[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE VIRGINIA POLYTECHNIC INSTITUTE]

Synthesis and Reactions of Some 9-Trichloromethyl-9,10-dihydroanthracenes[1,2]

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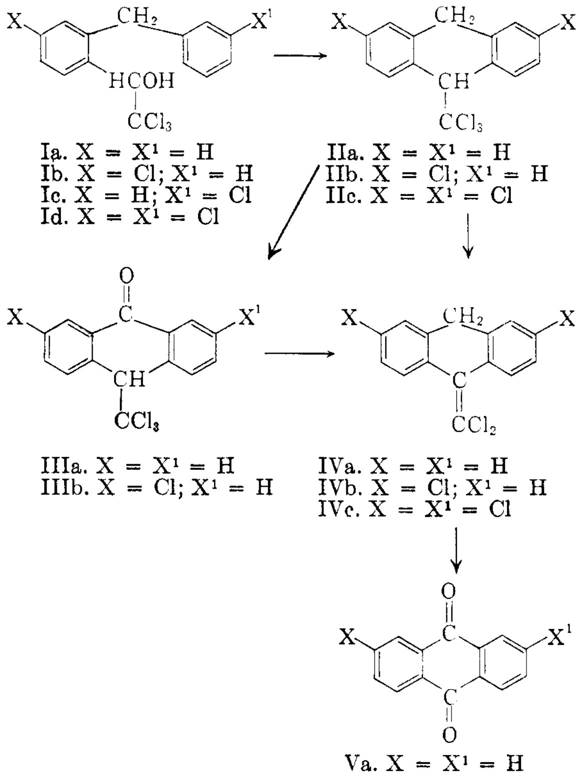
A series of new 9-trichloromethyl-9,10-dihydroanthracenes, which can be considered as analogues of the DDT-type molecule, have been prepared and several of their reactions studied. From the toxicity data against German cockroaches it would appear that these compounds have little if any insecticidal activity.

In connection with our preparation of compounds which are structurally and chemically analogous to the DDT-type molecule,[3,4] we have prepared a new series of 9-trichloromethyl-9,10-dihydroanthracenes (IIa–IIc). Essentially, the structural difference between DDT and the compounds under investigation is that of a methylene bridge linked across the positions of DDT *ortho* to the trichloromethyl moiety.

Although much work has been done in an attempt to relate structure to activity in the case of DDT,[5] it is still not possible to present a completely satisfactory theory of general applicability. Hass *et al.*[6,7] concluded that ascribing the quasi-independent toxic and lipoid-solubilizing properties to parts of the DDT molecule, as was done by many authors, is untenable and that the whole molecule must be considered *per se*. We thought compounds of the type II would be especially interesting to study in view of the suggestion of Riemschneider and Otto[8] and the important characteristics for the toxicity of compounds related to DDT are: molecular weight between 270 and 450; melting point below 180°; good lipoid solubility; and the type, number, and position of auxocontact substituents in the contactophore rings. Compounds of the type II meet all these requirements for high insecticidal activity.

Cyclization of Ia–Id[3] was effected essentially by the method of Ray *et al.*[9] The carbinol was heated with phosphoric anhydride, *in vacuo*, followed by distillation of the product from the reaction mixture. It was interesting to find that the cyclization could not be accomplished with sulfuric acid,[10,11] alumina,[12] or polyphosphoric acid.[13] The highest yield of IIa *via* phosphoric anhydride was obtained by carrying out the reaction in the dry state (61%); with xylene (45%); with toluene (7%). Thus all following cyclizations were carried out in the dry state. As was anticipated, cyclization of Ib under these conditions gave a comparable yield (54%) of IIb.



Ia. X = X^1 = H
Ib. X = Cl; X^1 = H
Ic. X = H; X^1 = Cl
Id. X = X^1 = Cl

IIa. X = X^1 = H
IIb. X = Cl; X^1 = H
IIc. X = X^1 = Cl

IIIa. X = X^1 = H
IIIb. X = Cl; X^1 = H

IVa. X = X^1 = H
IVb. X = Cl; X^1 = H
IVc. X = X^1 = Cl

Va. X = X^1 = H
Vb. X = Cl; X^1 = H
Vc. X = X^1 = Cl

On examination of the structure of Ic cyclization could be seen to afford two products, the desired

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(1) Presented before the Division of Organic Chemistry at the 136th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1959.

