720. *Researches on Acetylenic Compounds. Part XXVI. Further Reformatsky Reactions with Propargyl Bromides.*

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The modified Reformatsky reaction employing propargyl bromides has been extended to the vinylogous compounds ($R\cdot CHBr\cdot CH{=}CH\cdot C{\equiv}CH$). Smooth reactions take place with carbonyl compounds in the presence of zinc, leading to rearranged (unconjugated) carbinols.

Methyl γ-bromotetrolate has been prepared from propargyl alcohol, and has been found to condense normally with benzaldehyde in a Reformatsky reaction. Convenient methods of preparing tetrolic and γ-hydroxytetrolic acids are described.

In an earlier paper in this series (Henbest, Jones, and Walls, *J.*, 1949, 2696) it was shown that bromoacetylenes of the general formula $R\cdot CHBr\cdot C{\equiv}CR'$ (where R and R′ can be hydrogen or alkyl) undergo, in good yields, a Reformatsky type of reaction with carbonyl compounds in the presence of zinc. An extension of this reaction has now been investigated employing vinylogous bromides $R\cdot CHBr\cdot CH{=}CH\cdot C{\equiv}CH$, in the expectation that the double bond would transmit the considerable activation of the triple bond as in the analogous case of γ-bromocrotonic ester (Fuson, Arnold, and Cooke, *J. Amer. Chem. Soc.*, 1938, **60**, 2272; Ziegler *et al.*, *Annalen*, 1942, **551**, 80).

The bromides chosen for this work were the primary bromide, 1-bromopent-2-en-4-yne (I), and the secondary bromide, 4-bromohex-3-en-1-yne (II), which were readily prepared from pent-2-en-4-yn-1-ol (Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1583) and propenylethynylcarbinol respectively by reaction with phosphorus tribromide in the presence of pyridine at low temperatures.

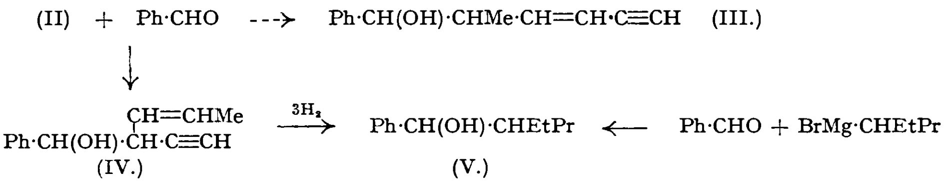
$$HO\cdot CH_2\cdot CH{=}CH\cdot C{\equiv}CH \longrightarrow Br\cdot CH_2\cdot CH{=}CH\cdot C{\equiv}CH \quad \text{(I.)}$$

$$Me\cdot CH{=}CH\cdot CH(OH)\cdot C{\equiv}CH \longrightarrow Me\cdot CHBr\cdot CH{=}CH\cdot C{\equiv}CH \quad \text{(II.)}$$

The former bromo-compound (I) was prepared previously as an intermediate in the preparation of 1-methoxypent-2-en-4-yne (Cheeseman, Heilbron, Jones, Sondheimer, and Weedon, *J.*, 1949, 1516), but was not isolated in a state of purity. The formation of the secondary bromide (II) is accompanied by an anionotropic rearrangement similar to that occurring during the preparation of the corresponding chloro-compound by the action of thionyl chloride or hydrochloric acid on propenylethynylcarbinol (Heilbron, Jones, Lacey, McCombie, and Raphael, *J.*, 1945, 77). The two bromo-compounds so prepared are unpleasant-smelling liquids which deteriorate slowly on storage. The light-absorption properties of these compounds, noted in the Table, are in keeping with their structures, the considerable bathochromic and hyperchromic effects produced by the bromine atom being particularly marked.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
$Br\cdot CH_2\cdot CH{=}CH\cdot C{\equiv}CH$ (I)	2350	17,000
$Me\cdot CHBr\cdot CH{=}CH\cdot C{\equiv}CH$ (II)	2350	16,500
$Me\cdot CHCl\cdot CH{=}CH\cdot C{\equiv}CH$	2260	14,000
$Me\cdot CH(OH)\cdot CH{=}CH\cdot C{\equiv}CH$	2230	13,500

