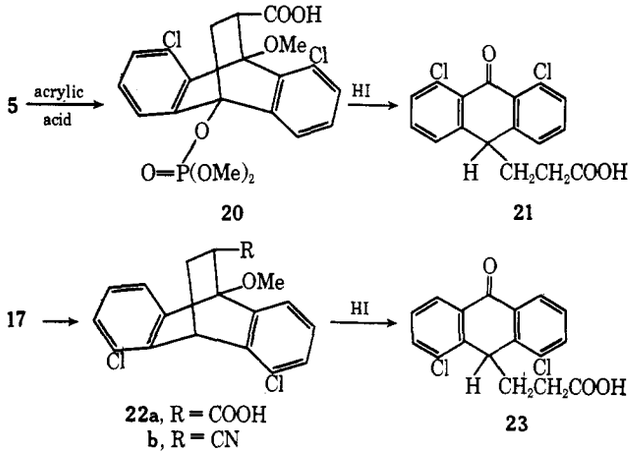
Since compound **5** gave **6** on treatment with hydriodic acid, it was expected that the adduct **15** would likewise have the methyl ether group cleaved and the ring would open before the anthryl phosphate bond was broken. This would lead preferentially to acid **16** and this acid was formed as expected. The isomeric succinic acid **19** was prepared by condensing maleic anhydride with 4,5-dichloro-9-methoxyanthracene (**17**) and treating the adduct **18** with hydriodic acid. In this case the positions of the chlorine atoms are known to be *peri* to the succinic acid moiety.



15 **16**

When compound **5** was condensed with acrylic acid only one adduct was isolated. This was shown to be **20** since the ring opening occurred with hydriodic acid which led to the keto acid **21**. Similarly, the isomeric keto acid, **23** was prepared from the acrylic acid and acrylonitrile adduct of 4,5-dichloro-9-methoxyanthracene. The bridgehead proton of **22b** appeared as a triplet which is additional proof that the adduct had the vicinal structure.

These results show that the vicinality[14] of a methoxy group is greater than that of a hydrogen atom and presumably more than a dimethylphosphato group.



20 **21**

Experimental Section

All nmr spectra were run on Varian A-50 and A-60-A spectrometers using tetramethylsilane as an internal standard. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer. Melting points were obtained on a Fisher-Johns melting point block. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Dimethyl 10-Methoxy-9-anthryl Phosphate (3).—Trimethyl phosphite (10 ml) was added to 6 g (28.2 mmol) of anthraquinone; the mixture was corked and placed on a steam bath for 2–3 days. The first day a yellow solution formed which turned red and then green. The solution was concentrated by a stream of air and gave 10.37 g of a dark, viscous oil. By adding ethyl acetate, filtering and reconcentrating the filtrate several times, several crops of yellow crystals of bianthronyl (**10**) were collected which, after washing well with ethyl acetate and pentane, weighed 1.12 g (20%) and decomposed at 250–255° (lit.[15] 256–258° dec). They were identical with an authentic sample obtained from the Aldrich Chemical Company.

The yellow filtrate was then washed with water, alkaline sodium hydrosulfite and again with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to a yellow oil. This procedure was repeated a second time and gave 4.78 g (79%) of a viscous, yellow oil identified as phosphate **3**: nmr ($CDCl_3$) δ 8.4–8.0, 7.6–7.2 (m, 8, aromatic protons), 4.06 (s, 3, C–OC**H**$_3$), and 3.38 ppm (d, 6, J = 11.5 Hz, POC**H**$_3$); ir (NaCl smear), 7.87 (P=O) and 9.65 μ (P–O–C).[3]

Dimethyl 4,5-dichloro-10-methoxy-9-anthryl phosphate (5) was obtained *via* the same procedure as used for phosphate **3**, starting with 6 g (22.2 mmol) of 1,8-dichloroanthraquinone in 10 ml of trimethyl phosphite. A red solution, which formed within 1 hr, turned green and deposited yellow crystals. Crystals (2.5 g) were filtered, washed with chloroform and then pentane. Treatment with Norit followed by crystallization from a large volume of acetone–petroleum ether (bp 60–70°) gave 2 g (29%) of a pale yellow phosphate (**12**). An analytical sample turned yellow at about 240° and decomposed at 250°; nmr (DMSO-d_6), δ 7.8–6.65 (m, 12, aromatic protons), 5.12 (s, 1, benzhydrylic proton), and 3.60 ppm (d, 6, J = 11.5 Hz, POC**H**$_3$); ir (KBr), 5.9 (C=O), 6.3, 6.9, 6.96 (sh) and 9.6–9.83 μ (d, P–O–C).

