tions investigated. The reaction appears to be general for all analogs and homologs of acetonechloroform; three new α-alkoxyacids have thus been synthesized. A reaction mechanism has been suggested for this somewhat surprising reaction, and the analogous reaction of acetonechloroform and aniline has been discussed.

The dealkoxylation of the esters of the α-alkoxyacids to α,β-unsaturated esters has been investigated and a number of known and new esters of this series have been prepared.[25]

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[25] (Note added February 19, 1948): In the November, 1947, issue of THIS JOURNAL (p. 2667), McElvain and Stevens describe the formation of ethyl α-ethoxyisobutyrate from acetonechloroform and 3 moles of sodium ethoxide in absolute alcohol. They also quote the British Patent 578,082 corresponding to the present paper (*C. A.*, **41**, 2075 (1947); applied in 1943; compare Weizmann, British Patent 587,545, applied in 1944).

LONDON, S. W. 1 RECEIVED APRIL 29, 1947

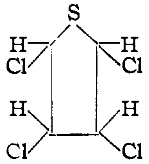
[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DEPARTMENT OF SOCONY-VACUUM LABORATORIES, A DIVISION OF SOCONY-VACUUM OIL CO., INC.]

The Chlorination of Thiophene. I. Addition Products

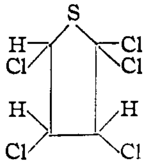
BY HARRY L. COONRADT AND HOWARD D. HARTOUGH

A study of the reaction of thiophene with chlorine was undertaken in these Laboratories when it became evident that the reaction was much more complex than had been indicated in the literature. Prior investigators reported[1] that when the reaction products were distilled, hydrogen chloride was evolved throughout the distillation and the presence of addition products was indicated since the substitution products distilled without decomposition. A study of addition products formed in the reaction was made by the present authors in order to determine, in part, their chemical potentialities since these compounds had been destroyed in the past by the methods used in processing the chlorinated mixtures.

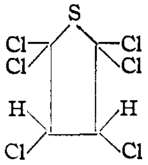
The addition compounds isolated from the reaction mixture were α-2,3,4,5-tetrachlorothiolane,[2] m.p. 111.5–113.5°, (I), β-2,3,4,5-tetrachlorothiolane, m.p. 44.5–46°, (II), 2,2,3,4,5-pentachlorothiolane (III), and 2,2,3,4,5,5-hexachlorothiolane (IV).



I, m. p. 111.5–113.5°
II, m. p. 44.5–46°



III



IV

The addition products were described previously by Steinkopf and Köhler[3] as "hydrogen chloride addition products." The assumption of addition products was based on the separation of a liquid material from exhaustively chlorinated thiophene, 2-thiophenecarboxylic acid or 4,5-dibromo-2-thiophenecarboxylic acid to which was assigned the structure of 2,3,4,5,5-pentachloro-2-thiolene or 2,3,4,4,5-pentachloro-2-thiolene. We isolated no such addition product from exhaustively chlorinated thiophene, and it seems probable that the material of Steinkopf and Köhler was not a single compound. The present work indicates that the addition compounds are chlorine addition products. Hydrogen chloride did not form addition products with 2,5-dichlorothiophene at 0° or −40° nor with 2,3,4,5-tetrachlorothiophene at 0°.

There are six possible geometrical isomers of 2,3,4,5-tetrachlorothiolane. Two were isolated and identified. These compounds may be viewed as the products of the addition of chlorine to thiophene. The *alpha* isomer, I, was obtained as a white crystalline product when partially chlorinated thiophene was cooled and filtered. The *beta* isomer, II, was obtained when partially chlorinated thiophene was distilled to remove the more volatile components, the residue cooled to crystallize and separate I, and the filtrate fractionated under reduced pressure. The higher boiling fractions contained II.

The structures of I and II were indicated by the method of synthesis and analysis. Further evidence for the structure assigned to I was obtained by dehydrohalogenation. Pyrolysis yielded hydrogen chloride and dichlorothiophenes composed of about 50% 2,3-dichlorothiophene, and 50% 2,4-dichlorothiophene with a trace of 2,5-dichlorothiophene. However, when I reacted with ethanolic potassium hydroxide, dichlorothiophenes composed of approximately 54% 3,4-dichlorothiophene, 44% 2,4-dichlorothiophene, 2% 2,5-dichlorothiophene, and no 2,3-dichlorothiophene were obtained. This conversion of I to all four possible dichlorothiophenes is evidence for the structure assigned. II upon treatment with ethanolic potassium hydroxide yielded a mixture of dichlorothiophenes.

