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# SELECTIVE CATALYTIC HYDROGENATION OF ACETYLENES

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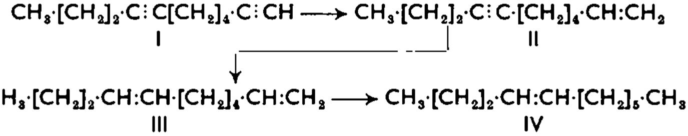
**Abstract**—The products of the stepwise catalytic hydrogenation of undeca-1,7-diyne (I) have been examined and the sequence of the reduction established. The ethynyl group may be protected during catalytic hydrogenation by conversion into the corresponding 1-bromoacetylene.

Certain palladium catalysts have been shown to produce substantial amounts of *trans*-ethylene in the catalytic partial reduction of several acetylenic hydrocarbons. Catalytic stereomutation of *cis*- to *trans*-ethylene has been observed, the extent of which depends on the relative proportions of catalyst and unsaturated hydrocarbon.

The successful partial chemical reduction of undeca-1,7-diyne (I) to *trans*-undec-7-en-1-yne[1] prompted an investigation into the feasibility of attaining an analogous differentiation of the two triple bonds in the case of catalytic hydrogenation. It would be especially valuable if some method could be devised for the protection of the ethynyl group during a catalytic partial hydrogenation of the internal triple bond to the *cis*-ethylene. As an essential preliminary, the stepwise catalytic reduction of undeca-1,7-diyne (I) itself was studied employing 10 per cent palladium–charcoal.



$$\underset{\text{I}}{CH_3\cdot[CH_2]_2\cdot C\vdots C[CH_2]_4\cdot C\vdots CH} \longrightarrow \underset{\text{II}}{CH_3\cdot[CH_2]_2\cdot C\vdots C\cdot[CH_2]_4\cdot CH{:}CH_2}$$

$$\underset{\text{III}}{CH_3\cdot[CH_2]_2\cdot CH{:}CH\cdot[CH_2]_4\cdot CH{:}CH_2} \longrightarrow \underset{\text{IV}}{CH_3\cdot[CH_2]_2\cdot CH{:}CH\cdot[CH_2]_5\cdot CH_3}$$

Separate experiments were stopped at hydrogen uptakes corresponding to the absorption of one, two and three moles of hydrogen. In a surprisingly clearcut manner each experiment gave essentially one hydrocarbon, the products obtained being respectively undec-1-en-7-yne (II), undeca-1,7-diene (III) and undec-4-ene (IV). These constitutions were proved by the obvious methods of analysis, microhydrogenation, infra-red absorption and ozonolysis (see Experimental) which showed that no appreciable double bond migration had taken place.[2,3] Thus the precedence of catalytic reduction seems to be ethynyl:disubstituted triple bond:vinyl:1,2-disubstituted double bond. That this was so, even when the triple bonds concerned were in different molecules, was shown by the catalytic partial reduction of an equimolar mixture of oct-1-yne and oct-4-yne. After the absorption of one mole of hydrogen, the products were oct-1-ene and unchanged oct-4-yne; a take-up of two moles of hydrogen produced oct-1-ene and oct-4-ene.

The acetylenic hydrogen of undeca-1,7-diyne was then replaced by various

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[1] N. A. Dobson and R. A. Raphael, *J. Chem. Soc.* 3558 (1955).

[2] W. G. Young, R. L. Meier, J. Vinograd, H. Bollinger, L. Kaplan and S. L. Linden, *J. Amer. Chem. Soc.* 69, 2046 (1947).

[3] J. B. Bream, D. C. Eaton and H. B. Henbest, *J. Chem. Soc.* 1974 (1957).

removable blocking groups in order to ascertain if this process would afford any protection of the terminal triple bond during hydrogenation. Use of the mercury salt was unsuccessful owing to poisoning of the catalyst. Hydrogenation of the lithium salt or Grignard derivative took place readily, but work-up after the absorption of one mole of hydrogen furnished predominantly undec-1-en-7-yne (II). More successful was the use of the bromoderivative. Thus initial experiments showed that 1-bromohept-1-yne was very resistant to attempted catalytic hydrogenation. Hydrogenation of 1-bromo-octa-1,7-diyne and 1-bromoundeca-1,7-diyne (V) led to the rapid absorption of two moles of hydrogen with the formation of 1-bromo-oct-1-yne and 1-bromoundec-1-yne respectively.