Anal. Calcd for $C_{30}H_{19}Cl_4O_5P$: C, 56.99; H, 3.03; Cl, 22.43; P, 4.90. Found: C, 56.76; H, 3.09; Cl, 22.27; P, 4.93.

The yellow filtrate remaining after removal of compound **12** was reduced in volume. Methanol was added and after further

(12) J. S. Meek, P. A. Monroe, and C. J. Bouboulis, *J. Org. Chem.*, **28**, 2572 (1963).

(13) J. Sauer and B. Schroeder, *Ber.*, **100**, 678 (1966).

(14) Vicinality of a group is hereby defined as the ability to polarize a diene so that a negatively monosubstituted dienophile gives the vicinal adduct as the predominant product.

(15) Aldrich Chemical Company.

concentrating, phosphate **5** crystallized. After washing with ethyl acetate and petroleum ether, a yield of 6.38 g (71%), mp 114–116°, was obtained. Crystallization from acetone–petroleum ether gave an analytical sample of bright yellow needles: mp 116–117°; nmr ($CDCl_3$), δ 8.3–8.15 (q, 2), 8.7–7.2 (m, 4), 3.88 (s, 3, C–OCH_3), and 3.85 ppm (d, 6, J = 11 Hz, $POCH_3$); ir (KBr), 7.33, 7.64 (d, P=O) and 9.55 μ (m, P–O–C).

Anal. Calcd for $C_{17}H_{15}Cl_2O_5P$: C, 50.89; H, 3.77. Found: C, 50.95; H, 3.86.

An nmr spectrum ($CDCl_3$) of the oily residue remaining after evaporation of the mother liquors from phosphate **5** showed peaks belonging to its isomer, dimethyl 1,8-dichloro-10-methoxy-9-anthryl phosphate, at δ 3.88 (d, 6, J = 11 Hz) and 3.85 ppm (s, 3, C–OCH_3).

9-Methoxy-10-dimethylphosphato-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Acid Anhydride (13).—Dimethyl 10-methoxy-9-anthryl phosphate (**3**) (1.7 g, 5.12 mmol) and maleic anhydride (0.49 g, 5.12 mmol) were refluxed in 2 ml of xylene for 4 hr. White needles (1.9 g, 95%) crystallized from the dark solution and melted with decomposition between 205–215° after being filtered and washed with benzene and acetone. The product was purified by treatment with Norit in acetone and recrystallization from acetone petroleum ether (bp 60–70°). The analytical sample of white needles decomposed at 224–229°: nmr (DMSO-d_6), 8.0–7.2 (m, 8), 4.94 (d, 1, J = 15 Hz, H-11), 4.40 (d, 1, J = 15 Hz, H-12), 4.07 (s, 3, $COCH_3$), 4.06 (d, 3, J = 18 Hz, $POCH_3$), and 4.02 ppm (d, 3, J = 18 Hz, $OPCH_3$); ir (KBr), 5.35–5.58 (d, C=O), 6.87, 7.75–8.4 (m, P=O) and 9.3–10.0 (m, P–O–C).

Anal. Calcd for $C_{21}H_{19}O_8P$: C, 58.61; H, 4.45. Found: C, 58.81; H, 4.34.