(2) This paper has been abstracted from the Doctorate thesis of P. E. Newallis presented to the Virginia Polytechnic Institute in 1957.

(3) F. A. Vingiello, G. J. Buese, and P. E. Newallis, *J. Org. Chem.*, **23**, 1139 (1958).

(4) F. A. Vingiello and P. E. Newallis, *J. Org. Chem.*, **23**, 1786 (1958).

(5) R. L. Metcalf, *Organic Insecticides*, Interscience Publishers, Inc., New York, N. Y., 1956.

(6) T. A. Jacob, G. B. Bachman, and H. B. Hass, *J. Org. Chem.*, **16**, 1572 (1951).

(7) H. B. Hass, M. B. Neher, and R. T. Blinkenstaff, *Ind. Eng. Chem.*, **43**, 2875 (1951).

(8) R. Riemschneider and H. Otto, *Z. Naturforsch.*, **9b**, 95 (1954).

(9) M. Ray, J. C. Bardham and K. C. Bhattacharyya, *J. Chem. Soc.*, 1344 (1956).

(10) D. Perlmar, D. Davidson, and M. T. Bogert, *J. Org. Chem.*, **1**, 288 (1937).

(11) C. K. Bradsher and D. Beavers, *J. Am. Chem. Soc.*, **78**, 3193 (1956).

(12) F. A. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, **78**, 3205 (1956).

(13) J. Koo, *J. Am. Chem. Soc.*, **75**, 1891 (1953).

product IIb and one corresponding to cyclization into the position *ortho* to the chlorine substituent. Only the desired product, IIb, was obtained, *albeit* in low yields (26%). As expected, this cyclization into a ring containing a chlorine atom results in a marked decrease in yield.

Similarly, cyclization of Id could be expected to result in the formation of two products. Apparently this was the case, as a yield of 27% of a mixture was realized. The desired compound, IIc, was obtained after the mixture was chromatographed on alumina and recrystallized numerous times from ethanol. As the known anthraquinone Vc was obtained as the oxidation produce of IIc, the positions of the chlorine atoms were established.

Attempted oxidation of IIa with either selenium dioxide or alkaline potassium permanganate yielded starting material along with a trace of the quinone Va. Heating IIa with a potassium dichromate–acetic acid mixture under reflux conditions gave 28% of anthrone IIIa. Employing a chromic anhydride–acetic acid mixture resulted in an increase in the yield of anthrone IIIa to 60%. Compound IIb was oxidized in the same manner to IIIb in 71% yield. Apparently, the trichloromethyl group exerts a stabilizing effect which makes the adjacent carbon atom resistant to oxidation.[14]

Dehydrochlorination of IIa with alcoholic potassium hydroxide under reflux conditions gave only a yellow gum. A good yield (89%) of IVa could be realized however, by heating a pyridine solution of IIa under reflux for twenty-four hours. Compound IVb was obtained in 75% yield in like manner. Compound IVc, which contains the dichloromethylene group, was not isolated but was subjected to oxidation. Our only interest in compounds IVa–IVc was that they provided a good means of preparing the anthraquinones which were needed for proof of structure.

The oxidation of compounds IVa–IVc with a chromic anhydride–acetic acid mixture proceeded smoothly and in fair yields, Va (42%), Vb (54%), and Vc (53%).

Entomological testing[15] of the new DDT analogs was undertaken by Dr. James M. Grayson and his staff at the Virginia Polytechnic Institute Entomology Department using standard methods of assay. From the toxicity data against German cockroaches it would appear that the new compounds have little if any insecticidal activity.

This work corroborates the view of many workers in this field that the correlation of chemical structure with insecticidal activity is a complex problem. It also indicates that hypotheses assigning specific properties to portions of the molecule are of doubtful value and that the entire molecule must be considered as a unit. Of the compounds prepared and tested, 2,7-dichloro-9-trichloromethyl-9,10-dihydroanthracene (IIc) has the strongest structural semblance of the DDT molecule. It also fulfills most of the requirements proposed for insecticidal activity by various authors, yet this compound is inactive.

Although any conclusion regarding the inactivity of IIc drawn at this time would necessarily be speculative, we feel that the ease of dehydrochlorination exhibited by IIc may be pertinent and that a detoxification mechanism *via* premature dehydrochlorination is a plausible explanation for the failure of IIc to show insecticidal activity.

