369. *Researches on Acetylenic Compounds. Part XXXIII.* The Preparation of Monosubstituted Derivatives of Diacetylenes.*

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By treatment of the mono- and di-sodium derivatives of diacetylene with alkyl halides or carbonyl compounds under suitable conditions, monosubstituted diacetylenes can be prepared. Some observations bearing on the mechanism of the reaction are discussed and syntheses of iododiacetylenic compounds are described.

As a continuation of the work on disubstituted derivatives of diacetylene already reported (Armitage, Jones, and Whiting, *J.*, 1951, 44), a number of monosubstituted derivatives have now been prepared, partly to make more complete the investigation of the light-absorption properties of diacetylenes reported in the next paper but more especially because of the possibility of coupling these compounds, to give conjugated alkatetraynes (see *J.*, 1952, p. 2014).

Hitherto only four monosubstituted derivatives of diacetylene have been prepared. 2-Methylhexa-3 : 5-diyn-2-ol (I; $R^1 = R^2 = Me$) was prepared by heating the corresponding glycol (II; $R^1 = R^2 = CMe_2\cdot OH$) with alkaline reagents (Zalkind and Aizikovich, *J. Gen. Chem.*, *U.S.S.R.*, 1939, **9**, 961). Penta-1 : 3-diyne (III; R = Me) has recently been obtained from sodium acetylide and either methylene di-iodide or propargyl bromide, reactions which imply a double prototropic rearrangement of the initially-formed penta-1 : 4-diyne (Schlubach and Wolf, *Annalen*, 1950, **568**, 141). The hydrocarbon so prepared had physical constants differing considerably from those recorded by Prévost (*Compt. rend.*, 1926, **182**, 854) for a compound, obtained by the dehydrobromination of 1 : 2 : 3 : 4-tetrabromopentane, to which the structure (III; R = Me) was assigned. Schlubach and Franzen have very recently obtained phenyldiacetylene, and have also disproved Grignard and Tcheoufaki's claim (*Compt. rend.*, 1929, **188**, 359) to have made 1-iododiacetylene and have prepared this compound themselves (*Annalen*, 1951, **573**, 105, 115). In addition, the existence of methyl-, ethyl- and vinyl-diacetylenes in the high-boiling residues from the Hüls acetylene-synthesis process has been deduced, though these compounds were not isolated (see Copenhaver and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold, p. 302). In Baeyer's synthesis of tetra-acetylenedicarboxylic acid (*Ber.*, 1885, **18**, 2272) a salt of (III; $R = CO_2H$) was assumed to be an intermediate.

$$\underset{\text{(I)}}{HO\cdot CR^1R^2\cdot C{\equiv}C\cdot C{\equiv}CH} \qquad \underset{\text{(II)}}{R^1C{\equiv}C\cdot C{\equiv}CR^2} \qquad \underset{\text{(III)}}{RC{\equiv}C\cdot C{\equiv}CH}$$

The method previously described (Armitage, Jones, and Whiting, *loc. cit.*), whereby 1 : 4-dichlorobut-2-yne is dehydrohalogenated by sodamide in liquid ammonia to a sodium derivative of diacetylene which may then react *in situ* with alkyl halides or carbonyl compounds, has now been applied to the preparation of several monosubstituted diacetylenes. When three molecular proportions of sodamide were employed, a monosodium derivative was presumably formed, and addition of alkyl halides then resulted in the usual alkylation reactions. Thus methyl iodide gave penta-1 : 3-diyne (III; R = Me) with physical constants agreeing with those quoted by Schlubach and Wolf (*loc. cit.*). This unambiguous synthesis confirms the interesting rearrangement postulated by the latter authors. Penta-1 : 3-diyne is very volatile and unstable, and it apparently forms an azeotrope with ammonia; the only satisfactory method of isolation devised involved extraction of the liquid-ammonia solution with butane, from which the pentadiyne was readily separated by distillation.

