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}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}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}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}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

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[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

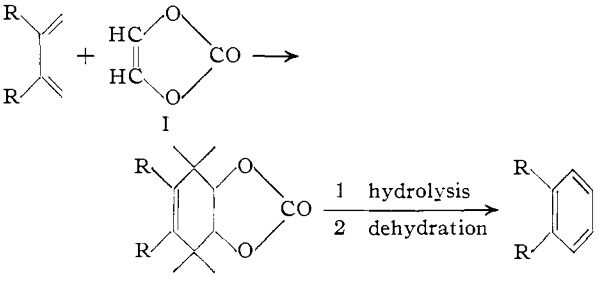
BY MELVIN S. NEWMAN AND ROGER W. ADDOR[1]

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

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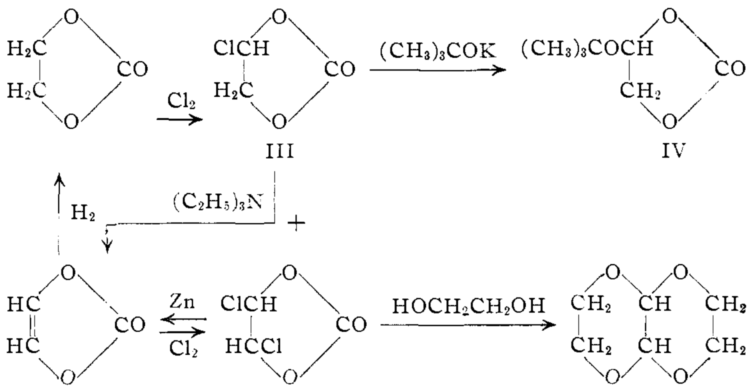
[1] Taken from the Ph.D. thesis of R. W. A., The Ohio State University, 1954. The authors wish to acknowledge with thanks a grant from the Research Corporation in support of this work.

[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).

monochloroethylene carbonate range made difficult the isolation of any pure III. The dichloro compound could be converted into I in 29% yield by treatment of V with zinc dust in a mixture of 1,2-dimethoxyethane and benzene. Since the same dichloro compound V was obtained by adding chlorine to I as by chlorination of ethylene carbonate, V is assumed to be the *trans* isomer.

The structure of vinylene carbonate is established from the following facts: elemental analysis; catalytic reduction to ethylene carbonate; strong absorption bands at 3.12 μ (carbon–hydrogen) and 5.48 μ (strained ring carbonyl); and hydrolysis followed by treatment with excess phenylhydrazine to yield glyoxal phenylosazone, m.p. undepressed by admixture with an authentic sample,[4] m.p. 168–170°. The structures of monochloroethylene and dichloroethylene carbonates are considered established by their analyses, their method of formation, and their reactions. As previously pointed out,[3] the boiling points of ethylene carbonate, 248°, chloroethylene carbonate, 212°, dichloroethylene carbonate, 178°, and vinylene carbonate, 162°, are of interest.

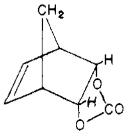


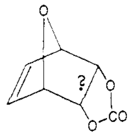
III IV I V VI

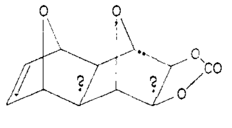
(*cis* and *trans*)

The Diels–Alder reaction was carried out successfully between vinylene carbonate and the following dienes: 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, cyclopentadiene, hexachlorocyclopentadiene, furan and anthracene. In every case except that of the hexachlorocyclopentadiene adduct, the structure was established by hydrolysis of the corresponding glycols followed by conversion of the latter to known substances. These conversions are described in the Experimental part. The structure of the chlorinated adduct was not proved. Unfortunately, no adduct was obtained on heating I with 3,4,3',4'-tetrahydro-7,7'-dimethyl-1,1'-binaphthyl, an intermediate in the synthesis of coronene.[5]

The adduct from cyclopentadiene, VII, is shown in the *endo* structure since work on the diol obtained on hydrolysis supports this structure.[6] The adduct VIII from I and furan was obtained in two stereoisomeric forms (*endo* and *exo*) in a ratio of about 4 to 1. We have not established the fine structure of either.[7] In addition to the 1:1 adducts, VIII, there were obtained a diadduct, IX, and a mixture of polymeric adducts which are probably compounds of a similar structure except for additional 1,4-epoxycyclohexane rings. The 1:1 adducts, VIII, were obtained in fair yield (20–35%) only when a large excess of I was present.