Reformatsky reactions with these bromo-compounds were investigated with benzaldehyde and *cyclo*hexanone; in each case, a smooth reaction ensued leading to the isolation of carbinols.



$$\text{(II)} + Ph\cdot CHO \dashrightarrow Ph\cdot CH(OH)\cdot CHMe\cdot CH{=}CH\cdot C{\equiv}CH \quad \text{(III.)}$$

$$\underset{\text{(IV.)}}{Ph\cdot CH(OH)\cdot \overset{CH=CHMe}{C}H\cdot C{\equiv}CH} \xrightarrow{3H_2} \underset{\text{(V.)}}{Ph\cdot CH(OH)\cdot CHEtPr} \longleftarrow Ph\cdot CHO + BrMg\cdot CHEtPr$$

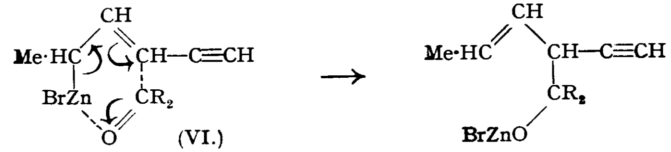
The expected product of the reaction between benzaldehyde and 4-bromohex-3-en-1-yne (II) was the carbinol (III), but the compound isolated, although analysing correctly for (III), did not possess the high-intensity light absorption in the 2300-A. region exhibited by vinylacetylenic compounds. It has now been shown that a rearrangement takes place during the reaction to give the isomeric unconjugated carbinol (IV). This was proved (*a*) by ozonolysis, which gave acetaldehyde, and (*b*) by hydrogenation, which led to uptake of three molecules of hydrogen to give a product whose 3 : 5-dinitrobenzoate was identical with that of the carbinol (V), prepared from benzaldehyde and 3-hexylmagnesium bromide. This type of rearrangement also occurred in the other three reactions examined, the carbinols obtained showing no appreciable light absorption in the 2300-A. region.

A similar rearrangement occurring in a Reformatsky reaction was encountered by Jones, O'Sullivan, and Whiting (*J.*, 1949, 1415). These authors found that the reaction between benzaldehyde and γ-bromocrotonic ester gave some of the rearranged product $\mathrm{Ph{\cdot}CH(OH){\cdot}CH(CO_2Me){\cdot}CH{=}CH_2}$, although the unrearranged ester

$$\mathrm{Ph{\cdot}CH(OH){\cdot}CH_2{\cdot}CH{=}CH{\cdot}CO_2Me}$$

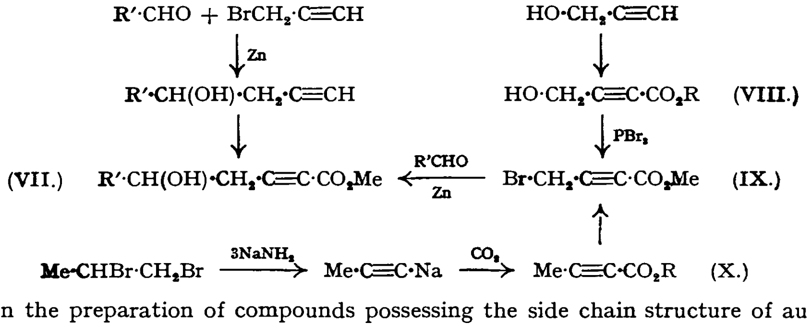
was the major product of the reaction. Several more examples of this type of behaviour have been discovered by English, Gregory, and Trowbridge (private communication).

The reaction of cinnamyl and geranyl halides in Grignard condensation with carbon dioxide and carbonyl compounds also leads predominantly to rearranged unconjugated compounds (cf. review by Barnard and Bateman, *J.*, 1950, 932). Although much work has been done on the Grignard reactions of allylic halides the precise reaction mechanisms are still uncertain, and the factors influencing the extent of possible rearrangements are not yet fully understood (cf. Barnard and Bateman, *loc. cit.*). However, it appears that reactions of mesomeric anions tend to occur at the point of highest charge density (Birch, *Quart. Reviews*, 1950, **4**, 69). For instance, in the reduction of $\overset{-}{\overbrace{\mathrm{Ph{\cdot}CH{-}CH{-}CMe_2}}}$ to $\mathrm{Ph{\cdot}CH_2{\cdot}CH{=}CMe_2}$, addition of a proton occurs at the position adjacent to the charge-stabilising phenyl group. In view of the somewhat similar electronic effects of the phenyl and the acetylenyl groups, it is likely that the highest density in the anion $\overset{-}{\overbrace{\mathrm{Me{\cdot}CH{-}CH{-}CH}}}\mathrm{{\cdot}C{\equiv}CH}$ derived from (II) will be located on the carbon atom next to the acetylenyl group. On this basis, the formation of unconjugated carbinols in the Reformatsky reaction under discussion would be expected, but it does not rule out the possibility that the reaction proceeds *via* a cyclic transition complex (VI) analogous to those