The 2,2,3,4,5-pentachlorothiolane (III) was separated in low yield by the fractionation under reduced pressure of chlorinated thiophene. A superior method of preparation was found to be

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[1] W. Steinkopf, "Die Chemie des Thiophens," Theodor Steinkopff, Dresden, 1941, p. 35.

[2] This terminology is in accord with that in Patterson, "The Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940, p. 44. Other terminology, except that derived from thiacyclopentane, is cumbersome and occasionally misleading. The *alpha* and *beta* isomers of tetrachlorothiolane have been so designated by the present authors.

[3] Steinkopf and Köhler, *Ann.*, **532**, 250 (1937).

the chlorination of 2-chlorothiophene at low temperatures and subsequent crystallization of III at low temperatures from the reaction mixture. The structure assigned to III was based on the latter synthesis and on analysis. Further evidence for the structure assigned was the conversion of III to trichlorothiophenes by pyrolysis and by dehydrohalogenation with ethanolic potassium hydroxide. Of the trichlorothiophenes formed by pyrolysis, infrared absorption spectra indicated that 92% was 2,3,5-trichlorothiophene and 8% was 2,3,4-trichlorothiophene. However, of the trichlorothiophenes formed by the reaction of III with ethanolic potassium hydroxide similar analysis showed that 35% was 2,3,5-trichlorothiophene and 65% was 2,3,4-trichlorothiophene.

The 2,2,3,4,5,5-hexachlorothiolane (IV) was obtained from chlorinated thiophene by fractionation under reduced pressure. The same compound, IV, also was prepared by the direct addition of chlorine to 2,5-dichlorothiophene. The position of the two hydrogen atoms was indicated by the latter synthesis, and by the formation of 2,5-dichlorothiophene by the action of zinc on IV. IV reacted with ethanolic potassium hydroxide to give 2,3,4,5-tetrachlorothiophene. Pyrolysis of IV yielded hydrogen chloride and 2,3,4,5-tetrachlorothiophene.

The formation of the addition product, IV, as the principal product of the exhaustive chlorination of thiophene at 80–130° showed that at the latter stage of the reaction the ratio of addition to substitution products increased markedly. This is in contrast to the early stages of the chlorination where more chlorine reacted to form substitution than addition products. When two moles of chlorine was treated with one mole of thiophene at 70–80°, only 20% of the chlorine reacted to form addition products. The balance of the chlorine reacted to form substitution products as calculated from the weight of chlorine added and the weight of the reaction products.

The effect of temperature on the ratio of addition to substitution products was determined in part. When two moles of chlorine per mole of thiophene was used, the chlorine that reacted to form addition products was 20% at 70–80°, 30% at 30°, and 40% at −30°; the balance of the chlorine reacted to form substitution products. When the exhaustive chlorination of thiophene was conducted at reflux temperatures up to 200°, with concomitant pyrolysis, the yield of the addition product, IV, was low due to its dehydrohalogenation to tetrachlorothiophene. When the exhaustive chlorination was conducted at 80–130°, IV was obtained directly by distillation of the reaction product and was purer than the IV obtained when the chlorination was conducted at a lower temperature. This was clarified when I was found to react with chlorine at 115°, but not at 40°. The impurity in IV formed by chlorination near room temperature was thus indicated to be I and possibly other addition products which accumulated in the reaction mixture at lower temperatures and decomposed when IV was fractionated. I was found to react more readily than IV with cold sodium carbonate solution. Treatment of the crude reaction product with the alkaline solution destroyed the more unstable addition products so that IV could be distilled satisfactorily.

The purity of the addition products reported in this paper was indicated by the melting point, and infrared absorption spectrograms of carbon tetrachloride solutions of I, II and IV. Similar absorption spectrograms for I, II, IV and thiolane were obtained. The white crystalline addition products isolated had relatively high vapor pressures at room temperatures, but were quite stable under such conditions as was indicated by a constant melting point on standing. The addition products had a slight vesicant and lachrymatory action.