$CH_3\cdot[CH_2]_2\cdot C{:}C\cdot[CH_2]_4\cdot C{:}CBr$ V $\quad$ $CH_3\cdot[CH_2]_2CH{:}CH\cdot[CH_2]_4\cdot C{:}CBr$ VI

Absorption of one mole of hydrogen by 1-bromoundeca-1,7-diyne gave substantially *cis*-1-bromoundec-7-en-1-yne (VI). Attempts at characterization by converting VI into the Grignard derivative by treatment with magnesium[4] and subsequent carboxylation were abortive. However, structure VI was confirmed by its coupling under conditions specific for the —C⋮CBr function[5] and catalytic hydrogenation of the product to the crystalline n-docosane. Thus although some measure of the required protection for the ethynyl group during catalytic hydrogenation was achieved, the process seems too cumbersome to be of practical value, and was not investigated further.

The stereochemistry of the formation of the central double bond during the stepwise hydrogenation of undeca-1,7-diyne proved to be unusually complex. As expected from many precedents[6] of the partial catalytic hydrogenation of disubstituted triple bonds, the infra-red absorption of the undeca-1,7-diene (III) showed the central double bond to possess predominantly the *cis*-configuration. It was therefore unexpected when the infra-red absorption of the next product, undec-4-ene (IV), showed it to contain a substantial proportion (ca. 50 per cent) of the *trans*-isomer (strong absorption near 970 $cm^{-1}$). This was confirmed by comparison with the infra-red spectra of authentic pure *trans*-undec-4-ene (obtained by sodium-ammonia reduction of undec-4-yne) and of pure *cis*-undec-4-ene (prepared from the *trans*-compound by a well-established three-step stereomutation procedure[7]). This result prompted the study of the partial catalytic reduction of undec-4-yne over palladium on various supports (Table 1). In this process almost pure *cis*-undec-4-ene was produced only when Lindlar catalyst (case *a*) was used; unusually high percentages of the *trans*-isomer being formed in all other cases. There was a remarkable variation in the results. The amount of *trans*-isomer produced seemed unpredictable, although there was some indication of dependence on pH (cases *g* and *h*) and especially in the origin (cases *d* and *e*) and quantity (cases *e* and *f*) of catalyst. The last factor was subsequently investigated further and is discussed below.

There seemed to be no correlation with the speed of the hydrogenation. The effect also seemed dependent on the particular acetylene used (see Experimental).

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[4] H. Normant and J. Cuvigny, *Bull. Soc. Chim. Fr.* 1447 (1957).

[5] P. Cadiot and W. Chodkiewicz, *Bull. Soc. Chim. Fr.* 298 (1958).

[6] R. A. Raphael, *Acetylenic Compounds in Organic Synthesis* p. 22 et seq. Butterworths, London (1955); R. L. Burwell, *Chem. Rev.* 57, 895 (1957); P. H. Emmett (Editor) *Catalysis* vol. III, pp. 49–148 and 413–452. Reinhold, New York (1955).

[7] M. C. Hoff, K. W. Greenlee and C. E. Boord, *J. Amer. Chem. Soc.* 73, 3329 (1951).

From this work, and other indications in the literature, it seems clear that the Lindlar catalyst[6,8,9] and possibly Raney nickel[7,9] are substantially stereoselective for the production of *cis*-ethylenes from acetylenic hydrocarbons, while the use of other substrates for the palladium produces an unpredictable and often large content of *trans*-isomer.

One obvious explanation of these results involves stereomutation of initially formed *cis*-undec-4-ene at the catalyst surface. This simple idea has been discounted in the past[6] in view of the findings that *cis*-ethylenes did not undergo stereomutation in contact with the catalyst alone. We have confirmed this point in the present case by the observation that no stereomutation occurred when a solution of *cis*-undec-4-ene in cyclohexane was shaken in an atmosphere of air or nitrogen with palladium-charcoal catalyst derived in the following ways; untreated; prehydrogenated; used initially in a simple hydrogenation. However, it was found that stereomutation at the catalyst surface *did occur in an atmosphere of hydrogen.*[10] This could be shown in a particularly striking manner when the amount of catalyst used was reduced to such an extent that virtually no hydrogenation of the double bond occurred. In such circumstances substantially pure *cis*-undec-4-ene was transformed in one hour at room temperature into a mixture containing about 70 per cent of the *trans*-isomer (see Table 2, case *i*), at which point no further stereomutation seemed to occur (cases *i* and *j*). In an attempt to see whether this represented a true equilibrium value, these same minimal catalyst stereomutation conditions were tried on pure *trans*-undec-4-ene; most surprisingly one mole of hydrogen was absorbed with such rapidity that no accurate estimate of isomer proportions was possible (case *k*). These results would certainly seem to indicate not only that the pure *trans*-isomer undergoes hydrogenation much more rapidly than the *cis* but also that in mixtures of the two

