655. *Studies of Compounds Related to Natural Perfumes. Part III. The Diels–Alder Reaction with Acetylenic Aldehydes. The Synthesis of 4-Methylsafranal.**

By J. C. Lunt and Franz Sondheimer.

2 : 5-Dihydrobenzaldehydes have been prepared by the Diels–Alder reaction between two acetylenic aldehydes (tetrolaldehyde and hept-2-yn-1-al) and butadienes. The dehydrogenation, partial hydrogenation, and isomerisation of the tetrolaldehyde adducts have been investigated. In particular, it is shown that the aldehyde (VI), obtained from tetrolaldehyde and 1 : 1 : 3-trimethylbutadiene, undergoes a smooth rearrangement in the presence of acids to give 4-methylsafranal (X).

The ultra-violet light absorption properties of the adducts are recorded and briefly discussed.

In connexion with the synthesis of analogues of β-*cyclo*citral and β-ionone (Heilbron, Jones, *et al.*, *J.*, 1949, 737, 1827, 2028; Lunt and Sondheimer, previous communication), it became desirable to investigate the Diels–Alder reaction between butadienes and acetylenic aldehydes.

Until recently, the use of acetylenic compounds as dienophiles in the Diels–Alder reaction had been restricted mainly to acetylenic acids and esters (for reviews, see Bowden and Jones, *J.*, 1946, 52; Holmes, " Organic Reactions," John Wiley, New York, 1948, **4**, 60). The employment of αβ-acetylenic ketones in such reactions had been restricted to isolated examples (Allen and Sheps, *Canadian J. Res.*, 1934, **11**, 171; Dupont and Paquot, *Compt. rend.*, 1937, **205**, 805), but was recently more extensively investigated (Bowden and Jones, *loc. cit.*; Braude, Jones, Sondheimer, and Toogood, *J.*, 1949, 607). It was found that αβ-ethynyl ketones (containing the group •CO•C⋮CH) could be condensed with dienes in good yield, while substituted ketones (•CO•C⋮CR) reacted considerably less readily to give rather poor yields of adducts. The only authenticated example of the employment of an αβ-acetylenic aldehyde in a Diels–Alder type reaction is the condensation between 3-phenylprop-2-yn-1-al and the highly reactive tetraphenyl*cyclo*pentadienone (which even reacts with acetylene itself) to give an aromaticized product (Dilthey, Schommer, and Trösken, *Ber.*, 1933, **66**, 1627). In addition, the patent literature (Naef et Cie., F.P. 672,025; *Chem. Zentr.*, 1930, I, 2796) records the reaction both of propargylaldehyde and tetrolaldehyde (Me•C⋮C•CHO) with a number of substituted butadienes to give substituted dihydrobenzaldehydes. Unfortunately, very few details and no yields are given, and from our experience, the reaction conditions (usually *ca.* 150—200° for 1—2 days) would have resulted in the dehydrogenation of the primary adducts to benzenoid derivatives. It may be noted that in the same patent the successful use of 1 : 1-dimethylbutadiene and 1 : 1 : 4 : 4-tetramethylbutadiene in Diels–Alder reactions is reported, a fact which has not since been substantiated.

It has been found that only by careful attention to reaction conditions could 2 : 5-dihydrobenzaldehydes be obtained by the reaction between acetylenic aldehydes and dienes; the temperature range below which only little reaction occurred, and above which considerable aromaticization of the adduct set in, was not large. Even when the expected product was formed, it was usually difficult to obtain it pure by distillation, and significant results were only obtained by careful characterisation through a solid derivative.

The acetals of tetrolaldehyde (I; R = Me) have been prepared both by the dehydrobromination of the acetals of α-bromocrotonaldehyde (Claisen, *Ber.*, 1911, **44**, 1161; Viguier, *Ann. Chim.*, 1913, **28**, 447) and also by the reaction between propynylmagnesium bromide and ethyl orthoformate (Viguier, *loc. cit.*, p. 450). Both these methods have been investigated; modifications in the experimental procedures have been introduced, and the acetylenic acetal can be obtained in yields of 75—80% by either method. Hydrolysis of the acetal to the aldehyde by means of dilute mineral acids results in considerable polymerisation (Claisen, *loc. cit.*), but Viguier (*loc. cit.*, p. 481) found that heating the acetal with aqueous oxalic acid produced the aldehyde in 35% yield. This result could not be substantiated, considerably lower yields of (I; R = Me) being obtained under Viguier's conditions. It was, however, found that by shaking the acetal with cold aqueous tartaric acid, followed by removal of most of the ethanol with calcium chloride solution, a 55% yield (35% conversion) of tetrolaldehyde (2 : 4-dinitrophenylhydrazone) could be obtained. As the hydrolysis of the acetal to the aldehyde presented some difficulty, a direct synthesis of tetrolaldehyde itself was also investigated. Acetylenic aldehydes