Experimental

Chlorination.—Thiophene of better than 99.5% purity, as determined by infrared absorption analysis, was used. The chlorinations were conducted in a flask fitted with stirrer, efficient condenser, thermometer and chlorine gas inlet tube that led below the surface of the liquid. The chlorine was measured by a rotameter.

α-2,3,4,5-Tetrachlorothiolane, I.—Five moles (420 g.) of thiophene was chlorinated at 30° with from two and one-half to ten moles of chlorine. The products were placed in stoppered flasks and immersed in a Dry Ice–acetone-bath at −70° for four hours. The cold reaction mixtures were filtered and the precipitates washed with cold petroleum ether. The white crystalline products so obtained had melting points of about 106–112° which were not substantially changed by repeated recrystallizations from ASTM naphtha. The moles of chlorine used per mole of thiophene and the yields of I, m. p. 106–112°, based on chlorine were as follows: 0.5, 9.9%; 0.8, 13.2%; 1.0, 11.1%; 2.0, 8.2%. The best yield of I based on thiophene was obtained with two moles of chlorine per mole of thiophene. The effect of the temperatures of chlorination on the yields under such conditions was as follows: 70–80°, 3.5%; 30°, 8.2%; −30°, 3.8%. Addition of petroleum ether to the more highly chlorinated mixtures before crystallization reduced coprecipitation and facilitated separation of I. Under such conditions the moles of chlorine used and the yields of I, m. p. 106–112°, based on chlorine were as follows: 3.0, 1.9%; 4.0, 0.0%. I of m. p. 111.5–113.5° was obtained by fractional crystallization from carbon tetrachloride by the addition of ASTM naphtha or from benzene by the addition of petroleum ether. I boiled at 111.5° (3.4 mm.) with partial decomposition, as was indicated by hydrogen chloride evolution and a distillate with a lower melting point. I gave an immediate precipitate with alcoholic silver nitrate.

Anal. Calcd. for $C_4H_4Cl_4S$: C, 21.26; H, 1.79; Cl, 62.8; S, 14.2; mol. wt., 226. Found: C, 21.27; H, 1.78; Cl, 62.5; S, 14.8; mol. wt., 226.

β-2,3,4,5-Tetrachlorothiolane, II.—Ten moles of chlorine was added to ten moles (840 g.) of thiophene over a two-hour period during which time the temperature was allowed to rise at a constant rate from 50 to 100°. Then nitrogen was passed through the reaction mixture for forty minutes while the mixture was heated at 90°. The cold reaction mixture was washed in turn with water, 5% sodium carbonate solution and water, and then dried over sodium sulfate. The mixture was distilled until the vapor temperature reached 150°. Hydrogen chloride was evolved during the distillation. The 404 g. of residue was divided. One-half (202 g.) was distilled directly under 4 mm. pressure. The major portion of the distillate was chlorine substitution products. In addition, there was a higher boiling fraction consisting of 8 g. of liquid, b. p. 112° (4 mm.), from which no II was obtained, and 74 g. of black tarry residue from which 7 g. of I was isolated by recrystallization from ASTM naphtha.

The other one-half (202 g.) of the mixture was kept at −30° for eighteen hours and then at room temperature for twenty-four hours. The precipitate, I (25 g.) that formed was separated by filtration. The filtrate was fractionated under reduced pressure (5 mm.) and gave, in addition to the chlorine substitution products, 47 g. of II, b. p. 110–118° (5 mm.), and 12 g. of black crystalline residue. The residue was recrystallized from ASTM naphtha and gave 2 g. of white crystalline product, m. p. 64–69°. II was recrystallized from ASTM naphtha; m. p. 44.5–46°; $n^{50}\text{D}$ 1.5688.

Anal. Calcd. for $C_4H_4Cl_4S$: C, 21.26; H, 1.79; Cl, 62.8; S, 14.2. Found: C, 21.26; H, 1.87; Cl, 62.9; S, 14.2.