TABLE 1. UPTAKE OF 1 MOLE OF HYDROGEN BY UNDEC-4-YNE IN THE PRESENCE OF PALLADIUM CATALYSTS AT ROOM TEMPERATURE

(in ethyl acetate, unless otherwise stated)

| Case | *a* | *b* | *c* | *d* | *e* | *f* | *g* | *h* |
|---|---|---|---|---|---|---|---|---|
| Catalyst | 4·8% Pd–$CaCO_3$ + $Pb(OAc)_2$ | 10% Pd–$CaCO_3$ | 10% Pd–$BaSO_4$ | 10% Pd–C | 10% Pd–C | 10% Pd–C | 10% Pd–C + $Et_3N$ | 10% Pd–C + AcOH |
| % Catalyst* | 8·9 | 10·1 | 11·2 | 9·8 | 10 | 17·4 | 11·5 | 10·5 |
| % *trans* in ethylenic content | 4 | 63 | 40 | 32 | 68 | 31 | 17 | 49 |

* i.e. 100 × wt of catalyst/wt of acetylene.

*Cases*

(*a*) 'Lindlar' catalyst; a few drops of quinoline were added to the hydrogenation mixture. A duplicate run gave a closely similar result.

(*e*) and (*f*) Cyclohexane as solvent and Baker catalyst (all other cases Johnson-Matthey) were used.

(*g*) and (h) 0·5 ml of $Et_3N$ and AcOH added respectively.

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[8] M. Svoboda and J. Sicher, *Chem. & Ind.* 290 (1959).

[9] B. Loev and C. R. Dawson, *J. Org. Chem.* **24**, 981 (1959).

[10] S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.* **82**, 6082, 6087 (1960); J. F. Sauvage, R. H. Baker and A. S. Hussey, *Ibid.* **82**, 6090 (1960).

the *cis*-isomer preferentially occupies the hydrogenation sites and thus inhibits the hydrogenation of the *trans*.

This latter phenomenon would account for the inhibition of hydrogenation of the *trans*-rich mixture obtained by the stereomutation, under conditions in which ready hydrogenation of the pure *trans*-isomer occurred (cases *i*, *j*, *k*).

When sufficient catalyst was used to overcome the poisoning effect of the *cis*-isomer, hydrogenation and isomerization proceeded side by side; the proportion of *trans*-isomer in the ethylenic content of the reaction first rose rapidly and then fell, in agreement with the above suggestion of more rapid hydrogenation of the *trans*-isomer (case *l*).

TABLE 2. STEREOMUTATION OF UNDEC-4-ENE ON 10% Pd–C (BAKER) IN CYCLOHEXANE AT ROOM TEMPERATURE

| Case | *i* | *j* | *k* | *l* |
|---|---|---|---|---|
| % Catalyst | 2·3 | 1·7 | 2·1 | 8·4 |
| Time (min) | 0 30 60 120 | 0 39 60 90 120 | 0 18 | 0 15 30 50 80 120 |
| % Molar hydrogen absorption | < 5 | No absorption | 0 98 | 0 17 42 58 81 94 |
| % *trans* in ethylenic* product | 6·6 50 71 74 | 68 70 72 72 72 | 100 – | 6·6 58 55 50 37 ~23 |

* The percentage *trans* given for zero time is that of the undec-4-ene before addition to hydrogenation flask.

When the above low catalyst concentration conditions were applied to substantially pure *cis*-undeca-1,7-diene (III, prepared by Lindlar reduction of I) hydrogenation of the terminal double bond proceeded fairly rapidly with concurrent substantial stereomutation (79 per cent) of the central double bond (see Experimental).