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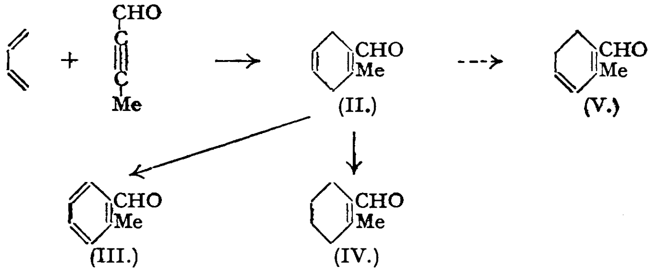
* A preliminary account of part of the work described in this paper was published in *Nature* (1949, **164**, 1051).

have been prepared by condensation of the sodium salt of substituted acetylenes with ethyl formate in ether (Charon and Dugoujon, *Compt. rend.*, 1903, **137**, 126; Moureu and Delange, *Bull. Soc. chim.*, 1902, **27**, 374; 1904, **31**, 1327; Brachin, *ibid.*, 1906, **35**, 1165), although rather poor conversions (11—28%) were obtained with aliphatic acetylenes. We prepared sodiopropyne in ether by reaction of methyl iodide with sodium acetylide in liquid ammonia, adding another mole of sodamide in liquid ammonia (cf. Zoss and Hennion, *J. Amer. Chem. Soc.*, 1941, **63**, 1151; Raphael and Sondheimer, *J.*, 1950, 115; Sondheimer, *J.*, 1950, 877) and displacing the ammonia by ether. However, when this complex reacted with ethyl formate under the usual conditions, no trace of tetrolaldehyde could be detected. This may well have been caused by the low solubility of sodiopropyne in ether (sodium acetylide itself in ether is extremely unreactive owing to its low solubility), for when sodiohex-1-yne in ether reacted with ethyl formate under the same conditions, hept-2-yn-1-al (I; R = Bu^n) (2 : 4-dinitrophenylhydrazone) could be isolated in 24% yield.

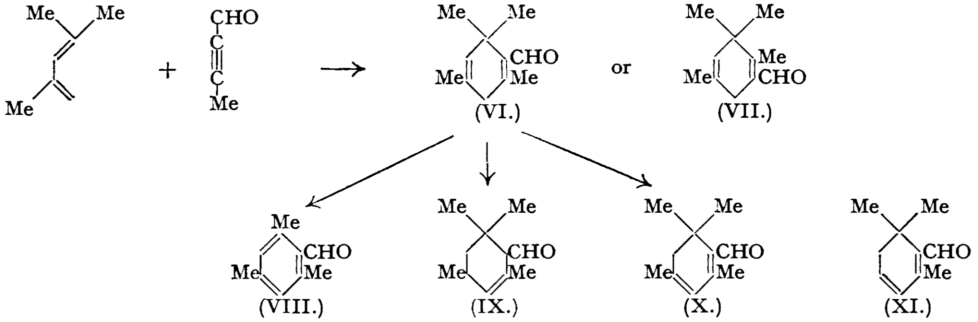
$$\mathrm{R{\cdot}C{\vdots}C{\cdot}Na + H{\cdot}CO_2Et \longrightarrow [R{\cdot}C{\vdots}C{\cdot}CH(ONa){\cdot}OEt] \longrightarrow R{\cdot}C{\vdots}C{\cdot}CHO} \quad \text{(I.)}$$



Tetrolaldehyde was caused to react with butadiene under various conditions, inhomogeneous products being usually obtained. However, by heating the components at 120° for 7 hours, and again bringing the recovered aldehyde into reaction with butadiene, pure 3 : 6-dihydro-*o*-tolualdehyde (II) (2 : 4-dinitrophenylhydrazone; semicarbazone) could be isolated in 31% yield. The structure was confirmed by heating it under reflux, whereupon *o*-tolualdehyde (III) was formed. The methyl ketone corresponding to (II) had already been partially hydrogenated (Braude, Jones, Sondheimer, and Toogood, *loc. cit.*) and, when the aldehyde (II) was allowed to absorb 1 mole of hydrogen in the presence of a palladium–calcium carbonate catalyst, 2-methyl*cyclo*hexenealdehyde (IV) was readily isolated. This aldehyde proved identical with that already prepared by dehydrobromination of the corresponding saturated bromo-aldehyde (Heilbron, Jones, Richardson, and Sondheimer, *J.*, 1949, 737). Several attempts were made to rearrange the isolated double bond in (II) to the conjugated diene aldehyde (V) (or the other possible isomer), under both acidic and basic conditions. This could not be effected, and (II) was either recovered unchanged or (under strongly alkaline conditions) was dehydrogenated to *o*-tolualdehyde (III).