EXPERIMENTAL[16,17]

9-Trichloromethyl-9,10-dihydroanthracene (IIa). A mixture of 4.35 g. (0.014 mole) of the alcohol Ia[3] and 4.35 g. (0.032 mole) of phosphoric anhydride was heated *in vacuo* (5 mm.) in a metal bath kept at 130–140° for 1 hr. The temperature of the bath was then gradually raised so that a yellow oil distilled. This oil crystallized on standing for a few minutes and was recrystallized from ethanol (Norit) yielding white needles, m.p. 122–123°; yield 2.48 g. (60%). The compound displayed a weak green fluorescence in ethanol and was only slightly soluble in concd. sulfuric acid.

Anal. Calcd. for $C_{15}H_{11}Cl_3$: C, 60.53; H, 3.73. Found: C, 60.35; H, 3.86.

2-Chloro-10-trichloromethyl-9,10-dihydroanthracene (IIb). A. *Via* Ib. This compound (IIb) was prepared using substantially the procedure given above for IIa with Ib being used in place of Ia. The product (54%) melted at 107.5–108.5°.

Anal. Calcd. for $C_{15}H_{10}Cl_4$: C, 54.25; H, 3.04. Found: C, 54.47; H, 3.06.

B. *Via* Ic. Repeating the above experiment using Ic as the starting material instead of Ib gave the same product (IIb) (26%), m.p. 107.5–108.5°. A melting point determination of a mixture of this product with that obtained from Ib showed no depression.

2,7-Dichloro-10-trichloromethyl-9,10-dihydroanthracene (IIc). This compound was prepared using substantially the procedure given above for IIa. This gave a mixture (27%) which was chromatographed in the usual way on alumina using petroleum ether (b.p. 30–60°) as the eluent. This gave a solid, m.p. 142–146°, which after fifteen recrystallizations from ethanol gave long, fine white needles, m.p. 152–153°.

Anal. Calcd. for $C_{15}H_9Cl_5$: C, 49.15; H, 2.48. Found: C, 49.17; H, 2.58.

9-Keto-10-trichloromethyl-9,10-dihydroanthracene (IIIa). A mixture of 1.0 g. (0.003 mole) of IIa, 3.5 g. (0.035 mole) of chromic anhydride,[18] and 35 ml. of glacial acetic acid was heated under reflux for 6 hr. This was poured into an ice

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[14] The DDT molecule was also found to be resistant to oxidation when a chromic anhydride–acetic acid mixture was employed under reflux conditions. However, oxidation to the corresponding benzophenone was effected *via* the ethylenic derivative under comparable conditions. O. Grummitt, A. Buck, and A. Jenkins, *J. Am. Chem. Soc.*, **67**, 155 (1945).

[15] Dr. James M. Grayson of the Entomology Department at the Virginia Polytechnic Institute was responsible for conducting the assays. We are grateful to him for this work.

[16] All melting points were taken on a Fisher-Johns melting point block and are uncorrected.

[17] All analyses were carries out by the Micro-Tech Laboratories, Skokie, Illinois.

[18] In another experiment, the ratio of chromic anhydride to the dihydro compound was 5 to 1. A small amount of anthraquinone was isolated in addition to the main product.

water mixture and the greenish solid was filtered. The solid was washed with water and recrystallized from ethanol (Norit). Colorless rods, m.p. 172–174°, were obtained; 0.54 g. Concentration of the mother liquor gave an additional 0.09 g. A total of 0.63 g. (60%) was obtained.

An analytical sample was obtained by repeated recrystallization from ethanol; m.p. 177–178°.

Anal. Calcd. for $C_{15}H_9Cl_3O$: C, 57.82; H, 2.91. Found: C, 57.87; H, 3.34.

2-Chloro-9-keto-10-trichloromethyl-9,10-dihydroanthracene (IIIb). This compound was prepared using substantially the procedure given above for IIIa. The product, IIIb, (71%) melted at 144–145° (from ethanol).

Anal. Calcd. for $C_{15}H_8Cl_4O$: C, 52.06; H, 2.33. Found: C, 51.83; H, 2.21.

