21. *Studies in the Polyene Series. Part XVIII. The Formation of Ethers from Propenylethynylcarbinol and Related Compounds.*

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Isomerisation of propenylethynylcarbinol (I) with sulphuric acid in alcoholic solution gives the ethers (II; R = OMe and OEt) of the conjugated vinylethynylcarbinols. The etherification appears to occur essentially as a consequence of the anionotropic rearrangement. An analogous dual etherification-isomerisation can be effected with the acetylenyl glycol (III) from crotonaldehyde.

When the carbinol (I) is distilled in the presence of a small quantity of sulphuric acid, self-etherification accompanies the rearrangement, yielding the divinylacetylenyl C_{12} ether (V).

An improved procedure for the preparation of propenylethynylcarbinol (I) is described.

Several methods of obtaining ethers of acetylenylcarbinols are known but the most effective appears to consist simply in treating the carbinol with the appropriate alcohol in the presence of concentrated sulphuric acid (Moureu, Dufraisse, and Blatt, *Bull. Soc. chim.*, 1924, **35**, 1412; Dufraisse and Rocher, *ibid.*, 1935, **2**, 2235). This method appears to be applicable particularly to tertiary carbinols, and Nazarov (*Bull. Acad. Sci. U.R.S.S.*,

1938, 706), who used alcoholic sulphuric acid at 50—80° to make ethers of vinylacetylenylcarbinols of the type $CH_2{:}CH{\cdot}C{:}C{\cdot}C(OH)R_1R_2$, mentions that secondary alcohols form ethers only with difficulty.

A convenient synthesis of ethers of ethynyl- and vinylacetylenyl-carbinols derived from αβ-unsaturated carbonyl compounds was desired, and it seemed possible that compounds such as (II) might be obtained by effecting the anionotropic rearrangement (Jones and McCombie, J., 1943, 261) of propenylethynylcarbinol (I) in the presence of an excess of the required alcohol, using concentrated sulphuric acid. This proved to be the case, and when the carbinol (I) was treated with methyl-alcoholic sulphuric acid at 20°, *2-methoxyhex-3-en-*

(I.) $CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{:}CH$ $CH_3{\cdot}CHR{\cdot}CH{:}CH{\cdot}C{:}CH$ (II.)

5-yne (II; R = OMe) was isolated in 65% yield. The *ethyl ether* (II; R = OEt) was obtained (40% yield) in an analogous manner. The high volatility of these ethers renders their isolation difficult, and better yields could undoubtedly be obtained by a more detailed study of the reaction conditions. The structures of the two ethers are adequately established by their absorption spectra (Table) which are characteristic of the conjugated vinylacetylene chromophore (see Parts VIII—X, XIV—XVII). Further evidence is forthcoming from the observation that the methyl ether can also be isolated from the product obtained by treating 2-chlorohex-3-

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
2-Methoxyhex-3-en-5-yne (II; R = OMe)	2235	12,500
	*2320	11,000
2-Ethoxyhex-3-en-5-yne (II; R = OEt)	2230	12,500
	*2290	10,500
Hex-3-en-5-yn-2-ol [1] (II; R = OH)	2230	13,500
	*2300	9,500
Di-2-(hex-3-en-5-ynyl) ether (V)	2240	26,500
	*2310	23,000
2 : 9-Diethoxydeca-3 : 7-dien-5-yne (IV; R = OEt)	2650	23,000
	2800	17,000
Deca-3 : 7-dien-5-yne-2 : 9-diol [2] (IV; R = OH)	2650	21,500
	2800	19,000

* Inflexion.

[1] Jones and McCombie, *loc. cit.* [2] Heilbron, Jones, and Raphael, J., 1943, 268.

en-5-yne (II; R = Cl), described in the preceding paper, with methyl alcohol in the presence of pyridine or other bases.

No ether formation could be detected when the rearrangement product of (I), *i.e.*, hex-3-en-5-yn-2-ol (II; R = OH), was treated with methyl alcohol and sulphuric acid. This supports Nazarov's finding (*loc. cit.*) that secondary carbinols cannot readily be etherified in this way and, together with the results described in the next paragraph, provides a strong indication that etherification occurs during, and as a result of, the anionotropic rearrangement under the influence of acids.