Hexa-1 : 3-diyne (III; R = Et) and octa-1 : 3-diyne (III; R = Bu) were readily prepared from the corresponding bromides in about 45% yields; substitution of lithium, potassium, or calcium for sodium had little effect on the yields, and the use of alkyl iodides

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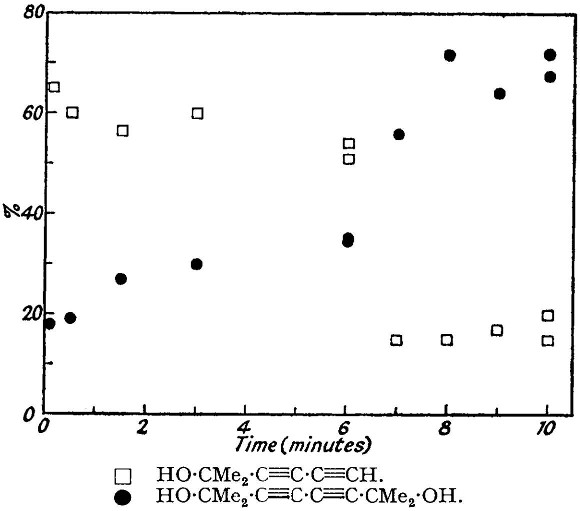
* Part XXXII, *J.*, 1951, 2652.

also made no improvement, while ethyl toluene-*p*-sulphonate failed to react under the usual conditions. Allyl bromide gave a small yield of a hydrocarbon, b. p. 42°/150 mm., n_D^{19} 1·4038, which may have been hept-1-ene-4 : 6-diyne (III; R = $H_2C{:}CH{\cdot}CH_2$) (but see Armitage, Jones, and Whiting, *loc. cit.*); it could not be investigated fully because of the facility with which it decomposed explosively.

Carbonyl compounds also reacted with monosodiodiacetylene. Thus acetone gave 2-methylhexa-3 : 5-diyn-2-ol (I; $R^1 = R^2 =$ Me), which crystallised on cooling and melted sharply; its physical constants agreed only moderately well with those recorded by Zalkind and Aizikovich (*loc. cit.*), who obtained their specimen by regeneration from the silver derivative under rather drastic conditions. Benzophenone, butaldehyde, acetaldehyde, and formaldehyde similarly gave diacetylenic alcohols, that obtained from formaldehyde being particularly unstable.

It was observed that in all these reactions an appreciable quantity of the corresponding diacetylenic glycol was formed. Because of this unexpected observation, and because of the importance of the reaction as a model for the synthesis of triacetylenic alcohols, the reactions of acetone with mono- and di-sodiodiacetylenes were studied semiquantitatively. The two products, the alcohol (I; $R^1 = R^2 =$ Me) and the glycol (II; $R^1 = R^1 = CMe_2{\cdot}OH$), can readily be isolated in a state of purity with fairly small and constant experimental losses; the results are tabulated in the experimental section, and those obtained for the reaction between two molecules of acetone and one of disodiodiacetylene at −62° are illustrated in the diagram. It is obvious that these do not accord with the simplest representation of the reaction, as one involving two consecutive second-order reactions of the bifunctional addend C_4^{--}; but attempts to find a satisfactory quantitative interpretation have proved unsuccessful. It is at least evident that the reaction (at −62°) takes place in two phases, the first leading to the formation of *ca.* 0·65 mol. of the alcohol and 0·18 mol. of the glycol (as their sodium derivatives) within a few seconds, the second to the conversion of the sodium derivative of the alcohol into that of the glycol very much less rapidly. The reason for the discontinuity after about 6 minutes is obscure.

Alcohol and glycol formation from disodiodiacetylene and acetone.