postulated as intermediates in the Grignard reactions of cinnamyl halides (Johnson, *J. Amer. Chem. Soc.*, 1933, **55**, 3029; Young and Roberts, *ibid.*, 1946, **68**, 1472). This mechanism would gain support from the fact that the C–ZnX bond would be more covalent than in the corresponding Grignard reagent, and thus less likely to give rise to ions of the form discussed above.

The second part of this paper is concerned with the preparation of methyl γ-bromotetrolate, and its possible use as a component in Reformatsky reactions. The products from such Reformatsky condensations should be δ-hydroxy-$\alpha\beta$-acetylenic esters (VII), which are intermediates in the preparation of compounds possessing the side chain structure of auxin-b (see *J.*, 1950, 3628, 3634). This alternative synthesis of these esters is outlined in the accompanying scheme, together with the original method.

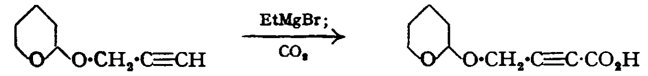


Treatment of methyl tetrolate (X; R = Me) with *N*-bromosuccinimide appeared to be the obvious way of making methyl γ-bromotetrolate (IX; R = Me). The reaction between these compounds was found to be slow and the only products isolated were unchanged ester together with some methyl $\alpha\beta$-dibromocrotonate. [This reaction has been performed with ethyl tetrolate

(English and Gregory, *J. Amer. Chem. Soc.*, 1949, **71**, 1115) with similar results.] However, a convenient method of preparing tetrolic acid was devised in the course of this investigation. The readily accessible propylene dibromide was converted by the action of sodamide in liquid ammonia into sodiopropyne, which reacted readily with carbon dioxide to give tetrolic acid in 65% overall yield.

An alternative method of preparing methyl γ-bromotetrolate was then sought, and a route *via* methyl γ-hydroxytetrolate (VIII; R = Me) was investigated. The first stage in this series, the preparation of γ-hydroxytetrolic acid (VIII; R = H), did not look very promising. There is only one reference to its preparation, that of Lespieau (*Ann. Chim.*, 1912, **27**, 178), who passed carbon dioxide through a suspension of the Grignard derivative of propargyl alcohol in ether for fourteen days; no yield was stated. This reaction was repeated using the carbon dioxide-under-pressure technique of Haynes and Jones (*J.*, 1946, 503), and ether being replaced by benzene. However, the Grignard complex was not appreciably soluble (and was therefore rather unreactive) even in the latter solvent, and long reaction periods were necessary to obtain a useful yield—sixteen days gave a 35% yield of γ-hydroxytetrolic acid.

(XI.)



(XII.)

Attention was then turned to the elegant method of protecting hydroxyl groups by an addition reaction with 2 : 3-dihydropyran to give acetals. These adducts are easily converted back into the parent alcohol by means of dilute acid (Woods and Kramer, *J. Amer. Chem. Soc.*, 1947, **69**, 2246) and are stable to organometallic reagents (Parham and Anderson, *J. Amer. Chem. Soc.*, 1948, **70**, 4187). Propargyl alcohol and 2 : 3-dihydropyran gave the adduct (XI) in 90% yield, and, as expected, this compound gave a more soluble mono-Grignard derivative, which was readily carboxylated to give (XII). This acid adduct could be transformed into methyl γ-hydroxytetrolate by hydrolysis to γ-hydroxytetrolic acid followed by esterification (55% from XI), or, preferably (since it avoids isolating the very water-soluble γ-hydroxytetrolic acid), by direct treatment of the magnesium complex from the carboxylation with methanol containing sulphuric acid to give the desired ester (65%) together with 2-methoxypyran, easily separable by distillation.