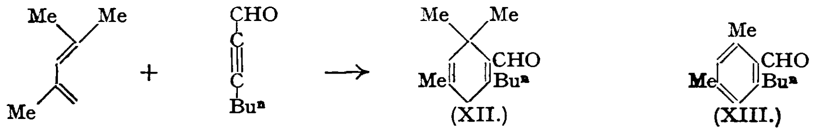
It was thought that the condensation between tetrolaldehyde and 1 : 1 : 3-trimethylbutadiene would be more easily effected than the reaction with butadiene, as the expected adduct could not undergo dehydrogenation, although of course two products, (VI) or (VII), might be formed. However, when this reaction was carried out either at 140° or 160°, an inhomogeneous product was obtained, containing a considerable proportion of 2 : 4 : 6-trimethylbenzaldehyde (VIII) as indicated by the formation of its semicarbazone and 2 : 4-dinitrophenylhydrazone. The aromatic aldehyde must have been formed from (VI) by the loss of methane, and this was supported by the fact that considerable pressure was observed at the end of the reaction. Only by heating the components at 125° for 16 hours could the required reaction be effected. Even under these optimum conditions, and inhomogeneous product was formed, but by converting the crude adduct into the semicarbazone, and regeneration with dilute sulphuric acid, the pure 2 : 2 : 4 : 6-tetramethyl*cyclo*hexa-3 : 6-dienealdehyde (VI) (2 : 4-dinitrophenylhydrazone) could be obtained. It was assigned structure (VI) rather than (VII), for when it was heated under reflux, methane was evolved, and 2 : 4 : 6-trimethylbenzaldehyde (VIII) was again formed.

Partial hydrogenation both of the aldehyde (VI) and of its semicarbazone in the presence of a palladium–calcium carbonate catalyst gave complex mixtures. The product obtained from (VI), after absorption of one mole of hydrogen, had maximal ultra-violet light absorption of such low intensity as to preclude the presence of the expected product, 4-methyl-β-*cyclo*citral (Lunt and Sondheimer, *J.*, 1950, 2957), as a major component. However, a pure 2 : 4-dinitrophenylhydrazone was obtained after chromatographic purification, which showed the properties expected of the derivative of 4-methyl-α-*cyclo*citral (IX). This aldehyde may well have been produced by the rearrangement of (VI) to (X) (see below) by the palladium catalyst, followed by 1 : 4-hydrogenation. Such a rearrangement is of interest owing to the close structural relationship of (X) to the important androtermone safranal (XI). This aldehyde (derived from picrocrocin, the bitter principle of saffron) was shown to play a remarkable rôle in controlling the sexual characteristics of the hermaphroditic green alga *Chlamydomonas eugametos f. synoica*, causing the cells to become male even at a dilution of 10 molecules per cell (Kuhn, Moewus, and Wendt, *Ber.*, 1939, **72**, 1702). An isomer of safranal had been synthesised by Fischer and Loewenberg (*Annalen*, 1932, **494**, 263), and safranal itself was synthesised in very poor yield by the direct dehydrogenation of β-*cyclo*citral, the product being isolated as a semicarbazone of 85% purity (Kuhn and Wendt, *Ber.*, 1936, **69**, 1549). A further synthesis envisaged by Karrer and Ochsner (*Helv. Chim. Acta*, 1947, **30**, 2092) has not proved successful.



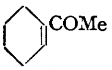
It was found that the rearrangement of (VI) to 4-methylsafranal (X) could be effected easily, the 2 : 4-dinitrophenylhydrazone of (X) being formed merely by treating the unconjugated isomer with the hot reagent (in methanol and sulphuric acid). It appears that the hyperconjugation effect of the 4-methyl group is sufficient to enable isomerisation to take place in this case. The best preparative method for obtaining the conjugated isomer was found to be heating (VI) with methanolic sulphuric acid, and isolating the product as the semicarbazone, from which regeneration with dilute sulphuric acid yielded the pure 4-methylsafranal (X). This aldehyde is being tested for any termonic activity by Dr. R. A. Lewin of the Osborn Botanical Laboratories, Yale University. This investigation will throw light on the structural specificity associated with this type of activity.

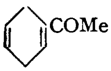
The reaction between 1 : 1 : 3-trimethylbutadiene and hept-2-yn-1-al (I; R = Bu^n) required rather higher temperatures than the reaction with tetrolaldehyde. It could be effected by heating the components at 150° for 5½ hours, whereupon impure 2 : 2 : 4-trimethyl-6-*n*-butyl*cyclo*hexa-3 : 6-dienealdehyde (XII) was obtained, characterised by its 2 : 4-dinitrophenylhydrazone. The product was assigned structure (XII) rather than the other possible structure by analogy with the tetrolaldehyde adduct, but the correctness of this assumption has not been confirmed otherwise. On careful redistillation, the aldehyde was found not to be completely homogeneous. It was suspected that some aromaticization had occurred at the rather high reaction temperature employed, and this was confirmed by the fact that a small amount of another 2 : 4-dinitrophenylhydrazone could be isolated, believed to be the derivative of the unknown 2 : 4-dimethyl-6-*n*-butylbenzaldehyde (XIII).