1,8-Dichloro-9-methoxy-10-dimethylphosphato-9,10-ethanoanthracene-11,12-dicarboxylic Acid Anhydride (15).—Dimethyl 4,5-dichloro-10-methoxy-9-anthryl phosphate (**5**) (3 g, 7.48 mmol) and 0.98 (10 mmol) of maleic anhydride were dissolved in xylene and refluxed for 12 hr. The solvent was removed by distillation under reduced pressure and the resulting solid was washed well with ethyl acetate and pentane. This yielded 3.22 g (86%) of white needles, mp 230–240° dec. Recrystallization from acetone–petroleum ether gave analytically pure white needles, mp 232–241° dec.

Anal. Calcd for $C_{21}H_{17}Cl_2O_8P$: C, 50.52; H, 3.43. Found: C, 50.60; H, 3.57.

An nmr spectrum (DMSO-d_6–acetone-d_6) showed two doublets at 3.95, 3.9 (3 H, J = 11 Hz), one singlet at 3.74 (3 H), and one multiplet at 7.05–7.85 ppm (6 H). The 11,12-CH protons were obscured by the phosphate and solvent peaks. An infrared spectrum showed peaks at λ_{max} 5.35–5.58 (d, C=O), 7.7–8.45 (m), 9.3–9.9 (m, P=O) and 10.4–11.2 μ (m, P–O–C).

1,8-Dichloro-9-methoxy-10-dimethylphosphato-9,10-dihydro-9,10-ethanoanthracene-12-carboxylic Acid (20).—Dimethyl 4,5-dichloro-10-methoxy-9-anthryl phosphate **5** (1 g, 2.49 mmol), and 1.0 g of hydroquinone were refluxed in 2 ml of freshly distilled acrylic acid for 50 min. The resulting hot, viscous solution was decanted, leaving acrylic acid polymer behind. Since the reaction was slow, a longer period of refluxing only gave more polymer, which was difficult to separate from the adduct.

An ethyl acetate–chloroform solution of the product was washed with water, treated with Norit, dried over anhydrous magnesium sulfate, and partially concentrated. After several days at 5°, 0.20 g (24%) of white crystals formed, mp 240–260° dec. Recrystallization from acetone–petroleum ether gave an analytical sample melting at 244–264° dec.

Anal. Calcd for $C_{20}H_{19}Cl_2O_7P$: C, 50.87; H, 3.84. Found: C, 50.78; H, 4.06.

An infrared spectrum showed peaks at λ_{max} 3.85 (broad m, OH), 5.73 (C=O), 7.9–8.23 (t, P=O) and 9.35–9.85 μ (m, P–O–C).

4,5-Dichloro-9-methoxyanthracene (17).—This procedure was adapted from Toji's method.[16] Sodium borohydride (6 g, 159 mmol) was added slowly over a 0.5-hr period to a magnetically stirred solution of 9 g (32.6 mmol) of 1,8-dichloroanthraquinone suspended in 500 ml of absolute methanol at room temperature. The solution turned red after each addition owing to the formation of a side product, but air reoxidized it to the anthraquinone and the final solution was yellow. This solution was evaporated by a stream of air and the resulting semisolid yellow product was stirred with 500 ml of water, filtered, and washed well with water to remove most of a yellow impurity. This gave 8.79 g (96%) of nearly colorless *trans*-1,8-dichloro-9,10-dihydro-9,10-anthradiol which turned yellow at 155° and melted with decomposition between 160–170°. Treatment of an acetone solution of the product with Norit followed by crystallization from acetone–petroleum ether yielded white needles which turned yellow at 160° and decomposed at 170° (lit.[16] turned yellow at 160° and melted with decomposition at 176°).

All reagents used below were boiled or treated with a stream of nitrogen to deoxygenate them. Exclusion of air is critical since the anion of anthrone is readily oxidized to anthraquinone.

To a solution of 7.64 g (26.5 mmol) of the diol in 40 ml of 2-propanol under a nitrogen atmosphere was added 40 ml of 20% sodium hydroxide solution. The resulting dark red solution was boiled while 35 ml of methyl tosylate was added during a 10–20 min period. Refluxing was continued until the solution became pale yellow and the product began to crystallize. Cold water was added; the yellow needles were washed well with water and air dried to give 7.35 g (quantitative yield), mp 140°. One recrystallization from acetone raised the melting point to 144–146° (lit.[17] 145°).

