13. *Researches on Acetylenic Compounds. Part I. The Preparation of Acetylenic Ketones by Oxidation of Acetylenic Carbinols and Glycols.*

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A new and convenient route to acetylenic ketones has been devised, consisting of chromic acid oxidation of the corresponding secondary alcohols, best in acetone solution, and simple ethynyl ketones ($-\mathrm{CO{\cdot}C{\vdots}CH}$), hitherto practically unknown, have now become readily available. In the various cases examined, which include the ethylenic acetylenyl-carbinol, propenylethynylcarbinol, the yields range from 40—80%, the ease of oxidation of the alcohols [$\mathrm{R{\cdot}CH(OH){\cdot}C{\vdots}C}-$] being in the order R = Ph, $\mathrm{CH_3{\cdot}CH{:}CH} >$ Pr $>$ Me. Both vinylacetylenyl and acetylenylvinyl ketones can also be produced by this means, but because of their instability low yields are obtained and, where possible, preparation by means of the vinylacetylenic Grignard reagents is preferable.

The acetylenic hydrogen of the ethynyl ketones is markedly acidic and although the ketones show no appreciable tendency to polymerise they undergo a variety of addition reactions with considerable facility. These additions have been investigated in detail and some of the results are described in the following papers. A study of the light absorption properties of a number of *αβ*-acetylenic ketones and of their 2 : 4-dinitrophenylhydrazones reveals essential similarities to the ethylenic analogues.

The acetylenic di-secondary glycols from crotonaldehyde and benzaldehyde are smoothly oxidised to the diketones, but the glycol from butaldehyde gives mainly the keto-alcohol (XII), the further oxidation to the diketone being much more difficult.

Only one example of an αβ-ethynyl * ketone ($-\mathrm{CO{\cdot}C{\vdots}CH}$) has as yet been described in the literature and although many routes to αβ-acetylenic keto-compounds of the type, $\mathrm{R{\cdot}CO{\cdot}C{\vdots}CR'}$ (I) (R′ = alkyl or aryl) are known, comparatively few are of general applicability.

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* The term " ethynyl " is applied to the group $-\mathrm{C{\vdots}CH}$, containing one active hydrogen atom.

The method most frequently employed consists of treatment of alkali metal acetylides with acid bromides (the chlorides are frequently less effective) or anhydrides in inert media such as benzene or ether (*inter alia*, André, *Ann. Chim.*, 1913, **29**, 557; Moureu and Brachin, *Bull. Soc. chim.*, 1904, **31**, 345; 1906, **33**, 134; 1907, **35**, 1176; Nightingale and Wadsworth, *J. Amer. Chem. Soc.*, 1945, **67**, 416), the process having been applied mainly to arylacetylenes. Both aryl- and alkyl-acetylenylmagnesium halides react with acetic anhydride or acetyl chloride giving acetylenic ketones (Kroeger and Nieuwland, *J. Amer. Chem. Soc.*, 1936, **58**, 1861), the secondary reactions due to further condensation between the ketones and the Grignard reagents being said to be minimised by employing the acetylenylmagnesium chlorides and by carrying out the reactions at − 25°. Both the Grignard complexes and the alkali metal derivatives of acetylenes can be employed in condensations with esters, the formates yielding aldehydes (I; R = H), and other esters giving ketones, except when the acetylide is so basic as to bring about Claisen condensations with the esters (Moureu and Delange, *Bull. Soc. chim.*, 1902, **27**, 375; 1904, **31**, 1329).

Other applications of Grignard reagents to the preparation of acetylenic keto-compounds include their interaction with phenylpropiolic esters (Hurd and Cohen, *J. Amer. Chem. Soc.*, 1931, **53**, 1072) and reactions between acetylenic Grignard complexes and α-chloro-ketones (Tiffeneau and Deux, *Compt. rend.*, 1941, **213**, 753; 1942, **214**, 892), when the primary products undergo a type of hydrobenzoin rearrangement on heating to 110°, giving either αβ- or βγ-acetylenic ketones depending upon the nature of the substituent groups present.

$$\mathrm{C_5H_{11}{\cdot}C{\vdots}C{\cdot}MgBr \xrightarrow{Et{\cdot}CO{\cdot}CH_2Cl} C_5H_{11}{\cdot}C{\vdots}C{\cdot}CEt(OMgBr){\cdot}CH_2Cl \longrightarrow C_5H_{11}{\cdot}C{\vdots}C{\cdot}CO{\cdot}CH_2Et + MgBrCl}$$

The partial hydration of conjugated diacetylenes (Grignard and Tchéoufaki, *Rec. trav. chim.*, 1929, **48**, 901; Griner, *Ann. Chim.*, 1892, **26**, 359) and Friedel–Crafts reactions with substituted propiolyl halides (Krafft and Heizmann, *Ber.*, 1900, **33**, 3590; Simonis and Lear, *Ber.*, 1926, **59**, 2908) have both been applied to the production of acetylenic ketones. The only example of the oxidation of an acetylenylcarbinol to the corresponding ketone, is that given by André (*Ann. Chim.*, 1913, **29**, 564), although a number of instances of similar oxidations of aromatic *bis*-secondary acetylenic glycols (Dupont, *Bull. Soc. chim.*, 1914, **15**, 606) and of secondary di-acetylenylcarbinols, $\mathrm{RC{\vdots}C{\cdot}CH(OH){\cdot}C{\vdots}CR}$ (Liang, *ibid.*, 1933, **53**, 44; Chauvelier, *Compt. rend.*, 1941, **212**, 793), are known.

$$\mathrm{Ph{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}Ph \xrightarrow{CrO_3—AcOH} Ph{\cdot}CO{\cdot}C{\vdots}C{\cdot}Ph}$$

The ready availability of the secondary acetylenyl-carbinols (II) and glycols suggested an investigation of their oxidation, especially of the aliphatic ethynylcarbinols, with chromic acid and good yields of ketones have been obtained in practically every case.

$$\text{(II.)}\quad \mathrm{R_1C{\vdots}C{\cdot}CH(OH){\cdot}R \xrightarrow{CrO_3} R_1C{\vdots}C{\cdot}CO{\cdot}R}\quad \text{(III.)}$$

The nature of the solvent employed, the concentrations of the reagents and the reaction temperature all have a marked influence on the reaction. The most satisfactory procedure consists in the addition of a solution of chromic anhydride in dilute sulphuric acid to an acetone solution of the carbinol; in some cases a sharp end-point is observed after the addition of the theoretical amount of the oxidising agent. Acetone is preferred as a solvent since the oxidations proceed at a far greater rate in this medium than in acetic acid. The most suitable conditions for the oxidation of any given carbinol are best determined by preliminary titration of small quantities (*ca.* 1 g.) with a standard chromic acid solution.