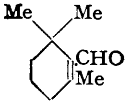


The ultra-violet light absorption properties of the various compounds described in this paper, together with those of related substances, are set out in the table. It had already been noticed (Bowden and Jones, *loc. cit.*; Braude, Jones, Sondheimer, and Toogood, *loc. cit.*) that introduction of a 3 : 4-double bond into acetyl*cyclo*hexene (XIV) to give 2 : 5-dihydroacetophenone (XV), increases $\lambda_{max.}$ by *ca.* 150 A. and lowers $\varepsilon_{max.}$ to *ca.* 30% of its former value. The introduction of a 3 : 4-double bond into 1-acetyl-2-alkyl*cyclo*hexenes has comparatively little effect, but in this case the original acetyl*cyclo*hexenes already have abnormally low $\varepsilon_{max.}$ values (Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890). When we now consider the light-absorption properties of the diene aldehydes described in this paper, it becomes apparent that introduction of a 3 : 4-double bond into 2-methyl*cyclo*hexenealdehyde (IV) (which shows normal light absorption), to give (II), increases $\lambda_{max.}$ by only *ca.* 60 A. and lowers $\varepsilon_{max.}$ to only *ca.* 60% of its former value. A similar effect is observed on introducing a 3 : 4-double bond (and an extra methyl group) into β-*cyclo*citral (XVI) to give (VI).* Thus the introduction of a 3 : 4-double bond into *cyclo*hexenealdehydes does not cause as marked an effect on the light absorption as in the case of the acetyl*cyclo*hexenes.

	Carbonyl compound.		Semicarbazone.		2 : 4-Dinitrophenylhydrazone.†	
	$\lambda_{max.}$, A.	$\varepsilon_{max.}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.}$.
(XIV)	2320	12,500 [1]	—	—	—	—
(XV)	2450	4,000 [2]	—	—	—	—
(IV)	2420	11,200 [3]	2740	23,200 [3]	3870	29,500 [3]
	2510	11,200	*2800*	*21,700*		
(II)	2270	6,100 *	2720	23,900	3830	27,600
	2500	7,100	2780	22,500		
	2570	7,100				
(XVI)	2490	11,600 [4]	2730	24,500 [5]	3860	26,600 [6]
(VI)	2330	7,000 *	2750	19,700	3860	25,800
	2560	5,000				
(XII)	2600	7,200 ‡	—	—	3850	27,800
(X)	3080	10,700 *	3240	15,300	3980	27,500
(XI)	3020	— [7]	3230	— [7, 8]	—	—


(XIV.)


(XV.)


(XVI.)

All light-absorption data, unless stated otherwise, were determined in ethanol. Data in italics refer to inflexions.

In *n*-hexane. † In chloroform. Main band only. ‡ Not quite pure.

Braude, Jones, Koch, Richardson Sondheimer, and Toogood, *J.*, 1949, 1890. [2] Brande, Jones, Sondheimer, and Toogood, *J.*, 1949, 607. [3] Heilbron, Jones, Richardson, and Sondheimer, *J.*, 1949, 737. [4] Young and Linden, *J. Amer. Chem. Soc.*, 1947, **69**, 2072. [5] Andrews, Cristol, Lindenbaum, and Young, *ibid.*, 1945, **67**, 715. [6] Lunt and Sondheimer, preceding paper. [7] Kuhn and Winterstein, *Ber.*, 1934, **67**, 344. Values read from graph. [8] Kuhn and Wendt, *ibid.*, 1936, 69, 1549.

The semicarbazones and 2 : 4-dinitrophenylhydrazones of the unconjugated diene aldehydes all have the properties expected of derivatives of αβ-unsaturated aldehydes with αββ-substitution. 4-Methylsafranal (X) and its semicarbazone exhibit $\lambda_{max.}$ values in good agreement with those of safranal and its semicarbazone (a slight increase would be expected owing to the extra alkyl substitution). Unfortunately, no comparison of the $\varepsilon_{max.}$ values can be made because of the uncertainty of the method used by Kuhn for calculating these values.

EXPERIMENTAL

(Absorption spectra, unless stated otherwise, were determined in alcoholic solution; m. p.s and b. p.s are uncorrected.)

