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Rearrangement of Polyynes. IX.[1] Dimers of Tri-*t*-butylethynylmethyl Halides

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In an early attempt to prepare hexaacetylenic ethanes, Gray and Marvel[2] treated tri-*t*-butylethynylcarbinol (I) with phosphorus trichloride and obtained a halogen compound which, although having the expected composition, did not show reactions which would be given by tri-*t*-butylethynylmethyl chloride (II). Later Salzberg and Marvel[3] were able to prepare the bromide (III) and show that it had the structure indicated. They observed that this bromide readily rearranged to a higher melting compound of the same composition, but they did not report further on the properties of this rearrangement product.

$$[(CH_3)_3CC{\equiv}C]_3C{-}OH \qquad [(CH_3)_3CC{\equiv}C]_3C{-}Cl$$

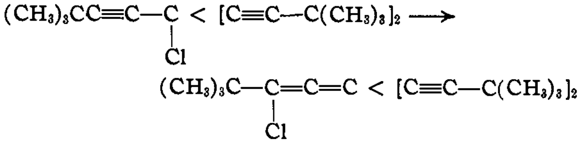
I II

$$[(CH_3)_3CC{\equiv}C]_3C{-}Br$$

III

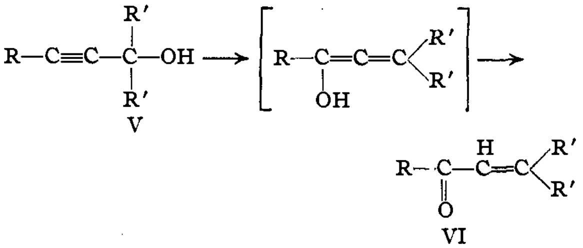
In the present investigation it has been found that the chloride of Gray and Marvel and the higher melting bromide of Salzberg and Marvel are produced by the rearrangement and dimerization of the simple halides (II and III). Each dimer contains one halogen atom which reacts with molecular silver and one halogen atom which does not react with this reagent. The product of the reaction of the dimeric halide and silver is a molecule of four times the original molecular weight minus the weight of the two halogen atoms removed by the action of silver. When the dimeric bromide is heated to its melting point, it decomposes with the evolution of hydrogen bromide and the formation of tar. When small amounts of the chloride are melted, a further rearrangement occurs, giving a new dimeric chloride in which both chlorine atoms are inert toward molecular silver.

In seeking an explanation for the ready dimerization of the tri-*t*-butylethynylmethyl halides (II and III) it occurred to us that a rearrangement of the acetylenic halide to an allenic halide (IV) might be an intermediate step. Such a shift of halogen atom from the 1- to the 3-position would be strictly analogous to the rearrangement of an acetylenic carbinol (V) to an unsaturated ketone (VI) which has been reported by Meyer and Schuster.[4] Salkind and Kruglow[5] have observed



$$(CH_3)_3CC{\equiv}C{-}\underset{\displaystyle Cl}{C} < [C{\equiv}C{-}C(CH_3)_3]_2 \longrightarrow (CH_3)_3C{-}\underset{\displaystyle Cl}{C}{=}C{=}C < [C{\equiv}C{-}C(CH_3)_3]_2$$

IV



$$R{-}C{\equiv}C{-}\underset{\displaystyle R'}{\overset{\displaystyle R'}{C}}{-}OH \longrightarrow \left[R{-}\underset{\displaystyle OH}{C}{=}C{=}C\begin{smallmatrix}R'\\R'\end{smallmatrix}\right] \longrightarrow R{-}\underset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle H}{C}{=}C\begin{smallmatrix}R'\\R'\end{smallmatrix}$$

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(1) For the eighth paper, see THIS JOURNAL, **58**, 29 (1936).

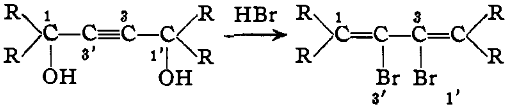
(2) Gray and Marvel, *ibid.*, **47**, 2796 (1925).

(3) Salzberg and Marvel, *ibid.*, **50**, 1737 (1928).

(4) Meyer and Schuster, *Ber.*, **55**, 819 (1922).