Preparation of 9-dichloromethylene-9,10-dihydroanthracene (IVa) *and oxidation to* Va. A mixture of 0.4 g. of the dihydro compound IIa and 20 ml. of anhydrous pyridine was protected from moisture and heated under reflux for 24 hr. The mixture was poured into an ice water mixture. The white precipitate was filtered and recrystallized from ethanol to give 0.18 g. of white needles, m.p. 84–86°. Concentration of the mother liquor gave an additional 0.13 g. for a total yield of 0.31 g. (89%).

A mixture of 0.12 g. of the above olefin, 0.6 g. of chromic anhydride, and 10 ml. of glacial acetic acid was heated under reflux for 4 hr. Worked up in the usual way this mixture gave 42% of the known anthraquinone Va; m.p. 282–284°.

2-Chloro-10-dichloromethylene-9,10-dihydroanthracene (IVb). This compound was prepared using substantially the procedure given above for IVa. The dihydro compound IIb on dehydrohalogenation with pyridine gave IVb (75%); m.p. 131–132°.

Anal. Calcd. for $C_{15}H_9Cl_3$: C, 60.94; H, 3.07. Found: C, 60.74; H, 3.12.

Oxidation of 2-chloro-10-dichloromethylene-9,10-dihydroanthracene (IVb). This oxidation was effected using chromic anhydride in substantially the way IVa was oxidized. The yield of the known 2-chloroanthraquinone (Vb), m.p. 212–213° was 54%.

Dehydrohalogenation of 2,7-dichloro-10-trichloromethyl-9,10-dihydroanthracene (IIc) *and subsequent oxidation to* Vc. The dihydrocompound IIc was dehydrohalogenated with pyridine as was IVa above. The tan solid was then oxidized with chromic anhydride in 53% yield to the known 2,7-dichloroanthraquinone, m.p. 231–232°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Addition of Halogens and Halogen Compounds to Allylic Chlorides. IV. Effect of Reactivity upon the Orientation of Electrophilic Olefinic Addition

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The orientation of electrophilic olefinic addition is governed by the various electronic effects (such as electromeric, hyperconjugative, and inductive) which are in turn influenced both by the presence of substituents in the olefinic compound and by the nature of the electrophilic reagent. Three generalizations summarize the experimentally observed behavior with a series of allylic chlorides and related compounds: (1) When both the reagent and the olefinic compound are of low reactivity, the orientation is controlled by electromeric or hyperconjugative electron displacements. If this type of displacement cannot be induced, the orientation is controlled by the inductive effect. (2) When either the reagent or the olefinic compound is of high reactivity, the orientation is controlled chiefly by the inductive effect, although hyperconjugative effects may also be involved. (3) When both the reagent and the olefinic compound are of high reactivity, the normal orientation is controlled by the inductive effect, plus a certain amount of random orientation. Increasing the number of chlorine atoms in the allylic position does not appear to reduce the electron density of the double bond sufficiently to alter the nature of the attack by electrophilic reagents.

The literature of organic chemistry provides an abundance of information on the orientation and mechanism of additions of halogen and halogen compounds to unsaturated compounds containing various kinds and numbers of substituents. Some apparent contradictions and inconsistencies in the results reported prompted the present investigation of the addition of halogens and halogen compounds to a selected series of allylic chlorides and related compounds. Part I of this series of papers[2] was concerned with the addition of hydrogen chloride and hydrogen iodide, Part II dealt with the additions of hypochlorous acid, and Part III involved a study of the relative rates of halogen addition. The object of this concluding paper of the series is to review the experimental results and point out the relationships and possible theoretical interpretations of the data. A comparison of olefinic addition and certain aspects of aromatic substitution will be made as an aid to the interpretation of the observed behavior.

DISCUSSION

Effect of allylic halogen. The principal products obtained by the addition of hydrogen chloride, hydrogen iodide, and hypochlorous acid to a series of allylic chlorides and related compounds are summarized in Table I. The addition of hydrogen chloride and hydrogen iodide to propene is according to Markownikoff's rule. Similar orientation of the additions of hydrogen chloride and hydrogen iodide is observed in the case of allyl chloride in

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[1] This is an abstract of a part of the doctoral thesis submitted by Lieng-huang Lee. Present address: The Dow Chemical Company, Midland, Mich.

[2] Part I, *J. Org. Chem.*, **23**, 1876 (1958); Part II, *J. Org. Chem.*, **24**, 1271 (1959); Part III, *J. Org. Chem.*, **25**, 428 (1960).