Tetrolaldehyde Diethyl Acetal (1 : 1-*Diethoxybut*-2-*yne*).—(*a*) α-Bromocrotonaldehyde was prepared from crotonaldehyde and bromine, followed by dehydrobromination with potassium acetate, as described by Claisen (*Ber.*, 1911, **44**, 1161). The diethyl acetal was prepared from the bromo-aldehyde (87 g.), ethyl orthoformate (95 g.), ethanol (103 c.c.), and concentrated hydrochloric acid (1 c.c.), Claisen's conditions (*loc. cit.*) for the preparation of the dimethyl acetal being used. The ethyl acetal, obtained in 73% yield, had b. p. 83—85°/15 mm., $n_D^{19.5}$ 1·4574 (Viguier, *loc. cit.*, gives b. p. 86°/15 mm., n_D^{21} 1·4565).

The α-bromocrotonaldehyde diethyl acetal (85 g.) and a solution of potassium hydroxide (30 g.) in methanol (125 c.c.) were heated under reflux for 2 hours. Most of the solvent was distilled off through a

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* It has recently been found in these laboratories (Braude, Jones, and Sondheimer, forthcoming publication) that some aldehydes in ethanolic solution exhibited inconsistent $\varepsilon_{max.}$ values, probably owing to hemiacetal formation. The light-absorption data of most of the aldehydes described in this paper have therefore been determined in *n*-hexane. In consequence, a strict comparison with related aldehydes, determined previously in ethanolic solution, cannot be made.

short column, enough water added to the residue to dissolve the inorganic matter, the organic layer separated, and the aqueous layer washed with ether (4 × 100 c.c.). The combined organic extracts were dried and evaporated, and the residue was distilled. The recovered bromo-acetal (26 g.) was again heated for 2 hours with a solution of potassium hydroxide (5·5 g.) in methanol (25 c.c.). Working up as before and redistillation of the combined crude products then gave pure tetrolaldehyde diethyl acetal (42 g., 78%), b. p. 60—62°/11 mm., $n_D^{17.5}$ 1·4310 (Viguier, *loc. cit.*, gives b. p. 63—65°/13 mm., n_D^{16} 1·4271). The preparation of the ethyl acetal in methanolic solution, whereby no alkoxyl interchange is observed, has the advantage over the methods of Viguier and Claisen in that no specially efficient fractionation of the product is necessary.

(*b*) Propyne was prepared by adding 1 : 2-dibromopropane (450 g.) dropwise to a refluxing solution of potassium hydroxide (500 g.) in *n*-butanol (1 l.) contained in a copper flask, during 6 hours. The gas was passed through water, a calcium chloride tower, and then into a stirred and ice-cooled ethereal solution of ethylmagnesium bromide (prepared from magnesium, 40·0 g., and ethyl bromide, 190 g.) in a nitrogen atmosphere. After all the dibromopropane had been added, the butanol solution was refluxed until no more gas was evolved; next morning ethyl orthoformate (210 g.) in ether (100 c.c.) was added to the stirred and gently refluxing Grignard reaction mixture (which had separated into two layers) during 4 hours. After another hour's refluxing, the ether was distilled off, dry benzene (50 c.c.) added to the residue, and the mixture heated under reflux without stirring on the steam-bath for 1 hour, then cooled in ice; a solution of ammonium chloride (250 g.) in water (1 l.) was added all at once, and the mixture was stirred vigorously. Complete decomposition of the solid complex required several hours, occasional external cooling being necessary. The product was then isolated with ether in the usual way. Pure tetrolaldehyde diethyl acetal (160 g., 80% based on the ethyl orthoformate) was obtained, b. p. 62—63·5°/14 mm., $n_D^{17.5}$ 1·4300.

Tetrolaldehyde (*But*-2-*yn*-1-*al*) (I; R = Me).—The ethyl acetal (90 g.) and a trace of quinol were shaken overnight with a saturated aqueous tartaric acid solution (80 c.c.) in a nitrogen atmosphere. Saturated aqueous calcium chloride (360 c.c.) was added, and the shaking continued for 2—3 minutes. The aldehyde and unchanged acetal were extracted with ether, the dried ethereal solution was evaporated, and the residue distilled through a small column. The tetrolaldehyde (average yield; 15 g., 35%) had b. p. 105—110°/755 mm., n_D^{19} 1·446 (Viguier, *loc. cit.*, p. 482, gives b. p. 106·5—107°, n_D^{17} 1·4467, for a specially purified sample). Light absorption : Maxima, 2250 and 3160 A.; ε = 2,800 and 85, respectively. In addition, unchanged acetal (*ca.* 33 g.; 37% recovery) could be isolated. There was some resinous residue. The 2 : 4-*dinitrophenylhydrazone*, prepared from the aldehyde or the acetal, crystallised from ethanol in yellow needles, m. p. 136° (Found : N, 22·95. $C_{10}H_8O_4N_4$ requires N, 22·6%). Light absorption (in chloroform; main band only) : Maximum, 3630 A.; ε = 25,000.