Perhaps the only conclusion which can be drawn with certainty is that the reactions between the diacetylide ion and the $Me_2C(O^-){\cdot}C_4^-$ ion, and acetone, are extremely rapid, more rapid by several powers of ten than might be estimated from the usual reaction times allowed for the Nef reaction in liquid ammonia. It follows that the further reactions responsible for the second phase must be controlled by some process in which either the $Me_2C(O^-){\cdot}C_4^-$ ion, or acetone, is formed slowly. The possibility that this reaction might be the slow dissociation of 2-amino*iso*propanol, which might be formed rapidly from acetone and ammonia, was eliminated by an experiment in which the acetone was added as a solution in liquid ammonia; the results were unaffected. It seems more probable that all the acetone which does not react by addition to the acetylide type ions present is converted by proton transfer into its conjugate anion, $CH_3\cdot C(O^-){:}CH_2$, at a comparable rate in a competing reaction [alternatively, the ammonia-adduct of the enolate ion, $(CH_3)_2C(O^-)\cdot NH_2$,

$$(CH_3)_2CO + RC{\equiv}C^- \begin{array}{l} \xrightleftharpoons[k_2]{k_1} CH_3\cdot C(O^-){=}CH_2 + RC{\equiv}CH \\ \xrightleftharpoons[k_4]{k_3} (CH_3)_2C(O^-)\cdot C{\equiv}CR \end{array} \quad . \; . \; . \quad \text{(i)}$$

$$[R = HC{\equiv}C,\ \ {}^-C{\equiv}C \text{ or } Me_2C(O^-)\cdot C{\equiv}C]$$

might be formed]. This would then slowly regenerate acetone by the reversal of the reaction by which it was formed; of course the relative rates of the various reactions will differ according to the nature of the substituent R.

The results for the reaction with monosodiodiacetylene (see Experimental) suggest that in liquid ammonia, even at —62°, rapid equilibrium is reached in the system:

$$H\cdot C_4^- + Me_2C(O^-)\cdot C_4H \rightleftharpoons H_2C_4 + Me_2C(O^-)\cdot C_4^- \quad . \; . \; . \; . \; . \; . \; . \quad \text{(ii)}$$

with the result that the glycol is formed [by further reaction of $Me_2C(O^-)\cdot C_4^-$ with acetone] along with the alcohol even in a short period at —62°. The glycol then continues to be formed very slowly, now at the expense of the alcohol, the sodium derivative of which presumably disproportionates:

$$Me_2C(O^-)\cdot C{\equiv}C\cdot C{\equiv}CH \xrightleftharpoons[k_4]{k_3} Me_2CO + {}^-C{\equiv}C\cdot C{\equiv}CH \quad . \; . \; . \; . \; . \; . \quad \text{(iii)}$$

The acetone then may condense with $Me_2C(O^-)\cdot C{\equiv}C\cdot C{\equiv}C^-$, present because of equilibrium (ii). Evidence of these reactions was obtained when an attempt was made to prepare (II; $R^1 = CMe_2\cdot OH$, $R^2 = I$) by the action of iodine on the disodium derivative of (I; $R^1 = R^2 = Me$). The only product isolated was the diacetylenic glycol, formed by disproportionation. Similarly attempts to prepare unsymmetrical diacetylenic glycols by condensation of carbonyl compounds with the disodium derivatives of diacetylenic alcohols have given heterogeneous products.

The difficulty of preparing penta-1 : 3-diyne in quantity renders its use in synthetic work inconvenient, and an attempt was therefore made to effect simultaneous alkylation and condensation by treating disodiodiacetylene with a mixture of methyl iodide and a carbonyl compound. In this way hexa-2 : 4-diyn-1-ol and 2-methylhepta-3 : 5-diyn-2-ol (IV; R = H and Me, respectively) were obtained in moderate yields. Other compounds of this type could probably be prepared more easily by two-stage methods *via* the alka-1 : 3-diynes.

$$MeC{\equiv}C\cdot C{\equiv}C\cdot CR_2\cdot OH \quad \text{(IV)}$$

The preparation of a group of 4-alkyl-1-iododiacetylenes by treating the sodio-derivative with iodine (cf. Vaughn and Nieuwland, *J. Amer. Chem. Soc.*, 1933, **55**, 2150) proceeded smoothly. Although good yields of iodo-diacetylenes could also be obtained from an alkyl halide, monosodiodiacetylene, and iodine in equimolecular proportions, spectroscopic examination suggested that these were somewhat heterogeneous, except for the crystalline 1-iodopenta-1 : 3-diyne. One specimen of 1-iodo-octa-1 : 3-diyne prepared in this manner detonated on distillation, the only substance (apart from triacetylene) obtained during the work on polyacetylenes in these laboratories which was responsible for a potentially dangerous explosion.

