305. *Researches on Acetylenic Compounds. Part XX. Some Reactions of the Acetylenic–Ethylenic Aldehyde, 3-Methylpent-2-en-4-yn-1-al.*

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The preparation of the methylpentenynal (I) has been improved and a general survey of its reactions has been made. These included addition of ammonia and amines, conversion into the acetal, and partial hydrogenation of the latter to the diene-acetal, and oxidation and condensation reactions of the aldehyde group. The preparation of methyl 2 : 2-dichlorovinyl ketone and certain of its Grignard reactions are also described.

In Part VI of this series (Jones and Weedon, *J.*, 1946, 937) the preparation and rearrangement of carbinols derived from methyl 2-chlorovinyl ketone were described, 3-methylpent-2-en-4-yn-1-al (I) being obtained by the action of dilute acids on the carbinol resulting from the condensation of acetylene itself with the ketone. This aldehyde represents a novel type of acetylenic compound, and its ready availability and interesting multi-functionality suggested that a survey of its reactions would be desirable.

Repetition of the earlier work resulted in improvements in the preparation both of the carbinol and of the aldehyde; in the latter case yields of up to 90% were obtained by prolonging the acid isomerisation treatment.

Many examples of the β-addition of amines to the acetylenic bond in αβ-acetylenic carbonyl compounds are now known (cf. Bowden, Braude, Jones, and Weedon, *J.*, 1946, 45). Methylpentenynal reacted readily with diethylamine in ethereal solution, giving an *adduct* (II), m. p. 57·5—58°, in 40% yield. As was expected from an analogous reaction with a similarly constituted ketone (Bowden *et al.*, *loc. cit.*), the amine addition occurred at the acetylenic linkage, light-absorption data (see below) providing conclusive evidence of the extended conjugated

(II)	$\lambda_{max.}$, A. ……	2360	2580 *	3,970
	$\varepsilon_{max.}$ ……	5000	4000	59,500

* Inflexion.

(III)[1]	$\lambda_{max.}$, A. …	2270	2420	3,780
	$\varepsilon_{max.}$ …	3500	3000	46,500

[1] Bowden, *et al.*, *loc. cit.*

system ($N{\cdot}[C{:}C]_2{\cdot}C{=}O$ chromophore). The considerable water solubility of the adduct and also its feeble basic and aldehydic properties suggest that the dipolar resonance form ($Et_2\overset{+}{N}{=}CH{\cdot}CH{=}CMe{\cdot}CH{=}CH{\cdot}O^-$) contributes very largely towards the resonance hybrid.

$HC{\equiv}C{\cdot}CMe{:}CH{\cdot}CHO$ (I.) $Et_2N{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3$ (III.)

$Et_2N{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CHO$ (II.) $[p\text{-}C_6H_4Me{\cdot}NH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}N{\cdot}C_6H_4Me\text{-}p],HCl$ (IV.)

In its reactions with primary amines, methylpentenynal (I) behaves strictly as a vinylogue (Fuson, *Chem. Reviews*, 1935, **16**, 1) of propargyl aldehyde (cf. Claisen, *Ber.*, 1903, **36**, 3665). In the reaction between the latter aldehyde or its acetal and aniline, Claisen recorded the formation of a monoadduct which he formulated as $HC{\equiv}C{\cdot}CH(OH){\cdot}NHPh$ but which is probably more correctly represented as the anilino-aldehyde, $NHPh{\cdot}CH{=}CH{\cdot}CHO$. On treatment with aniline hydrochloride, or by treatment of the parent aldehyde with two molecular proportions of the hydrochloride, the hydrochloride of the Schiff's base, $[NHPh{\cdot}CH{:}CH{\cdot}CH{:}NPh],HCl$, is produced (cf. for analogous reactions, Reitzenstein and Schwerdt, *J. pr. Chem.*, 1907, **75**, 412; Reitzenstein and Bönitsch, *ibid.*, 1912, **86**, 1; Viguier, *Ann. Chim.*, 1913, **28**, 433; Dieterle and Riester, *Chem. Zentr.*, 1937, I, 3910; 1937, II, 714). With aniline, methylpentenynal gave a yellow monoadduct, m. p. 60—63° (presumably $NHPh{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CHO$), and this with aniline hydrochloride gave the dark violet hydrochloride of an anilino-anil ($[NHPh{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}NPh],HCl$), m. p. 153°. The former of these two compounds was too unstable and the latter too insoluble and unstable to permit of further purification. With *p*-toluidine hydrochloride, however, a more amenable deep violet *hydrochloride* (IV), m. p. 145°, was obtained and an analogous compound was formed with *p*-aminobenzoic acid. In similar reactions with appropriate heterocyclic nitrogen compounds methylpentenynal yields cyanine-type dyes (Jones and Read, B.P. 616,223).