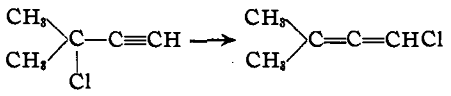
(5) Salkind and Kruglow, *ibid.*, **59**, 1936 (1926).

that treatment of certain acetylenic glycols (VII) with hydrogen bromide gives rise to unexpected products (VIII). This rearrangement must have



VII VIII

involved a double 1,3-shift of bromine atoms. Quite recently Favorsky and Favorskaja[6] have reported the rearrangement of the chloride of dimethylethynylcarbinol (IX) to 1-chloro-3-methyl-1,2-butadiene (X). This chloroallene apparently did not dimerize spontaneously.



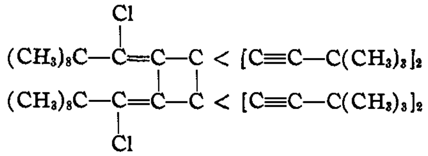
IX X

Evidence has been obtained that a 1,3-shift of the chlorine atom in the tri-*t*-butylethynylmethyl halide (II) actually occurs on heating. When the acetylenic methyl chloride was dissolved in acetic acid and warmed, the dimeric chloride was obtained in practically quantitative yields. If chromic anhydride was added to a solution of the chloride in acetic acid and the mixture was warmed, oxidation occurred and one product of the oxidation was di-*t*-butylethynyl ketone (XI).

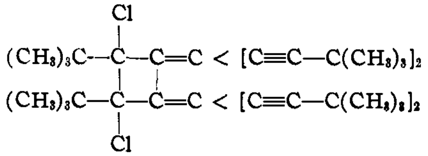
XI $[(CH_3)_3C—C \equiv C]_2 > C = O$

When the dimeric chloride was prepared first and then chromic anhydride was added to the mixture, the only oxidation product which could be isolated was one containing as many carbon and hydrogen atoms as were present in the dimeric chloride. Di-*t*-butylethynyl ketone would not be produced by any normal oxidation of tri-*t*-butylethynylmethyl chloride (II), but would be one of the expected oxidation products if a 1,3-shift of the chlorine atom to give the allenic chloride (IV) preceded oxidation.

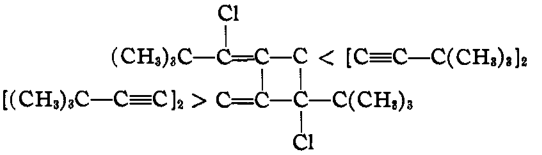
Acceptance of this allenic chloride (IV) as an intermediate in the dimerization of tri-*t*-butylethynylmethyl halides affords also a ready explanation of the properties of the dimeric halides. Work by Lebedev and Mereshovski[7,8] has shown that unsymmetrically substituted allenes on dimerization may produce any one of the three possible cyclobutane derivatives containing conjugated divinyl systems. On the basis of their work, it is possible to predict that the allenic chloride (IV) would give one or more of three cyclobutanes (XII, XIII or XIV) on dimerization.



XII

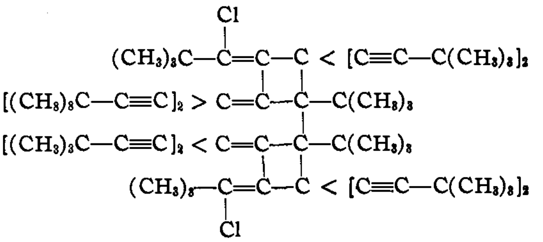


XIII



XIV

Of these possible dimers, formula XIV alone accounts for the properties of the dimeric halide which has been obtained by the low temperature rearrangement of the normal chloride. It is apparent that this molecule has one chlorine atom of the vinyl type which would not be expected to react with molecular silver. It also has an active chlorine atom of the allyl chloride type which should be removed by silver giving rise to the substituted dicyclobutyl XV. The compound obtained by the action of molecular silver on the dimeric chloride has the correct composition and molecular weight for such a dicyclobutyl.



XV

The dimeric bromide, which likewise contains an active bromine atom and an inactive bromine atom, must have a structure analogous to that of XIV and treatment of the dimeric bromide with molecular silver gives a compound $C_{76}H_{108}Br_2$, which must have a structure analogous to that of the chlorine analog (XV).

As mentioned earlier in this paper, the dimeric chloride (XIV) rearranged with the liberation of considerable heat when heated to its melting point. If more than a half gram of the dimeric

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(6) Favorsky and Favorskaja, *Compt. rend.*, **200**, 839 (1935).