Pyrolysis of α-2,3,4,5-Tetrachlorothiolane, I.—Forty grams of I was refluxed at about 180° for thirteen hours. Hydrogen chloride was evolved throughout the heating period. The liquid product had a refractive index, $n^{30}\text{D}$, of 1.5698. Distillation at atmospheric pressure gave 22 g. of dichlorothiophenes, b. p. 160–168°, and 8 g. of residue. The dichlorothiophene fraction was analyzed by infrared spectrograms which indicated the composition was 50% 2,3-dichlorothiophene and 50% 2,4-dichlorothiophene which contained a trace of 2,5-dichlorothiophene.

Reaction of α-2,3,4,5-Tetrachlorothiolane with Ethanolic Potassium Hydroxide.—A solution of 168 g. (3 moles) of potassium hydroxide in 504 g. of absolute ethanol was heated to 65–70°. The heater was removed and 226 g. (1 mole) of I, m. p. 106–110°, was added over a two-hour period so that the temperature was maintained at 65–70°. Considerable heat was evolved. The mixture then was refluxed at 80° for twenty-two hours. Water was added and the mixture was steam distilled into approximately 250 ml. fractions. Water was added to each fraction to precipitate an oil. The oily layers from the first three fractions were combined. The water layers were extracted twice with petroleum ether; the petroleum ether solution was distilled and the residual oil, 15 ml., added to the main body of the oil. The combined oil was washed with water to remove alcohol and then treated again with a mixture of 10 g. of sodium hydroxide and 10 g. of potassium hydroxide at 100–125° for five hours to react with any I that might remain. The excess alkali and any salt formed was removed by filtration and 124 g. (81%) of dichlorothiophenes was obtained as filtrate. The dichlorothiophenes, b.p. 155–185°, were separated by fractionation and analyzed by infrared absorption spectrograms. The analysis indicated a dichlorothiophene composition of approximately 2% 2,5-dichlorothiophene, 44% 2,4-dichlorothiophene, no 2,3-dichlorothiophene, and 54% 3,4-dichlorothiophene.

Reaction of α-2,3,4,5-Tetrachlorothiolane with Chlorine.—One mole of chlorine was passed into a solution of 34 g. (0.15 mole) of I, m.p. 110–112°, in 500 ml. of carbon tetrachloride at 40° during a two-hour period. The resultant product was evaporated on a steam-bath, and the crystalline residue, 34 g., m.p. 104–110°, showed no depression of the melting point with I.

Anal. Calcd. for $C_4H_4Cl_4S$: Cl, 62.8. Found: Cl, 63.3.

Four moles of chlorine was passed into 113 g. (0.5 mole) of I, m.p. 110–112°, at 115° during a one hundred-minute period. The product was a liquid which weighed 120 g., 7 g. more than the original I. The product was washed in turn with water, 5% sodium carbonate solution and water. The product gave 80 g. of distillate, b.p. 57–113° (4 mm.), and 10 g. of residue.

2,2,3,4,5-Pentachlorothiolane, III.—Two moles of chlorine was passed into 1 mole (119 g.) of 2-chlorothiophene at −30 to −35° during an eighty-minute period. Nitrogen was passed through the cold mixture for five minutes. The mixture was transferred to a stoppered flask and placed in a Dry Ice–acetone-bath at −70°, but crystallization was slow. The addition of 25 ml. of petroleum ether facilitated crystallization. After four hours the cold mixture was filtered. The precipitate (46 g.) after recrystallization from petroleum ether melted at 31–32°; $n^{35}\text{D}$ 1.5755; $\Delta n\text{D}/\Delta t = -0.0005$. The calculated refractive index, $n^{20}\text{D}$, was 1.5830.

Anal. Calcd. for $C_4H_3Cl_5S$: C, 18.45; H, 1.16; Cl, 68.1; S, 12.3. Found: C, 18.32; H, 1.09; Cl, 67.9; S, 12.5.

Pyrolysis of 2,2,3,4,5-Pentachlorothiolane, III.—Twelve grams of III with refractive index, $n^{33}\text{D}$, of 1.5740 was refluxed for twenty-four hours. Evolution of hydrogen chloride had practically ceased after that time. The condenser was inverted and 9 g. of light red oil was obtained by distillation. Redistillation gave a colorless product, b.p. 190–195°. Infrared absorption analysis indicated that of the trichlorothiophenes present 92% was 2,3,5-trichlorothiophene and 8% 2,3,4-trichlorothiophene.