Treatment of methyl γ-hydroxytetrolate with phosphorus tribromide under mild conditions gave methyl γ-bromotetrolate (IX), slightly contaminated with an isomeric impurity not easily separated by fractional distillation. This impurity may be the bromo-allenic ester ($CH_2{=}C{=}CBr{\cdot}CO_2Me$), formed by anionotropic rearrangement. The Reformatsky reaction between methyl γ-bromotetrolate and benzaldehyde proceeded smoothly to give the expected ester (VII; R′ = Ph) in 40% yield. The crystalline acid obtained by hydrolysis of this ester was identical with that obtained by the original route by Henbest and Jones (*J.*, 1950, 3628).

Although the preparation of δ-hydroxy-αβ-acetylenic esters employing a Reformatsky reaction with methyl γ-bromotetrolate has been achieved, the original route employing propargyl bromide seems preferable; the yields are somewhat higher and the carboxylation stage is more easily carried out.

EXPERIMENTAL.

(Light absorptions were determined in ethanol solution with a Beckman spectrophotometer.)

5-*Bromohex*-3-*en*-1-*yne* (II).—A solution of phosphorus tribromide (31 g.) in dry ether (50 c.c.) was added dropwise with stirring to a mixture of propenylethynylcarbinol (30 g.; Heilbron, Jones, and Weedon, *J.*, 1945, 83) and dry pyridine (5 c.c.), the internal temperature being kept at −15°. The mixture was then allowed to attain room temperature and stirring was continued for a further hour. The product was isolated with ether, and careful distillation gave 5-*bromohex*-3-*en*-1-*yne* (34·5 g.), b. p. 50°/12 mm., n_D^{20} 1·5212 (Found: C, 45·65; H, 4·5. C_6H_7Br requires C, 45·3; H, 4·45%). Light absorption: see Table. The bromo-compound darkened fairly quickly when kept at 0°, but after a month most of the material could be recovered by distillation.

4-1′-*Hydroxy*cyclo*hexylhex*-2-*en*-5-*yne*.—A solution of the above bromo-compound (16 g.) and pure, dry *cyclo*hexanone (13 g.) in ether (70 c.c.) was added to zinc wool (6 g.) and benzene (20 c.c.)—the reaction proceeded at a vigorous rate. Isolation of the product with ether gave the *carbinol* (6·5 g.), b. p. 59°/0·01 mm., n_D^{20} 1·4979 (Found: C, 80·5; H, 10·35. $C_{12}H_{18}O$ requires C, 80·85; H, 10·2%). It showed no selective light absorption in the region 2200—3000 A.

2-*Ethynyl*-1-*phenylpent*-3-*en*-1-*ol* (IV).—A solution of 5-bromohex-3-en-1-yne (16 g.) and benzaldehyde (11 g.) in ether (70 c.c.) was added to zinc wool (6 g.) in benzene (20 c.c.), a vigorous reaction occurring. Isolation with ether gave the *carbinol* (7·6 g.), b. p. 78—79°/0·01 mm., n_D^{20} 1·5416 (Found: C, 83·7; H, 7·85. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). It showed no selective light absorption in the region 2200—3000 A.

Reactions of the Carbinol (IV).—(a) *Ozonolysis.* Ozonised oxygen (3%; *ca.* 400 mg. of ozone per hour) was passed into a solution of the carbinol (1 g.) in carbon tetrachloride (15 c.c.) at 0° until the outgoing gas rapidly turned starch–potassium iodide paper blue. The solvent was removed *in vacuo*, and the residual ozonide was decomposed by the addition of zinc dust (5 g.) and acetic acid (15 c.c.). Water (50 c.c.) was added, and the mixture was then distilled, portions of distillate being collected in tubes containing a saturated aqueous solution of 2 : 4-dinitrophenylhydrazine hydrochloride. The first fractions yielded acetaldehyde 2 : 4-dinitrophenylhydrazone (combined weight, 0·31 g.; 30%), m. p. and mixed m. p. with an authentic sample, 167—168°.