1,8-Dichloro-10-methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Acid Anhydride (18).—4,5-Dichloro-9-methoxyanthracene (1 g, 3.7 mmol) ground together with 0.36 g (3.7 mmol) of maleic anhydride was placed in a test tube immersed in a nitrobenzene bath. The bath was refluxed overnight during which time the reaction mixture darkened. The dark semisolid product, **18**, was dissolved in ethyl acetate and treated with Norit which resulted in a yellow solution. After refrigeration, 0.5 g (36%) of white crystals, mp 230–240° dec, was filtered. Recrystallization from acetone–petroleum ether raised the decomposition range to 232–241°: nmr (DMSO-d_6–acetone-d_6), 7.65–7.26 (m, 6), 5.69 (d, 1, J = 3 Hz, H-9), 4.36 (d, 1, J = 16 Hz, H-11), 4.08 (s, 3, OCH_3), and 4.03 ppm (q, 1, J = 3 Hz, 16, H-12); ir, 5.84–5.55 (d, C=O), 6.87–7.03 (d, C=C), 8.05–8.26 (t), 9.3–9.45 (d), 10.65, and 12.85.

Anal. Calcd for $C_{19}H_{12}Cl_2O_4$: C, 60.82; H, 3.22. Found: C, 60.75; H, 3.44.

1,8-Dichloro-9-methoxy-9,10-dihydro-9,10-ethanoanthracene-12-carboxylic Acid (22a).—A solution of 1.6 g (5.78 mmol) of 4,5-dichloro-9-methoxyanthracene with 0.1 g of hydroquinone in 1.8 ml of acrylic acid was refluxed for 40 min. The resulting yellow oil was dissolved in ethyl acetate–acetone and treated with Norit. The solution was partially evaporated and gave 1.26 g (60%) of white crystals, mp 215–230° slight dec. Further recrystallization from methanol did not raise the decomposition range.

Anal. Calcd for $C_{18}H_{14}Cl_2O_3$: C, 62.09; H, 3.76. Found: C, 61.90; H, 4.01.

An infrared spectrum showed peaks at λ_{max} 3.88 (m, OH), 5.83, 6.87–7.02 (d), 7.52–7.74 (d), 7.9–8.7 (m), 10.0 and 12.6–12.75 μ (d). The compound was not soluble enough in DMSO to permit nmr analysis.

1,8-Dichloro-10-methoxy-9,10-dihydro-11-cyano-9,10-ethanoanthracene (22b).—A solution of 5.0 g (18.5 mmol) of 1,8-dichloro-9-methoxyanthracene and 0.1 g of hydroquinone in 25 ml of acrylonitrile was placed in a bomb at 150° for 5 hr. The resulting pale yellow solution was filtered to remove a powdery residue and the filtrate was evaporated by a stream of air to yield 7.4 g of pale yellow crystals, mp 160–190°. Several recrystallizations from methanol of acetone–petroleum ether gave 5 g (87%) of white needles, mp 173–175°. An analytical sample melted at 174–175°: nmr (acetone-d_6) 7.2–6.6 (m, 6), 4.85 (t, 1, J = 3, Hz, H-9), 3.48 (s, 3, OCH_3), 3.3–3.05 (m, 1, H-11), and 2.0–1.3 ppm (m, 2, H-12).

Anal. Calcd for $C_{18}H_{13}Cl_2NO$: C, 65.47; H, 3.97. Found: C, 65.49; H, 4.07.

Attempted Diels–Alder Reaction.—Dimethyl 4,5-dichloro-10-methoxy-9-anthryl phosphate did not form an adduct in any appreciable amount after 3 weeks of refluxing in acrylonitrile.