The iodo-derivative of (I; $R^1 = R^2 = Me$), not obtainable *via* the disodium derivative, was readily prepared by the action of iodine on the Grignard derivative.

EXPERIMENTAL

All manipulations described in the following account were carried out as far as possible at or below room temperature, all distillations were effected in an atmosphere of purified nitrogen, and all monosubstituted diacetylenes were stored at —70° if they had to be kept for an appreciable time.

General Method (*Small Scale*).—To a suspension of sodamide, prepared without mechanical stirring in a small vacuum-flask from liquid ammonia (100 c.c.), sodium (6·9 g.), and ferric nitrate (0·05 g.) by the procedure described by Vaughn, Vogt, and Nieuwland (*J. Amer. Chem. Soc.*, 1934, **56**, 2120), 1 : 4-dichlorobut-2-yne (12·3 g.) was added slowly with shaking. After 1 minute the second reactant was added, the mixture was set aside, and the product was extracted, usually with ether, from the inorganic residue after the ammonia had been allowed to evaporate.

Penta-1 : 3-*diyne* (III; R = Me).—The reaction was carried out in a 3-l. vacuum-flask fitted with stirrer and inlet tube. To a suspension of sodamide, prepared from liquid ammonia (2 l.), sodium (82·8 g.), and ferric nitrate (0·5 g.), 1 : 4-dichlorobut-2-yne (147·6 g.) was slowly added. After 5 minutes methyl iodide (170·4 g.) was added, and the mixture was stirred for 3 hours. Most of the ammonia was then allowed to evaporate, butane (600 c.c.) was added with stirring, and the butane extracts were poured off and combined. Removal of the butane through a lagged 50-cm. Fenske column, fitted with a solid carbon dioxide–carbon tetrachloride condenser for partial reflux, left a brown liquid which was fractionated to give penta-1 : 3-diyne (19 g., 25%), b. p. 76·5°/742 mm., $n_{\rm D}^{15}$ 1·4790 (Found : C, 93·5; H, 6·5. Calc. for C_5H_4 : C, 93·7; H, 6·3%) (Schlubach and Wolf, *Annalen*, 1950, **568**, 141, give b. p. 76—77°, $n_{\rm D}^{20}$ 1·4717).

Hexa-1 : 3-*diyne* (III; R = Et).—The reaction was carried out in a 2-l. vacuum-flask fitted with a stirrer. To a suspension of sodamide, prepared from liquid ammonia (800 c.c.), sodium (23·0 g.), and ferric nitrate (0·2 g.), 1 : 4-dichlorobut-2-yne (41·0 g.) was slowly added. After 5 minutes ethyl iodide (52·0 g.) was added, and the solution was stirred for 3 hours. After ether (100 c.c.) had been added, the ammonia was allowed to evaporate overnight and the product was extracted with ether (5 × 100 c.c.). The combined ether extracts were distilled through a 30-cm. Fenske column, and the residue fractionated to give *hexa*-1 : 3-*diyne* (11·5 g., 45%), b. p. 59°/200 mm., $n_{\rm D}^{16.5}$ 1·4772 (Found : C, 92·3; H, 7·9. C_6H_6 requires C, 92·3; H, 7·7%).

Hydrogenation. Hexa-1 : 3-diyne (0·307 g.) was dissolved in ethyl acetate (50 c.c.), platinic oxide (Adams) catalyst (10 mg.) added, and the suspension shaken with hydrogen. The hydrogen uptake was 380 c.c. at 758 mm./18°, corresponding to 4·0 mol.

Octa-1 : 3-*diyne* (III; R = Bu^n).—As prepared by the general method from sodium (3·4 g.), 1 : 4-dichlorobut-2-yne (6·1 g.), and butyl bromide (6·9 g.) in liquid ammonia (100 c.c.) with a reaction period of 3 hours, this hydrocarbon (2·5 g., 47%) had b. p. 49°/47 mm., $n_{\rm D}^{19}$ 1·4755 (Found : C, 90·5; H, 9·4. C_8H_{10} requires C, 90·5; H, 9·5%).