(7) Lebedev and Mereshovski, *J. Chem. Soc.*, **104**, 1285 (1913).

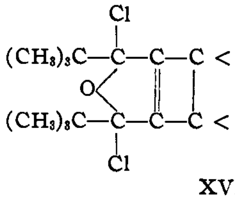
(8) Mereshovski, *ibid.*, **106**, 369 (1914).

chloride was melted, the reaction could not be controlled and tarry products resulted. However, by working with small samples it was possible to isolate a new dimeric chloride. In this new dimeric chloride, neither of the chlorine atoms was removed by the action of molecular silver. When this dimeric chloride was exposed to air or oxygen, it rapidly absorbed one atom of oxygen and then the chlorine atoms became so reactive that they could be removed by the action of hot alcohol with resulting formation of a dialkoxyl derivative.

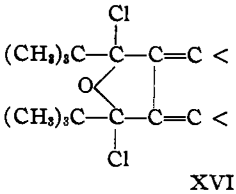
This behavior of the new dimeric chloride establishes its structure as that of a second of the possible dimers (XII) of the simple allene chloride. This structure accounts for the inactivity of the two halogen atoms as well as the ready oxidation of the molecule by air with consequent activation of the halogen atoms. The only organic halogen derivatives which react with alcohols to give replacement of the halogen by alkoxyl are acid chlorides and alpha-chloro ethers. The air oxidation product of the new dimeric chloride cannot be a diacid chloride because it is deficient in oxygen, and because it hydrolyzes to give a neutral and not an acidic compound. It must, therefore, be of the alpha-chloro ether type.

Kogerman[9] has shown that 2,3-dimethyl-1,3-butadiene absorbs only one atom of oxygen per molecule. He did not isolate the oxidation products. In the case at hand, we have been able to isolate the dihydrofuran which results from 1,4-addition of one atom of oxygen to a conjugated diene.

The product of air oxidation of the new dimeric chloride must have either structure XVI or structure XVII. On stereochemical grounds, formula XVII seems to be the more logical one, as formula XVI has a cyclobutene ring fused to a dihydrofuran ring, and this would seem to be a highly strained configuration.



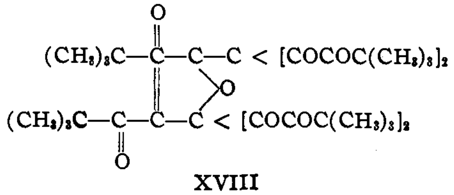
XVI



XVII

The chlorine atoms in this dichloro ether were replaced by methoxyl, ethoxyl, *n*-butoxyl and *n*-dodecanoxyl groups to give acetals which were stable toward alkalies, but which could be hydrolyzed with acids. Hydrolysis of any one of the acetals produced a compound which had the composition of the expected diketone, but no derivatives of the carbonyl groups could be prepared.

Oxidation experiments showed that the dimeric products were unexpectedly stable. Hot nitric acid converted the simple dimeric chloride, the rearranged dimeric chloride and any of the derivatives of the autoxidized dimeric chloride to a yellow solid which was not highly crystalline and which melted at about 60–65°. This rather poorly defined product seemed to vary in oxygen content from one experiment to the next, but it is expecially significant that carbon and hydrogen analyses on various samples invariably showed that the ratio of carbon to hydrogen in them was identical with the ratio of carbon to hydrogen in the skeletal molecule before oxidation; *i. e.*, $C_{38}H_{54}$. This establishes definitely that the various rearrangements which have been observed do not involve shifts of methyl groups which then could be easily removed by oxidation. The oxygen content of this oxidation product indicated ten or eleven atoms of oxygen in the molecule. To account for this amount of oxygen, it is necessary to assume that the nitric acid has oxidized the acetylenic groups to α-diketones, a reaction which is known to occur in certain less complicated molecules.[10] Assuming this change occurs in the oxidation, the molecule $C_{38}H_{54}O_{11}$ seems to be the most probable for our product, and its structure is very likely that shown in formula XVIII.



