[Contribution from the Department of Chemistry of the University of Wisconsin]

Ketene Acetals. XXXIII. The Addition of Halogens and Cyanogen Compounds to Methylketene Diethylacetal

By S. M. McElvain and William L. McLeish[1]

Received February 18, 1955

Salts of the type $[\mathrm{CH_3CHXC(OEt)_2}]^+\mathrm{X}^-_{n-1}$ (*n* is 4 when X = I; *n* is 0 and 2 when X = Br) have been isolated and shown to be the intermediates through which certain dimeric products are formed when these halogens react with methylketene diethylacetal. Cyanogen does not react with this ketene acetal, but both bromocyanogen and iodocyanogen add readily as $\mathrm{X} \rightarrow\!-\,\mathrm{CN}$ to give only $\mathrm{CH_3CHXC(OEt)_2CN}$ in high yields. Hydrogen cyanide reacts exothermically with the ketene acetal to yield mono- and dimeric addition products XII and XIII.

The formation of methyl ortho-α-bromoisobutyrate from the bromination of dimethylketene dimethylacetal in the presence of an orthoester[2] indicates the transitory existence of the cationic species, $\mathrm{(CH_3)_2CBr\overset{+}{C}(OMe)_2}$, which doubtless is stabilized by the contributing bromonium and oxonium structures. In the present paper the isolation and characterization of salts of such onium cations and polyhalide anions are reported.

The addition of an ethereal solution of iodine to methylketene diethylacetal (I) in ether at 25° consumed approximately 46% of an equivalent of iodine and produced the iodoester III (8%), ethyl α-methyl-β,β-diethoxy-γ-iodovalerate (VI) (66%), and the dimer of the ketene acetal VII (15%). The ratio of the yields of III and VI is considerably lower than that of analogous products obtained in the bromination of this ketene acetal,[2] but are of the order that would be expected when an excess of the ketene acetal is present during a large part of the reaction period. However, the formation of the dimer VII was quite unexpected and led to a further study of this reaction.

When the order of addition of the reactants was reversed and the reaction run at 0°, a precipitate that appeared crystalline and changed in color from brown to brick-red separated from the ether solution as the ketene acetal was added. After an equivalent of the ketene acetal had been added, the composition of the brick-red precipitate corresponded to IV, $n = 4$; lesser amounts of the ketene acetal produced a brown precipitate, for which the value of n approached 6. The composition of IV was determined by removal of the supernatant liquid, treatment of the precipitate with cold water and ether, titration of the mixture first with a standard solution of sodium thiosulfate and then with base. These titrations give, respectively, the amount of iodine (n) in the anion and a measure of the iodine that had added to I to form the cation of II and/or IV. The ether, after separation from the titrated aqueous layer, contained *only* the iodoester III in an amount corresponding to the acid that was titrated in the aqueous layer. It thus appears that the large excess of iodine present during the early part of this reaction makes possible reaction 2.

The salt IV, which melted to a black, intractable oil when allowed to warm to room temperature, could be dissolved and decolorized by further treatment with the ketene acetal at 0°. The reaction products in this case were III, VI and VII. Titration of iodine with the ketene acetal in ether at 25° produced no precipitate and yielded III (64%) and VI (23%); under these conditions *no VII was formed.*

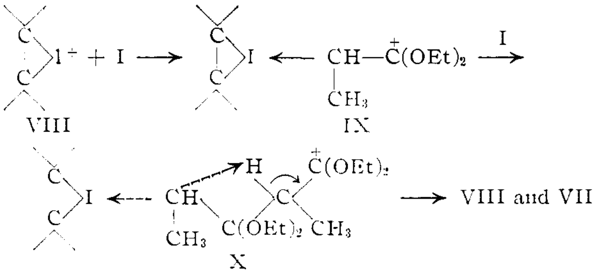
$$\underset{\mathrm{I}}{\mathrm{CH_3CH{=}C(OEt)_2}} + \mathrm{I_2} \longrightarrow \underset{\mathrm{II}}{[\mathrm{CH_3CHIC(OEt)_2}]^+\mathrm{I}^-} \longrightarrow \underset{\mathrm{III}}{\mathrm{CH_3CHICOOEt}} + \mathrm{EtI} \qquad (1)$$