The reagent concentrations can usually be adjusted so that an upper layer, consisting mainly of an acetone solution of the ketonic product, separates during the course of the oxidation from the lower green (usually saturated) solution of chromium salts. The segregation of the product in this way appears to be of considerable importance in protecting it from further oxidation; the colour of this upper layer also gives a useful indication of the presence of any excess of chromic acid. When the ketone produced is itself readily oxidised, it is advisable to introduce the chromic acid solution well below the surface of the liquid, so as to avoid undue contact with the upper layer.

With readily oxidisable carbinols, satisfactory results can usually be obtained by using the theoretical quantity of oxidising agent but, in those cases where oxidation is slow, the use of an excess of chromic acid is desirable. The particular temperature employed, in the range 0—20°, depends upon the ease of oxidation of the carbinol; the temperature and the rate of addition of the chromic acid solution are mutually adjusted so that the reaction proceeds at a reasonable rate without any appreciable excess of oxidising agent ever being present in the reaction medium.

Oxidation of oct-3-yn-2-ol (IV) by this method gave, in 80% yield, the same oct-3-yn-2-one (V) as was obtained by the method of Kroeger and Nieuwland (*loc. cit.*) from 1-hexynylmagnesium chloride and acetic anhydride.

$$\underset{\text{(IV.)}}{\mathrm{Bu^aC{\vdots}C{\cdot}CH(OH){\cdot}Me}} \longrightarrow \underset{\text{(V.)}}{\mathrm{Bu^aC{\vdots}C{\cdot}CO{\cdot}Me}} \xleftarrow{(Ac)_2O} \mathrm{Bu^aC{\vdots}CMgCl}$$

The only αβ-ethynyl ketone hitherto described in the literature is methyl ethynyl ketone, which was prepared by Petrov (*J. Gen. Chem. Russia*, 1940, **10**, 1682) by acid hydrolysis of its enol methyl ether, the latter being obtained from butadiene by a multi-stage process. These ketones are now easily prepared by employing the oxidation procedure described above and compounds of the type, $\mathrm{R{\cdot}CO{\cdot}C{\vdots}CH}$ (VI), *viz.*, *phenyl ethynyl ketone* (VI; R = Ph) (80% yield), *propyl ethynyl ketone* (VI; R = Pr) (70%) and methyl ethynyl ketone (VI; R = Me) (40%) have been obtained in this way. In the latter case, because of the difficulty of separating the ketone from acetone, the reaction was carried out in water, with which methylethynylcarbinol is completely miscible.

Only a few rather complex examples of the ethylenic acetylenic ketones have so far been synthesised (Worrall, *J. Amer. Chem. Soc.*, 1938, **60**, 1266; Rossander and Marvel, *ibid.*, 1929, **51**, 934; cf. Nightingale and Wadsworth, *loc. cit.*). The oxidation method is again applicable for the preparation of such compounds and oxidations of propenylethynylcarbinol and its isomer, hex-3-en-5-yn-2-ol, have yielded *propenyl ethynyl ketone*, $\mathrm{Me{\cdot}CH{:}CH{\cdot}CO{\cdot}C{\vdots}CH}$ (VII) (75% yield), and *hex-3-en-5-yn-2-one*, $\mathrm{Me{\cdot}CO{\cdot}CH{:}CH{\cdot}C{\vdots}CH}$ (VIII), (50%). Only one example of the oxidation of a carbinol derived from a vinylacetylene has been investigated, and the ketone *5-methylhex-5-en-3-yn-2-one*, $\mathrm{Me{\cdot}CO{\cdot}C{\vdots}C{\cdot}CR{:}CH_2}$ (IX; R = Me), was isolated only, however, in 10% yield, a large quantity of undistillable resin being formed. This was not surprising since the ketone has been found to be very unstable and appears to polymerise readily. The ketone synthesis involving the reaction of acetylenic Grignard reagents and acetic anhydride (Kroeger and Nieuwland, *loc. cit.*) has been reported to fail (see Nazarov and Elizarova, *Bull. Acad. Sci. U.R.S.S.*, 1940, 189) when applied to vinylacetylene. However, by addition of an ethereal suspension of methylvinylacetylenyl- or vinylacetylenyl-magnesium chloride to an excess of acetic anhydride at − 30°, the ketone (IX; R = Me) and the unsubstituted vinylacetylenyl ketone, *hex-5-en-3-yn-2-one* (IX; R = H), have been obtained in 25 and 16·5% yields respectively. On reversing the mode of addition, as originally advocated by Kroeger and Nieuwland, further condensation ensues between the ketone initially produced and the Grignard reagent and, from one experiment carried out in this way, only a 10% yield of (IX; R = Me) was obtained, the main product being the acetate of the tertiary carbinol, $\mathrm{CH_2{:}CMe{\cdot}C{\vdots}C{\cdot}CMe(OH){\cdot}C{\vdots}C{\cdot}CMe{:}CH_2}$ (X).

With certain exceptions, the acetylenic ketones described above are stable substances which can be kept indefinitely at 0° in the presence of a little quinol. In sharp contrast to the vinyl ketones, propyl ethynyl ketone was practically unaffected by heating with 1% of benzoyl peroxide for 48 hours at 100°. The vinyl acetylenic ketones (VIII and IX; R = Me) are not stable under the storage conditions mentioned above and with 1% of benzoyl peroxide at 20° during 48 hours, the ketone (IX; R = Me) was converted into a rubber-like polymer but its lower homologue (IX; R = H) did not polymerise appreciably on keeping.

The ketones containing the free ethynyl group possess marked lachrymatory and sternutatory properties. They readily form acetylides with ammoniacal cuprous and silver salts and they attack metallic copper with remarkable rapidity. The high reactivity of the ethynyl hydrogen atom is further evidenced by the fact that these ethynyl ketones quantitatively liberate methane from methylmagnesium iodide at ordinary temperatures, thus behaving analogously to compounds in which the ethynyl group is conjugated with an ethylenic linkage (Cymerman, Heilbron, and Jones, *J.*, 1945, 90); the mechanism of this activation is undoubtedly similar.