Reaction of 2,2,3,4,5-Pentachlorothiolane, III, with Ethanolic Potassium Hydroxide.—Twelve grams of pentachlorothiolane with refractive index, $n^{33}\text{D}$, of 1.5740 was refluxed with 50 ml. of 20% ethanolic potassium hydroxide for eight hours. The mixture was diluted with 100 ml. of water and steam distilled. The steam distillate was extracted with ether; the ether solution was washed with water, dried over calcium chloride, and then distilled. The distillate, b.p. 198–212°, weighed 8 g. and infrared absorption analysis indicated that of the trichlorothiophenes present 65% was 2,3,4-trichlorothiophene and 35% was 2,3,5-trichlorothiophene.

2,2,3,4,5,5-Hexachlorothiolane, IV.—Twenty-six and one-half moles of chlorine was added to 420 g. (5 moles) of thiophene over a five and one-half hour period. The temperature was maintained at 40° except during the last hour when it was lowered to 5°. The mixture evolved some chlorine at room temperature. A 400-g. sample of the 1284 g. of product was washed in turn with water, 5% sodium carbonate solution, and water. The alkaline and water solutions were extracted with carbon tetrachloride. The organic material was combined and dried over sodium sulfate. The carbon tetrachloride was distilled and the residue fractionated; the yield of IV was 354 g. (77%); b.p. 100–105° (1 mm.). The compound was recrystallized by adding just sufficient petroleum ether to dissolve the crystals and then cooling the solution slowly to 0°. The white crystalline product melted at 45–46°; $n^{50}\text{D}$ 1.5590, $\Delta n\text{D}/\Delta t = -0.0005$. IV gave an immediate precipitate with alcoholic silver nitrate.

Anal. Calcd. for $C_4H_2Cl_6S$: C, 16.29; H, 0.69; Cl, 72.2; S, 10.9. Found: C, 16.31; H, 0.64; Cl, 71.8; S, 10.8.

Chlorination of 2,5-Dichlorothiophene.—Five moles of chlorine was passed, during a two-hour period, into 100 g. (0.65 mole) of 2,5-dichlorothiophene at 5–10°. The product weighed 130 g. There was 20 g. of distillate, b.p. 115–120° (5 mm.), which after recrystallization from petroleum ether had a m.p. 45–46°. This material gave no depression of the melting point with IV prepared from thiophene as described above.

Pyrolysis of 2,2,3,4,5,5-Hexachlorothiolane, IV.—Forty-five grams of IV was refluxed (about 215°) for seventy-two hours. Hydrogen chloride evolution was rapid at first, but very slow near the end. Upon distillation there was obtained 7 g., b.p. 76–83 (3 mm.), and 17 g. of 2,3,4,5-tetrachlorothiophene, b.p. 75–77° (2 mm.), m. p. 29°. The latter material gave no depression of the melting point with pure tetrachlorothiophene, m. p. 29.09°.

Reaction of 2,2,3,4,5,5-Hexachlorothiolane, IV, with Ethanolic Potassium Hydroxide.—A solution of 20 g. of potassium hydroxide in 180 g. of absolute alcohol was heated to 60° and 45 g. of IV added over a ten-minute period. The mixture was refluxed for eighteen hours.

Water was added and the mixture steam distilled. The organic layer was separated and the water layer extracted four times with 30-ml. portions of petroleum ether. The combined organic material was dried over calcium chloride, filtered and fractionated. The 2,3,4,5-tetrachlorothiophene weighed 7 g., mixed m.p. 29°.

Reaction of 2,2,3,4,5,5-Hexachlorothiolane, IV, with Zinc.—A suspension of 150 g. of 90% zinc dust in 500 ml. of water was heated to 95°, and 250 g. of IV added over a one and one-quarter hour period. The unreacted metal was removed by filtration and the organic layer separated. The water layer was extracted with ether and yielded 21 g. of product. The organic material was combined and the ether distilled. The distilled 2,5-dichlorothiophene weighed 85 g.; b.p. 160–163°; n^{20}_D 1.5624.