VII

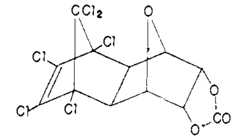

VIII


IX

The gross structure of IX is supported by analysis, by the fact that on hydrogenation only one mole of hydrogen was absorbed and by the similarity of the infrared absorption spectrum of IX to that of VIII. The absorption spectra of various fractions of the polymeric adducts also were similar to those of VIII and IX. Diadducts of this type have been reported previously[8] although the structures were not proved. Analogous 2:1 adducts have been reported for the reactions of cyclopentadiene with allyl cyanide,[9] 1,2-dichloroethylene,[9] vinyl chloride[10] and vinyl acetate.[10] In the case of cyclopentadiene and vinylene carbonate, a small yield of 2:1 compound was isolated.

Since the adduct VIII from furan and I appeared to be so receptive to further additive attack by furan, it was thought that VIII might add other dienes. This proved to be the case as VIII reacted with perchlorocyclopentadiene to yield an adduct X, the fine geometry of which has not been established.

A few experiments showed that vinylene carbonate could be polymerized by heating with benzoyl peroxide. The polymeric mixtures formed ranged from clear viscous liquids to tough plastic solids which became hard and brittle on exposure to air.


X

A film of plastic polymer deposited from acetone in which it was soluble showed strong carbonyl absorption at 5.55 μ (1800 cm.$^{-1}$). Infrared examination of the gelatinous solid which precipitated from the solution obtained by treating polymer with potassium hydroxide solution showed hydroxyl absorption at 3.0 μ (3320 cm.$^{-1}$) and a lack

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[4] H. J. H. Fenton and H. Jackson. *J. Chem. Soc.*, 578 (1899).

[5] M. S. Newman, THIS JOURNAL, **62**, 1683 (1940).

[6] H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954).

[7] Furan and maleic anhydride yield the *exo* adduct in ether, J. A. Norton, *Chem. Revs.*, **31**, 498 (1942), whereas furan and maleic acid yield the *endo* adduct in water, R. B. Woodward and H. Baer, THIS JOURNAL, **70**, 1161 (1948).

[8] O. Diels and S. Olsen, *J. prakt. Chem.*, **156**, 285 (1940), reported a 2:1 adduct of furan and dimethyl acetylenedicarboxylate.

[9] K. Alder and E. Windemuth. *Ber.*, **71**, 1939 (1938).

[10] K. Alder and H. Rickert. *Ann.*, **543**, 1 (1939).

of carbonyl absorption. Partial hydrolysis of another sample of polymer with ammonium hydroxide followed by evaporation of excess ammonia on a steam-bath afforded a dark solid which absorbed in the 2.9–3.1 μ (OH) and the 5.7–5.8 μ (CO) regions. Evidently this sample was a partly hydrolyzed polymeric material.

Experimental

Vinylene Carbonate (I).—Chloroethylene carbonate (III) was prepared as previously described[3] in yields which varied from 65–75%. The apparatus for chlorination consisted of a wide tube (*ca.* 60 cm.) in which a quartz U-tube was sealed by means of graded seals at the top. A gas bubbling tube was sealed in the side so that gas could be introduced at the bottom. The quartz tube, evacuated and partly filled with mercury vapor, served as an ultraviolet light source. Chlorination occurred over a wide temperature range but a temperature near 70° is recommended.