It was observed by Moureu, Dufraisse, and Houghton (*Bull. Soc. chim.*, 1927, **41**, 53) that the tertiary acetate, $CPh_2(OAc){\cdot}C{:}C{\cdot}Ph$, could be converted into the corresponding methyl ether merely by heating it with methyl alcohol. No such conversion could be effected with the acetate of (I) by boiling with methyl alcohol for 6 hours, and a repetition of the experiment in the presence of anhydrous potassium carbonate merely resulted in hydrolysis. The failure of the first experiment appears to be due only partly to the fact that (I) is a secondary carbinol, and more especially to the comparatively low mobility of the propenylethynyl system, since etherification does occur in the case of the acetate of a more readily isomerised secondary carbinol (see Part XX).

It is noteworthy that although conjugated vinylacetylenes, particularly *s.*-divinylacetylenes, undergo Diels–Alder addition reactions (Norton, *Chem. Reviews*, 1942, **31**, 319), yet no reaction could be induced between the ether (II; R = OMe) and maleic anhydride in benzene solution, even at 150°.

The dual rearrangement of the acetylenyl glycol (III), derived from crotonaldehyde, to the *s.*-divinylacetylenyl glycol (IV; R = OH) has already been described (Part XI). In the presence of alcoholic sulphuric acid, simultaneous etherification accompanies the isomerisation, yielding *2 : 9-diethoxydeca-3 : 7-dien-5-yne* (IV; R = OEt), which exhibits light absorption similar to that of the corresponding glycol.

(III.) $CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{:}C{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CH_3$ $CH_3{\cdot}CHR{\cdot}CH{:}CH{\cdot}C{:}C{\cdot}CH{:}CH{\cdot}CHR{\cdot}CH_3$ (IV.)

One experiment involving the rearrangement of propenylethynylcarbinol (I) in the usual manner with dilute sulphuric acid proceeded anomalously, the main product being a liquid of much higher b. p. than the expected isomeride (II; R = OH). Attempts to repeat this experiment were fruitless until, investigating the possibility that all traces of acid had not been removed prior to distillation of the product, we distilled the carbinol (I) with a small quantity of dilute sulphuric acid, whereupon this high-boiling compound, which proved to be a C_{12} ether, was produced in 45% yield. This ether must be *di-2-(hex-3-en-5-ynyl) ether*, $O(CHMe{\cdot}CH{:}CH{\cdot}C{:}CH)_2$ (V), since (*a*) it exhibits intense light absorption (Table) corresponding to the presence of two conjugated vinylacetylene systems in the molecule, (*b*) it readily forms a silver salt with ammoniacal silver nitrate, and (*c*) on complete hydrogenation it gives a compound which is probably di-2-(*n*-hexyl) ether. This self-etherification reaction is quite analogous to the simple etherification described above, and in

accordance with this view, treatment of the rearranged carbinol (II; R = OH) with sulphuric acid in a similar fashion gave a much poorer yield of (V).

The n-*butyl ether* of propenylethynylcarbinol (I) was obtained, although in very low yield, by treatment of the intermediate sodio-compound, obtained by condensing crotonaldehyde with sodium acetylide, with an excess of the appropriate alkyl bromide. The replacement reaction would appear to be largely incomplete in liquid ammonia solution since much of the carbinol (I) was also isolated, but no trace of the *C*-alkylated product was obtained.

In Part VI (J., 1942, 733) the preparation of propenylethynylcarbinol (I) from crotonaldehyde and sodium acetylide in liquid ammonia solution was described, the sodium acetylide employed in this and related preparations being prepared *in situ* directly from sodium. It has now been found preferable to obtain the sodium acetylide from sodamide, the latter being prepared by means of a ferric nitrate–sodium oxide catalyst (Vaughn, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120); the acetylide appears to be produced in a considerably more reactive condition than that formed by the direct interaction of acetylene with sodium in liquid ammonia. By using this method the preparation of propenylethynylcarbinol has now been appreciably improved in that, not only can yields of 75% be obtained regularly, but the main operations involved in an experiment on a 15 M. scale can be completed in about 14 hours. Similarly improved results have been obtained in other preparations of ethynylcarbinols. Hennion and Lieb (*J. Amer. Chem. Soc.*, 1944, **66**, 1289) describe a preparation of propenylethynylcarbinol which gives a 46% yield.

Experimental.

(Absorption spectra were determined in alcoholic solutions.)