Acknowledgment.—The authors are grateful to Dr. D. E. Badertscher and Dr. C. C. Price for their advice and interest in this problem, to Miss Emily Burns who carried out a great many of the laboratory experiments, and to Mr. J. G. Ehlers for infrared spectrographic analyses.

Summary

Thiophene reacts with chlorine to produce both addition and substitution products in proportions dependent upon the reaction conditions and the ratio of chlorine to thiophene.

Chlorine addition products were isolated. These are identified as α-2,3,4,5-tetrachlorothiolane, β-2,3,4,5-tetrachlorothiolane, 2,2,3,4,5-pentachlorothiolane and 2,2,3,4,5,5-hexachlorothiolane. The compounds are white crystalline materials stable at room temperature.

Pyrolysis of α-tetrachlorothiolane and of pentachlorothiolane gave mixtures of dichlorothiophenes and trichlorothiophenes, respectively, varying in composition from the chlorothiophenes formed by dehydrohalogenation with ethanolic potassium hydroxide.

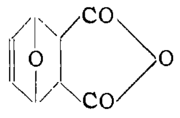
PAULSBORO, N. J. RECEIVED JULY 28, 1947

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Reaction of Furan with Maleic Anhydride[1]

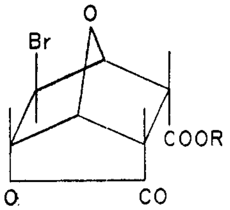
BY R. B. WOODWARD AND HAROLD BAER

In an attempt to synthesize cantharidine or cantharidine-like compounds, Diels and Alder[2] undertook the study of the reaction of furan with maleic anhydride. The two substances reacted in ether solution to give a crystalline adduct, m.p. 125°, which was shown to have the structure (I).



I

Subsequently, the same authors[3] observed that an aqueous solution of maleic acid dissolved furan on long shaking. When the resultant solution was treated with bromine a substance, $C_8H_7O_5Br$, m.p. 205°, was precipitated, to which the structure (II, R = H) was assigned. This bromolactonic acid was converted by diazomethane to a monomethyl ester (II, R = Me), m.p. 175°. Hydrobromic acid at 100° converted (II) to an isomer (III, R = H), from which an ester (III, R = Me), m.p. 168°, was obtained, while the same agent, at 160–170°, converted (II) to *o*-phthalic acid. These observations indicated that the solution of furan in aqueous maleic acid contained *endo-cis*-1,4-endoxo-Δ^5-cyclohexene-2,3-dicarboxylic acid (IV). It is significant that the German authors presented no evidence of the actual isolation from the solution of an adduct. *On the assumption that the acid obtained by the hydrolysis of the crystalline anhydride (I) was identical with the acid contained in the aqueous solution of furan in maleic acid, Diels and Alder assigned the structure (V) to the adduct, m.p. 125°.*



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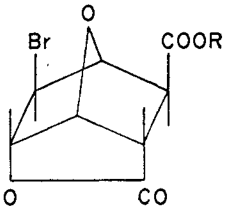

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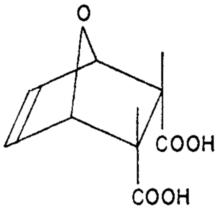

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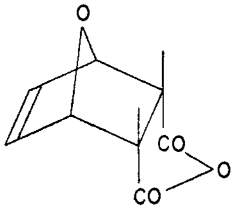
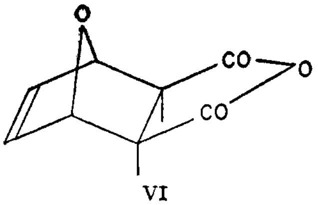


V

In this communication, it is shown that that assumption was incorrect and that, in fact, the product of the addition of maleic anhydride to furan is *exo-cis*-3,6-endoxo-Δ^4-tetrahydrophthalic anhydride (VI). When the anhydride, m.p.



VI

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(1) This paper is the third in a series of studies on diene addition reactions. For II, see Woodward and Baer, THIS JOURNAL, 66, 645 (1944).

(2) Diels and Alder, *Ber.*, 62, 557 (1929).

(3) Diels and Alder, *Ann.*, 490, 243 (1931).