To a stirred refluxing mixture of 150 g. (1.22 moles) of III in 150 ml. of dry ether was added 155 g. (1.53 moles) of redistilled pure triethylamine over four hours. After a total of 39 hours of refluxing the dark solid was collected and washed four times with benzene–ether. The amount obtained was 170 g. (theory for triethylamine hydrochloride is 163 g.). This solid gave about the same infrared absorption curve as triethylamine hydrochloride except that a small peak at 5.5 μ indicated the probable presence of quaternary salt. After distillation of solvent and excess triethylamine through a short column, further distillation at 30 mm. afforded 67.5 g. of I, b.p. 69–72°, and 9.0 g. of dark solid, b.p. 72–80°. Redistillation of the latter afforded 8.0 g. of I to bring the total yield to 71.6%. Rectification at 32 mm. afforded pure vinylene carbonate, b.p. 73–74°, m.p. 22.0° (time–temperature cooling curve), $n^{25}\text{D}$ 1.4190, $d^{25}{}_4$ 1.3541, strong infrared absorption at 3.12 and 5.48 μ.

Pure I also was obtained in 29% yield by refluxing a mixture of 10 g. of dichloroethylene carbonate (V) and 15 g. of zinc dust in 70 ml. of 35% ethylene glycol dimethyl ether in benzene for 12 hours.

Vinylene carbonate readily absorbed an equivalent of chlorine to yield a sample of V which had the same properties[3] as that isolated by vacuum rectification of the mixture produced when ethylene carbonate was chlorinated. However, small peaks at 9.3 and 9.8 μ, which accompanied strong peaks at 9.15 and 9.65 μ, were absent in the sample of V produced by addition of chlorine to I. Perhaps this means a small amount of *cis*-dichloroethylene carbonate is formed during chlorination of ethylene carbonate as the *trans* compound is undoubtedly formed on addition of chlorine to I. It is interesting that almost entirely *trans* dichloro compound V is formed in chlorination of ethylene carbonate.

Catalytic hydrogenation of I over a commercial platinic oxide catalyst[11] was very slow and incomplete. However, the theoretical amount of hydrogen was absorbed at room temperature in a 21-hr. hydrogenation at 35 p.s.i. over a 5% rhodium-on-alumina catalyst[11] to afford pure distilled ethylene carbonate in 76% yield.

Glyoxal Phenyl Osazones. a. From I.—One gram of I was dissolved in 4 ml. of concd. ammonium hydroxide. The solution was warmed for a few minutes, then cooled, neutralized and treated with excess phenylhydrazine. The gummy solid formed was recrystallized from 80% methanol several times to yield a small amount of glyoxal phenylosazone, m.p. 167–169°, undepressed by admixture with an authentic sample,[12] m.p. 168–170°. b. **From V.**—To 8 ml. of dilute ammonia was added 1.34 g. of V. After several minutes the solution was neutralized and treated with aqueous 2,4-dinitrophenylhydrazine reagent to yield 2.5 g. (87%) of glyoxal 2,4-dinitrophenylosazone, m.p. about 320° dec.[13]

4-*t*-Butoxy-1,3-dioxol-2-one (IV).—To a solution of 8.0 g. of III in 60 ml. of 1:1 *t*-butyl alcohol–ether was added dropwise with stirring 50 ml. of a 1.23 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol. After 22 hours at 0° the still basic reaction mixture was held one hour at 25°, after which time it was neutral. Distillation of the filtered solution afforded 1.2 g. of an almost completely solid distillate, b.p. 128–130° at 5–6 mm., which, on crystallization from petroleum ether, b.p. 65–110°, afforded 0.59 g. of colorless needles of IV, m.p. 73.2–74.0°, strong carbonyl absorption at 5.60 μ.

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.5; H, 7.6. Found: C, 52.6; H, 7.6.

The molecular weight, as determined cryoscopically in benzene, was 188 (theory 160). In connection with the abnormally high b.p. of ethylene carbonate, 248° at 760 mm., it is of interest that the molecular weight (cryoscopic in benzene) was 113 (average of two experiments) (theory 88).