XVIII

In the course of this investigation, it has been found that the chlorine compound obtained by the action of titanium trichloride on tri-*t*-butylethynylcarbinol[11] is not $C_{38}H_{56}Cl_2$, but $C_{38}H_{54}Cl_2$,

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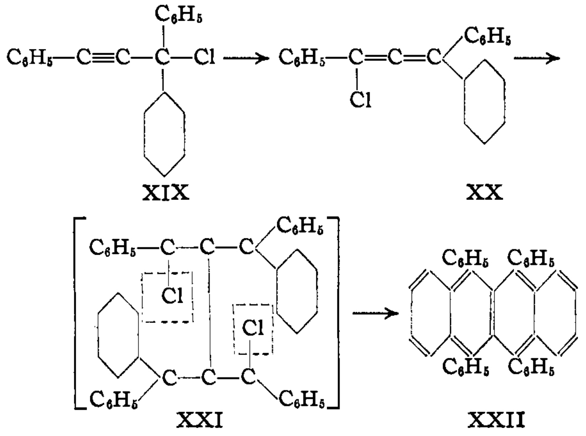
[9] Kogerman, Trans. 2nd World Power Conf., Berlin, **8**, 33 (1930); *C. A.* **25**, 5549 (1931).

[10] For example, see Overbeck, *Ann.*, **140**, 62 (1866).

[11] Sweet and Marvel, THIS JOURNAL, **54**, 1184 (1932).

and is identical with the dimeric chloride (XIV) obtained by the low temperature rearrangement of the normal chloride (II). Moreover, it has not been possible to repeat the experiment in which this chloride was believed to have been converted to the hydrocarbon $C_{38}H_{54}$ by the action of sodamide. Undoubtedly the previous sample of the chloride contained some of the hydrocarbon as an impurity.

This rearrangement of an acetylenic methyl halide to an allenic chloride is of some considerable interest in connection with the conversion of phenylethynyldiphenylchloromethane (XIX) to rubrene. Dufraisse and Velluz[12] have shown that rubrene is 9,10,11,12-tetraphenylnaphthacene (XXII). A very logical mechanism to account for this transformation of the chloro compound to the naphthacene derivative is to assume that phenylethynyldiphenychloromethane first rearranges to an allene chloride (XX), and then in the process of dimerization (XXI) loses hydrogen chloride before the cyclobutane ring is established.


XIX XX XXI XXII

Some incidental reactions of the dimeric chloride are recorded in the experimental part.

Experimental

Tri-*t*-butylethynylmethyl Chloride.—To a solution of 1 g. of tri-*t*-butylethynylcarbinol in 100 cc. of petroleum ether was added 0.2 g. of phosphorus trichloride. After allowing the mixture to stand for thirty minutes at room temperature, it was washed with 5% sodium bicarbonate solution, dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure at room temperature. The residue was dissolved in 20 cc. of dry ether, 5 cc. of alcohol was added and solvent was removed under reduced pressure at room temperature until crystals began to appear. After standing a short time, the mixture was filtered and the crystals were air dried at room temperature. The yield was 0.5 g. of chloro compound melting with rearrangement at 73°.

Anal. Calcd. for $C_{19}H_{27}Cl$: Cl, 12.3; mol. wt., 291. Found: Cl, 12.2; mol. wt. (cryoscopic in benzene), 306.

This same chloride was readily prepared by dissolving 1 g. of the carbinol in 5 cc. of ethyl alcohol and adding water until the mixture was barely turbid at 0°. The solution was then saturated with hydrogen chloride at 0°. The chloride which precipitated was filtered off, washed with water and recrystallized from alcohol and ether. The yield was 0.8 g. of a product melting at 73–74°.

Dimerization of Tri-*t*-butylethynylmethyl Chloride.—Attempts to prepare the monomeric chloride without careful control of the temperature resulted in the formation of a dimer. The compound described as tri-*t*-butylethynylchloromethane by Gray and Marvel[2] is really the dimer of the normal chloride. The method of preparation described there is the best procedure for getting the pure dimer. Also, the compound obtained by Sweet and Marvel[11] by the action of a solution of titanium trichloride on tri-*t*-butylethynylcarbinol is this same dimeric chloride. The dimer is most conveniently prepared from the normal chloride in the following manner. Six grams of the normal chloride was melted in a test-tube and heated in a boiling water-bath for five minutes. After recrystallization from alcohol and ether, 5.6 g. of dimeric chloride, melting at 176°, was obtained.

Anal. Calcd. for $C_{38}H_{54}Cl_2$: C, 78.5; H, 9.2; Cl, 12.3; mol. wt., 581. Found: C, 78.46; H, 9.19; Cl, 12.4; mol. wt. (cryoscopic in benzene), 553, 543.