The hydrogenation-stereomutation behaviour revealed even by the above relatively crude study is complex and would certainly merit a physico-chemical investigation involving rigidly-standardized quantitative measurements.

## EXPERIMENTAL

Routine infra-red spectra were determined as liquid films or Nujol mulls with Perkin-Elmer spectrophotometers, Models 13, 21 or 137 (NaCl prisms). Light petroleum was generally of b.p. 60–80°.

Unless stated to the contrary, hydrogenations were performed at atmospheric pressure in an apparatus of the conventional type (mechanical shaking) on about 0·02 mole of the acetylene dissolved in the stated solvent in the presence of ca. 10% by weight of the particular catalyst (Johnson–Matthey and Co. Ltd). After removal of the catalyst by filtration and of the solvent by evaporation, the product was distilled and its composition investigated.

*Alkynes*. The hydrocarbons hept-1-yne,[11] oct-1-yne,[11] hept-2-yne,[12] dec-4-yne,[13] undec-4-yne,[14]

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[11] *Organic Synthesis* Vol. 30, p. 15. John Wiley, New York (1950).

[12] G. F. Hennion and C. J. Pillar, *J. Amer. Chem. Soc.* **72**, 5317 (1950).

[13] T. H. Vaughn, G. F. Hennion, R. R. Vogt and J. A. Nieuwland, *J. Org. Chem.* **2**, 1 (1937).

[14] B. Gredy, *C.R. Acad Sci., Paris* **196**, 1121 (1933); *Liebigs Ann.* **4**, [11], 15 (1935).

undec-5-yne,[15] oct-4-yne,[16] dec-5-yne[17] and undeca-1,7-diyne[18] (I) were prepared by standard methods involving liquid ammonia as solvent; the yields and the physical constants were generally in agreement with those given in the literature.

trans-*Alkenes*. The standard sodium-liquid ammonia procedure for the reduction of the bilaterally-substituted acetylenic linkage furnished, with the appropriate alkynes (0·05–0·2 moles), *trans*-hept-2-ene[19] (59%) b.p. 98–100°, $n_D^{20}$ 1·4050, *trans*-dec-5-ene[17] (85%) b.p. 92–94°/32 mm, $n_D^{21}$ 1·4282 and trans-*undec-4-ene* (90%) b.p. 104–105°/40 mm, $n_D^{25}$ 1·4274. (Found: C, 86·0; H, 14·1. $C_{11}H_{22}$ requires: C, 85·6; H, 14·4%). The *trans*-ethylenes absorbed strongly at 968 cm$^{-1}$ and were shown to be free from the corresponding alkynes and saturated hydrocarbons by gas-liquid chromatography.[20]

*Hydrogenation of undeca*-1,7-*diyne* (I)

Unless stated otherwise, the hydrogenations were performed using undeca-1,7-diyne (7·4 g, 0·05 mole) in ethyl acetate (75 cc) with 10% palladium–charcoal catalyst (400 mg). The products were the same when n-hexane or tetrahydrofuran was substituted for ethyl acetate.

(a) *Absorption of one mole of hydrogen.* The product (7·2 g), b.p. 83–84°/12 mm, $n_D^{25}$ 1·4470–1·4479 was established as virtually pure *undec*-1-*en*-7-*yne* (II). (Found: C, 88·1; H, 11·9. $C_{11}H_{18}$ requires: C, 87·9; H, 12·1%) on the following basis. Microhydrogenation, Pd in acetic acid, found: 2·91 double bond equivalents ($C_{11}H_{18}$ requires: 3·0). No precipitate was formed on addition of silver nitrate solution (5% in 95% aqueous ethanol) and there was no absorption near 3300 cm$^{-1}$ (absence of the ethynyl group). Strong absorption at 908, 994 and 1610 cm$^{-1}$ substantiated the presence of the vinyl grouping.

The hydrocarbon (1·5 g, 0·01 mole) was subjected to ozonolysis in acetic acid (75 cc). The solution was then diluted with water (75 cc), zinc dust (2 g) added, and the mixture steam distilled. Excess of 2,4-dinitrophenylhydrazine reagent was added to the steam distillate and, after 2 hr, the precipitate of 2,4-dinitrophenylhydrazones was collected, washed, dried *in vacuo*, and chromatographed on bentonite-kieselguhr. Elution with benzene–chloroform (9:1) furnished the 2,4-*dinitrophenylhydrazone of dec*-6-*ynal*, yellow needles, m.p. 93–95° from light petroleum. (Found: C, 57·9; H, 6·0; N, 16·55. $C_{16}H_{20}O_4N_4$ requires: C, 57·8; H, 6·1; N, 16·9%). By elution with chloroform, formaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 155° from light petroleum, was obtained.