Penta-2 : 4-*diyn*-1-*ol* (I; $R^1 = R^2 = H$).—This very unstable alcohol was prepared by the general method from paraformaldehyde (6·0 g.) in ether (100 c.c.), a reaction period of 2 hours being used. Distillation of the crude product gave a liquid (6·0 g.), b. p. 33°/0·1 mm., $n_{\rm D}^{26}$ 1·5230, which solidified on storage; the *alcohol* was crystallised from pentane giving needles, m. p. 26—28° (Found : C, 74·5; H, 5·2. C_5H_4O requires C, 75·0; H, 5·0%).

Hexa-3 : 5-*diyn*-2-*ol* (I; $R^1 = H$, $R^2 = Me$).—Prepared by the general method from acetaldehyde (4·4 g.) in ether (50 c.c.), a reaction period of 2 hours being used, this *alcohol* (4·3 g., 46%) had b. p. 70°/11 mm., $n_{\rm D}^{17}$ 1·5050 (Found : C, 76·6; H, 6·9. C_6H_6O requires C, 76·6; H, 6·4%). Though more stable than its lower homologue, it became deep red within 5 minutes at room temperature. No crystalline 3 : 5-dinitrobenzoate could be obtained.

Octa-5 : 7-*diyn*-4-*ol* (I; $R^1 = H$, $R^2 = Pr$).—Application of the general method to butaldehyde (7·2 g.) in ether (50 c.c.), with a reaction period of 18 hours, gave after distillation *octa*-5 : 7-*diyn*-4-*ol* (4·3 g.), b. p. 45°/0·1 mm., $n_{\rm D}^{20}$ 1·4968 (Found : C, 78·4; H, 8·5. $C_8H_{10}O$ requires C, 78·6; H, 8·3%). This alcohol gave a crystalline 3 : 5-dinitrobenzoate, but a constant melting point and satisfactory analytical data could not be obtained because of rapid decomposition.

2-*Methylhexa*-3 : 5-*diyn*-2-*ol* (I; $R^1 = R^2 = Me$).—Two experiments, typical of those tabulated on p. 1997, are described. During the course of this work the procedure was improved in minor respects, and the results are not quite equally reliable.

(*a*) Sodamide was prepared from sodium (9·2 g.) in liquid ammonia (100 c.c.) with efficient mechanical stirring at −33°. The temperature was adjusted to −62° by direct addition of liquid nitrogen to the reaction mixture, while 1 : 4-dichlorobut-2-yne (12·3 g.) was slowly added. Acetone (11·6 g.) was added all at once, and after 6 seconds a solution of ammonium nitrate (15 g.) in liquid ammonia (50 c.c.), previously cooled to −62°, was quickly added. Isolation of the product gave a red oil which was distilled to give 2-methylhexa-3 : 5-diyn-2-ol (7·0 g., 65%), b. p. 39·5°/0·5 mm., $n_{\rm D}^{19}$ 1·4938, m. p. 8—9° (Found : C, 77·9; H, 7·5. Calc. for C_7H_8O : C, 77·7; H, 7·4%). The non-volatile residue was crystallised from water giving 2 : 7-dimethylocta-3 : 5-diyne-2 : 7-diol (3·0 g., 18%) as needles, m. p. 133°.

Reaction between sodium derivatives of diacetylene and acetone.