Hept-2-*yn*-1-*al* (I; R = Bu^n). A solution of sodamide in liquid ammonia (120 c.c.) was prepared from sodium (9·3 g.), Vaughn, Vogt, and Nieuwland's ferric nitrate catalyst (*J. Amer. Chem. Soc.*, 1934, **56**, 2120) being used. Hex-1-yne (33 g.) was added during 30 minutes to the stirred and cooled (alcohol–carbon dioxide) reaction mixture. After another hour's stirring at *ca.* −40°, the ammonia was evaporated from the light brown suspension on the steam-bath with continuous stirring, the volume being kept constant by gradual addition of dry ether. The stable ethereal suspension of sodio-hexyne thus obtained was added slowly to ethyl formate (59·2 g., 100% excess) with stirring and cooling (alcohol–carbon dioxide), the temperature being kept at −20° throughout. The reaction mixture was allowed to attain room temperature, whereupon a reddish-brown slightly turbid solution was obtained. This was stirred for 45 minutes at 20° and another 1 hour at 0°, and then acetic acid (27 g.) was gradually introduced. The mixture was poured into ice and water and the aqueous layer was extracted with ether (2 × 150 c.c.). The combined ethereal extracts were washed with water and excess of sodium hydrogen carbonate solution, and dried. Evaporation of ether and recovered starting materials left a residue which on distillation gave *hept*-2-*yn*-1-*al* (10·6 g., 24%), b. p. 52—54°/13 mm., n_D^{17} 1·4521 (Found : C, 76·6; H, 9·2. $C_7H_{10}O$ requires C, 76·3; H, 9·15%). Light absorption : Maxima, 2270 and 3240 A.; ε = 3,200 and 155, respectively. The 2 : 4-*dinitrophenylhydrazone* crystallised from aqueous methanol in yellow needles, m. p. 74° (Found : N, 19·6. $C_{13}H_{14}O_4N_4$ requires N, 19·3%).

3 : 6-*Dihydro*-o-*tolualdehyde* (II).—Tetrolaldehyde (12 g.), butadiene (12 g.), and a trace of quinol were heated in a stainless-steel autoclave for 7 hours at 120°. Distillation of the product gave a low-boiling fraction (6·5 g.) consisting largely of unchanged aldehyde, and crude 3 : 6-dihydro-*o*-tolualdehyde (5·9 g.), b. p. 60—70°/2 mm., n_D^{23} 1·524. The recovered tetrolaldehyde was added to a mixture of butadiene (8 g.) and more acetylenic aldehyde (3 g.) and the solution was brought into reaction as before. Distillation then gave another 3·4 g. of the crude adduct. The combined products were redistilled through a small Vigreux column to yield pure 3 : 6-*dihydro*-o-*tolualdehyde* (8·2 g.; 31%), b. p. 65—66°/2 mm., n_D^{28} 1·5246—1·5250 (Found : C, 78·9; H, 8·4. $C_8H_{10}O$ requires C, 78·65; H, 8·25%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in red needles, m. p. 219° (Found : C, 55·6; H, 4·75. $C_{14}H_{14}O_4N_4$ requires C, 55·6; H, 4·65%). The *semicarbazone* crystallised from methoxyethanol as a microcrystalline powder, m. p. 230° (Found : C, 60·1; H, 7·15. $C_9H_{13}ON_3$ requires C, 60·3; H, 7·3%). For light absorptions of the foregoing, see Table.

o-*Tolualdehyde* (III).—The dihydro-*o*-tolualdehyde (0·17 g.) was heated under reflux for 5½ hours in an atmosphere of nitrogen. The resulting dark brown liquid gave an orange 2 : 4-dinitrophenylhydrazone (0·11 g., 26%), which after crystallisation from ethyl acetate had m. p. 194—195°, undepressed on admixture with an authentic specimen of *o*-tolualdehyde 2 : 4-dinitrophenylhydrazone (m. p. 194°).

2-*Methyl*cyclo*hexenealdehyde* (IV).—A solution of dihydro-*o*-tolualdehyde (1·78 g.) in redistilled methyl acetate (30 c.c.) was shaken with a palladium–calcium carbonate catalyst (0·8 g.; 0·75% Pd) in hydrogen, until 368 c.c. of gas had been absorbed at 25°/760 mm., corresponding to 1·0 ⊨. Removal of the catalyst and solvent, followed by fractionation of the residue, gave 2-methyl*cyclo*hexenealdehyde (0·80 g.), b. p. 55—57°/2 mm., n_D^{27} 1·5020 (Heilbron, Jones, Richardson, and Sondheimer, *J.*, 1949, 737, give b. p. 103°/27 mm., n_{D}^{18} 1·5091). The 2 : 4-dinitrophenylhydrazone, after one crystallisation from ethyl acetate, formed red needles, m. p. 185°, undepressed on admixture with an authentic specimen (m. p. 186—187°).