Glyoxal Bis-ethylene Acetal, *cis* and *trans*, VI.—A solution of 2.64 g of V and 5.7 g. of ethylene glycol in 6 ml. of benzene was refluxed for 4 hours. Strong evolution of hydrogen chloride occurred. On removal of the benzene the residue yielded 1.75 g. of a colorless solid, which on fractional crystallization from ether (aided by separation of crystals by hand) yielded the two isomers[14] of VI, m.p. 111–113° and 134.6–135.6°.

Dibromoethylene Carbonate.—To a stirred refluxing mixture of 8.0 g. in I in 50 ml. of carbon tetrachloride was added 15 g. of bromine over a $2^1/_3$ hour period. The mixture was refluxed one hour more and then distilled to yield 21.4 g. (94%) of dibromoethylene carbonate as a nearly colorless solid, b.p. 93–102° at 12 mm. A colorless analytical sample, b.p. 96–97° at 10–11 mm., $n^{33.7}\text{D}$ 1.5288, $d^{33.7}\text{D}$ 2.2824, m.p. 29.0° by time–temperature cooling curve, was obtained after two redistillations. This compound had strong carbonyl absorption at 5.45 μ.

Anal. Calcd. for $C_3H_2O_3Br_2$: C, 14.7; H, 0.8; Br, 65.0; *MR*D (Eisenlohr), 32.7. Found: C, 15.2; H, 0.8; Br, 65.2; *MR*D, 33.2.

Diels–Alder Reactions. a. 1,3-Butadiene.—A mixture of 19.3 g. of I, 4.7 g. of 1,3-butadiene, 5.4. g. of benzene and 0.1 g. of hydroquinone was sealed in a nitrogen-flushed Pyrex tube and heated at 173–175° for 19 hours. After decantation of the reaction mixture from some polymeric material the benzene and 16.1 g. of vinylene carbonate were distilled under reduced pressure through a small packed column. Distillation of the residue afforded 3.2 g. (26%) of the cyclic carbonate of *cis*-4,5-dihydroxycyclohexene, b.p. 130–133° at 3–4 mm., m.p. 48–53°. Recrystallization from 30% chloroform in Skellysolve B (petroleum ether, b.p. 60–70°) yielded 2.97 g. in four crops which melted from 50–53°. The analytical sample, m.p. 52.4–53.2°, was obtained by recrystallization from ether and from 20% Skellysolve F (petroleum ether, b.p. 35–40°)–ether.

Anal. Calcd. for $C_7H_8O_3$: C, 60.0; H, 5.8. Found: C, 59.8; H, 5.9.

A sample was hydrolyzed by warming with 10% potassium hydroxide. After neutralization the *cis*-4,5-dihydroxycyclohexene, m.p. 78–80°, was obtained in 97% yield by continuous ether extraction. An analytical sample, m.p. 80.3–81.1°, was obtained by several recrystallizations from Skellysolve B–benzene mixtures.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.2; H, 8.8. Found: C, 63.3; H, 9.1.

On catalytic reduction in ethanol over previously reduced platinic oxide the theoretical uptake of hydrogen was complete after ten minutes. Two recrystallizations afforded *cis*-1,2-cyclohexanediol,[15] m.p. 98–99°.

b. **2,3-Dimethyl-1,3-butadiene.**—In the best of several runs a mixture of 4.29 g. of I, 1.08 g. of freshly distilled diene, a few crystals of hydroquinone and 1.1 g. of benzene was sealed under nitrogen in a Pyrex tube and heated at 175–185° for 15 hr. Distillation afforded 3.54 g. of I and 1.35 g. (61% based on diene) of adduct as a colorless oily solid, b.p. 132–134° at 2–3 mm. On recrystallization from ether–Skellysolve F 1.1 g. of crystals, m.p. 57.5–59.0°, was obtained. The analytical sample of the cyclic carbonate of *cis*-4,5-dihydroxy-1,2-dimethylcyclohexene melted at 57.1–57.7°.

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.3; H, 7.2. Found: C, 64.6; H, 7.4.

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[11] Baker and Co., Inc., Newark, N. J.

[12] H. J. H. Fenton and H. Jackson, *J. Chem. Soc.*, 578 (1899).