$$\mathrm{II} + (n/2)\mathrm{I_2} \longrightarrow \underset{\mathrm{IV}}{[\mathrm{CH_3CHIC(OEt)_2}]^+\mathrm{I}^-_{n+1}} \qquad (2)$$

$$\mathrm{II\ or\ IV} + \mathrm{I} \longrightarrow \underset{\mathrm{V}}{[\mathrm{CH_3CHIC(OEt)_2CH(CH_3)C(OEt)_2}]^+\mathrm{I}^-} \longrightarrow \qquad (3)$$
$$\underset{\mathrm{VI}}{\mathrm{CH_3CHIC(OEt)_2CH(CH_3)COOEt}} + \mathrm{EtI}$$

$$2\mathrm{I} \xrightarrow{\mathrm{II\ or\ IV}} \underset{\mathrm{VII}}{\mathrm{CH_3CH_2C(OEt)_2C(CH_3){=}C(OEt)_2}} \qquad (4)$$

It appears from the results described above that dimer VII is formed by the coördination of the ketene acetal I with the cation of II or IV, probably in its more stable iodonium form VIII to produce the cation IX which then reacts with another molecule of the ketene acetal to yield X. A proton shift then separates VII from the cation VIII. This mechanism assigns a catalytic role to VIII and is supported by the observation that ten mole per cent. of iodine converted the ketene acetal in ether solution at 0° to VI (7%) and VII (16%).



The intermediate II doubtless furnishes the cation VIII when VII is formed at 25° in the presence of an excess of the ketene acetal. However, when an excess of iodine is present during the early part of the reaction, it seems necessary to have the reaction temperature sufficiently low to permit the unstable salt IV to exist until the concentration of the ketene acetal builds up sufficiently for reaction 4 to proceed.

---

[1] Wisconsin Alumni Foundation Research Assistant 1951–1952, 1953–1954; National Science Foundation Fellow 1952–1953.

[2] S. M. McElvain and W. R. Davie, This Journal, **74**, 1816 (1952).

In contrast to I, dimethylketene dimethylacetal, $(CH_3)_2C{=}C(OMe)_2$, gives only methyl α-iodoisobutyrate (reaction 1) when treated with iodine at 0°. Apparently, the hindrance afforded by the *gem*-dimethyl groups prevents any dimerizations of this ketene acetal corresponding to reactions 3 and 4.

An orange bromide corresponding to II was precipitated when the ketene acetal I was added to a solution of bromine in carbon tetrachloride at −5 to 0°. Analysis of this salt (total bromine content 58.3%) indicated that it contained slightly more than one (1.2) bromine atom in the anion; ethyl α-bromopropionate was the only product isolated from this salt after treatment with potassium iodide followed by titration with sodium thiosulfate. When this reaction was conducted at −25°, a red salt containing 69.5% total bromine was formed; this analysis indicates the anion contains approximately three (2.7) bromine atoms.

These bromides, which like the polyiodide IV melt and decompose when allowed to warm to room temperature, appear to be intermediate in stability between the cations of type II previously proposed to explain the reaction of ketene acetals with bromine[2] and the di- and tetraphenylethylene–bromine complexes that contain a carbonium ion so unreactive toward the anion as to prevent the completion of the bromination.[3]

Treatment of iodine monochloride in carbon tetrachloride with the ketene acetal, I, at 0° gave no solid precipitate, but the separation of an insoluble maroon oil, which readily dissolved on continued addition of I, was observed. Approximately 1.85 equivalents of I was required to decolorize the halogen solution. The reaction products were ethyl α-chloropropionate (17%), the iodoester III (17%), the iodoketal VI (14%) and the ketene acetal dimer VII (26%). III, VI and VII doubtless result from the iodonium cation VIII from which these compounds were formed in the reaction of the ketene acetal with iodine. The high yield of VII with this mixed halogen may be related to the greater solubility of the intermediate chloride salt. These reaction products would be expected from the polarization, $I \rightarrow\!\!- Cl$, of iodine monochloride. The ethyl α-chloropropionate was probably the result of some disproportionation of iodine monochloride into iodine and chlorine and the reaction of the latter halogen with the ketene acetal.[4]

Reactions of Cyanogen Compounds.—No apparent reaction occurred when cyanogen was passed into the ketene acetal I at 100°. Bromocyanogen, however, added readily to I to yield α,α-diethoxy-β-bromobutyronitrile (XI) in high yields (97%). This single product was obtained regardless of the order of mixing of the reactants. Similarly, the reaction of iodocyanogen with I gave the corresponding iodo compound XIa in 88% yield (reaction 5). It is apparent from these reactions that these halocyanogens are polarized as $X \rightarrow\!\!- CN$. The absence of any dimeric reaction products shows that the cyanide anion reacts more rapidly with the intermediate cation than does the ketene acetal.