(b) *Hydrogenation.* A solution of the carbinol (1·86 g.) in methyl acetate (30 c.c.) was shaken in an atmosphere of hydrogen with platinum oxide (50 mg.) until absorption of hydrogen was complete; 740 c.c. were taken up at 22°/770 mm. (theor., 720 c.c.). Removal of the catalyst and solvent followed by distillation gave 3-α-hydroxybenzyl-*n*-hexane (V) (1·6 g.), b. p. 74—76°/0·01 mm., n_D^{20} 1·5012 (cf. succeeding experiment). A portion of the carbinol was warmed with a slight excess of 3 : 5-dinitrobenzoyl chloride for 5 minutes. Addition of water followed by a little methanol gave a solid product, which after recrystallisation from aqueous methanol gave the 3 : 5-*dinitrobenzoate* as platelets, m. p. 112° (Found : C, 61·9; H, 5·95; N, 7·45. $C_{20}H_{22}O_6N_2$ requires C, 62·2; H, 5·7; N, 7·3%).

3-α-*Hydroxybenzyl*-n-*hexane from* 3-*Bromohexane.*—Hydrogenation of hex-1-yn-3-ol (propylethynylcarbinol) (20 g.) in methyl acetate solution in the presence of platinum oxide (100 mg.) gave hexan-3-ol (18·8 g.), b. p. 68°/60 mm., n_D^{17} 1·4180. Treatment of a mixture of this carbinol (10 g.) and pyridine (5 g.) with a solution of phosphorus tribromide (10 g.) in ether (20 c.c.) at −10° led to 3-bromohexane (9·2 g.), b. p. 53°/20 mm., n_D^{18} 1·4483 (Shoule and Waldo, *J. Amer. Chem. Soc.*, 1933, **55**, 4649, give b. p. 66—67°/49 mm., n_D^{20} 1·4469).

A solution of 3-bromohexane (6 g.) in ether (10 c.c.) was added dropwise with stirring to magnesium (0·9 g.) in ether (10 c.c.). When the magnesium had dissolved, benzaldehyde (4·5 g.) was added to the Grignard solution, and stirring was continued for 30 minutes. Isolation of the product with ether in the usual way gave 3-α-hydroxybenzyl-*n*-hexane (V) (3·8 g.), b. p. 75—77°/0·01 mm., n_D^{20} 1·5008. The 3 : 5-dinitrobenzoate, prepared as described in the previous experiment, had m. p. 111°; on admixture with the previous material the m. p. was 111—112°.

1-*Bromopent*-2-*en*-4-*yne* (I).—A solution of pent-2-en-4-yn-1-ol (41 g.) [prepared by the method of Haynes, Heilbron, Jones, and Sondheimer (*J.*, 1947, 1583)] in dry ether (50 c.c.) containing pyridine (5 c.c.) was treated with phosphorus tribromide (50 g.) in ether (50 c.c.) under the conditions employed for the preparation of 5-bromohex-3-en-1-yne (see above). Distillation gave 1-bromopent-2-en-4-yne (53 g.), b. p. 43°/25 mm., n_D^{17} 1·5430 (Found : C, 41·5; H, 3·35. C_5H_5Br requires C, 41·7; H, 3·5%). Light absorption : see Table. This bromo-compound was rather less stable than its homologue (II).

3-α-*Hydroxybenzylpent*-1-*en*-4-*yne.*—This carbinol was prepared by adding a solution of 1-bromopent-2-en-4-yne (20 g.) and benzaldehyde (18 g.) in tetrahydrofuran (40 c.c.) to zinc wool (9 g.) in tetrahydrofuran (20 c.c.). Owing to the thermal instability of the carbinol it was necessary to perform a fairly rapid preliminary distillation at 0·1 mm. from a Claisen flask in order to separate it from unchanged benzaldehyde and polymeric material. Further rapid distillation then gave the *carbinol* (7·4 g.), b. p. 72—73°/0·04 mm., n_D^{21} 1·5470 (Found : C, 83·45; H, 7·2. $C_{12}H_{12}O$ requires C, 83·7; H, 7·05%). It showed no selective light absorption in the region 2200—3000 A.

Condensation of 1-bromopent-2-en-4-yne with *cyclo*hexanone in the presence of zinc proceeded smoothly, but the resultant carbinol decomposed considerably during distillation. The reaction between *cyclo*hexanone (15 g.), zinc (7 g.), and 1-bromopent-2-en-4-yne (15 g.) in tetrahydrofuran (100 c.c.) gave crude 3-1′-hydroxy*cyclo*hexylpent-1-en-4-yne (6·2 g.), b. p. 52°/0·1 mm., n_D^{16} 1·4970.