2 : 4-Dinitrophenylhydrazones were readily obtained from all of the ketones studied and, rather unexpectedly, these appear to be the normal derivatives, no cyclisation, such as has frequently been reported in reactions between acetylenic carbonyl compounds and hydrazine and its derivatives, having occurred. These derivatives show the expected light absorption properties and, in those cases where it would be anticipated, silver salts were readily formed. With semicarbazide acetate abnormal reactions ensue, phenyl ethynyl ketone, for example, giving a high melting product, probably the *di-semicarbazone* of *hydroxymethyleneacetophenone*, which has been formed by addition of semicarbazide to the acetylenic bond. The substituted ketone, oct-3-yn-2-one (V), gives a normal *semicarbazone* and a *phenylsemicarbazone*, the light absorption properties of the former being in good agreement with those of the semicarbazones of αβ-ethylenic carbonyl compounds (Evans and Gillam, *J.*, 1943, 565).

Dupont (*Bull. Soc. chim.*, 1914, **15**, 606), who effected the oxidation of several aromatic *bis*-secondary acetylenic glycols to the corresponding diketones with chromic acid in acetic acid, stated that the method was not applicable to aliphatic glycols, but gave no indication of the compounds examined or of the conditions employed. No aliphatic acetylenic diketones have been described in the literature, consequently the oxidation of several glycols by the method successfully developed for the carbinols has been investigated.

In view of the ease of oxidation of propenylethynylcarbinol, the corresponding glycol was examined first and, by using the theoretical quantity of chromium trioxide, a 40% yield of the *diketone* (XI) was obtained. The behaviour of the glycol from butaldehyde under similar conditions was unexpected. The oxidation proceeded much more slowly than that of the crotonaldehyde glycol and there was a marked diminution in the oxidation rate after one-half of the chromic acid required to form the diketone (XIII) had been added. Taking advantage of this fact, the *keto-alcohol* (XII) has been obtained in 60% yield. Its Zerewitinoff value is one; it can be characterised through its dinitrophenylhydrazone and it exhibits light absorption (see table) similar to that of an αβ-acetylenic ketone. The highly reactive *diketone* (XIII) appears to be unstable and readily polymerises, but it has been isolated in poor yield as a pale yellow liquid by direct oxidation of the glycol; a better yield was obtained by oxidation of the keto-alcohol (XII). The *product*, obtained by allowing the

(XI.) $\mathrm{Me{\cdot}CH{:}CH{\cdot}CO{\cdot}C{\vdots}C{\cdot}CO{\cdot}CH{:}CH{\cdot}Me}$ $\mathrm{Pr^{\alpha}{\cdot}CO{\cdot}C{\vdots}C{\cdot}CH(OH){\cdot}Pr^{\alpha}}$ (XII.)

(XIII.) $\mathrm{Pr^{\alpha}{\cdot}CO{\cdot}C{\vdots}C{\cdot}CO{\cdot}Pr^{\alpha}}$ $\mathrm{Pr^{\alpha}{\cdot}C({:}NDn){\cdot}CH{:}C(NHDn){\cdot}CO{\cdot}Pr^{\alpha}}$ (XIV.)

$[\mathrm{Dn} = 2:4\text{-}\mathrm{C_6H_3(NO_2)_2{\cdot}NH{\cdot}}]$

diketone to react with 2 : 4-dinitrophenylhydrazine, is probably best represented as (XIV). The two ***keto-alcohols*** (XV and XVI) have also been prepared in good yields by oxidation of the secondary–tertiary glycols.

(XV.) Me·CH:CH·CO·C⋮C·C(OH)Me$_2$ Me·CH:CH·CO·C⋮C·C(OH)Ph$_2$ (XVI.)

When the method described in this paper was applied to an aromatic acetylenic glycol, *viz.*, that from benzaldehyde, the oxidation proceeded rapidly and to completion, giving the diketone, dibenzoylacetylene, in 90% yield. In the various oxidations detailed above, it has invariably been observed that the acetylenic carbinols or glycols derived from aromatic or αβ-unsaturated aldehydes are much more readily oxidised than those from the saturated aldehydes. For carbinols or glycols of structure, R·CH(OH)·C⋮C–, the rate of oxidation for different values of R appears to be in the order Ph, CH$_3$·CH:CH > Pr > Me.

The ultra-violet light absorption properties of the various acetylenic ketones described above and of their 2 : 4-dinitrophenylhydrazones are listed in the table, together with comparative data which have been obtained for analogous ethylenic ketones. The locations of the maxima in the acetylenic and ethylenic series are practically identical, but as has already been noted for other conjugated systems containing acetylenic bonds (Jones and McCombie, *J.*, 1943, 261; Heilbron, Jones, and McCombie, J., 1944, 134; Heilbron, Jones, and Raphael, *J.*, 1944, 136), the molecular extinction coefficients of the acetylenic compounds are considerably lower than those of the corresponding ethylenic compounds. The lower intensity longer wave-length bands, usually observed with carbonyl compounds, are also exhibited by the acetylenic ketones. The general characteristics of the absorption of the dinitrophenylhydrazones are similar to those already recorded for ethylenic compounds (Braude and Jones, *J.*, 1945, 498) and the Δλ values, *i.e.*, differences between the locations of the main maxima of the derivatives and the parent ketones, are of the same order as for the ethylenic series.

In order to obtain the corresponding ethylenic compounds for spectrographic purposes, propyl and propenyl ethynyl ketones were semi-hydrogenated in the presence of a 0·3% palladium on barium sulphate catalyst. In both cases the reaction proceeded smoothly and by interrupting the experiments after one molar proportion of hydrogen had been absorbed it was possible to prevent any appreciable hydrogenation of the ethylenic linkages. The propyl vinyl ketone thus obtained was characterised by the preparation of the diethylamine and aniline adducts.

Light Absorption of Acetylenic Ketones and their 2 : 4-*Dinitrophenylhydrazones.*

(In alcohol except where stated otherwise.)