2-*Methoxyhex*-3-*en*-5-*yne* (II; R = OMe).—(*a*) Propenylethynylcarbinol (250 g.; see below) was added to a solution of concentrated sulphuric acid (125 g.) in dry methyl alcohol (1·25 l.), and the mixture kept at 20° for a week. After dilution (to 5 l.) with water, the product was isolated by means of ether, and distillation through a 24-cm. Dufton column gave 2-*methoxyhex*-3-*en*-5-*yne* (190 g.), b. p. 73—76·5° (mainly 75—76°)/120 mm., $n_D^{17°}$ 1·4537. The ether is a colourless mobile liquid with a pleasant odour (Found: C, 76·65; H, 9·4. $C_7H_{10}O$ requires C, 76·35; H, 9·15%). *Active hydrogen* (Zerewitinoff): The ether (71·5 mg.) gave 15·15 c.c. of methane (after heating to 90°) at 15°/765 mm., equivalent to 1·0 active hydrogen atom per mol.

When hex-3-en-5-yn-2-ol (18 g.; Jones and McCombie, J., 1943, 261) was added to a solution of concentrated sulphuric acid (9 g.) in methyl alcohol (90 c.c.) and the mixture kept for a week, no trace of the methyl ether was obtained on working up by the above method.

(*b*) A mixture of 2-chlorohex-3-en-5-yne (50 g.; previous paper), pyridine (50 g.), and dry methyl alcohol (50 g.) was refluxed for 17 hours. After dilution with dilute hydrochloric acid, isolation with ether gave 2-methoxyhex-3-en-5-yne (9 g.), b. p. 73—77°/120 mm., $n_D^{14·5°}$ 1·4547.

2-*Ethoxyhex*-3-*en*-5-*yne* (II; R = OEt).—Prepared by the method described under (*a*) above from the carbinol (30 g.), concentrated sulphuric acid (12 g.), and dry alcohol (120 c.c.), the *ether* (16 g.), a pleasant-smelling mobile liquid, had b. p. 81—81·5°/100 mm., $n_D^{14°}$ 1·4532 (Found: C, 77·6; H, 9·6. $C_8H_{12}O$ requires C, 77·4; H, 9·75%). *Active hydrogen* (Zerewitinoff): The ether (76 mg.) evolved 13·4 c.c. of methane (after heating to 90°) at 19°/760 mm. (0·9 active hydrogen atom per mol.).

Propenylethynylcarbinol from 3-*Acetoxyhex*-4-*en*-1-*yne*.—A solution of 3-acetoxyhex-4-en-1-yne (6 g.; Jones and McCombie, J., 1942, 733) in methyl alcohol (7 c.c.) was refluxed for 6 hours in the presence of anhydrous potassium carbonate (3 g.). Isolation of the product with ether in the usual manner gave propenylethynylcarbinol (3·1 g.), b. p. 86°/50 mm., $n_D^{16°}$ 1·4664. The *α-naphthylurethane* crystallised in needles from light petroleum (b. p. 60—80°) and had m. p. 98—99·5°, undepressed on admixture with a specimen made from an authentic sample of carbinol (Found: N, 5·35. $C_{17}H_{15}O_2N$ requires N, 5·3%).

2 : 9-*Diethoxydeca*-3 : 7-*dien*-5-*yne* (IV; R = OEt).—To a solution of concentrated sulphuric acid (2 g.) in alcohol (40 c.c.), deca-2 : 8-dien-5-yne-4 : 7-diol (3 g.; Heilbron, Jones, and Raphael, J., 1943, 268) was added, and the mixture was kept at about 20° for 5 days. Isolation by means of ether gave the *ether* (IV; R = OEt) (2·3 g.), b. p. 93—95°/0·03 mm., $n_D^{16°}$ 1·4991 (Found: C, 75·65; H, 10·05. $C_{14}H_{22}O_2$ requires C, 75·7; H, 9·9%).

Di-2-(*hex*-3-*en*-5-*ynyl*) *Ether* (V).—(*a*) A mixture of propenylethynylcarbinol (51 g.) and sulphuric acid (2 c.c.; 2N) was heated in a distilling flask at 80°/50 mm. for 10 minutes and then distilled in an atmosphere of nitrogen at the same pressure. The high-boiling fraction obtained after removal of water and hex-3-en-5-yn-2-ol was redistilled through a 24-cm. Dufton column, giving *di*-2-(*hex*-3-*en*-5-*ynyl*) *ether* (25 g.) as a colourless oil, b. p. 72—74°/5 mm., $n_D^{20·5°}$ 1·4950 (Found: C, 82·8; H, 8·0. $C_{12}H_{14}O$ requires C, 82·75; H, 8·05%).

(*b*) Repetition of the above procedure with hex-3-en-5-yn-2-ol (10 g.) gave the ether (2·5 g.), b. p. 66—68°/3·5 mm., $n_D^{15°}$ 1·4977.