[13] S. Glasstone and A. Hickling, *ibid.*, 820 (1936), reported a m.p. of 330°.

[14] J. Boeseken, F. Tellegen and P. C. Henriquez, *Rec. trav. chim.*, **50**, 909 (1931), give 109–112° and 133–136° as melting points for these isomeric acetals.

[15] P. Bedos and A. Ruyer, *Compt. rend.*, **204**, 1350 (1937).

Hydrolysis of this adduct by warming with 40% sodium hydroxide followed by acidification, ether extraction and crystallization afforded *cis*-4,5-dihydroxy-1,2-dimethylcyclohexene, m.p. 80–83°, in 96% yield. The analytical sample, m.p. 86.6–87.4°, was obtained after two recrystallizations from carbon tetrachloride.

Anal. Calcd. for $C_8H_{12}O_2$: C, 67.6; H, 9.9. Found: C, 67.7; H, 9.9.

Acetylation of 2 g. of the diol by reaction with acetic anhydride and pyridine yielded the diacetate (89%) as a colorless oil, b.p. 121–123° at 3–4 mm.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.7; H, 8.0. Found: C, 64.1; H, 8.2.

From a small syringe 2.67 g. of the diacetate was dropped over a 3-hour period through a 11 × 60 cm. tube which contained a few glass beads at the top and was held at 490–500°. A slow stream of nitrogen was passed through during the pyrolysis. In addition to 0.5 g. of recovered diacetate there was isolated 0.73 g. of *o*-xylene, b.p. 80–82° at 95 mm. The identity with authentic *o*-xylene was established by comparison of the infrared absorption curves and by m.p. and mixed m.p. of the sulfonamide derivative,[16] m.p. 144.8–145.6°.

c. **Cyclopentadiene.**—A mixture of 1.07 g. of freshly distilled cyclopentadiene dimer, 4.50 g. of freshly distilled I, 1 g. of benzene and a trace of hydroquinone was sealed in a nitrogen-flushed Pyrex tube and heated at 170–177° for 16 hours. Distillation of the mixture yielded 2.63 g. of I and 2.17 g. of an almost colorless solid, b.p. about 150° at 4 mm. Recrystallization from 50% carbon tetrachloride in Skellysolve B afforded 1.89 g. (77%) of adduct, VII, m.p. 107–112°. A pure sample, m.p. 114.4–115.0°, was obtained on further recrystallization (ref. 6 gives m.p. 113.2–113.5°).

By many recrystallizations of the material in the mother liquor a small amount of an adduct, m.p. 162–165°, which contained two units of cyclopentadiene to one of I was obtained.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.5; H, 6.5. Found: C, 71.9; H, 6.1.

On alkaline hydrolysis VII was converted into endo-*cis*-bicyclo[2,2,1]hept-5-ene-2,3-diol, m.p. 173–177°, in 86% yield. Vacuum sublimation raised the melting range to 176–179° dec. but repeated attempts at recrystallization failed to improve the melting behavior.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.6; H, 8.0. Found: C, 66.3; H, 8.0.

Catalytic hydrogenation over prereduced platinum catalyst[11] afforded the saturated glycol, *endo-cis* bicyclo[2,2,1]hepta-2,3-diol, as colorless needles, m.p. 210.6–212.4° in a sealed capillary.[17] Oxidation of 0.12 g. of this diol was effected in one hour at 13–15° with 15 ml. of a solution prepared by addition of 4.08 g. of potassium dichromate to 65 ml. of concd. sulfuric acid and 120 ml. of water.[18] The excess oxidant was destroyed with sodium bisulfite and the solution was extracted continuously with ether. After evaporation of ether, 0.15 g. of colorless crystals were obtained. After two recrystallizations from benzene–Skellysolve B the m.p. was 119–121°[19] and the neutral equivalent was 79.2. A m.p. of 120–121.5° is reported[19] for *cis*-1,3-cyclopentanedicarboxylic acid and the theoretical neutral equivalent is 79.1.