	Ketone.		2 : 4-Dinitrophenylhydrazone (main band only).		
	$\lambda_{max.}$ A.	$\epsilon_{max.}$	$\lambda_{max.}$ A.	$\epsilon_{max.}$	Δλ.
Me·CO·C⋮CH	*ca.* 2150	5,000	3590	21,000	1440
			3650 *	25,500	
Pr·CO·C⋮CH	*ca.* 2140	4,500	3600	25,500	1460
			3655 *	26,500	
Me·CO·C⋮C·Bu	2180 ‖	7,500	3660	32,500	1455
Pr·CO·C⋮C·CH(OH)·Pr	2200	7,500	3640	26,000	1440
	2280 †	6,500			
Me·CO·CH:CH$_2$	2100 [1]	6,500	—	—	—
Pr·CO·CH:CH$_2$	<2220	>6,000	—	—	—
Me·CO·CH:CHMe [1]	2240	9,700	—	—	—
Ph·CO·C⋮CH	2645	14,500	—	—	—
	(2340) ‡	4,000			
Ph·CO·CH:CH$_2$ [5]	2475	10,500	—	—	—
Me·CH:CH·CO·C⋮CH	2230	8,500	3740	33,000	1410
	2430	7,000			
Me·CH:CH·CO·C⋮C·C(OH)Me$_2$	2380	13,500	3850 *	31,500	1470
	2510 †	11,500			
Me·CH:CH·CO·C⋮C·C(OH)Ph$_2$	2240	21,000	—	—	—
	2420—2510	16,500			
Me·CH:CH·CO·CH:CH$_2$	2280	9,500	—	—	—
	2360	9,500			
CMe$_2$:CH·CO·CH:CMe$_2$	2655 [2]	23,000	3950 * [3]	24,500	1295
Me·CO·CH:CH·C⋮CH	2550	11,500	3780 *	30,000	1230
Me·CO·C⋮C·CH:CH$_2$	2510	8,500	3670	26,000	1160
	2580 †	8,000	3770 *	27,500	
Me·CO·C⋮C·CMe:CH$_2$	2500—2620	9,000	3660	28,000	1100
			3770 *	26,000	
Me·CO·CH:CH·CH:CH·Me	2710 [4]	22,500	—	—	—
Pr·CO·C⋮C·CO·Pr	2200	4,000	—	—	—
	2290	4,000			
Ph·CO·C⋮C·CO·Ph	2210 §	14,000	—	—	—
	2690	23,500			
Me·CH:CH·CO·C⋮C·CO·CH:CH·Me	2420	20,500	—	—	—
	2450	20,500			
Me·CO·CH:CH·CO·Me [6]	2260 ‖	14,500	—	—	—

* In CHCl$_3$. † Inflexion. ‡ Minimum. § In *cyclo*hexane. ‖ In hexane.

[1] B. p. 79°/757 mm., $n_D^{20°}$ 1·4071.
[2] Scheibe, *Ber.*, 1925, **58**, 586.
[3] Braude and Jones, *J.*, 1945, 498.
[4] Dimroth, *Angew. Chem.*, 1939, **52**, 545.
[5] Undistilled semi-hydrogenation product of phenyl ethynyl ketone.
[6] M. p. 78°.

EXPERIMENTAL.

Oct-3-yn-2-one (V).—(a) An authentic specimen of oct-3-yn-2-one was prepared by the method of Kroeger and Nieuwland (*J. Amer. Chem. Soc.*, 1936, **58**, 1861); it had the following physical properties: b. p. 74°/12 mm., $n_D^{16^\circ}$ 1·4487 (*idem, loc. cit.*, give b. p. 76—76·5°/15 mm., $n_D^{25^\circ}$ 1·4446). The 2 : 4-*dinitrophenylhydrazone* formed orange needles, m. p. 87—88°, from aqueous alcohol (Found: N, 18·4. $C_{14}H_{16}O_4N_4$ requires N, 18·4%). The *semicarbazone* crystallised from aqueous alcohol in needles, m. p. 109° (Found: N, 23·25. $C_9H_{15}ON_3$ requires N, 23·2%). Light absorption in alcohol: Maximum, 2600 A.; ε = 18,500. The *phenylsemicarbazone* formed needles, m. p. 104—104·5°, from aqueous alcohol (Found: N, 16·55. $C_{15}H_{19}O_3N$ requires N, 16·35%). Light absorption in alcohol: Maxima, 2290, 2730 and 2800 A.; ε = 17,000, 29,000 and 28,500, respectively.

(b) A solution of chromium trioxide (10·3 g.) in water (30 c.c.) and concentrated sulphuric acid (8·7 c.c.) was added during two hours to a stirred solution of oct-3-yn-2-ol (15 g.; for preparation, see below) in acetone (30 c.c.) at 5—10°. After stirring for a further 30 minutes, the mixture was diluted with water to 250 c.c. and the product isolated with ether; distillation then gave oct-3-yn-2-one (11·5 g.), b. p. 70·5—71·5°/14 mm., $n_D^{16^\circ}$ 1·4482. The semicarbazone had m. p. 109°, undepressed on admixture with an authentic specimen. The light absorption data of the ketone were identical with those of the material prepared as described above, (a).

Phenyl Ethynyl Ketone (VI; R = Ph).—To a stirred solution of phenylethynylcarbinol (342 g.; Jones and McCombie, *J.*, 1942, 733) in acetone (500 c.c.) a solution of chromium trioxide (175 g.) in water (500 c.c.) and concentrated sulphuric acid (148 c.c.) was slowly added; the operation, carried out at 5° in nitrogen, lasted 3—4 hours. After stirring for a further 30 minutes, the mixture was diluted with water and the product extracted with ether. Evaporation of the ethereal solution gave a yellow solid which was recrystallised from aqueous methanol to give *phenyl ethynyl ketone* (258 g.), as pale yellow needles, m. p. 50—51°, having an odour similar to that of benzaldehyde (Found: C, 83·1; H, 4·45. C_9H_6O requires C, 83·1; H, 4·65%). The 2 : 4-*dinitrophenylhydrazone* formed orange needles, m. p. 214° (decomp.), from benzene–ligroin (b. p. 80—100°) (Found: N, 18·0. $C_{15}H_{10}O_4N_4$ requires N, 18·05%). With alcoholic semicarbazide acetate, phenyl ethynyl ketone gave the *di-semicarbazone* of *hydroxymethylene-acetophenone* as pale yellow plates, m. p. *ca.* 235°. When this material was sublimed at 200° (bath temp.)/10^{-4} mm., it gave colourless needles, m. p. 115°, immediately solidifying and re-melting at 238—239° (Found: N, 32·5. $C_{11}H_{14}O_2N_6$ requires N, 32·05%).