Reactant (1 mol.)	Acetone, mols.	Temp., ° c.	Time, sec.	Alcohol, mols.	Glycol, mols.
C_4^{--}	2·00	−62	6	0·65	0·18
,,	2·00	−62	30	0·60	0·19
,,	2·00	−62	90	0·57	0·27
,,	2·00	−62	180	0·60	0·30
,,	2·00	−62	360	0·51	0·35
,,	2·00	−62	360	0·54	0·35
,,	2·00	−62	420	0·15	0·56
,,	2·00	−62	480	0·15	0·72
,,	2·00	−62	540	0·17	0·64
,,	2·00	−62	600	0·15	0·72
,,	2·00	−62	600	0·20	0·68
,,	2·00	−62	3,600	0	0·88
,,	2·00	−62	7,200	0	0·88
,,	2·00	−33	60	0·22	0·88
,,	2·00	−33	300	0·10	0·88
,,	2·00	−33	1,800	0	0·90
,,	2·00	−33	3,600	0	0·94
,,	1·00	−62	60	0·32	0·05
,,	1·00	−62	60	0·32	0·06
,,	1·00	−62	300	0·35	0·31
C_4H^-	1·00	−62	60	0·27	0·06
,,	1·00	−62	200	0·42	0·21
,,	1·00	−33	60	0·52	0·17
,,	1·00	−33	600	0·46	0·22
,,	1·00	−33	3,600	0·46	0·21
,,	1·00	−33	10,800	0·26	0·31
,,	1·00	−33	66,000	0·05	0·415

(*b*) Sodamide was prepared from sodium (6·9 g.) in liquid ammonia (100 c.c.) at −33° with efficient mechanical stirring. 1 : 4-Dichlorobut-2-yne (12·3 g.) was added slowly and then, after 5 minutes, acetone (5·8 g.). After 1 minute ammonium chloride (10 g.) was added quickly and the ammonia allowed to evaporate. Isolation of the product gave a red oil which was distilled to give the alcohol (5·6 g., 52%), b. p. 45°/0·8 mm., n_D^{20} 1·4940. The residue was crystallised from water, giving the glycol (2·8 g., 34%), m. p. 133° (Zalkind and Aizikovich, *loc. cit.*, give b. p. 59—61°/7 mm., n_D^{20} 1·4859, for the alcohol).

1 : 1-*Diphenylpenta*-2 : 4-*diyn*-1-*ol* (I; $R^1 = R^2 = Ph$).—Application of the general method to benzophenone (18·2 g.) in ether (50 c.c.) with a reaction period of 30 minutes gave, after chromatographic separation, the *alcohol* (3·0 g.) which crystallised from light petroleum (b. p. 40—60°) as rhombs, m. p. 55—56° (Found : C, 88·3; H, 5·4. $C_{17}H_{12}O$ requires C, 87·9; H, 5·2%).

1-*Iodopenta*-1 : 3-*diyne* (II; $R^1 = Me$, $R^2 = I$).—To a suspension of sodamide, prepared from liquid ammonia (100 c.c.), sodium (6·9 g.), and ferric nitrate (0·05 g.), 1 : 4-dichlorobut-2-yne (12·3 g.) was added dropwise with shaking. After 5 minutes methyl iodide (14·2 g.) was added, then, after a further 3 hours, iodine (25·4 g.), and the reactants were set aside for 3 hours. The ammonia was allowed to evaporate under ether, and the product extracted with ether (3 × 50 c.c.). The combined extracts were washed with saturated sodium thiosulphate solution and water, and evaporated under reduced pressure to give a pale brown solid (14·0 g.). This was sublimed at 50° (bath temp.)/10^{-5} mm. to give 1-*iodopenta*-1 : 3-*diyne* (12·0 g., 63%), m. p. 34—35° unchanged after crystallisation from pentane (Found : C, 31·6; H, 2·0. C_5H_3I requires C, 31·6; H, 1·6%).

1-*Iodohexa*-1 : 3-*diyne* (II; $R^1 = Et$, $R^2 = I$).—To a suspension of sodamide, prepared from liquid ammonia (100 c.c.), sodium (1·3 g.), and ferric nitrate (0·05 g.), hexa-1 : 3-diyne (4·5 g.) was added with shaking. After 5 minutes iodine (14·0 g.) was added; 3 hours later the ammonia was allowed to evaporate under ether, and the product was isolated with ether (3 × 50 c.c.). Removal of the ether under reduced pressure and distillation gave 1-*iodohexa*-1 : 3-*diyne* (9·0 g., 76%), b. p. 30°/0·01 mm., n_D^{20} 1·6158 (Found : C, 35·1; H, 2·7. C_6H_5I requires C, 35·3; H, 2·5%).