In a second experiment, the ozonolysis solution was totally hydrogenated (10% palladium–charcoal) prior to steam distillation and isolation of the derivatives of fission products as described above. Only two 2,4-dinitrophenylhydrazones, that of decanal, m.p. and mixed m.p. 90°, and that of formaldehyde, were isolated.

(b) *Absorption of two moles of hydrogen.* The product (7·3 g) b.p. 79–80°/13 mm, $n_D^{25}$ 1·4378 was established as predominately cis-*undeca*-1,7-*diene* (III). (Found: C, 86·7; H, 13·2. $C_{11}H_{20}$ requires: C, 86·8; H, 13·2%). Microhydrogenation, Pd in acetic acid, found: 1·95 double bond equivalents ($C_{11}H_{20}$ requires: 2·0). Light absorption: 724 *m.br.* [$(CH_2)_n$ and (—HC=CH-*cis*)] and 908 *s*, 994 *s* and 1610 *m* cm$^{-1}$ (—$CH{=}CH_2$). The ozonolysis procedure already described furnished the 2,4-dinitrophenylhydrazone of formaldehyde and that of butanal, m.p. 122° and the *bis*-2,4-*dinitrophenylhydrazone* of *hexanedial* as small orange prisms, m.p. 199–202° (decomp) from acetic acid. (Found: C, 45·8; H, 4·1; N, 23·4. $C_{18}H_{18}O_8N_8$ requires: C, 45·6; H, 3·8; N, 23·6%) undepressed on admixture with a genuine specimen prepared by ozonolysis of cyclohexene. When the hydrogenation was performed with palladium-calcium carbonate-traces of quinoline, the rate of absorption slowed markedly after 2 moles of hydrogen had been absorbed, but did not cease entirely. Lindlar catalyst[21] to which a few drops of synthetic quinoline had been added was specific as absorption ceased at this point. In both cases the product was almost pure *cis*-undeca-1,7-diene.

(c) *Absorption of three moles of hydrogen.* Undec-4-ene (IV) (7·2 g) b.p. 79–82°/10 mm, $n_D^{25}$ 1·4277–1·4282. (Found: C, 85·5; H, 14·2. Calc. for $C_{11}H_{22}$: C, 85·6; H, 14·4%) was the sole product. Microhydrogenation, found: 0·97 double bond equivalents ($C_{11}H_{22}$ requires: 1·0). There was no

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[15] K. N. Campbell and M. J. O'Connor, *J. Amer. Chem. Soc.* **61**, 2897 (1939).

[16] A. L. Henne and K. W. Greenlee, *J. Amer. Chem. Soc.* **67**, 484 (1945).

[17] K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.* **63**, 2684 (1941).

[18] R. A. Raphael and F. Sondheimer, *J. Chem. Soc.* 115 (1950).

[19] B. Gredy, *Bull. Soc. Chim. Fr.* **2**, (5), 1029 (1935).

[20] We are indebted to Dr. Davison (Unilever Research Department, Bedford) for his examination of undec-4-ene (IV).

[21] H. Lindlar, *Helv. Chim. Acta* **35**, 446 (1952).

absorption at 908, 994 or 1610 cm$^{-1}$ (absence of —CH=CH$_2$) but the presence of ~50% *trans*-isomer was inferred from the strong absorption at 968 cm$^{-1}$. Only butanal and heptanal 2,4-dinitrophenylhydrazones were isolated from the ozonolysis of the ethylene, a satisfactory separation on the bentonite–kieselguhr column being achieved with light petroleum–benzene (3 : 1; containing 2% ether) as eluent.

(d) *Absorption of four moles of hydrogen.* Undeca-1,7-diyne (1·1 g) furnished n-undecane (920 mg) b.p. 81°/15 mm, $n_D^{19}$ 1·4190, the infra-red spectrum of which was identical with that given in the file of the American Petroleum Institute (spectrum number 391).