The bromonitrile XI is quite stable to heat, but is slowly pyrolyzed at its reflux temperature (210°) into ethyl α-bromopropionate (23% after 5 hr.) hydrogen cyanide and, presumably, ethylene (reaction 6). However, the cyanide group of XI, because of its attachment to a carbon carrying two ethoxyl groups, is readily replaceable as shown by its reaction with aqueous silver nitrate to yield silver cyanide (92%) and ethyl α-bromopropionate (76%) together with 0.71 equivalent of a titratable acid (HNO_3) (reaction 7).

$$\begin{array}{lll} I + X\text{-}CN \longrightarrow & CH_3CHXC(OEt)_2CN & (5) \\ X = Br \text{ or } I & XI, X = Br & \\ & XIa, X = I & \end{array}$$

$$XI \xrightarrow{\Delta} CH_3CHBrCOOEt + HCN + CH_2{=}CH_2 \quad (6)$$

$$XI + H_2O + AgNO_3 \longrightarrow$$
$$AgCN + CH_3CHBrCOOEt + HNO_3 + EtOH \quad (7)$$

Hydrogen cyanide added exothermically to I to yield α,α-diethoxybutyronitrile (XII) (71%) and the dimeric product, α,α,γ,γ-tetraethoxy-β-methylcapronitrile (XIII) (25%). Reversal of the order of addition, *i.e.*, the ketene acetal to the acid, gave XII and XIII in 86 and 4% yields, respectively. The formation of XIII in this reaction indicates the existence of a more reactive intermediate cation (carbonium ion), which can attack another molecule of the ketene acetal, and supports the postulate that the presence of a halogen in the intermediate cation produces the more stable halonium structure of the type of VIII.

$$CH_3CH_2C(OEt)_2CN \quad XII$$
$$CH_3CH_2C(OEt)_2CH(CH_3)C(OEt)_2CN \quad XIII$$

Experimental

Reactions of Methylketene Diethylacetal (I) **with Iodine.** (a).—A solution of 16.0 g. (0.123 mole) of methylketene diethylacetal[5] in 300 ml. of ether at 25° was titrated with stirring to a permanent yellow color with a solution of iodine in ether over a period of 1.75 hr. At this point 14.4 g. (0.057 mole) of iodine, corresponding to an absorption of 46% of an equivalent of iodine, had been used. The solvent and ethyl iodide were distilled off and the last traces removed at 9 mm. pressure. Distillation of the residual material gave 3.5 g. (8%) of ethyl α-iodopropionate (III), 2.4 g. (15%) of the dimer (VII), and 14.5 g. (66%) of ethyl α-methyl-β,β-diethoxy-γ-iodovalerate (VI). The latter compound boils at 92° (0.25 mm.), $n^{25}D$ 1.4782, d^{25}_4 1.3509, liberates iodine when treated with bromine or on standing, and gives an immediate precipitate with silver nitrate.

Anal. Calcd. for $C_6H_8(OC_2H_5)_3IO$: I, 35.5; OC_2H_5, 38; *MR*D, 75.37. Found: I, 35.0; OC_2H_5, 36.5; *MR*D, 75.02.

When 13.2 g. of VI was heated for 15 min. at 210°, 6.86 g. of the ethyl iodide–ethyl alcohol azeotrope had distilled. From the dark brown residue was isolated 0.95 g. (17%) of ethyl α,γ-dimethyltetronate,[2] b.p. 153–168°, $n^{25}D$ 1.4731. Hydrolysis of this product gave the free acid,[2] m.p. 121.5–122.5°.