Treatment with anhydrous ammonia in ether left the aldehyde essentially unchanged, but with alcoholic solutions of aqueous ammonia or ammonium carbonate, (I) gave γ-picoline in 10—15% yields, presumably by internal condensation of the mono-adduct ($NH_2{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CHO$).

In order to render possible a study of the replacement reactions of the acetylenic hydrogen atom, the preparation of the *acetal* (V) of methylpentenynal was investigated. By using ethyl

(V.) $HC{\equiv}C{\cdot}CMe{=}CH{\cdot}CH(OEt)_2 \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CMe{=}CH{\cdot}CH(OEt)_2$ (VI.)

$H_2C{=}CH{\cdot}CMe{=}CH{\cdot}CH(OEt)_2$ (VII.)

orthoformate and ammonium nitrate in alcohol, a procedure successfully employed by Fischer and Baer (*Helv. Chim. Acta*, 1935, **18**, 514) to obtain acraldehyde acetal, the acetal was produced in 55% yield. It gave copper and silver derivatives, showed light-absorption properties typical of those of a conjugated en-yne and yielded the derivative of the parent aldehyde on treatment with acid and 2 : 4-dinitrophenylhydrazine.

The ethynyl hydrogen atom of propargyl acetal can be replaced in Grignard reactions (cf. Grard, *Ann. Chim.*, 1930, **13**, 343; Heilbron, Jones, and Koch, *J.*, 1942, 735) and the acetal (V) behaved similarly. With butaldehyde the hydroxy-acetal (VI) was obtained although it could not be distilled without undergoing some decomposition; on treatment with semicarbazide hydrochloride in aqueous methanol, however, the *semicarbazone* of the corresponding hydroxy-aldehyde was formed in good yield.

Semihydrogenation of (V) in the presence of a partially poisoned palladium catalyst yielded the *acetal* of 3-*methylpenta*-2 : 4-*dien*-1-*al* (VII), showing the expected light-absorption properties, and giving the *semicarbazone* and the 2 : 4-*dinitrophenylhydrazone* of the aldehyde on treatment with the appropriate reagent in acid media. As a possible alternative route to the diene-aldehyde the preparation and rearrangement of the vinyl-carbinol (VIII) have been studied; the results of this investigation, as yet incomplete, will be reported later.

(VIII.) $H_2C{:}CH{\cdot}CMe(OH){\cdot}CH{:}CHCl$ $HC{\equiv}C{\cdot}CMe{=}CH{\cdot}CH{=}CH{\cdot}COR$ (IX.)

Oxidation of the aldehyde with chromic acid in aqueous acetone solution gave the corresponding *acid* (XI; R = H) but, rather unexpectedly, the yield and conversion were much less satisfactory than in the case of the oxidation of pent-2-en-4-yn-1-ol to an analogous acid (Heilbron, Jones, and Sondheimer, *J.*, 1947, 1586). Other standard methods of aldehyde → acid conversion were even less successful. The aldehyde can be condensed with ketones in the presence of sodium hydroxide, and with acetophenone and acetone the *ketones* (IX; R = Ph and Me, respectively) were obtained, the former as a crystalline solid, m. p. 86—88°.

As an alternative route to acids of the type (XI), the possibility of effecting conversion of dichlorovinyl carbinols (X) into such acids was explored. *Methyl* 2 : 2-*dichlorovinyl ketone* was readily prepared by condensation of acetyl chloride with vinylidene chloride (cf. Catch, Elliott, Hey, and Jones, *J.*, 1948, 278). Unfortunately, on attempted condensation with sodium acetylide in liquid ammonia, none of the expected carbinol (X; R = H) could be obtained.

$$\text{(X.)}\quad R{\cdot}C{\equiv}C{\cdot}CMe(OH){\cdot}CH{=}CCl_2 \qquad\qquad R{\cdot}C{\equiv}C{\cdot}CMe{=}CH{\cdot}CO_2H\quad \text{(XI.)}$$