### *Hydrogenation of an equimolar mixture of oct-1-yne and oct-4-yne*

(a) A mixture of oct-1-yne (1·1 g, 0·01 mole) and oct-4-yne (1·1 g), dissolved in light petroleum, was hydrogenated in the presence of Lindlar catalyst (containing quinoline) until 0·01 mole (235 cc/776 mm and 19°) of hydrogen had been absorbed. The product gave no precipitate with alcoholic silver nitrate solution (5%) and had no absorption in the 3300 cm$^{-1}$ region (absence of —C≡C—H), but did absorb strongly at 910 and 990 cm$^{-1}$ (—CH=CH$_2$). Gas–liquid chromatography (4′ column: 20% by weight of a saturated solution of AgNO$_3$–triethylene glycol on Celite, Embacel 60–100 mesh. Temp 23°, flow 33 ml of argon/min. Pye "Argon Gas chromatograph") confirmed that the product was almost entirely a mixture of oct-4-yne (retention time 16·9 min) and oct-1-ene (7·0 min). Oct-4-ene (5·4 min) was present in traces only and oct-1-yne (32·8 min) was absent.

(b) When a mixture of oct-1-yne (0·01 mole) was similarly hydrogenated until absorption ceased (0·02 mole) the product was found to be a mixture of *cis*-oct-4-ene (715 br and 1655 cm$^{-1}$; retention time 5·4 min) and oct-1-ene (910, 990 and 1640 cm$^{-1}$; 7·0 min). Approx. 5% of the oct-4-ene was present as the *trans*-isomer (absorption at 968 cm$^{-1}$; 2·1 min).

### *Hydrogenation of undeca-1,7-diynylmagnesium bromide*

A solution of undeca-1,7-diyne (I) in tetrahydrofuran was added to an equivalent quantity of ethylmagnesium bromide in the same solvent and the mixture heated under reflux for 3 hr. The resulting solution was hydrogenated (dry hydrogen) over 10% palladium–charcoal until one double bond equivalent of hydrogen had been absorbed, the solvent removed under reduced pressure and the dry residue decomposed with cold dilute H$_2$SO$_4$. Isolation of the neutral fraction followed by distillation furnished a liquid (81%) b.p. 77°/12 mm, $n_D^{25}$ 1·4452. (Found: C, 87·7; H, 11·9. Calc. for C$_{11}$H$_{22}$: C, 87·9; H, 12·1%). Microhydrogenation, found: 3·02 double bond equivalents (C$_{11}$H$_{18}$ requires: 3·0). This product was shown to be largely (ca. 95%) undec-1-ene-7-yne by the following experiments.

The product (3·0 g) was first ozonized and then hydrogenated. The resulting saturated aldehydes were converted to their 2,4-dinitrophenylhydrazones which, after separation by chromatography on bentonite–kieselguhr, were identified as decanal 2,4-dinitrophenylhydrazone (5·81 g, 86%), m.p. and mixed m.p. 89–90° from ethanol, heptanal 2,4-dinitrophenylhydrazone (250 mg, 4·3%) m.p. 106–107° from ethanol, butanal 2,4-dinitrophenylhydrazone (200 mg, 4%), m.p. 122°, and formaldehyde 2,4-dinitrophenylhydrazone, m.p. 155° from light petroleum.

A solution of the product (1·5 g) in ethanol (95%; 50 cc) was treated with an aqueous solution of silver nitrate (7%; 50 cc) and the precipitate collected, washed and dried (212 mg; corresponding to ca. 5% C$_{11}$H$_{18}$ (Calc. as C$_3$H$_7$CH:CH—[CH$_2$]$_4$C ⋮ CAg.AgNO$_3$). The products obtained after the absorption of 2 and 3 double bond equivalents closely resembled those obtained by reduction of undeca-1,7-diyne itself. Further absorption of hydrogen was very slow.