Methyl-α,α-diethoxypropylketene diethylacetal (VII) boiled at 47° (0.25 mm.), $n^{25}D$ 1.4305, and showed a characteristic absorption peak in the infrared at 6.01 μ (the ketene acetal I shows an absorption peak at 5.97 μ). VII first added and then substituted bromine and slowly gave a green coloration with ferric chloride.

---

(3) R. E. Buckles and N. A. Meinhart, THIS JOURNAL, **74**, 1171 (1952).

(4) Evidence for a similar dissociation of iodine monobromide influencing the course of a halogenation reaction is reported by A. G. Sharpe, *J. Chem. Soc.*, 3713 (1953).

(5) S. M. McElvain and W. R. Davie, THIS JOURNAL, **73**, 1400 (1951).

Anal. Calcd. for $C_6H_8(OC_2H_5)_4$: OC_2H_5, 69.3. Found: OC_2H_5, 66.2.

A mixture of 6.85 g. of VII and 1.52 g. of water was heated at 85–95° with stirring for 30 minutes. The solution became deep red in color. It was dried and distilled to furnish 2.65 g. (64%) of ethyl α-propionylpropionate, which yielded a phenylpyrazolone, m.p. 108–110°.[6]

(b).—Dropwise addition of the ketene acetal I to 25.2 g. (0.10 mole) of iodine in 500 ml. of ether at 25° caused a fleeting yellow spot to appear as each drop struck the surface of the iodine solution, but no lasting precipitate was formed. After one hour, 16.5 g. (0.127 mole) of the ketene acetal had been added, and the iodine solution was nearly colorless. Distillation yielded 18.5 g. (64%) of the iodoester III and 5.3 g. (23%) of the iodoketal VI.

(c).—A solution of 2.17 g. (0.0085 mole) of iodine in 28 ml. of ether was added to 11.1 g. (0.085 mole) of I in 117 ml. of ether at 0° over a period of one hour. The products, 1.75 g. (16%) of the dimer VII and 1.05 g. (7%) of the iodoketal VI, were not completely separated, but their amounts were estimated from the iodine content of the distillation fractions. The results so obtained agreed with estimations made from the index of refraction. The recovered ketene acetal amounted to 8.0 g. (72%).

(d) **Preparation of the Polyiodide IV.**—To a solution of 61.0 g. (0.236 mole) of iodine in 450 ml. of ether at 0–5° was added with vigorous stirring 31.2 g. (0.240 mole) of the ketene acetal I over a period of 40 min. After approximately one-half of I had been added, the reddish color of the iodine had disappeared and only the greenish tint of the brown-black precipitate was visible; when all of the ketene acetal had been added, the precipitate was brick red. The light yellow, supernatant liquid was forced through a filter stick by pressure of dry nitrogen and the remaining solid was treated with 200 ml. of cold ether and 25 ml. of cold water. This mixture was titrated while stirring with a standard solution of sodium thiosulfate until colorless; this titration showed the presence of 0.118 mole of iodine in the precipitate. The ether and water layers then were separated and the aqueous layer titrated with standard base against phenolphthalein; this titration showed an aqueous layer contained 0.058 mole of acid, which is equivalent to the iodine that had added to I. Distillation of the ether layer yielded 11.8 g. (0.052 mole, 22%) of ethyl α-iodopropionate (III). These titrations show the anion of IV to be I_5^- ($1 + 2 \times 0.118/0.058 = 5$).

When a solution of 119.8 g. (0.472 mole) of iodine in 800 ml. of ether at *ca.* −3° was treated with 20.4 g. (0.157 mole) of the ketene acetal over a period of 15 min., a heavy, brown precipitate was formed. This precipitate, when treated as described above, was found to contain 0.315 mole of iodine by the sodium thiosulfate titration and to yield 0.12 mole of acid on reaction with water. From the ether layer 22.5 g. (0.10 mole, 63%) of ethyl α-iodopropionate (III), was obtained.

A precipitate of IV, prepared from 49.6 g. (0.196 mole) of iodine and 25.4 g. (0.196 mole) of I, was mixed with 100 ml. of cold ether. Titration of this ether suspension required 27.7 g. (0.213 mole) of the ketene acetal to destroy the iodine color. The products of this reaction, after removal of the ether, were 6.6 g. (0.029 mole) of III, 7.0 g. (0.027 mole) of VII, and 20.4 g. (0.057 mole) of VI; 3.5 g. (0.027 mole) of excess ketene acetal was recovered.