1,8-Dichloro-9-anthrone (6) and 4,5-Dichloro-9-anthrone (7).—A solution of 1.0 g (2.5 mmol) of dimethyl 4,5-dichloro-10-methoxy-9-anthryl phosphate, **5**, in 5 ml of hydriodic acid (sp gr 1.5) and 10 ml of glacial acetic acid was refluxed for 70 min. The initially colorless solution turned yellow. After cooling, 500 ml of cold water was added which caused precipitation of a bright yellow solid (probably the anthrol tautomer). The

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(17) E. B. Barnett and C. L. Hewlett, *J. Chem. Soc.*, 1452 (1932).

solution stood overnight and the solid which was now pale yellow was filtered and washed with water and then pentane to yield 0.63 g (100%), mp 143–170°. Three recrystallizations from methanol gave pale yellow crystals, mp 167–170° (lit.[5] 167°).

The nmr spectrum is discussed above. An infrared spectrum showed peaks at λ_{max} 5.95, 6.28, 6.87–6.97 (d), 8.0 and 10.63–11.37 μ (t).

The other isomer (**7**) may be prepared by the methods of Toji,[16] Barnett, Cook, and Matthews,[6] or by treatment of 4,5-dichloro-10-methoxy-9-anthrone (**8**) with hydriodic acid in acetic acid as described previously.

4,5-Dichloro-10-methoxy-9-anthrone (8).—The reaction was carried out under nitrogen and the reagents used were deoxygenated as in the preparation of 4,5-dichloro-9-methoxyanthracene (**17**).

To a boiling solution of 3 g (7.48 mmol) of dimethyl 4,5-dichloro-10-methoxy-9-anthryl phosphate (**5**) in 50 ml of 2-propanol was added 50 ml of 10% sodium hydroxide solution. The mixture immediately turned dark red and gradually became yellow after 20 hr of refluxing. The hot solution was acidified with concentrated hydrochloric acid; 2.02 g (100%) of **8**, mp 127–133°, was removed by filtration, washed with water and then pentane. Treatment with Norit and several recrystallizations from acetone gave white, diamond-shaped crystals melting at 134–136° (lit.[8] 136°): nmr ($CDCl_3$), 8.1–8.01 (q, 2, *peri* protons), 7.8–7.2 (m, 4), 6.4 (s, 1, H-10), and 2.96 ppm (s, 3, OCH_3); ir, 6.0 6.3 (sh), 6.35 (sh), 7.5–7.94 (t), 9.38–9.5 (d), and 13.37–13.78 (d). After standing overnight in a closed container, the crystals turned pink but there was no change in the nmr or infrared spectra or in the melting point.

(10-Keto-9,10-dihydro-9-anthryl)succinic acid (14).—A solution of 2.9 g (6.7 mmol) of 9-methoxy-10-dimethylphosphato-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride (**13**) in 15 ml of hydriodic acid and 30 ml of glacial acetic acid was refluxed for 15 hr. When the product was isolated following the procedure for compound **6**, 1.68 g (81%) of **14**, mp 190–195° dec was obtained. Recrystallization from acetone–petroleum ether gave colorless crystals melting at 196–198° dec (lit.[12] 194.3–195.3°). The acid was identified by comparison with an authentic sample prepared from 9-methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride.[12]

(4,5-Dichloro-10-keto-9,10-dihydro-9-anthryl)succinic Acid (16).—Hydriodic acid in acetic acid converted 1.34 g (2.69 mmol) of 1,8-dichloro-9-methoxy-10-dimethylphosphato-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride (**15**) into 0.84 g (72%) of acid **16**, mp 220–260° dec. After two recrystallizations, white crystals were obtained which turned yellow at 240° and melted at 260° dec.

Anal. Calcd for $C_{18}H_{12}Cl_2O_5$: C, 57.01; H, 3.19. Found: C, 56.97; H, 3.15.

An infrared spectrum showed peaks at λ_{max} 3.4 (broad s), 5.83–5.94 (d), 6.03 (sh), 6.87–7.07 (t), 7.77 and 8.05 μ.

(1,8-Dichloro-10-keto-9,10-dihydro-9-anthryl)succinic Acid (19).—The procedure was previously described. Cleavage of 2.16 g (5.76 mmol) of 1,8-dichloro-10-methoxy-9,10-dihydro-9,10-ethanoanthracene-11-12-dicarboxylic anhydride (**18**) gave 1.37 g (65%) of pale yellow crystals, mp 230–245° dec. The analytical sample melted at 245–255° dec.