d. **Hexachlorocyclopentadiene.**—A mixture of 13.0 g. of I, 8.2 g. of freshly distilled hexachlorocyclopentadiene,[20] b.p. 82–84° at 4 mm., and 5 g. of benzene was sealed in a tube and heated at 177–183° for 26 hours. Unchanged I, 7.9 g., was removed by vacuum distillation and the residue was taken up in benzene and passed through a small column of alumina. Crystallization of the material in the eluate from Skellysolve C (petroleum ether, b.p. 90–100°) and from Skellysolve B yielded 8.6 g. (80% based on diene) of the cyclic carbonate of *cis*-1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]hept-5-ene-2,3-diol, m.p. 240–243°. The analytical sample melted at 241.0–242.8° after sintering at 236°.

Anal. Calcd. for $C_8H_2O_3Cl_6$: C, 26.8; H, 0.6; Cl, 59.3. Found: C, 26.6; H, 0.5; Cl, 59.2.

e. **Furan.**—In the best of several experiments a mixture of 4.0 g. of furan and 25.0 g. of I (ratio of I/furan = 5) was heated for 21 hours at 123–127° in a sealed tube. On vacuum distillation 21.8 g. of I was recovered. Further distillation yielded 3.09 g. (34%) of a mixture of solids, b.p. 150–165° at 2 mm. Crystallization from benzene and a little Skellysolve B afforded 2.69 g. of colorless needles, m.p. 95–140°, which further study showed to be mainly a mixture of *exo* and *endo* furan–vinylene carbonate adducts.

In another experiment a 1.0-g. sample of crystalline product, m.p. 100–145°, was put on a 3.4 × 16 cm. column of 2:1 silicic acid (Mallinckrodt Chromatographic Grade)–Celite[21] in 50 ml. of benzene. After development with a solvent composed of 720 ml. of benzene, 120 ml. of Skellysolve C and 55 ml. of ether, the column was streaked with permanganate. Elution of the upper 4-cm. band with ether followed by crystallization of the product from 40% chloroform in carbon tetrachloride, yielded 0.15 g. of colorless needles of one isomer of VIII, m.p. 137.0–137.7°. A total of 0.78 g. of the second isomer of VIII, m.p. 148.8–149.6°, was obtained from the bottom band in the column and [mostly] from the developer solvent. That these two compounds were the *exo* and *endo* forms of the cyclic carbonate of oxabicyclo[2,2,1]hept-5-ene-2,3-diol was indicated by analysis and by comparison of the infrared absorption curves. We estimate the total yield of the two isomers in this experiment to be about 23% (based on furan).

Anal. Calcd. for $C_7H_6O_4$: C, 54.6; H, 3.9. Found (137° isomer): C, 54.5; H, 4.1. (149° isomer): C, 54.6; H, 4.1.

From a higher boiling fraction of the original reaction mixture products there was isolated 0.74 g. of another substance, m.p. 241.8–242.2° (sealed capillary), which was undoubtedly a diadduct IX. Insolubility of IX in benzene aided in isolation.

Anal. Calcd. for $C_{11}H_{10}O_5$: C, 59.5; H, 4.5. Found: C, 59.7; H, 4.6.

When 0.50 g. of a mixture of isomers of VIII and 0.88 g. of furan was heated for 20 hours at 135°, 0.60 g. of benzene-insoluble product was obtained. This material, as judged by infrared absorption, was probably a mixture of products similar to IX. The wide and high melting range, 230–300°, indicated that multiple addition of furan had occurred. This type of product and higher resinous materials predominated when the original reaction between furan and I was carried out with furan in equivalent amount or in excess.

The structure of the isomers VIII was established by hydrolysis, reduction of the unsaturated glycol to a saturated glycol and oxidation of the isomeric mixture of the latter to *cis*-2,5-tetrahydrofurandicarboxylic acid. Hydrolysis was accomplished by shaking 0.23 g. of VIII, m.p. 149°, with 5 ml. of 5% sodium hydroxide. After neutralization, continuous extraction with ether afforded 0.19 g. (100%) of *cis*-oxabicyclo[2,2,1]hept-5-ene-2,3-diol, m.p. 145–152°. Two recrystallizations from benzene and vacuum sublimation (100° at 10 mm.) did little to improve the melting range which became 147–152°.