Dimerization of Tri-*t*-butylethynylmethyl Bromide.—The high melting bromide (177–178°) reported by Salzberg and Marvel[8] was found to have a molecular weight of 609 and 613,[13] in benzene, and by the Rast method, using camphor as a solvent, of 652.[14] The same dimeric bromide was obtained by heating the normal bromide in alcohol solution or in toluene solution. The yields were not very satisfactory. On standing at room temperature, the normal bromide slowly changed into the dimer. A solid sample of normal bromide stored in the dark showed no change in melting point after two months; melted at 124–152° after eight months, at 150–161° after one year, and at 162–163° after two years. After recrystallization, this two-year-old sample melted at 177–178°.[13] The best yields of dimeric bromide were obtained by treating tri-*t*-butylethynylcarbinol with phosphorus tribromide, using toluene as a solvent. Evaporation of the toluene at 100° under reduced pressure causes dimerization of the normal bromide, and yields of as high as 60% of dimer have been obtained.[14]

Action of Silver Acetate on the Dimeric Bromide.—To a solution of 0.5 g. of this dimeric bromide in 50 cc. of glacial acetic acid was added 0.5 g. of silver acetate. A precipitate separated at once. After twelve hours, the mixture was poured into water and extracted with petroleum ether. After evaporation of this solvent, the residue was recrystallized from alcohol, and a bromine-containing compound, melting at 108–110°, was obtained.

Anal. Calcd. for $C_{38}H_{54}Br(OCOCH_3)$: Br, 12.4. Found: Br, 12.4, 12.9.

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(12) Dufraisse and Velluz, *Compt. rend.*, **201**, 1394 (1935).

(13) These experiments were carried out by P. L. Salzberg.

(14) This experiment was carried out by M. R. Lehman.

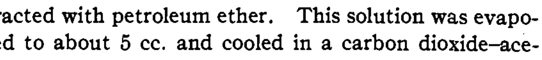
Action of Silver on the Dimeric Bromide.[13]—A solution of 0.7 g. of the dimeric bromide in benzene was boiled for two hours with 0.7 g. of molecular silver. This solution was then filtered, the solvent was evaporated and the residue was recrystallized from ether and alcohol. The yield was 0.31 g. (60% of the theoretical amount) of a product melting at 244–246°.

Anal. Calcd. for $C_{76}H_{108}Br_2$: C, 77.3; H, 9.15; Br, 13.61; mol. wt., 1180. Found: C, 77.16; H, 9.3; Br, 13.19, 14.0; mol. wt. (cryoscopic in benzene), 960, 961.

Action of Silver on the Dimeric Chloride.—Treatment of the dimeric chloride with silver under the same conditions as were used for the bromide did not give a definite product. Heating 0.5 g. of the dimeric chloride with 2 g. of molecular silver at 175° for thirty minutes did bring about a reaction. The mixture was extracted with ether, and the ether was evaporated. The residue, weighing 0.3 g., was recrystallized from alcohol and then melted at 241°.

Anal. Calcd. for $C_{78}H_{108}Cl_2$: Cl, 6.5. Found: Cl, 6.8.

Oxidation of the Normal Chloride.—A solution of 1 g. of the normal chloride and 1 g. of chromic anhydride in 50 cc. of glacial acetic acid was warmed slightly for three hours, and then poured into water. The aqueous mixture was extracted with petroleum ether, and this, in turn, was extracted with 10% sodium hydroxide solution. From this extract, trimethylacetic acid was isolated and identified as the *p*-bromophenacyl ester, melting at 76°.[15] The petroleum ether solution was evaporated and the residue was sublimed under slightly reduced pressure. About 0.1 g. of solid product, melting at 62–63°, was obtained. This compound has been shown to be di-*t*-butylethynyl ketone which was first described by Ivitsky,[16] and which has now been prepared by the oxidation of the unsaturated ketone



$$(CH_3)_3C\text{—}\underset{\underset{O}{\|}}{C}\text{—}CH{=}C{<}[C{\equiv}C\text{—}C(CH_3)_3]_2 \quad \text{(XXIII)}$$

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 81.9; H, 9.8.

Oxidation of the Ketone (XXIII).—A solution of 1 g. of the ketone, obtained by the action of sulfuric acid on tri-*t*-butylethynylcarbinol,[3] in 30 cc. of glacial acetic acid was heated to 75–80° with 3 g. of chromic anhydride for about thirty minutes. The solution was poured into water and extracted with petroleum ether. This solution was evaporated to about 5 cc. and cooled in a carbon dioxide–acetone bath. About 0.1 g. of crystals, melting at 61–62°, was obtained. This compound showed no depression in melting point when mixed with the product prepared by oxidation of the chloride.