Iodination of Dimethylketene Dimethylacetal.—To a solution of 10.2 g. (0.088 mole) of dimethylketene dimethylacetal[7] in 100 ml. of ether was added 21.3 g. (0.084 mole) of iodine in 200 ml. of ether at 0° over a period of three hours. This corresponded to an absorption of 95% of an equivalent of iodine. Distillation of the orange solution furnished 18.1 g. (90%) of methyl α-iodoisobutyrate, b.p. 64° (12 mm.), n^{25}D 1.5010.

Anal. Calcd. for $C_5H_9IO_2$: I, 55.7. Found: I, 55.3.

Preparation of $[CH_3CHBrC(OEt)_2]^+Br^-_{n+1}$. (a).—To a solution of 98.5 g. (0.616 mole) of bromine in 200 ml. of carbon tetrachloride at −5° was added with vigorous stirring 21.0 g. (0.162 mole) of the ketene acetal I in 100 ml. of carbon tetrachloride over a period of 35 min. A heavy, granular, red solid separated; after all of the ketene acetal had been added the color was orange. The solvent was removed through a filter stick, and the solid was shaken with 20 ml. of cold water until it had entirely liquefied. This mixture was treated with a solution of 100 g. of potassium iodide in water, and shaken until the reddish bromine color could not be seen. This mixture consumed sodium thiosulfate solution in an amount to indicate 0.303 mole of bromine, and then required 0.083 mole of sodium hydroxide to neutralize the acid in the water layer. The remaining organic layer was extracted and distilled; 12.2 g. (0.07 mole, 42%) of ethyl α-bromopropionate was obtained. The carbon tetrachloride solution which had been removed from the solid was shaken with a solution of 76 g. of potassium iodide in water, and decolorized with 0.345 equivalent of sodium thiosulfate; there remained, therefore, 0.173 mole of bromine in this supernatant carbon tetrachloride. Distillation of the carbon tetrachloride solution gave 8.8 g. (0.049 mole, 30%) of the bromoester. In another similar experiment the carbon tetrachloride solution, which had been removed from the solid and vigorously shaken with water, was shown by titration with base to contain a negligible amount of dissolved polybromide salt.

(b).—To a solution of 12.5 g. (0.078 mole) of bromine in 60 ml. of carbon tetrachloride at 0° was added with stirring 10.6 g. (0.081 mole) of ketene acetal I in 40 ml. of carbon tetrachloride over a period of 1 hr. Most of the solid which formed during the early part of the addition had been dissolved at the end, but 2.1 g. of an orange powder remained. It was dried at 0.1 mm. pressure and 0°; analyses for total bromine content (Stepanov) showed this salt to contain 58.3% bromine.

(c).—The red solid obtained from the addition of 2.6 g. (0.02 mole) of the ketene acetal I to a solution of 6.4 g. (0.04 mole) of bromine in 8 ml. of carbon tetrachloride at −25 to −30° amounted to 4.1 g., and contained 69.5% total bromine by the Stepanov analysis.

Reaction of I with Iodine Monochloride.—To 20.2 g. (0.124 mole) of iodine monochloride[8] in 100 ml. of carbon tetrachloride was added 30.1 g. (0.232 mole) of I at 0° over a period of 40 min. to form a colorless solution. No solid precipitate was observed during the addition, but an insoluble red to brown oil appeared, and was dissolved readily by more of the ketene acetal. Two distillations of the reaction mixture were required to separate it into 5.4 g. (17%) of ethyl α-chloropropionate, 9.1 g. (17%) of iodoester III, 7.9 g. (26%) of dimer VII and 5.7 g. (14%) of iodoketal VI.

Reaction of I with Cyanogen Compounds. (a) **Cyanogen.**—Gaseous cyanogen[9] was bubbled through 18.3 g. of I at 100° while the liquid was agitated with magnetic stirrer. After three hours the weight of the ketene acetal had not changed. On distillation 16.0 g. (87%) of the ketene acetal was recovered.