Propyl Ethynyl Ketone (VI; R = Pr).—A solution of chromium trioxide (57 g.) in water (165 c.c.) and concentrated sulphuric acid (48·3 c.c.) was added over a period of 2½ hours to a stirred and cooled solution of propylethynylcarbinol (75 g.; for preparation, see below) in acetone (240 c.c.), the operation being carried out in nitrogen. After stirring for a further 30 minutes, sufficient water was added to dissolve the precipitated chromium salts and the product was isolated by means of ether. Distillation gave *propyl ethynyl ketone* (53 g.) as a colourless mobile liquid with marked sternutatory and lachrymatory properties. It had b. p. 65—66°/100 mm., $n_D^{17^\circ}$ 1·4260 (Found: C, 75·05; H, 8·3. C_6H_8O requires C, 75·0; H, 8·4%). The 2 : 4-*dinitrophenylhydrazone* formed orange needles, m. p. 136—137° from alcohol (Found: N, 20·35. $C_{12}H_{12}O_4N_4$ requires N, 20·3%).

Methyl Ethynyl Ketone (VI; R = Me).—A solution of chromium trioxide (146 g.) in water (380 c.c.) and concentrated sulphuric acid (122 c.c.) was added over a period of 7—8 hours to a stirred solution of methylethynylcarbinol (150 g.; Macullum, U.S.P., 2,125,384) in water (325 c.c.) at 20° in an atmosphere of nitrogen. The mixture was stirred for a further 2—3 hours, set aside overnight and then extracted with ether. The ethereal solution was washed with water, dried and evaporated carefully through a Fenske column and the residue was distilled in nitrogen. The portion boiling below 100° was dried over calcium chloride and fractionation through a Dufton column (24 cm.), employing a partial reflux head, gave methyl ethynyl ketone (55 g.), b. p. 84·5—86°, $n_D^{22^\circ}$ 1·4050 (Petrov, *J. Gen. Chem. Russia*, 1940, **10**, 1682, gives b. p. 83·5—84·5°, $n_D^{20^\circ}$ 1·4070). The *p*-nitrophenylhydrazone formed reddish-brown needles, m. p. 142—143° from aqueous methyl alcohol (*idem, loc. cit.*, gives m. p. 140°) (Found: N, 20·85. Calc. for $C_{10}H_9O_2N_3$: N, 20·7%). The 2 : 4-*dinitrophenylhydrazone* formed yellow needles, m. p. 181°, from alcohol (Found: N, 22·65. $C_{10}H_8O_4N_4$ requires N, 22·55%).

Propenyl Ethynyl Ketone (VII).—This was prepared by a procedure analogous to that used for phenyl ethynyl ketone from propenylethynylcarbinol (250 g.; Heilbron, Jones and Weedon, *J.*, 1945, 81) in acetone (500 c.c.), and chromium trioxide (175 g.) and concentrated sulphuric acid (148 c.c.) in water (500 c.c.). Isolation by means of ether gave *propenyl ethynyl ketone* (193 g.) as a pungent smelling, colourless liquid, b. p. 145°/747 mm. and 75—77°/44 mm., $n_D^{20^\circ}$ 1·4770 (Found: C, 76·55; H, 6·75. C_6H_6O requires C, 76·6; H, 6·45%. Determination of active hydrogen (Zerewitinoff): The ketone (99·5 mg.) gave 25·5 c.c. of methane at 21°/766 mm., after heating to 90°, corresponding to 1·0 atom of active hydrogen per mol.). The 2 : 4-*dinitrophenylhydrazone* formed red needles, m. p. 162—163°, from alcohol (Found: C, 52·7; H, 4·1; N, 19·95. $C_{12}H_{10}O_4N_4$ requires C, 52·55; H, 3·7; N, 20·45%).

A solution of the ketone (1 g.) in ethyl acetate (10 c.c.) was shaken with Adams catalyst (10 mg.) and hydrogen until absorption was complete, 744 c.c. of hydrogen being absorbed at 21°/765 mm., corresponding to 2·9 |=. Removal of the catalyst and solvent gave ethyl propyl ketone which gave a 2 : 4-dinitrophenylhydrazone, m. p. 133—134°, undepressed on admixture with an authentic specimen.

Hex-3-en-5-yn-2-one (VIII).—A stirred and well cooled solution (0—5°) of hex-3-en-5-yn-2-ol (50 g.; see Part IV) in acetone (100 c.c.) was treated dropwise with a solution of chromium trioxide (35 g.) and concentrated sulphuric acid (29·6 c.c.) in water (100 c.c.) during 2½ hours, in an atmosphere of nitrogen in diffuse light. Isolation in the usual way gave *hex-3-en-5-yn-2-one* (23·5 g.) as a very pale yellow liquid, which rapidly darkened in air and light. It had b. p. 60—63°/20 mm., $n_D^{16^\circ}$ 1·4954 (Found: C, 76·45; H, 6·3. C_6H_6O requires C, 76·6; H, 6·45%. Determination of active hydrogen (Zerewitinoff): the ketone (59 mg.) gave 14·4 c.c. of methane at 22°/765 mm. (*i.e.*, 0·95 atom of active hydrogen per mol.). The 2 : 4-*dinitrophenylhydrazone* formed dark reddish-brown plates, m. p. 181° (decomp.), from alcohol–dioxan (2 : 1) (Found: N, 20·35. $C_{12}H_{10}O_4N_4$ requires N, 20·45%).

A solution of the ketone (2·9 g.) in methyl acetate (20 c.c.) was shaken with Adams catalyst (20 mg.) and hydrogen until absorption (2000 c.c. at 22°/760 mm.) ceased. After filtration and evaporation, the residue gave methyl butyl ketone (1·9 g.), b. p. 128°, $n_D^{18·5^\circ}$ 1·4038. The 2 : 4-dinitrophenylhydrazone crystallised from methyl alcohol in orange needles, m. p. 107—107·5°, undepressed on admixture with an authentic specimen.