Oxidation of the Dimeric Chloride.—One gram of the normal chloride was dissolved in glacial acetic acid and heated to 100° for twenty minutes. The mixture was poured into water, and the organic material isolated. After recrystallization from ethyl alcohol, there was obtained 0.73 g. of dimeric chloride melting at 175°.

One gram of this dimeric chloride was dissolved in 250 cc. of glacial acetic acid containing 3 g. of chromic anhydride, and the solution was heated to 100° for about four hours. After dilution with water, a yellow precipitate was filtered. After drying, this material melted at about 65°. It was not crystalline, and no solvent could be found for purification. Analysis showed that the carbon/hydrogen ratio was that in the original chloride, that the chlorine atoms were lost, and that approximately ten atoms of oxygen had been added to the molecule.

Anal. Calcd. for $C_{38}H_{54}O_{10}$: C, 68.1; H, 8.3. Found: C, 69.6; H, 8.3.

There was no indication that any di-*t*-butylethynyl ketone was formed by the oxidation of the dimer. A product closely resembling this oxidation product will be described later in this communication.

Other Reactions of the Dimeric Halides.—The dimeric bromide added bromine in a carbon tetrachloride solution, but the derivative was amorphous. With potassium cyanide, the dimeric bromide gave a red, resinous material. Heat converted the dimeric bromide to a red tar.

The dimeric chloride was heated with sodamide in boiling xylene for over an hour, but only resinous products resulted. No crystalline hydrocarbon, $C_{38}H_{54}$, previously reported[11] as a product of this reaction could be obtained. The dimeric chloride reacts with magnesium in dry ether. No acid was obtained by the action of carbon dioxide on the reagent. A crystalline solid, melting at 178° after crystallization from alcohol, was isolated from the reaction mixture. Analysis indicated that this product was formed by oxidation and hydrolysis of the Grignard reagent, but no further work was done on this product.

Anal. Calcd. for $C_{38}H_{56}O_2$: C, 84.0; H, 10.0. Found: C, 83.6; H, 10.3.

No addition products of the dimeric halides with maleic anhydride could be prepared. Alkaline reagents, such as aqueous sodium hydroxide, gave resinous products. The chlorine was partially removed by this treatment.

Rearrangement of the Dimeric Chloride.—When the dimeric chloride was heated much above its melting point, it decomposed violently with the liberation of hydrogen chloride and no definite products could be isolated from the residue. Heating 0.5-g. samples to 170°, with careful temperature control for ten minutes, gave a solid product. Recrystallization from benzene with exclusion of air gave a light yellow solid, melting at 257°.

Anal. Calcd. for $C_{38}H_{54}Cl_2$: C, 78.5; H, 9.2; Cl, 12.3. Found: C, 78.42; H, 9.34; Cl, 12.23.

This compound absorbed oxygen from the air very easily, and hence molecular weight determinations were difficult to obtain. Molecular weight determinations on its derivatives show that it is an isomer of the dimeric chloride which forms when the normal chloride undergoes rearrangement at low temperatures. The new dimeric chloride did not react readily with molecular silver.

Air Oxidation of the Rearranged Dimeric Chloride.—When the rearrangement product described above was recrystallized from benzene without exclusion of air, it oxidized to a new product which melted with decomposition at 250°.

Anal. Calcd. for $C_{38}H_{54}Cl_2O$: C, 76.3; H, 9.04; Cl, 12.2. Found: C, 76.1; H, 9.2; Cl, 12.0.

When a 0.1-g. sample of the dimeric chloride was heated in a sealed tube until rearrangement was complete and this

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(15) Powell, THIS JOURNAL, **53**, 1172 (1931).

(16) Ivitsky, *Bull. soc. chim.*, [4] **35**, 357 (1924).

tube was broken in an atmosphere of oxygen, the amount of gas absorbed was found to be 1.3 cc. The calculated amount (assuming one atom of oxygen per molecule of chloride) is 1.4 cc.

This oxidation product corresponds to either formula XVI or XVII in the previous discussion. Henceforth in this paper it will be called the dichloro ether derivative.