2 : 2 : 4 : 6-*Tetramethyl*cyclo*hexa*-3 : 6-*dienealdehyde* (VI).—Tetrolaldehyde (12·0 g.), 1 : 1 : 3-trimethylbutadiene (17·2 g.; 10% excess; Jitkow and Bogert, *J. Amer. Chem. Soc.*, 1941, **63**, 1979), and a trace of quinol were heated in a stainless-steel autoclave for 6½ hours at 125—130°. Distillation of a small amount of the product showed it to contain a considerable amount of unchanged starting materials. Heating at 125—130° was therefore continued for a further 10 hours. Distillation of the product gave a small fore-run of starting materials, and then the crude adduct (*ca.* 8 g.) as a pleasant smelling liquid, b. p. 67—76°/2 mm., $n_{\mathrm{D}}^{22 \cdot 5}$ 1·510. Distillation through a short column into six fractions showed the product to be inhomogeneous, as can be seen from the physical properties of three representative fractions: (ii) (0·8 g.), b. p. 65—67°/2 mm., $n_{\mathrm{D}}^{22 \cdot 5}$ 1·4960 (light absorption in *n*-hexane: maxima, 2480, 2550, and 2610 A.; ε = 5800, 7000, and 5800, respectively); (iv) (2·2 g.), b. p. 71—73°/2 mm., $n_{\mathrm{D}}^{22 \cdot 5}$ 1·5073 (light absorption: maxima, 2300, 2510, and 2570 A.; ε = 8300, 6100, and 6100 respectively); (vi) (1·0 g.), b. p. 76—86°/2 mm., $n_{\mathrm{D}}^{22 \cdot 5}$ 1·5150 (light absorption: maxima, 2280, 2510, and 2570 A.; ε = 7600, 6800, and 6800, respectively; inflexion, 2370 A.; ε = 7,100). The main fractions were recombined and converted into the semicarbazone in the usual way. The crude derivative after one crystallisation from aqueous methanol gave the *semicarbazone* of 2 : 2 : 4 : 6-tetramethyl*cyclo*hexa-3 : 6-dienealdehyde (5·8 g.; 15%) as regular needles, m. p. 146—148°; a small quantity was further crystallised to constant m. p. 149—151° (Found: C, 65·25; H, 8·65. $C_{12}H_{19}ON_3$ requires C, 65·1; H, 8·65%). Light absorption: see Table.

The semicarbazone (5·3 g.) was heated under reflux for 4 hours with a stirred mixture of light petroleum (50 c.c.; b. p. 60—80°) and 2N-sulphuric acid (50 c.c.) in a nitrogen atmosphere, two clear layers being obtained. Isolation in the usual manner gave the pure *aldehyde* (3·0 g.) as a mobile liquid, b. p. 75°/2 mm., $n_{\mathrm{D}}^{30 \cdot 5}$ 1·5095 (Found: C, 80·7; H, 9·9. $C_{11}H_{16}O$ requires C, 80·45; H, 9·8%). Light absorption: see Table. The regenerated aldehyde with semicarbazide acetate solution gave the original semicarbazone [m. p. (crude) 147—149°]. When the semicarbazone was cleaved by steam-distillation with oxalic acid, the aldehydic product had b. p. 69—70°/1·7 mm., n_{D}^{22} 1·5197. Light absorption: Maxima, 2360 and 3160 A.; ε = 4800 and 3900, respectively. Probably some rearrangement occurred during regeneration. The 2 : 4-*dinitrophenylhydrazone*, prepared either from the semicarbazone or from the pure aldehyde, crystallised from ethanol–ethyl acetate as red needles, m. p. 177—178° (Found: C, 59·7; H, 5·85. $C_{17}H_{20}O_4N_4$ requires C, 59·3; H, 5·85%). Light absorption: see Table.

2 : 4 : 6-*Trimethylbenzaldehyde* (VIII).—The diene-aldehyde (0·12 g.) was heated under reflux for 1 hour in a nitrogen atmosphere. The dark brown liquid product gave a red 2 : 4-dinitrophenylhydrazone (0·18 g.; 75%) which after two crystallisations from ethyl acetate–chloroform had m. p. 249—250°, undepressed on admixture with a sample (m. p. 250—251°) prepared from authentic 2 : 4 : 6-trimethylbenzaldehyde.

When the original reaction between tetrolaldehyde and 1 : 1 : 3-trimethylbutadiene was carried out at higher temperatures (140° or 160°) considerable pressure was observed on opening the autoclave. The products on distillation were found to be quite inhomogeneous, and the main fractions gave a 2 : 4-dinitrophenylhydrazone, m. p. 249—251°, and a semicarbazone, m. p. 188—189°. Neither of these m. p.s was depressed on admixture with the derivatives (m. p. 250—251° and 188—189°, respectively) prepared from authentic 2 : 4 : 6-trimethylbenzaldehyde.