(b) **Bromocyanogen.**—Slow addition with stirring of 51.1 g. (0.393 mole) of I to a solution of 41.7 g. (0.393 mole) of bromocyanogen[10] in 70 ml. of ether caused the ether to reflux steadily during the addition period (25 min.); any interruption of the ketene acetal addition stopped the reflux within a few seconds. Distillation furnished a total of 90.4 g. (97%) of crude α,α-diethoxy-β-bromobutyronitrile (XI). The pure material boiled at 108° (16 mm.), n^{25}D 1.4463, d^{25}_4 1.2611; it showed a weak absorption at 4.45 μ in the infrared.

Anal. Calcd. for $C_8H_{14}BrNO_2$: C, 40.70; H, 5.96; N, 5.93; OC_2H_5, 38.2; *MR*D, 50.03. Found: C, 40.97; H, 6.03; N, 5.80; OC_2H_5, 38.2; *MR*D 49.92.

A stirred solution of 19.6 g. (0.15 mole) of I in 150 ml. of ether was treated with a solution of 18.0 g. (0.17 mole) of bromocyanogen in 50 ml. of ether. Distillation furnished 28.9 g. (81%) of XI as the only isolable reaction product.

A solution of 4.32 g. (0.0254 mole) of silver nitrate in 5 ml. of water was shaken eight hours with 6.00 g. (0.0254 mole) of **XI**. The precipitated silver cyanide was separated, washed well with ether and dried; it weighed 3.5 g. (92%). The water solution contained 0.181 mole (71%) of acid. Distillation of the ether washings yielded 3.5 g. (76%) of ethyl α-bromopropionate, b.p. 54° (14 mm.), n^{25}D 1.4427.

---

(6) O. Emmerling and L. Kristeller, *Ber.*, **39**, 2450 (1906).

(7) S. M. McElvain and C. L. Aldridge, This Journal, **75**, 3587 (1953).

(8) J. Cornog and R. A. Karges, *Inorganic Syntheses*, **1**, 165 (1939).

(9) G. Hahn and W. Leopold, *Ber.*, **68**, 1974 (1935).

(10) W. W. Hartman and E. E. Dreger, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 150.

The hydrogen cyanide evolved during a 5.5-hr. period of refluxing (210°) of 10 g. of XI formed 1.2 g. (21%) of silver cyanide when passed into a solution of silver nitrate. Distillation of the residual material at 16 mm. gave 23% of impure ethyl α-bromopropionate as three fractions boiling between 60 and 106°, $n^{25}\text{D}$ 1.4414–1.4433; 63% of the original XI was recovered.

(c) **Iodocyanogen.**—A solution of 11.4 g. (0.075 mole) of iodocyanogen[11] in 50 ml. of ether was caused to reflux gently by dropwise addition of 9.7 g. (0.075 mole) of I. Distillation furnished 18.5 g. (88%) of α,α-diethoxy-β-iodobutyronitrile (XIa); a middle fraction boiled at 84–89° (0.15 mm.), $n^{25}\text{D}$ 1.4798.

Anal. Calcd. for $C_8H_{14}INO_2$: N, 4.95; OC_2H_5, 31.8. Found: N, 4.89; OC_2H_5, 31.7.

(d) **Hydrogen Cyanide.**—To 2.45 g. (0.091 mole) of hydrogen cyanide at −10° was added with stirring 11.8 g. (0.091 mole) of I. A small amount of white precipitate that formed was dissolved as the addition was continued. Distillation yielded 12.2 g. (86%) of α,α-diethoxybutyronitrile (XII), b.p. 62–63° (10 mm.), $n^{25}\text{D}$ 1.4040, d^{25}_4 0.9113, and 0.5 g. (4%) of $\alpha,\alpha,\gamma,\gamma$-tetraethoxy-$\beta$-methylcapronitrile (XIII), b.p. 70° (0.25 mm.), $n^{25}\text{D}$ 1.4330, d^{25}_4 0.9641.

Anal. Calcd. for $C_8H_{15}NO_2$: N, 8.92; OC_2H_5, 57.3; *MR*D, 42.19. Found: N, 8.78; OC_2H_5, 57.3; *MR*D, 42.19. Calcd. for $C_{15}H_{29}NO_4$: N, 4.88; OC_2H_5, 62.7; *MR*D, 77.81. Found: N, 4.69; OC_2H_5, 62.8; *MR*D, 77.53.