### *Hydrogenation of the lithium salt of undeca-1,7-diyne* (I)

A standardized solution of phenyllithium (0·052 mole) was blown by a stream of nitrogen into a solution of undeca-1,7-diyne (7·4 g, 0·05 mole) in ether (50 cc) and the mixture heated under reflux for 30 min. The ether was then replaced by dry tetrahydrofuran (100 cc) and the cooled solution hydrogenated in the presence of 10% palladium–charcoal (500 mg) in tetrahydrofuran (50 cc) until one double-bond equivalent had been absorbed. The product was then isolated by the procedure already described for the Grignard derivative. The product (6·9 g) b.p. 82–86°/12 mm, $n_D^{26}$ 1·4480 was shown to be predominantly undec-1-en-7-yne (II). (Found: C, 87·8; H, 11·9. Calc, for C$_{11}$H$_{18}$: C, 87·9; H, 12·1%). Microhydrogenation required 2·87 double bond equivalents. The amount of ethynyl compound present was estimated by the silver salt precipitation method to be 11%. The presence of both the ethynyl and vinyl groups was confirmed by the infra-red absorption. The standard ozonolytic degradation procedure resulted in the separation and identification of butanal 2,4-dinitrophenylhydrazone, m.p. 122°, formaldehyde 2,4-dinitrophenylhydrazone, m.p. 155°, dec-6-yn-1-al 2,4-dinitrophenylhydrazone, m.p. 94–95° and, what is presumed to be, *hex-1-yn-6-al 2,4-dinitrophenylhydrazone*, orange needles, m.p. 106–107° from ethanol–ethyl acetate. (Found: C, 53·6; H, 4·8; N. 19·0. $C_{13}H_{14}O_4N_4$ requires: C, 53·8; H, 4·9; N, 19·3%).

Absorption of two double-bond equivalents of hydrogen furnished almost exclusively undeca-1,7-diene (III) while the product resulting from the absorption of three double bond equivalents was shown to contain undec-1-ene (ca. 30%) in addition to undec-4-ene (IV). Some control by the lithium atom is therefore evident at this stage. Further hydrogen absorption was very slow.

### *Attempted hydrogenation of mercury derivative of undeca*-1,7-*diyne* (I)

Attempts to hydrogenate the mercury salt, m.p. 38°, with either benzene or ethyl acetate as solvent and either Adams' platinum oxide, 10% palladium–charcoal or Raney nickel as catalyst all failed owing to the almost immediate deposition of metallic mercury on the catalyst, whereupon absorption ceased.

### 1-*Bromo-octa*-1,7-*diyne*

Octa-1,7-diyne (26·5 g, 0·25 mole) was added slowly to a solution of ethylmagnesium bromide (0·5 mole) in ether (250 cc) and the resultant suspension stirred vigorously under reflux for 3 hr. The mixture was cooled to 0° and bromine (70 g, 0·44 mole) added at such a rate that the yellow colour did not persist for more than 20 sec. Isolation of the product in the usual way furnished 1-*bromo-octa*-1,7-*diyne* (8·4 g, 18%), b.p. 84–87°/23 mm, $n_D^{25}$ 1·5093. (Found: C, 51·7; H, 4·7; Br, 42·8. $C_8H_9Br$ requires: C, 51·9; H, 4·9; Br, 43·2%) and 1,8-dibromo-octa-1,7-diyne[23] (15·3 g, 23%) b.p. 108–110°/0·1 mm, $n_D^{25}$ 1·5307.

### 1-*Bromoundeca*-1,7-*diyne* (V)

(a) Treatment of the Grignard derivative of undeca-1,7-diyne (I, 29·6 g, 0·2 mole) with bromine (25·6 g, 0·16 mole) at —35° furnished 1-*bromoundeca*-1,7-*diyne* (19·5 g, 43%) as a colourless pungent oil, b.p. 126°/14 mm, $n_D^{25}$ 1·4929, (Found: C, 58·3; H, 6·5; Br, 34·6. $C_{11}H_{15}Br$ requires: C, 58·2; H, 6·64; Br, 35·3%) which slowly yellowed on keeping. Absorption bands due to the grouping $C{\equiv}CBr$ (e.g. 2200 $cm^{-1}$*m*), but not to ethynyl, ethylenic or carbonyl groupings, were present.

(b) Undeca-1,7-diyne (I, 7·4 g, 0·05 mole) was stirred for 16 hr at room temp with a solution of sodium hypobromite [from ice (25 g) 10 N sodium hydroxide solution (12·5 cc) and bromine (2·75 cc)] Isolation of the product with ether furnished the impure bromodiyne (1·95 g), $n_D^{22}$ 1·4822, the infra-red. spectrum of which indicated the presence of ethynyl, ethylenic and carbonyl groups.