Anal. Calcd. for $C_6H_8O_3$: C, 56.2; H, 6.3. Found: C, 56.2; H, 6.6.

When a mixture of the isomers of VIII was used for hydrolysis, the glycol mixture was formed in equally high yield and the melting range was 85–122°. This mixture was hydrogenated in ethanol over prereduced catalyst[11] to a mixture of saturated glycols, 0.25 g. of which was oxidized by heating with 3 cc. of nitric acid (d. 1.42) for two hours at 75–80°. There was isolated 0.26 g. (84%) of slightly yellow crystals of *cis*-tetrahydrofuran-2,5-dicarboxylic acid,[22] m.p. 124–126°. This acid had a neutralization equivalent of 80.4 (theoretical 80.1).

When 0.18 g. of a mixture of the isomers of VIII was refluxed for two days with 5 ml. of 48% hydrobromic acid

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(16) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N.Y., 1941, 3rd printing, p. 524.

(17) The m.p. of a sample of diol (sent by Drs. Kwart and Vosburgh, reported m.p. 201.2–201.7°, ref. 6) in a sealed Pyrex capillary was 207.1–208.4°. There was no depression when our diol was mixed with it.

(18) L. Semichon and M. Flanzy, *Compt. rend.*, **195**, 254 (1932).

(19) F. W. Semmler and K. Bartelt, *Ber.*, **41**, 866 (1908).

(20) We thank the Shell Development Co. for a generous sample of hexachlorocyclopentadiene.

(21) Diatomaceous earth, Johns–Manville product.

(22) W. N. Haworth, W. G. M. Jones and L. F. Wiggins, *J. Chem. Soc.*, 1 (1945), give m.p. 126–127°.

there was isolated 50 mg. of catechol, m.p. and mixed m.p. 101–103°, from the reaction product.

A mixture of 0.34 g. of VIII, m.p. 149°, 0.66 g. of hexachlorocyclopentadiene and 2 ml. of benzene was heated in a sealed tube at 155–160° for 21 hours. The mixture was taken up in 10 ml. of benzene and passed through a short column of alumina to remove much of the color. Concentration and addition of a little Skellysolve C yielded a total of 0.80 g. (85%) of crystalline X, m.p. 198–203°. Recrystallization from Skellysolve B containing a little benzene afforded a good yield of a fairly pure isomer, m.p. 200.0–200.6°, of the cyclic carbonate of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-epoxy-5,8-methanonaphthalene-2,3-diol (X).

Anal. Calcd. for $C_{12}H_6O_4Cl_6$: C, 33.8; H, 1.4; Cl, 49.8. Found: C, 33.7; H, 1.4; Cl, 49.8.

f. **Anthracene.**—A mixture of 0.52 g. of pure anthracene 2.06 g. of I and 4 ml. of dry benzene was sealed in a tube and heated at 160–170° for 12 hours. After removal of unchanged I by distillation there was obtained 0.68 g. (88%) of adduct, m.p. 254–257° by crystallization from benzene Skellysolve B. The analytical sample of the cyclic carbonate of *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-diol formed colorless needles, m.p. 259.0–259.6°.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.2; H, 4.6. Found: C, 77.3; H, 4.8.

On hydrolysis of this adduct with warm 40% sodium hydroxide for one hour there was obtained a quantitative yield of *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-diol, m.p. 201.9–202.7°.[23]

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 80.7; H, 5.9. Found: C, 80.9; H, 6.0.

Oxidation of 0.13 g. of diol at 13–17° for 5 hours and at 0° for 11 hours with acid dichromate[18] afforded a small yield of *cis*-9,10-dihydroanthracene-9,10-dicarboxylic acid,[24] m.p. 281–284°.

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[23] All melting points for analytical samples are corrected. Analyses by Galbraith and Clark Analytical Laboratories.