γ-*Hydroxytetrolic Acid* (3-*Hydroxyprop*-1-*yne*-1-*carboxylic Acid*) *and its Methyl Ester* (VIII; R = H and Me).—(a) *By carboxylation of propargyl alcohol.* Propargyl alcohol (14 g.) was carboxylated by the method of Haynes and Jones (*loc. cit.*). In order to obtain appreciable yields of acid it was necessary to treat the Grignard complex in an autoclave with carbon dioxide for longer periods—a 16 day reaction period led to a 35% yield of γ-hydroxytetrolic acid, m. p. 115°, after crystallisation from benzene (Lespieau, *loc. cit.*, gives m. p. 115—116°). Isolation of the acid from aqueous solutions during the working-up processes had to be effected by continuous ether-extraction.

(b) Via 2-*prop*-2′-*yn*-1′-*yloxytetrahydropyran* (XI). Phosphorus oxychloride (100 mg.) was added to a mixture of propargyl alcohol (8·4 g.) and 2 : 3-dihydropyran (12·6 g.). The mixture rapidly became warm and was cooled in ice to moderate the reaction. After 2 hours at room temperature, potassium hydroxide solution was added and the product isolated with ether. Distillation gave 2-*prop*-2′-*yn*-1′-*yloxytetrahydropyran* (18·6 g., 90%) as a pleasant-smelling liquid, b. p. 78°/25 mm., n_D^{20} 1·4570 (Found : C, 68·45; H, 8·35. $C_8H_{12}O_2$ requires C, 68·5; H, 8·6%). This compound gave a precipitate with ammoniacal silver nitrate in methanol solution, confirming the presence of an ethynyl group.

A solution of this adduct (14 g.) in benzene (200 c.c.) was added to a solution of ethylmagnesium bromide prepared from magnesium (2·4 g.) in ether (100 c.c.), the complex formed being largely retained in solution. The product obtained after a carboxylation period of 24 hours was decomposed with 20% sulphuric acid with vigorous shaking, which hydrolysed the labile acetal grouping to give γ-hydroxytetrolic acid, isolated as in the previous experiment by continuous ether-extraction. The yield of acid was 5·1 g. (51%), improved to 64% by substituting tetrahydrofuran (200 c.c.) for benzene in the first stage of the preparation.

For esterification, γ-hydroxytetrolic acid (8 g.) was dissolved in methanol (100 c.c.) containing sulphuric acid (2 c.c.). After 24 hours at room temperature, sodium hydrogen carbonate (3 g.) was added and most of the methanol was removed *in vacuo.* Water (20 c.c.) was added, and the ester was isolated by several extractions with ether, the ethereal extract then being processed in the usual way. The above isolation procedure, in which most of the methanol is removed before the addition of water and ether, was found to be very convenient for obtaining this water-soluble ester. Distillation gave *methyl* *γ-hydroxytetrolate* (7·6 g.), b. p. 73°/0·5 mm., n_D^{20} 1·4712 (Found : C, 52·25; H, 5·35. $C_5H_6O_3$ requires C, 52·6; H, 5·3%).

This ester was also obtained by a shortened procedure. A solution of the dihydropyran adduct (28 g.) of propargyl alcohol in benzene (400 c.c.) was added to a solution of ethylmagnesium bromide, prepared from magnesium (4·8 g.) in ether (100 c.c.), at 0°. After the mixture had been treated with carbon dioxide in an autoclave for 24 hours, methanol (300 c.c.) containing sulphuric acid (28 g.) was added to the complex, and the mixture was kept overnight at room temperature. The ether and some of the benzene and methanol were removed by distillation, which removed much of the water formed during the esterification, the reaction mixture then being kept for a further 24 hours at room temperature. Sodium hydrogen carbonate was added to neutralise the mineral acid, the mixture was filtered, and three-quarters of the solvent removed by distillation. Water (200 c.c.) was added and the ester was isolated with ether in the usual way. Distillation gave the ester (14·4 g., 65%), b. p. 63°/0·1 mm., n_D^{20} 1·4721.