1-*Iodo-octa*-1 : 3-*diyne* (II; $R^1 = Bu^n$, $R^2 = I$).—Treatment of the sodio-derivative of octa-1 : 3-diyne (5·3 g.) with iodine (12·7 g.) as described for the lower homologue gave, after isolation, the *iodo*-compound (9·6 g., 74%), b. p. 74°/10^{-3} mm., n_D^{16} 1·5878 (Found : C, 41·2; H, 4·0. C_8H_9I requires C, 41·4; H, 3·9%).

6-*Iodo*-2-*methylhexa*-3 : 5-*diyn*-2-*ol*.—To a solution of ethylmagnesium bromide, prepared from magnesium (0·67 g.) in dry ether (30 c.c.), 2-methylhexa-3 : 5-diyn-2-ol (2·7 g.) was added and the solution refluxed for 1 hour under nitrogen. A solution of iodine (3·1 g.) in dry ether (25 c.c.) was added and the reaction mixture was refluxed for a further 1½ hours. The solution was cooled and poured on ice, and the product isolated with ether. Distillation gave the *iodo-alcohol* (1·0 g., 34%) as a pale yellow, viscous liquid, b. p. 50°/10^{-5} mm., n_D^{20} 1·6095, which solidified when kept and was crystallised from pentane, giving needles, m. p. 53—54° (Found : C, 35·6; H, 3·2. C_7H_7OI requires C, 35·9; H, 3·0%).

Hexa-2 : 4-*diyn*-1-*ol* (II; R^1 = Me, R^2 = $CH_2{\cdot}OH$).—To a suspension of sodamide, prepared from liquid ammonia (100 c.c.), sodium (9·2 g.), and ferric nitrate (0·1 g.) in a small vacuum-flask, 1 : 4-dichlorobut-2-yne (12·3 g.) was added slowly with shaking. After 1 minute a mixture of dried paraformaldehyde (3·0 g.) and methyl iodide (14·2 g.) was added and the mixture was set aside for 18 hours before ammonium chloride (12 g.) was added. Isolation of the crude product and distillation gave the alcohol as a pale yellow, viscous liquid, b. p. 55°/0·1 mm., which solidified completely when kept and then had m. p. 36—38°. *Hexa*-2 : 4-*diyn*-1-*ol* (1·5 g.; 11%) crystallised from light petroleum (b. p. 40—60°) as laths, m. p. 42—43°, which became salmon-pink when kept in light for 1 minute (Found : C, 76·4; H, 6·4. C_6H_6O requires C, 76·6; H, 6·4%).

2-*Methylhepta*-3 : 5-*diyn*-2-*ol*.—(*a*) To a suspension of sodamide, prepared from liquid ammonia (100 c.c.), sodium (4·6 g.), and ferric nitrate (0·05 g.) in a vacuum-flask, 1 : 4-dichlorobut-2-yne (6·1 g.) was added slowly with shaking After 1 minute a mixture of acetone (2·9 g.) and methyl iodide (7·1 g.) was added, and the mixture was set aside for 3 hours before ammonium chloride (12 g.) was added. Isolation of the crude product and distillation gave the alcohol (2·5 g., 40%), b. p. 84—94°/11 mm. It solidified on storage; 2-*methylhepta*-3 : 5-*diyn*-2-*ol* separated from light petroleum (b. p. 40—60°) as needles (2·0 g., 33%), m. p. 42—43° (Found : C, 78·1; H, 8·0. $C_8H_{10}O$ requires C, 78·6; H, 8·2%). This compound was quite stable in light even at room temperature.

(*b*) To a suspension of sodamide, prepared from liquid ammonia (100 c.c.), sodium (1·2 g.), and ferric nitrate (0·05 g.), penta-1 : 3-diyne (3·2 g.) was added with stirring After 5 minutes acetone (2·9 g.) was added; then after a further hour ammonium chloride (5 g.) was added, and the product isolated in the usual way. Distillation gave the alcohol (3·0 g.), b. p. 80°/11 mm., which was crystallised from light petroleum (b. p. 40—60°), giving needles (2·0 g., 33%), m. p. 43°.

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