5-*Methylhex-5-en-3-yn-2-one* (IX; R = Me).—(a) A suspension of 2-methylvinylacetylenylmagnesium chloride (from magnesium 7·7 g.) in ether (500 c.c.) was cooled to − 30° and a solution of acetic anhydride (65 g.) in ether (100 c.c.) was gradually added over 2½ hours. The mixture was stirred at − 30° for a further 2 hours and then at − 5° for 2 hours after which ice and water were added and the mixture set aside overnight. The ethereal layer was separated, the aqueous mother liquors were extracted once with ether and the combined ethereal solutions were washed with water and saturated sodium bicarbonate solution until free from acetic acid. The residue on distillation in nitrogen gave two fractions. (i) 5-*Methylhex-5-en-3-yn-2-one* (*ca.* 3 g.) was a pungent, colourless mobile liquid, b. p. 73·5°/44 mm., $n_D^{16^\circ}$ 1·4787 (Found: C, 77·65; H, 7·55. C_7H_8O requires C, 77·75; H, 7·45%). The 2 : 4-*dinitrophenylhydrazone* formed orange needles, m. p. 133·5—134·5°, from alcohol (Found: N, 19·2. $C_{13}H_{12}O_4N_4$ requires N, 19·45%). (ii) The *acetate* of 2 : 5 : 8-

trimethylnona-1 : 8-*dien*-3 : 6-*diyn*-5-*ol* (X) (7·5 g.) was a colourless liquid, b. p. 69·5°/0·2 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·5042 (Found : C, 77·5; H, 7·85. $C_{14}H_{16}O_2$ requires C, 77·75; H, 7·45%). Light absorption in alcohol : Maximum, 2230 A.; ε = 22,000.

(b) A suspension of 2-methylvinylacetylenylmagnesium chloride (from magnesium 7·7 g.) in ether (500 c.c.) was slowly added over 2½ hours to a solution of acetic anhydride (65 g.) in ether (150 c.c.), at − 30°. Stirring was continued for 1½ hours at − 30° and then for 2 hours at − 5°. Ice and water were added, the solution was kept overnight and after stirring at room temperature for 4 hours to ensure complete hydrolysis of the excess acetic anhydride, the product was isolated as in (a). Distillation in nitrogen gave 5-methylhex-5-en-3-yn-2-one (8·4 g.), b. p. 73—74°/40 mm. and 42—44°/11 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4794.

(c) A solution of 5-methylhex-5-en-3-yn-2-ol (10 g.; Nazarov and Elizarova, *Bull. Acad. Sci. U.R.S.S.*, 1940, 189) in acetone (20 c.c.) was cooled to 5° and treated in nitrogen in the usual way with chromium trioxide (6·35 g.) in sulphuric acid (5·3 c.c.) and water (20 c.c.). Isolation by means of ether and distillation gave 5-methylhex-5-en-3-yn-2-one (1·0 g.), b. p. 74°/40 mm., $n_{\mathrm{D}}^{15^\circ}$ 1·4798. The 2 : 4-dinitrophenylhydrazone had m. p. 133·5—134·5°, undepressed on admixture with a specimen from (a).

Hex-5-*en*-3-*yn*-2-*one* (IX; R = H).—A suspension of vinylacetylenylmagnesium chloride (from magnesium 8 g.) in ether (500 c.c.) was added to acetic anhydride (68 g.) in ether (200 c.c.) as described in the case of the methyl analogue (b). *Hex*-5-*en*-3-*yn*-2-*one* was obtained as a colourless, mobile, sternutatory liquid (5·1 g.) that rapidly developed a yellow colouration on standing. It had b. p. 62—63·5°/40 mm., $n_{\mathrm{D}}^{15^\circ}$ 1·4891 (Found : C, 76·35, 76·25; H, 6·65, 6·75. C_6H_6O requires C, 76·6; H, 6·45%). The 2 : 4-*dinitrophenylhydrazone* separated from methanol in orange needles, m. p. 162° (Found : C, 53·0; H, 3·8. $C_{12}H_{10}O_4N_4$ requires C, 52·55; H, 3·7%).

Deca-2 : 8-*dien*-5-*yn*-4 : 7-*dione* (XI).—Deca-2 : 8-dien-5-yn-4 : 7-diol (3 g.; Heilbron, Jones, and Raphael, *J.*, 1943, 268) was oxidised in the usual manner in acetone (20 c.c.) with a solution of chromium trioxide (2·45 g.) in water (10 c.c.) and concentrated sulphuric acid (2·3 c.c.). Isolation by means of ether gave *deca*-2 : 8-*dien*-5-*yn*-4 : 7-*dione* (1·2 g.) as an oil, b. p. 80—81°/0·005 mm., 50° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{21\cdot5^\circ}$ 1·5289 (Found : C, 74·05; H, 6·3. $C_{10}H_{10}O_2$ requires C, 74·05; H, 6·2%. Determination of active hydrogen (Zerewitinoff) : The diketone (49 mg.) gave only 0·5 c.c. methane at 24° and 755 mm. Semimicro-hydrogenation : A solution of the diketone (0·8 g.) in ethyl acetate (10 c.c.) shaken with Adams catalyst (25 mg.) absorbed 476 c.c. of hydrogen at 19°/761 mm. Calc. for 4 |= per mol. : 472 c.c.).

Dec-5-*yn*-4-*ol*-7-*one* (XII).—To a stirred and cooled solution of dec-5-yn-4 : 7-diol (15 g.; for preparation, see below) in acetone (75 c.c.) a solution of chromium trioxide (8·8 g.) in water (45 c.c.) and concentrated sulphuric acid (8·0 c.c.) was added during 2 hours. After stirring for a further 30 minutes the product was isolated by means of ether giving, on distillation, *dec*-5-*yn*-4-*ol*-7-*one* (8·8 g.) as a colourless liquid, b. p. 91—92°/0·4 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4672 (Found : C, 71·3; H, 9·55. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). Determination of active hydrogen (Zerewitinoff) : The product (59 mg.) gave 8 c.c. of methane at 21° and 761 mm., *i.e.*, 0·95 atom of active hydrogen per mol.). The 2 : 4-*dinitrophenylhydrazone* crystallised from aqueous methanol in yellow needles, m. p. 84—85° (Found : N, 15·7. $C_{16}H_{20}O_5N_4$ requires N, 16·1%).