Anal. Calcd for $C_{18}H_{12}Cl_2O_5$: C, 57.01; H, 3.19. Found: C, 57.30; H, 3.39.

An infrared spectrum showed peaks at λ_{max} 3.2 (broad s), 5.55 (sh), 5.85–5.95 (d), 6.25, 6.3 (sh), 6.9, 7.65, 8.8 and 13.5 μ.

3-(4,5-Dichloro-10-keto-9,10-dihydro-9-anthryl)propionic Acid (21).—From a hydriodic acid cleavage as before, a quantitative yield of acid **21**, mp 200–205° dec, was obtained from 0.37 g (0.748 mmol) of 1,8-dichloro-9-methoxy-10-dimethylphosphato-9,10-dihydro-9,10-ethanoanthracene-12-carboxylic acid (**20**). The analytical sample melted at 204–206° dec.

Anal. Calcd for $C_{17}H_{12}Cl_2O_3$: C, 60.91; H, 3.61. Found: C, 60.83; H, 3.53.

An infrared spectrum showed peaks at λ_{max} 3.43 (broad m), 5.88–5.93 (d), 6.27–6.35 (d), 6.88–7.12 (t), 8.04–8.15 (d), 10.58–10.97 (t), and 12.45–12.72 μ (t).

3-(1,8-Dichloro-9-keto-9,10-dihydro-10-anthryl)propionic Acid (23).—A solution of 0.65 g (1.97 mmol) of 1,8-dichloro-10-methoxy-9,10-dihydro-9,10-ethanoanthracene-12-carboxylic acid (**22a**) or the cyano derivative (**22b**) in 5 ml of hydriodic acid and 10 ml of glacial acetic acid was refluxed for 2.5 hr. The same open acid (**23**) was obtained from both starting materials in quantitative yield and the analytical sample melted at 175–178°.

Anal. Calcd for $C_{17}H_{12}Cl_2O_3$: C, 60.91; H, 3.61. Found: C, 61.06; H, 3.64.

An infrared spectrum showed peaks at λ_{max} 3.4 (broad m), 5.75 (sh), 5.83–5.97 (d), 6.26, 6.85–9.4 (t), 7.6–8.0 (m), 8.8, 10.48 and 12.72–13.70 μ (t).

Registry No.—**5**, 16622-38-1; **8**, 16622-39-2; **12**, 16622-40-5; **13**, 16622-41-6; **15**, 16622-42-7; **16**, 16622-43-8; **18**, 16622-44-9; **19**, 16622-45-0; **20**, 16622-46-1; **21**, 16622-47-2; **22a**, 16622-48-3; **22b**, 16622-49-4; **23**, 16622-50-7.

Isoprene Chlorination

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The chlorination of isoprene does not appear to be a free-radical chain reaction either in the liquid or the gas phase at low temperatures. A mixture of substitution and addition products is obtained regardless of phase; somewhat more 1-chloro-2-methylbutadiene and less 1,4-dichloride were obtained in the gas phase. Dichlorides were obtained in greater yield when the chlorination was carried out in the presence of chloride ion.

Isoprene has been chlorinated in both liquid[1–4] and gas phase[4–7] to give products of substitution and addition. Because isoprene resembles both butadiene and isobutylene one might expect a common mechanism; however, in a recent study[8] Poutsma favors a radical mechanism for the chlorination of undiluted butadiene in the liquid phase. Isobutylene has been shown to undergo polar chlorination in the liquid phase.[9] Using *t*-butyl hypochlorite rather than chlorine, Oroshnik and Mallory[10] found that with undiluted isoprene in the liquid phase the orientation of 1,4 addition is that typical of a radical mechanism.

In Table I are shown true product yields obtained by chlorination below room temperature in neat liquid isoprene and in the gas phase at 100°. The liquid-phase results are corrected in that the addition products of hydrogen chloride are considered as recoverable isoprene. The conversion was complete with respect to

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