Reactions of the Dichloro Ether

(a) Replacement of the Chlorine Atoms by Alkoxyl Groups.—When an attempt was made to purify the dichloro ether by crystallization from alcohol, it was found that the chlorine atoms were replaced, and alkoxyl groups appeared in the molecule. The methoxyl, ethoxyl, *n*-butoxyl and *n*-dodecanoxyl derivatives were prepared by heating the oxidized chloro compound with an excess of alcohol and recrystallizing the derivative from the same alcohol. The *n*-dodecanoxyl derivative was recrystallized from acetone. The properties of these compounds are listed in the table.

ALKOXYL DERIVATIVES FROM THE DICHLOROETHER

Alkoxyl group	M. p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H	Mol. wt. (Rast) Calcd.	Found
CH_3O	250	$C_{40}H_{60}O_3$	81.7	10.2	82.4	10.2	588	596
C_2H_5O	217	$C_{42}H_{64}O_3$	81.8	10.4	81.4	10.1	632	660
n-C_4H_9O	132	$C_{46}H_{72}O_3$	82.2	10.7	82.4	10.7	672	...
n-$C_{12}H_{25}O$	85	$C_{62}H_{104}O_3$	83.0	11.7	83.7	11.8	966	...

(b) Hydrolysis.—Two grams of the dichloro ether was refluxed for two hours with 100 cc. of 50% sulfuric acid. The main product was a chlorine-free solid melting at 169°.

Anal. Calcd. for $C_{38}H_{54}O_2$: C, 83.8; H, 10.3; mol. wt., 542. Found: C, 83.0; H, 10.4; mol. wt. (Rast), 598.

Hydrolysis with alkalies gave no definite products.

Hydrolysis of the Alkoxyl Derivatives.—The alkoxyl derivatives prepared from the dichloro ether were not hydrolyzed with alkaline reagents, but were hydrolyzed by boiling with 50% sulfuric acid for about two hours. The methoxyl, ethoxyl and *n*-butoxyl derivatives were thus hydrolyzed and all gave the same product (m. p. 170°) which has been described before under the hydrolysis of the dichloro ether. From 0.2 g. of the dibutoxyl derivative, 0.15 g. of the hydrolysis product was obtained. This is presumably the diketone corresponding to the cyclic acetal.

A 0.1-g. sample of this hydrolytic product was boiled for ten minutes with 2 cc. of concentrated nitric acid. A rather gummy product was obtained. After washing out the acid, this material solidified and melted at about 60°. Analysis for carbon and hydrogen showed that these elements were present in the same ratio as in the original compounds of the series. This compound is probably identical with the one which was obtained by the chromic anhydride oxidation of the original dimeric chloride. Neither product could be purified sufficiently to melt sharply.

Anal. Calcd. for $C_{38}H_{54}O_{11}$: C, 66.4; H, 7.8. Found: C, 65.8; H, 7.6.

Oxidation of the Rearranged Dimer.—Treatment of 0.2 g. of the rearranged dimer with 0.04 g. of potassium permanganate in 100 cc. of acetone at room temperature for twenty hours with subsequent removal of the manganese dioxide gave a product which, after crystallization from acetone, melted at 260–263°.

Anal. Calcd. for $C_{38}H_{54}O_3$: C, 81.7; H, 9.67; mol. wt., 558. Found: C, 82.1; H, 9.62; mol. wt. (Rast), 460. C/H in $C_{38}H_{54}$: 89.5/10.5. Found: 89.5/10.5.

Treatment of 0.5 g. of the dichloro ether with moist silver oxide in benzene gave this same product. It did not hydrolyze with sulfuric acid to give the diketone which had been obtained by acid hydrolysis of the cyclic acetals. No satisfactory structure has been assigned to this compound.

Summary

1. Tri-*t*-butylethynylmethyl chloride and bromide readily undergo an allylic type of rearrangement to yield allene derivatives which rapidly dimerize to cyclobutane derivatives.

2. The intermediate allene derivative has not been isolated, but by allowing the rearrangement to occur in the presence of an oxidizing agent, the oxidation products characteristic of the allene have been obtained.

3. Two of the possible dimers of the chloroallene have been obtained. One of these isomers having chlorine atoms in the 1,4-positions of a butadiene system readily oxidizes with air to give a cyclic α,α'-dichloro ether. This is believed to be the first isolation of a dihydrofuran by the addition of one atom of oxygen to a conjugated system.

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