Hexynylmagnesium bromide, however, yielded the *carbinol* (X; R = Bu^n); with acetylenedimagnesium bromide a small yield of the *glycol*, m. p. 98°, was obtained, and methylmagnesium bromide gave the *carbinol*, $CMe_2(OH){\cdot}CH{:}CCl_2$. Using conditions (cf. Jones and Weedon, *loc. cit.*) under which chlorovinyl-carbinols were converted smoothly into aldehydes, none of the above dichlorovinyl compounds could be converted into acids or acid derivatives. These results were not entirely unexpected, as the effect of the additional chlorine substituent would be to reduce still further the electron availability at the reacting centre, *i.e.*, the hydroxyl group (cf. Braude and Jones, *J.*, 1946, 122, 128). They are also in line with the observations of Kirrmann *et al.* (*Bull. Soc. chim.*, 1940, [v], **7**, 586; 1948, [v], **15**, 168) that in the systems, $CH_2{:}CR{\cdot}CCl_3 \rightleftarrows CH_2Cl{\cdot}CR{:}CCl_2$, the equilibria lie almost entirely on the side of the dichlorovinyl compounds.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions, except where stated otherwise).

1-*Chloro*-3-*methylpent*-1-*en*-4-*yn*-3-*ol* (cf. Jones and Weedon, *loc. cit.*).—The rate of addition of the methyl chlorovinyl ketone to the liquid ammonia solution of sodium acetylide has much influence on the yield. By adding the ethereal solution of the ketone very slowly (200 g. during at least 6 hours) and employing an acetylide : ketone ratio of 2·7 : 1, yields of up to 55% have been obtained in fairly large-scale experiments. In the presence of a little quinol and in an atmosphere of nitrogen the carbinol can be kept at 0° without appreciable alteration for several months.

3-*Methylpent*-2-*en*-4-*yn*-1-*al* (I) (cf. Jones and Weedon, *loc. cit.*).—1-Chloro-3-methylpent-1-en-4-yn-3-ol (30 g.) was added to 2N-sulphuric acid (2500 c.c.). A trace of quinol was added, the air displaced by nitrogen, and the mixture kept in the dark at room temperature (about 15°). After about one day the carbinol dissolved; after two days an oil began to separate and the liquid, originally very pale yellow, turned orange. After four days the solution was saturated with ammonium sulphate and extracted three times with ether. In some experiments, when the room temperature was 25°, the rearrangement was completed after two days. After addition of a trace of quinol, the ethereal solution was dried and evaporated, and the residue fractionated in nitrogen, giving the aldehyde as a very pale yellow liquid (19 g.; 90%), b. p. 45°/12 mm.; $n_D^{21°}$ 1·5018 (Jones and Weedon, *loc. cit.*, give b. p. 53—54°/20 mm.; $n_D^{23°}$ 1·4993).

5-*Diethylamino*-3-*methylpenta*-2 : 4-*dien*-1-*al* (II).—A solution of diethylamine (1·5 g.) in ether (10 c.c.) was slowly added to a solution of methylpentenynal (1·9 g.) in ether (10 c.c.) with ice cooling in an atmosphere of nitrogen. The mixture was kept for 2 hours at room temperature and 12 hours at 0° in the dark. The solution, separated from a little dark oil that had been deposited, was dried and evaporated. Distillation of the residue gave (i) dark red oil (0·5 g.), b. p. 105—110°/0·05 mm., and (ii) red oil (0·8 g.), b. p. 110—111°/0·05 mm. Fraction (ii) crystallised on cooling, and (i) crystallised after seeding. Recrystallisation of the combined material from ether–light petroleum (b. p. 40—60°) in the cold in nitrogen gave the *diethylamino-aldehyde* as golden-yellow leaflets, m. p. 57·5—58° (Found : C, 71·45; H, 9·55; N, 8·25. $C_{10}H_{17}ON$ requires C, 71·8; H, 10·25; N, 8·35%).

Hydrochloride of 1-p-*Toluidino*-5-p-*tolylimino*-3-*methylpenta*-1 : 3-*diene* (IV).—A solution of methylpentenynal (1 g.) in methanol (5 c.c.) was added slowly to *p*-toluidine (2·2 g.) in methanol (10 c.c.) and 2N-hydrochloric acid (10 c.c.), under nitrogen, the temperature being kept below 20°. The mixture turned deep violet and on standing for 3 hours at 0° crystals were deposited which after recrystallisation from methanol gave the *hydrochloride* (1·2 g.) as fine deep violet needles, m. p. 145° (Found : C, 73·5; H, 7·3; N, 8·75. $C_{20}H_{23}N_2Cl$ requires C, 73·5; H, 7·1; N, 8·55%). Light absorption : Maximum, 5250 A.; ε = 41,000.