Partial Hydrogenation of 2 : 2 : 4 : 6-*Tetramethyl*cyclo*hexa*-3 : 6-*dienealdehyde* (VI).—The aldehyde (1·0 g.), dissolved in redistilled methyl acetate (12 c.c.), was shaken with a palladium–calcium carbonate catalyst (0·5 g.; 0·75% Pd) in hydrogen until 148 c.c. of gas had been absorbed at 24°/770 mm., corresponding to 1·0 ⊨. Removal of catalyst and solvent gave a residue, $n_{\mathrm{D}}^{26 \cdot 5}$ 1·4760. Light absorption (in *n*-hexane): Maxima, 2420 and 2500 A.; $E_{1\,\mathrm{cm.}}^{1\%}$ = 150 and 100, respectively. Distillation into several fractions showed the material to be inhomogeneous. The combined fractions were converted into the 2 : 4-dinitrophenylhydrazone in the usual way. The crude derivative was dissolved in benzene and poured on a column of alumina. The chromatogram was developed with benzene, three bands being obtained. Only small quantities of impure materials were isolated from the upper two bands, but the lowest, most intense band yielded what is believed to be the 2 : 4-*dinitrophenylhydrazone* of 4-methyl-α-*cyclo*citral (IX). It crystallised from ethyl acetate–ethanol in yellow needles, m. p. 213—215° (Found: C, 58·9; H, 6·6. $C_{17}H_{22}O_4N_4$ requires C, 58·95; H, 6·4%). Light absorption (in chloroform; main band only): Maximum, 3610 A.; ε = 24,800.

2 : 2 : 4 : 6-*Tetramethyl*cyclo*hexa*-4 : 6-*dienealdehyde* (4-*Methylsafranal*) (X).—The unconjugated diene aldehyde (0·30 g.) was added to a solution of concentrated sulphuric acid (0·2 c.c.) in methanol (1·5 c.c.) and water (0·5 c.c.) at 60°. The solution was kept at this temperature for *ca.* 1 minute, and a solution of potassium acetate in methanol was added dropwise, unil the precipitation of potassium sulphate was complete. The cooled mixture was filtered, and the filtrate concentrated and treated with a solution of semicarbazide acetate in aqueous methanol; after several hours' storage at room temperature and overnight at 0°, a solid was precipitated. Crystallisation from aqueous methanol yielded 4-*methylsafranal semicarbazone* (0·21 g.) as light yellow plates, m. p. 157° (Found: C, 65·55; H, 8·7. $C_{12}H_{19}ON_3$ requires C, 65·1; H, 8·65%). Light absorption: see Table.

The semicarbazone (0·19 g.) was heated under reflux for 2½ hours with a stirred mixture of light petroleum (20 c.c.; b. p. 60—80°) and 2N-sulphuric acid (10 c.c.) in a nitrogen atmosphere, two clear layers being obtained. Isolation in the usual manner gave 4-*methylsafranal* (0·10 g.), b. p. 80—85° (bath temp.)/0·2 mm. (Found: C, 80·6; H, 9·75. $C_{11}H_{16}O$ requires C, 80·45; H, 9·8%). Light absorption: see Table. The 2 : 4-*dinitrophenylhydrazone* was prepared from the regenerated aldehyde, from the semicarbazone, and also from the unrearranged aldehyde by treating it with the hot reagent (in methanol and sulphuric acid). In all cases the derivative crystallised from ethyl acetate in purple plates, m. p. 195° (Found: C, 59·3; H, 5·95. $C_{17}H_{20}O_4N_4$ requires C, 59·3; H, 5·85%). Light absorption: see Table.

2 : 2 : 4-*Trimethyl*-6-n-*butyl*cyclo*hexa*-3 : 6-*dienealdehyde* (XII).—Hept-2-yn-1-al (4·5 g.), 1 : 1 : 3-trimethylbutadiene (4·5 g.; 15% excess) and a trace of quinol were heated in a stainless-steel autoclave at 150° for 5 hours. Distillation of the product yielded the crude adduct (3·4 g.; 40%) as a mobile liquid, b. p. 96—100°/1 mm., n_D^{22} 1·5071. Light absorption: see Table. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol in red needles, m. p. 140—141° (Found: C, 62·2; H, 6·8. $C_{20}H_{26}O_4N_4$ requires C, 62·15; H, 6·8%). Light absorption: see Table. On careful redistillation into several fractions, the adduct was found not to be completely homogeneous (n_D^{22} 1·5040—1·5105). A small amount of another 2 : 4-dinitrophenylhydrazone, believed to be that of 2 : 4-dimethyl-6-*n*-butylbenzaldehyde, could be isolated. It crystallised from ethyl acetate in orange plates, m. p. 159—160°. Light absorption (in chloroform; main band only): Maximum, 3860 A.; $\varepsilon = 30,900$.

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