Methyl γ-Bromotetrolate (*Methyl* 3-*Bromoprop*-1-*yne*-1-*carboxylate*) (IX).—A solution of phosphorus tribromide (12 g.) in ether (50 c.c.) was added to a stirred mixture of methyl γ-hydroxytetrolate (12 g.) and pyridine (1 g.) in ether (50 c.c.) during an hour, the internal temperature being kept at —50°. After the mixture had been stirred at this temperature for an hour, the product was isolated with ether. Distillation gave the *ester* (8·9 g.), b. p. 60—67°/0·5 mm., n_D^{19} 1·5240—1·5280. The homogeneity could not be improved by further distillation; analytical data obtained with a middle fraction were: Found : C, 33·5; H, 3·2; Br, 45·35. $C_5H_5O_2Br$ requires C, 33·7; H, 3·4; Br, 44·9%.

Methyl 4-*Hydroxy*-4-*phenylbut*-1-*yne*-1-*carboxylate* (VII; R′ = Ph).—A solution of methyl γ-bromotetrolate (2·5 g.) and benzaldehyde (1·8 g.) in ether (5 c.c.) and tetrahydrofuran (5 c.c.) was added dropwise to activated zinc wool (1·2 g.) in ether (2·5 c.c.) and tetrahydrofuran (2·5 c.c.). Addition of a little mercuric chloride initiated the reaction, which was finally completed by heating the mixture under reflux for 10 minutes. Isolation with ether gave a product from which unchanged benzaldehyde was removed at 60°/0·01 mm.; the remainder then distilled as a viscous liquid (1·55 g., 40%) at 100° (bath-temp.; short-path still)/10^{-4} mm., n_D^{19} 1·5480. Henbest and Jones (*loc. cit.*) give n_D^{18} 1·5400 for the pure methyl ester.

Proof of structure for the ester was obtained by (*a*) alkaline hydrolysis (potassium hydroxide in aqueous methanol) to give the corresponding acid, m. p. and mixed m. p. with an authentic sample, 104°, and (*b*) benzoylation to yield the benzoate, m. p. and mixed m. p. 72° (cf. Henbest and Jones, *loc. cit.*).

Tetrolic Acid and its Methyl Ester (X; R = H and Me).—A solution of sodamide in liquid ammonia (2·5 l.) was prepared from sodium (69 g.) by the method of Vaughn, Vogt, and Nieuwland (*J. Amer. Chem. Soc.*, 1934, **56**, 2120), the reaction being carried out in a 5-l. 3-necked flask equipped with a mechanical stirrer and surrounded by cork-dust lagging. Propylene dibromide (150 g.) (or propylene dichloride, 84 g.) in dry ether (150 c.c.) was added dropwise with stirring to the sodamide solution, a strongly exothermic reaction taking place. When the addition of the dibromide was complete, the mixture was stirred for 30 minutes. Dry ether (1 l.) was then added, the cork lagging was removed, and the mixture was stirred overnight during which most of the ammonia evaporated. Moisture was excluded in all these operations by means of soda lime guard-tubes. After an additional 500 c.c. of dry ether had been added, the remainder of the ammonia was removed by passing a gentle stream of dry nitrogen into the well-stirred suspension of sodiopropyne, the internal temperature being kept at *ca.* 25° by warming as necessary. The mixture was poured on solid carbon dioxide (2 lbs.) in an autoclave, which was then sealed and kept at room temperature for 24 hours. Isolation of the acid fraction with ether (4 extractions necessary from aqueous solutions of tetrolic acid) gave tetrolic acid (41 g., 65%) as a light-brown solid, m. p. 71—75°, which was used directly for esterification. The pure acid, m. p. 76°, could be obtained by extracting the crude acid with hot light petroleum (b. p. 60—80°) and cooling the extract to 0°.

A solution of tetrolic acid (41 g.) in methanol (150 c.c.) containing sulphuric acid (1·5 c.c.) was heated under reflux for 16 hours. Isolation with ether followed by distillation gave homogeneous methyl tetrolate (38·2 g.), b. p. 76—77°/80 mm., n_D^{12} 1·4400.

Microanalyses were carried out by Mr. E. S. Morton and Mr. H. Swift. One of us (I. M. S. W.) thanks the Department of Scientific and Industrial Research for a Maintenance Grant.

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[*Received, July* 29*th*, 1950.]