Hydrochloride of 1-p-*Carboxyanilino*-5-p-*carboxyanilo*-3-*methylpenta*-1 : 3-*diene*.—A solution of methylpentenynal (5 g.) in methanol (10 c.c.) was slowly added to a solution of *p*-aminobenzoic acid (15 g.), methanol (40 c.c.), and 2N-hydrochloric acid (25 c.c.) under nitrogen, the temperature being kept below 20°. The mixture turned deep violet and a solid separated which was only partly soluble in boiling methanol. On cooling the solution, crystals (0·7 g.) were deposited which on recrystallisation from methanol gave the *hydrochloride* as reddish-violet prisms, m. p. indefinite, decomposition above 180—200° (Found : N, 6·8. $C_{20}H_{19}O_4N_2Cl$ requires N, 7·25%). Light absorption : Maxima, 2280, 4300, and 5250 A.; ε = 22,500, 7000, and 9500, respectively. The deep red alcoholic solution of the compound lost its colour after a few hours at room temperature, which explains the low intensity of the long-wave maximum.

γ-Picoline from Methylpentenynal.—(*a*) Methylpentenynal (1 g.) was added to concentrated aqueous ammonia (50 c.c.) and the mixture was made homogeneous by addition of alcohol. After 12 hours, water (100 c.c.) was added and the product was isolated with ether. Distillation at 100 mm. gave an oil (0·1 g.) which yielded γ-picoline picrate, m. p. 167°, undepressed on admixture with an authentic specimen.

(*b*) (Cf. Bowden and Jones, *J.*, 1946, 953.)—Ammonium carbonate (1 g.) was dissolved in the minimum amount of water, and alcohol (3 c.c.) was added; this solution was added to a solution of methylpentenynal (1 g.) in alcohol (3 c.c.) and the mixture was heated under reflux for ½ hour. Isolation with ether and distillation at 100 mm. gave an oil (0·15 g.) which yielded a picrate identical with that obtained in (*a*).

Acetal of 3-*Methylpent*-2-*en*-4-*yn*-1-*al* (V).—To a mixture of methylpentenynal (3 g.) and ethyl orthoformate (4 g.) was added a hot solution of ammonium nitrate (0·2 g.) in alcohol (8 c.c.) and the mixture was heated under reflux for 5 minutes. After cooling, ether (20 c.c.) was added and the mixture was shaken repeatedly with dilute aqueous ammonia until no more amorphous material separated. After drying and evaporation, distillation under reduced pressure gave a pale yellow oil (3·6 g.). This was shaken with concentrated aqueous sodium hydrogen sulphite solution, the residual oil was isolated with ether, and distillation gave 1 : 1-*diethoxy*-3-*methylpent*-2-*en*-4-*yne* (2·8 g.), b. p. 77°/12 mm., $n_D^{18^\circ}$ 1·4500 (Found: C, 71·25; H, 9·55. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). Light absorption: Maximum, 2230 A.; ε = 12,000. The acetal gave a white silver salt with ammoniacal silver nitrate. Steam distillation in the presence of 2N-sulphuric acid gave an oil, and thence a 2 : 4-dinitrophenylhydrazone, m. p. 144°, undepressed on admixture with an authentic specimen of methylpentenynal 2 : 4-dinitrophenylhydrazone, m. p. 144—145° (Jones and Weedon, *loc. cit.*), was prepared.