[24] J. Mathieu, *Ann. chim.*, [11] **20**, 215 (1945), gives m.p. 283°.

COLUMBUS 10, OHIO

[CONTRIBUTION NO. 334 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Synthesis and Polymerization of Vinyl Sulfonates[1]

BY J. C. SAUER AND J. D. C. WILSON

RECEIVED FEBRUARY 9, 1955

Monomeric vinyl sulfonates have been prepared by the direct vinylation of the sulfonic acid with acetylene in yields of 50–75%. Vinyl methanesulfonate has been homopolymerized and copolymerized with a variety of vinyl monomers.

Esters of vinylsulfonic acid (I), in which R is an alkyl group, and their polymers are known.[2] However, monomeric vinyl esters of sulfonic acids (II) have not hitherto been reported.

$$\underset{\text{I}}{CH_2{=}CH{-}SO_3R} \qquad \underset{\text{II}}{R{-}SO_3CH{=}CH_2}$$

Copolymers of vinyl sulfonates (II) have been prepared indirectly by partially esterifying a preformed polyvinyl alcohol or a hydrolyzed ethylene/vinyl acetate copolymer with a sulfonyl chloride.[3] Homopolymers of vinyl sulfonates (II) or other copolymers have not been reported, due to the inaccessibility of the monomeric vinyl esters needed for such an investigation.

It has been found that monomeric vinyl sulfonates II can be prepared by the direct vinylation of a sulfonic acid with acetylene in an ether solvent in the presence of mercuric oxide catalyst.[4]

$$R{-}SO_3H + HC{\equiv}CH \xrightarrow{HgO} RSO_3CH{=}CH_2$$

The R group can be methyl, butyl, phenyl or *p*-tolyl, and the yields range from 50 to 75%.

An ether solvent such as dioxane or dibutyl ether has given best results in this synthesis; oxonium salt formation of the sulfonic acid with the ether group may be involved. Attempts to isolate vinyl esters in the absence of solvent or in the presence of benzene were unsuccessful.

A convenient procedure for carrying out the synthesis involved injecting acetylene at 7–18 atmospheres pressure into a rocker bomb containing the sulfonic acid, solvent, and catalyst heated to 50–60°. Acetylene was repressured as required. The vinyl esters were isolated by distillation. These products were characterized by spectral and elemental analyses, hydrogen number and saponification number. In addition, vinyl benzenesulfonate was hydrogenated to ethyl benzenesulfonate which was compared with an authentic sample.

Polymerization studies were carried out mainly with vinyl methanesulfonate. A low softening homopolymer was obtained in conversions up to 30% in aqueous medium using a persulfate–bisulfite initiator. Vinyl methanesulfonate was also found to copolymerize with a variety of vinyl monomers yielding compositions containing vinyl methanesulfonate in a wide range of proportions. However, the yields, inherent viscosities, and stick temperatures of the copolymers decreased with increasing vinyl methanesulfonate content.

Vinyl benzenesulfonate was converted into viscous, tacky homopolymers with polymerization initiators of the ionic or free radical types.

During the course of this work, one of us developed a sensitization to unidentified substances. Several other persons who worked with the vinyl sulfonates were not affected. Although the adverse physiological effects have not been definitely assigned to the vinylsulfonates, care should be used in handling them.

Experimental

Source and Purification of the Materials.—Methanesulfonic acid was purchased from the Eastman Kodak Company and was purified by distillation at the lowest pressure

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[1] Presented at the Cincinnati Meeting of the American Chemical Society, March, 1955.

[2] Abstracts of the September, 1950, meeting of the American Chemical Society at Chicago, p. 10-J. V. V. Alderman and W. E. Hanford, U. S. 2,348,705 (1944). Z. Földi, *Ber.*, **53B**, 1836 (1920).

[3] D. D. Reynolds and W. O. Kenyon, THIS JOURNAL, **72**, 1584 (1950); W. H. Sharkey, U. S. Patent 2,395,347 (1946).

[4] J. C. Sauer, U. S. 2,667,469 (1954).