To 17.1 g. (0.13 mole) of methylketene diethylacetal in a flask cooled by an ice–salt mixture was added 3.9 g. (0.14 mole) of liquid hydrogen cyanide over a period of 20 min. Considerable heat was evolved in this reaction. After standing at 25° for 1.5 days, the reaction mixture was distilled; 14.6 g. (71%) of XII and 4.7 g. (25%) of XIII were obtained.

MADISON, WISCONSIN

---

[11] H. T. Comastri, *Anales asoc. quim. argentina*, **27**, 45 (1939); *C. A.*, **33**, 6743 (1939).

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Synthesis and Reactions of Vinylene Carbonate

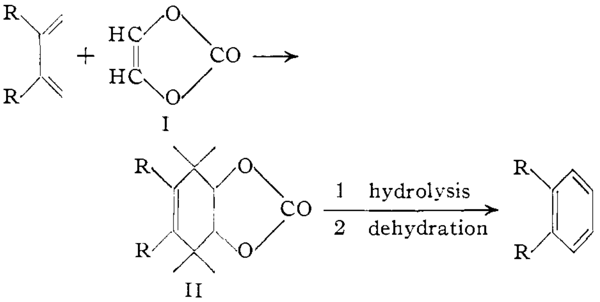
BY MELVIN S. NEWMAN AND ROGER W. ADDOR[1]

RECEIVED FEBRUARY 3, 1955

The synthesis of vinylene carbonate by chlorination of ethylene carbonate followed by dehydrochlorination of chloroethylene carbonate is described. Diels–Alder reactions of vinylene carbonate which lead to syntheses of aromatics and of *cis*-glycols have been effected.

Maleic anhydride is the most widely used dienophile in Diels–Alder reactions as it reacts readily with a wide variety of dienes. However, if the synthesis of a new six-carbon ring without substituents is desired, one must either remove the adjacent carboxyl groups from the adduct or use a dienophile which has groups more readily removed than carboxyl. The former problem still awaits a good general solution.[2] We therefore thought of the latter alternative. Furthermore, in seeking to rationalize the reasons for the superior activity of maleic anhydride in the Diels–Alder reaction, we thought that the shape of the molecule was of importance in addition to the polar characteristics imparted by the anhydride function. Conceivably the flat structure would offer a minimum of steric hindrance to the formation of the addition complex which probably orients the diene and dienophile prior to actual bond formation. Accordingly, the structure, vinylene carbonate (I), was conceived as a structure which would not only approximate maleic anhydride from the steric aspect but also would yield an adduct II, readily convertible to an aromatic structure.

Upon further thought vinylene carbonate was of interest from two other points of view. Adducts of structure II on hydrolysis should yield *cis*-diols, substances ordinarily not obtained too easily. In addition vinylene carbonate was expected to be of interest in the field of polymerization, since on hydrolysis of its polymers (or copolymers), polymers containing adjacent hydroxyl groups would be obtained.



The synthesis of vinylene carbonate[3] (I) was accomplished by chlorination of ethylene carbonate to chloroethylene carbonate (III), which was dehydrochlorinated by means of triethylamine to I. A large number of other dehydrochlorinating agents were tried but triethylamine was the best. When tertiary amines of smaller steric requirements were used, quaternization caused a drop in yield. With trimethylamine an almost quantitative yield of quaternary salt was obtained. Pyrolysis of the latter afforded no vinylene carbonate. When dehydrochlorination was attempted with a solution of potassium *t*-butylate in *t*-butyl alcohol a small yield of 4-*t*-butoxy-1,3-dioxol-2-one (IV) was obtained but no I.

When ethylene carbonate was chlorinated under optimum conditions (70–80°) for monochlorination, some dichloroethylene carbonate (V) also was obtained. If the temperature of chlorination were higher (120–125°) the yield of V was greater, but the formation of other compounds boiling in the

---

[1] Taken from the Ph.D. thesis of R. W. A., The Ohio State University, 1954. The authors wish to acknowledge with thanks a grant from the Research Corporation in support of this work.

[2] W. E. Doering, M. Farber and A. Sayigh, THIS JOURNAL, **74**, 4371 (1952). In a conversation Dr. Doering said that the published method failed when any sample of lead dioxide other than the original one was used.

[3] M. S. Newman and R. W. Addor, THIS JOURNAL, **75**, 1263 (1953).