Condensation of the Acetal with Butaldehyde.—Ethylmagnesium bromide (from magnesium, 0·9 g.) was prepared in ether (50 c.c.) and the ether was evaporated and replaced by dry benzene (50 c.c.). This solution was dropped into a solution of 1 : 1-diethoxy-3-methylpent-2-en-4-yne (6 g.) in dry benzene (40 c.c.) in an atmosphere of nitrogen with stirring and ice cooling during 1 hour. After a further 3 hours' stirring at 0°, butaldehyde (3 g.) in dry benzene (30 c.c.) was slowly added and stirring was continued for a further 4 hours at room temperature. The Grignard complex was decomposed with an ice-cold solution of ammonium chloride (20 g.) in water (100 c.c.), the benzene layer separated, and the aqueous layer extracted with benzene. The combined benzene solutions were washed and dried and evaporated under reduced pressure. Fractionation of the residue gave (i) recovered acetal (3 g.), b. p. 80°/0·05 mm., $n_D^{20^\circ}$ 1·4460, and (ii) crude condensation product (3 g.), b. p. 102—104°/0·01 mm., $n_D^{20^\circ}$ 1·4649. The latter could not be fractionated without some decomposition; consequently, a sample (200 mg.) was gently heated with a solution of semicarbazide hydrochloride (150 mg.) in aqueous methanol. Crystals (200 mg.; 80%) separated on cooling, and recrystallisation from alcohol gave the *semicarbazone* of 3-*methylnon*-2-*en*-4-*yn*-6-*ol*-1-*al* as needles, m. p. 197—198° (Found: N, 19·0. $C_{11}H_{17}O_2N_3$ requires N, 18·8%). Light absorption: Maximum, 2940 A.; ε = 31,000; inflexion, 3040 A.; ε = 27,000.

Acetal (VII), *Semicarbazone, and* 2 : 4-*Dinitrophenylhydrazone of* 3-*Methylpenta*-2 : 4-*dien*-1-*al*.—1 : 1-Diethoxy-3-methylpent-2-en-4-yne (9 g.) in methyl acetate (20 c.c.) was shaken in an atmosphere of hydrogen in the presence of a partially poisoned palladium catalyst (1 g.; Isler, Huber, Ronco, and Kofler, *Helv. Chim. Acta*, 1947, **30**, 1911). The hydrogenation was interrupted when the required amount of hydrogen had been absorbed (1280 c.c., corresponding to 1 mol. of hydrogen). The catalyst and solvent were removed and the residue was shaken with concentrated aqueous sodium hydrogen sulphite and extracted with ether. After the ethereal solution had been washed with water, dried, and evaporated, fractionation of the residue gave the *diene acetal* (5·5 g.), b. p. 79—80°/18 mm., $n_D^{23^\circ}$ 1·4550 (Found: C, 69·7; H, 10·6. $C_{10}H_{18}O_2$ requires C, 70·55; H, 10·65%). Light absorption: Maximum, 2230 A.; ε = 20,500; inflexion, 2280 A.; ε = 18,500.

The diene acetal easily gave the 2 : 4-*dinitrophenylhydrazone*, which separated from ethyl acetate–methanol as deep purple needles, m. p. 131—132° (Found: N, 19·9. $C_{12}H_{12}O_4N_4$ requires N, 20·3%). Light absorption in chloroform: Maxima, 2600, 3029, and 3900 A.; ε = 12,500, 10,000, and 30,000, respectively. On treatment of the acetal with semicarbazide hydrochloride in aqueous methanol, the *semicarbazone* was obtained as needles from ethyl acetate, m. p. 166—167° (Found: N, 27·5. $C_7H_{11}ON_3$ requires N, 27·45%). Light absorption: Maximum, 2940 A.; ε = 38,000.

2-*Methylbut*-1-*en*-3-*yne*-1-*carboxylic Acid* (XI; R = H).—A solution of chromium trioxide (5 g.) and concentrated sulphuric acid (8 g.) in water (20 c.c.) was added during an hour to a stirred solution of methylpentenynal (6 g.) in acetone (45 c.c.) in an atmosphere of nitrogen, the temperature being kept below 25°. The mixture was allowed to stand with occasional stirring for 2 hours; it was then diluted with water, saturated with potassium chloride, and thoroughly extracted with ether. The combined ethereal extracts were shaken four times with 2N-sodium hydrogen carbonate solution (90 c.c. in all), the extracts were acidified with 2N-sulphuric acid (100 c.c.) and saturated with potassium chloride, and the acidic material was isolated by thorough extraction with ether. Evaporation gave an orange-yellow oil (1·0 g.) which crystallised partially on trituration with light petroleum (b. p. 60—80°). Recrystallisation from this solvent (charcoal) gave 2-*methylbut*-1-*en*-3-*yne*-1-*carboxylic acid* (200 mg.) as flat needles, m. p. 107·5—109° (Found: C, 65·2; H, 5·5. $C_6H_6O_2$ requires C, 65·45; H, 5·5%). Light absorption: Maximum, 2480 A.; ε = 16,000. Some 3·2 g. of aldehyde were recovered from the neutral portion of the product.