Dec-5-*yn*-4 : 7-*dione* (XIII).—Chromium trioxide (3·0 g.), in water (15 c.c.) and concentrated sulphuric acid (2·7 c.c.) was added over 1½ hours to a stirred solution of dec-5-yn-4-ol-7-one (5·9 g.) in acetone (25 c.c.). Stirring was continued for a further 15 minutes and, after diluting with water, the product was isolated by means of ether. Distillation in nitrogen gave *dec*-5-*yn*-4 : 7-*dione* (1·45 g.), as a pale yellow liquid which polymerised extensively on distillation. It had b. p. 74—75°/0·4 mm., 61·5°/0·3 mm., $n_{\mathrm{D}}^{12\cdot5^\circ}$ 1·4593 (Found : C, 72·25; H, 8·7. $C_{10}H_{14}O_2$ requires C, 72·25; H, 8·5%). With 2 : 4-dinitrophenylhydrazine sulphate, the diketone gave a *derivative* which crystallised from ethyl acetate in orange needles, m. p. 183—184° (Found : N, 20·3. $C_{22}H_{24}O_9N_8$ requires N, 20·55%). Light absorption in chloroform : Maximum, 3870 A.; ε = 45,000.

Decane-4 : 7-*dione*.—(a) A solution of dec-5-yn-4 : 7-dione (325 mg.) in ethyl acetate (10 c.c.) was shaken in hydrogen in the presence of Adams catalyst (10 mg.) until absorption was complete (96 c.c. at 15·5°/780 mm.; theoretical 90 c.c.). After removal of catalyst and evaporation of solvent, the residue was distilled and gave decane-4 : 7-dione (170 mg.), b. p. 53·5°/0·1 mm. The dioxime was crystallised from benzene and had m. p. 108°, undepressed on admixture with the specimen prepared according to (b).

(b) (With G. H. Hargreaves.) Oxidation of decane-4 : 7-diol (4 g.) (obtained by complete hydrogenation of dec-5-yn-4 : 7-diol) with chromic acid in sulphuric acid gave the *diketone* (2·5 g.) which, after distillation at 10^{-4} mm., solidified and had m. p. 22° (Found : C, 70·65; H, 10·6. $C_{10}H_{18}O_2$ requires C, 70·55; H, 10·65%). The *dioxime* was obtained from benzene in flat needles, m. p. 108° (Found : N, 13·9. $C_{10}H_{20}O_2N_2$ requires N, 14·0%). It is appreciably soluble in water.

2-*Methyloct*-6-*en*-3-*yn*-2-*ol*-5-*one* (XV).—A solution of 2-methyloct-6-en-3-yn-2 : 5-diol (10 g.; for preparation, see below) in acetone (40 c.c.) at about 4° was treated during 30 minutes with a solution of chromium trioxide (4·5 g.) in water (22 c.c.) and concentrated sulphuric acid (4 c.c.), stirring was continued for a further 15 minutes and the mixture was diluted with water and the product isolated by means of ether. Distillation gave 2-*methyloct*-6-*en*-3-*yn*-2-*ol*-5-*one* (6·2 g.) as a colourless liquid, b. p. 96—99°/0·03 mm. and 65—66°/0·003 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4988 (Found : C, 70·4; H, 7·9. $C_9H_{12}O_2$ requires C, 71·05; H, 7·95%). The 2 : 4-*dinitrophenylhydrazone* formed red prismatic needles, m. p. 172—173° from alcohol (Found : C, 54·3; H, 4·85. $C_{15}H_{16}O_5N_4$ requires C, 54·2; H, 4·85%).

1 : 1-*Diphenylhept*-5-*en*-2-*yn*-1-*ol*-4-*one* (XVI).—A stirred solution of 1 : 1-diphenylhept-5-en-2-yn-1 : 4-diol (4 g.; Cymerman, Heilbron, Johnson, and Jones, *J.*, 1944, 141) in acetone (40 c.c.) was treated at *ca.* 0° with chromium trioxide (1 g.) in water (5 c.c.) and concentrated sulphuric acid (0·8 c.c.) during 40 minutes. After stirring for a further 10 minutes and isolation of the product with ether in the usual way a solid (3·85 g.), m. p. 118°, was obtained; this, after fractional crystallisation from aqueous alcohol, yielded 1 : 1-*diphenylhept*-5-*en*-2-*yn*-1-*ol*-4-*one* (2 g.) as colourless needles, m. p. 134°, depressed on admixture with the starting material (Found : C, 82·45; H, 5·9. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·85%).

Dibenzoylacetylene.—A solution in acetone (15 c.c.) of a mixture (m. p. 129—130°) of the stereoisomers of 1 : 4-diphenylbut-2-yn-1 : 4-diol (2 g.; Dupont, *Ann. Chim.*, 1913, **30**, 507) was cooled to 0—5° and treated over a period of 15 minutes with a solution of chromium trioxide (1·5 g.) in concentrated sulphuric acid (1·36 c.c.) and water (4 c.c.). After shaking for a further 5 minutes, the mixture was diluted to 100 c.c. with water and the pale yellow solid separated and washed well with water to remove all traces of chromium salts. Recrystallisation from either ligroin (b. p. 80—100°) or alcohol gave dibenzoylacetylene (1·8 g.) as very pale yellow leaflets, m. p. 111—112° (Dupont, *Bull. Soc. chim.*, 1914, **15**, 606, gives m. p. 112°).

Propyl Vinyl Ketone.—Propyl ethynyl ketone (30 g.) in methyl acetate (90 c.c.) was shaken in hydrogen in the presence of a palladium on barium sulphate catalyst (4·5 g., 0·3% Pd) until 7·5 litres had been absorbed. After filtration and rapid removal of solvent, the residue was distilled through a Dufton column to give propyl vinyl ketone (21 g.), b. p. 65·5—66°/100 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4231 (Courtot and Pierron, *Compt. rend.*, 1929, **188**, 1503, give b. p. 88—90°/150 mm., $n_{\mathrm{D}}^{14^\circ}$ 1·4275).

1-*Diethylaminohexan*-3-*one* (cf. Delaby, *Compt. rend.*, 1926, **182**, 140).—Diethylamine (2·25 g.) was slowly added to a solution of propyl vinyl ketone (3 g.) in ether (10 c.c.) and, after 2 days at room temperature, 1-diethylaminohexan-3-one

(3·8 g.), b. p. 101°/18 mm., $n_{\mathrm{D}}^{18\cdot5^{\circ}}$ 1·4363, was obtained. The picrate crystallised in yellow prisms, m. p. 81—81·5°, from methanol (Delaby, *loc. cit.*, gives m. p. 81°).