Di-2-(n-*hexyl*) *Ether*.—The above ether (14·2 g.) in ethyl acetate (200 c.c.) was completely hydrogenated in the presence of platinic oxide (40 mg.). Isolation of the product in the usual manner gave di-2-(*n*-hexyl) ether (13·5 g.), b. p. 95—97°/22 mm., $n_D^{22°}$ 1·4183 (Found: C, 77·25; H, 13·95. Calc. for $C_{12}H_{26}O$: C, 77·35; H, 14·05%) (Vernimmen, *Bull. Soc. chim. Belg.*, 1924, **33**, 96, gives b. p. 200°/760 mm., $n_D^{20°}$ 1·4152).

3-n-*Butoxyhex*-4-*en*-1-*yne*.—A solution of crotonaldehyde (140 g.) in ether (200 c.c.) was added during 1½ hours to a liquid ammonia solution (1·5 l.) of sodium acetylide, prepared from sodium (47 g.) as described below. After an hour's stirring, *n*-butyl bromide (274 g.) in ether (150 c.c.) was added during 1½ hours, followed after a further 1½ hours by ammonium chloride (120 g.), and the solvent was allowed to evaporate off overnight. The product, isolated with ether, was distilled, and the portion with b. p. above 62°/145 mm. was redistilled through a 24-cm. Dufton column. In this way there were obtained: (i) propenylethynylcarbinol (67 g.), b. p. 74—76°/30 mm. (α-naphthylurethane, m. p. and mixed m. p., 98—99°); (ii) 3-n-*butoxyhex*-4-*en*-1-*yne* (12 g.), a colourless liquid with a pleasant odour, b. p. 88—89°/30 mm., $n_D^{19·5°}$ 1·4453 (Found: C, 79·2; H, 10·8. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The ether shows no appreciable light absorption in the range 2200—4000 A. *Active hydrogen* (Zerewitinoff): The ether (81 mg.) evolved 12·5 c.c. of methane at 25°/772 mm. (after heating to 90°) (1·0 active hydrogen atom per mol.).

Improved Preparation of Propenylethynylcarbinol.—The reaction vessel consisted of a 3-necked, 10-l. flask set up in an alcohol and "dry-ice" cooling bath. The flask was fitted with an efficient mercury-seal stirrer, a gas inlet leading nearly to the bottom of the flask, thermometer, and a gas outlet tube packed with soda-lime. The solid materials were introduced by removing the stopper from one of the necks of the flask, and the liquid (crotonaldehyde in ether) by means of a dropping-funnel temporarily inserted in one of the necks.

About 6 l. of liquid ammonia were run into the reaction flask, the latter being cooled to — 40°; then finely powdered hydrated ferric nitrate (3 g.) was added, and the mixture stirred for a few minutes to effect solution, which was followed by addition of sodium (10 g.). The mixture was stirred until the colour changed from blue to a brownish-black.

In some cases it may be necessary to pass dry air through the mixture in order completely to remove the blue colour. At this point a slow stream of dry nitrogen was introduced, and the bath temperature was raised by addition of alcohol until the internal temperature reached — 35°. Sodium (345 g.), cut in cubes of about ½ inch size, was added piecemeal into the mixture, and stirring continued until the colour changed from a deep blue to a light grey, indicating conversion of sodium into sodamide (25—50 minutes). While the temperature was kept at about — 35°, acetylene, purified by passage through a tower (90 × 3 cm.) of silica gel and by bubbling through concentrated sulphuric acid, was introduced with the nitrogen at a rate of about 3 l./min. After 2—2½ hours the mixture again turned black, corresponding to the completion of the formation of sodium acetylide (cf. Kreimeier, U.S.P. 2,106,181). The acetylene flow was then reduced to 50—100 c.c./min., and a solution of redistilled crotonaldehyde (1050 g.) in about twice its volume of dry ether added over a period of 4 hours, the temperature being maintained at about — 32°. The mixture was stirred for a further 3 hours. At this point the reaction was stopped by the gradual addition of ammonium chloride (825 g.), a considerable amount of heat being evolved in this process. The mixture was stirred for a further 30 minutes to complete the decomposition of the sodio-compound. The reaction flask was then removed from the cooling bath and the ammonia allowed to evaporate off overnight, the mixture being stirred gently throughout. The suspension of salt thus obtained was filtered off at the pump, and the solid washed thoroughly with ether. Evaporation of the ethereal solution gave a residue which on distillation in nitrogen gave propenylethynylcarbinol (1085 g.; 75% yield based on the crotonaldehyde), b. p. 74—75°/30 mm., $n_D^{21°}$ 1·4645.

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