1-*Benzoyl*-4-*methylhexa*-1 : 3-*dien*-5-*yne* (IX; R = Ph).—Methylpentenynal (0·5 g.) and acetophenone (0·6 g.) were mixed under nitrogen at room temperature and sodium hydroxide (0·2 g.), dissolved in water (2 c.c.) and alcohol (1 c.c.), was added, the temperature being kept below 20° by external cooling. The mixture became very dark and after 15 minutes an excess (3 c.c.) of 2N-sulphuric acid was added. A dark red oil separated which crystallised partly when kept overnight at 0°. The crystals (200 mg.) m. p. 82—85°, were freed from oil on a porous plate and several recrystallisations from aqueous methanol gave the *ketone* as dark yellow flat needles, m. p. 86—88° (Found: C, 85·5; H, 6·05. $C_{14}H_{12}O$ requires C, 85·7; H, 6·15%). Light absorption in methanol: Maxima, 2280 and 3240 A.; ε = 10,000 and 32,000, respectively.

6-*Methylocta*-3 : 5-*dien*-7-*yn*-2-*one* (1-*Acetyl*-4-*methylhexa*-1 : 3-*dien*-5-*yne*) (IX; R = Me).—Methylpentenynal (3 g.) was dissolved in acetone (6 c.c.) and the solution was cooled in ice in an atmosphere of nitrogen. Sodium hydroxide (0·8 g.), dissolved in water (3 c.c.) and alcohol (3 c.c.), was added; the solution darkened considerably and after ½ hour acidification with 2N-sulphuric acid precipitated a dark red oil which was taken up in ether. The ethereal solution was washed and dried, and after evaporation at room temperature under reduced pressure, the residue was distilled, giving the *ketone* (1·5 g.; 30%)

as a very pale yellow oil, b. p. 44—46°/10^{-3} mm., $n_{\mathrm{D}}^{18^\circ}$ 1·5630. This oil solidified on keeping at 0° and melted a little above room temperature (Found: C, 80·2; H, 7·45. $C_9H_{10}O$ requires C, 80·55; H, 7·5%). Light absorption: Maximum, 2390 A.; ε = 12,500. At the end of the distillation, the residue sometimes exploded if heated above *ca.* 75°. The *semicarbazone* separated from alcohol as very pale yellow needles. It decomposed above about 185° without melting sharply (Found: N, 21·95. $C_{10}H_{13}ON_3$ requires N, 22·0%). Light absorption: Maxima, 3110 and 3260 A.; ε = 51,500 and 45,000, respectively.

6-*Methyloctan*-2-*one*.—A solution of the above ketone (0·85 g.) in alcohol (50 c.c.) was shaken in an atmosphere of hydrogen in presence of platinic oxide catalyst (20 mg.), 610 c.c. of hydrogen being absorbed in a little more than ½ hour (theoretical amount: 565 c.c.). The catalyst was filtered off, and the solvent removed under reduced pressure: the remaining oil was distilled, giving 6-*methyloctan*-2-*one* (0·6 g.) as a pleasant-smelling liquid, b. p. 70°/10 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4250 (Found: C, 76·25; H, 13·05. $C_9H_{18}O$ requires C, 76·0; H, 12·75%). The *semicarbazone* formed leaflets from aqueous alcohol, m. p. 131° (Found: N, 20·9. $C_{10}H_{21}ON_3$ requires N, 21·1%).

Methyl 2 : 2-*Dichlorovinyl Ketone*.—Acetyl chloride (50 g.) was cooled in a freezing mixture and finely powdered aluminium chloride (50 g.) was slowly added with vigorous stirring. The freezing mixture was then replaced by a water-bath at room temperature, and vinylidene chloride (30 g.) was slowly dropped in during 1½ hours. At first the mixture became less viscous but the viscosity subsequently increased considerably. After being stirred for a further ½ hour the reaction mixture was poured on crushed ice (600 g.); a heavy oil separated which soon crystallised in long white needles, melting at about room temperature. This product was taken up in carbon tetrachloride and the aqueous solution was extracted several times with the same solvent. The combined solutions (250 c.c.) were washed twice with water, and then hot water (250 c.c.) was added and steam was passed through. The distilled organic layer was separated and the aqueous phase was extracted twice with carbon tetrachloride.