1-*Anilinohexan*-3-*one*.—Propyl vinyl ketone (1 g.) and aniline (0·95 g.) were mixed together in ligroin (2 c.c., b. p. 40—60°) and allowed to stand at room temperature for 2 days. The large colourless plates deposited were separated and recrystallised from the same solvent to give 1-anilinohexan-3-one (1·7 g.), m. p. 60—61°, undepressed on admixture with an authentic specimen prepared according to Blaise and Maire (*Bull. Soc. chim.*, 1908, **3**, 660) who give m. p. 60°.

Vinyl Propenyl Ketone.—Propenyl ethynyl ketone (9·4 g.) in ethyl acetate (40 c.c.) was shaken in hydrogen in the presence of a palladium-barium sulphate catalyst (0·94 g., 0·3% Pd) with exclusion of bright light. When the theoretical amount of hydrogen had been absorbed, the catalyst was separated and the solvent removed under reduced pressure at room temperature. Distillation of the residue gave vinyl propenyl ketone (3·5 g.), b. p. 38·5—39·5°/10 mm., $n_{\mathrm{D}}^{18\cdot5^{\circ}}$ 1·4696 (Nazarov and Okolskaya, *Bull. Acad. Sci. U.R.S.S.*, 1941, 314, give b. p. 30—31°/7·5 mm., $n_{\mathrm{D}}^{20^{\circ}}$ 1·4690).

Oct-3-*yn*-2-*ol*.—A solution of 1-hexyne (90 g.) in ether (100 c.c.) was added to ethylmagnesium bromide (from 24·3 g. magnesium) in ether (250 c.c.) and the mixture was heated under reflux for 3 hours in nitrogen and then cooled while freshly distilled acetaldehyde (48 g.) in ether (75 c.c.) was added over 30 minutes. After stirring for 2 hours, the solution was set aside overnight. The complex was decomposed with a cold solution of ammonium chloride and isolation of the product with ether gave oct-3-yn-2-ol (104 g.), b. p. 101·5—103°/40 mm., $n_{\mathrm{D}}^{17\cdot5^{\circ}}$ 1·4503 (Campbell, Campbell, and Eby, *J. Amer. Chem. Soc.*, 1938, **60**, 2882, give b. p. 88°/40 mm., $n_{\mathrm{D}}^{20^{\circ}}$ 1·4347) (Found : C, 76·15; H, 11·1. Calc. for $C_8H_{14}O$: C, 76·15; H, 11·2%). The *α-naphthylurethane* crystallised from ligroin (b. p. 40—60°) as needles, m. p. 63·5—64·5° (Found : N, 4·5. $C_{19}H_{21}O_2N$ requires N, 4·75%).

n-*Propylethynylcarbinol*.—A solution of sodium (69 g.) in liquid ammonia (1500 c.c.) was converted to sodamide, in the presence of hydrated ferric nitrate (0·6 g.) and sodium oxide (from 2 g. sodium), and then into sodium acetylide in the manner already described (Heilbron, Jones, and Weedon, *J.*, 1945, 81). A solution of butaldehyde (216 g.) in ether (400 c.c.) was then added over 2—3 hours and after stirring for a further 2 hours, the reaction was terminated by the gradual addition of ammonium chloride (165 g.). When the ammonia had evaporated, sufficient water was added to dissolve the inorganic salts and the product was isolated by means of ether. Distillation through a 12 inch Fenske column gave *n*-propylethynylcarbinol (136 g.), b. p. 89°/100 mm., $n_{\mathrm{D}}^{16\cdot5^{\circ}}$ 1·4382 (Lespieau, *Ann. Chim.*, 1912, **27**, 137, gives b. p. 141°). The *acetyl derivative* (39 g.), prepared from the carbinol (41 g.) and acetic anhydride (43 g.) in pyridine (40 g.), had b. p. 74°/30 mm., and 65·5—66°/19 mm., $n_{\mathrm{D}}^{19^{\circ}}$ 1·4257 (Found : C, 68·7; H, 8·8. $C_8H_{12}O_2$ requires C, 68·55; H, 8·65%).

Dec-5-*yn*-4 : 7-*diol*.—A slow stream of pure dry acetylene was passed during 24 hours into a stirred ethereal solution of ethylmagnesium bromide (from magnesium 24 g.). A solution of *n*-butaldehyde (72 g.) in ether was then added over a period of 2 hours, stirring was continued for a further 2 hours and the complex was decomposed with ammonium nitrate (180 g.) and ice water. Isolation by means of ether and distillation gave dec-5-yn-4 : 7-diol (63 g.) as a pale yellow viscous oil, b. p. 134—137°/3 mm., $n_{\mathrm{D}}^{17^{\circ}}$ 1·4694 (Marvel and Williams, *J. Amer. Chem. Soc.*, 1939, **61**, 2716, give b. p. 113—114°/1 mm., $n_{\mathrm{D}}^{20^{\circ}}$ 1·4678).

2-*Methyloct*-6-*en*-3-*yn*-2 : 5-*diol* (with G. H. Hargreaves).—Propenylethynylcarbinol (106 g.) in ether solution was added during one hour to an ice-cooled ethereal solution of ethylmagnesium bromide (from 48 g. of magnesium), and the mixture was refluxed for 2 hours. After ice-cooling, a solution of acetone (58 g.) in ether was added dropwise (45 minutes), the mixture stirred overnight in nitrogen and finally refluxed for one hour. After cooling to 0°, the Grignard complex was decomposed with ammonium chloride and ice and isolated by means of ether to give the *glycol* (90 g.), b. p. 120°/10^{-2} mm., $n_{\mathrm{D}}^{23^{\circ}}$ 1·4861 (Found : C, 69·9; H, 8·95. $C_9H_{14}O_2$ requires C, 70·1; H, 9·15%. Determination of active hydrogen (Zerewitinoff) : The glycol (57 mg.) evolved 16·8 c.c. of methane at 19°/766 mm., equivalent to 1·9 atoms of active hydrogen per mol.). The glycol exhibited no absorption of appreciable intensity in the ultraviolet.

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