The combined tetrachloride solutions were washed with water and dried and evaporated (after the addition of traces of quinol and magnesium oxide) under reduced pressure below 30° through a Dufton column (8″). The residual ketone was then rapidly distilled under reduced pressure and subsequent fractionation gave *methyl* 2 : 2-*dichlorovinyl ketone* (32·5 g.; 80%), b. p. 45°/10 mm., 58°/15 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4940 (Found: C, 34·6; H, 2·8. $C_4H_4OCl_2$ requires C, 34·55; H, 2·9%). Light absorption: Maximum, 2390—2420 A.; ε = 12,000. As with methyl chlorovinyl ketone, the immediate fractionation of the crude product was found to be essential. The 2 : 4-*dinitrophenylhydrazone* crystallised from benzene in orange-red prisms, m. p. 195° (Found: N, 17·2. $C_{10}H_8O_4N_4Cl_2$ requires N, 17·55%). Light absorption in chloroform: Maximum, 3740 A.; ε = 30,000.

1 : 1-*Dichloro*-3-*methylnon*-1-*en*-4-*yn*-3-*ol*.—Ethylmagnesium bromide was prepared from magnesium (2·1 g.) in ether. Hex-1-yne (9 g.), dissolved in dry ether (100 c.c.), was added during 2 hours with ice cooling, and the mixture was then heated under reflux for 3 hours. Methyl 2 : 2-dichlorovinyl ketone (10 g.) in dry ether (100 c.c.) was added slowly with cooling; the Grignard complex separated as a white suspension and the mixture was set aside overnight. The complex was decomposed with an ice-cold solution of ammonium chloride (27 g.) in water (100 c.c.) and the product was isolated in the usual manner. Distillation gave 1 : 1-*dichloro*-3-*methylnon*-1-*en*-4-*yn*-3-*ol* (13·5 g.; 85%), b. p. 90°/0·5 mm., 65°/0·05 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4909 (Found: C, 54·45; H, 6·6. $C_{10}H_{14}OCl_2$ requires C, 54·3; H, 6·4%). The carbinol showed no absorption of appreciable intensity in the range 2200—4000 A.

1 : 1-*Dichloro*-3-*methylbut*-1-*en*-3-*ol*.—Methylmagnesium bromide was prepared from magnesium (1·8 g.) in ether, and methyl 2 : 2-dichlorovinyl ketone (10 g.) in ether (100 c.c.) was dropped in with ice cooling. The mixture was stirred for 4 hours at room temperature and the complex which had separated was decomposed with an ice-cold solution of ammonium chloride (22 g.) in water (100 c.c.). The product was isolated with ether and distillation gave 1 : 1-*dichloro*-3-*methylbut*-1-*en*-3-*ol* (5·8 g.; 55%), b. p. 63°/13 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4814 (Found: C, 37·8; H, 4·9; Cl, 44·35. $C_5H_8OCl_2$ requires C, 38·7; H, 5·2; Cl, 45·7%). The p-*nitrobenzoate* crystallised from alcohol as very pale yellow leaflets, m. p. 97—98° (Found: N, 4·85. $C_{12}H_{11}O_4NCl_2$ requires N, 4·6%).

1 : 1 : 8 : 8-*Tetrachloro*-3 : 6-*dimethylocta*-1 : 7-*dien*-4-*yn*-3 : 6-*diol*.—Ethylmagnesium bromide was prepared from magnesium (2·4 g.) and ethyl bromide (11 g.) in ether (100 c.c.). The ether was then distilled off and at the same time replaced by dry benzene (200 c.c.). Distillation was continued until the temperature of the vapours reached 70°. The reaction flask was then cooled and a fairly rapid stream of acetylene was passed in for 4 hours with ice cooling. Acetylenedimagnesium bromide separated as a white crystalline powder. Methyl 2 : 2-dichlorovinyl ketone (14 g.) in dry benzene (75 c.c.) was then added during ½ hour with cooling. The mixture was stirred at room temperature for a further 3 hours and the Grignard complex was decomposed with an ice-cold solution of ammonium chloride (30 g.) in water (150 c.c.). The product (13 g.) was isolated *via* benzene, the solution being treated with charcoal, and partly crystallised on standing at 0°. The crystals (2 g.; 15%) were washed free from oil with light petroleum (b. p. 40—60°) and crystallisation from light petroleum (b. p. 60—80°) gave the *diol* (1·5 g.) as long fine needles, m. p. 98° (Found: C, 40·0; H, 3·25. $C_{10}H_{10}O_2Cl_4$ requires C, 39·5; H, 3·3%).

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