(c) A solution of bromine (4·4 g, 0·028 mole) in dry carbon tetrachloride (200 cc) was added slowly to a stirred and cooled solution (−10°) of bis-undeca-1,7-diynyl mercury (7·4 g, 0·15 mole) in carbon tetrachloride (250 cc). The precipitated mercuric bromide was removed by filtration and the filtrate was washed successively with acidified potassium iodide solution, dilute sodium hydroxide solution and water. After removal of the solvent the residue was dissolved in light petroleum (b.p. 40–60°) and the solution passed down a column of charcoal containing a small quantity of admixed palladium–charcoal (to remove residual mercuric bromide). The bromodiyne (4·1 g, 60%) had b.p. (bath) 90–100°/1 mm, $n_D^{19}$ 1·4935.

### 1-*Chloroundeca*-1,7-*diyne*

Undeca-1,7-diyne (I, 29·6g, 0·2 mole) was added with vigorous stirring to a suspension of sodamide (7·8 g, 0·2 mole) in benzene, and a solution of *p*-toluenesulphonyl chloride (41·9 g, 0·22 mole) in benzene (100 cc) then added slowly. After heating under reflux for 1 hr, the reaction mixture was decomposed with dil hydrochloric acid and the benzene layer separated, washed, dried and evaporated to give the *chloride* (22·9 g, 63%) b.p. 114°/13 mm, $n_D^{25}$ 1·4757. (Found: C, 71·9; H, 8·15; Cl, 19·7. $C_{11}H_{15}Cl$ requires: C, 72·3; H, 8·2; Cl, 19·5%). Undeca-1,7-diyne (23%) was recovered from the fore-run.

Similar treatment of the lithium salt of undeca-1,7-diyne with *p*-toluenesulphonyl chloride in ether furnished the chloride in 30% yield.

### *Catalytic hydrogenation of 1-bromo-octa-1,7-diyne*

1-Bromo-octa-1,7-diyne (7·4 g, 0·04 mole) was hydrogenated in light petroleum in the presence of 10% palladium–charcoal (1·5 g) until 0·08 mole of hydrogen had been absorbed (50 min), whereupon the reaction was stopped. After the reaction mixture had been washed with sodium hydrogen carbonate solution, the product was isolated in the usual way, to give 1-bromo-oct-1-yne[22] (3·95 g, 52%), b.p. 86°/12 mm, $n_D^{25}$ 1·4725. (Found: C, 50·7; H, 6.7; Br, 42·0. Calc. for $C_8H_{13}Br$; C, 50·8; H, 6·9; Br, 42·3%).

When a similar hydrogenation of 1-bromohept-1-yne (prepared in 55% yield[23]) was attempted, uptake of hydrogen was very slow (30 hrs). The product was markedly inhomogeneous and was not studied further.

### *Catalytic hydrogenation of 1-bromoundeca-1,7-diyne* (V)

1-Bromoundeca-1,7-diyne (2·06 g) was hydrogenated in light petroleum in the presence of 10% palladium–charcoal until hydrogen equivalent to one mole had been absorbed (215 cc at 763 mm, 17°). After the catalyst had been removed the pale yellow filtrate was washed with sodium carbonate solution and water and then dried and evaporated. Chromatography of the residue in light petroleum (b.p. 40–60°) over alumina (Grade III) gave the somewhat impure *cis*-1-bromoundec-7-en-1-yne (VI, 1·85 g, 89%) b.p. 90–100° (bath)/0·64 mm. (Found: C, 60·8; H, 7·8; Br, 31·2. $C_{11}H_{17}Br$ requires: C, 57·65; H, 7·4; Br, 34·9%). The presence of ca. 10% of vinyl compound, presumably undec-1-en-7-yne, seems to be indicated by the analysis figures and by the infra-red spectrum. Hydrogenolysis occurred when 1-chloroundeca-1,7-diyne was subjected to catalytic hydrogenation.

Several unsuccessful attempts were made to convert the bromoenyne via the Grignard derivative to undec-7-en-1-yne-1-carboxylic acid, by heating the substance with magnesium in tetrahydrofuran or ether.[4] The formation of the Grignard derivative appeared to be extremely slow. A similar experiment with 1-bromophenylacetylene gave a 23% yield of phenylpropiolic acid.

A solution of 1-bromoundec-7-en-1-yne (VI, 458 mg) in benzene was added dropwise to a solution of cuprous chloride (294 mg) in n-butylamine (10 cc) and benzene (10 cc). The reaction mixture was then poured into dil acid and the product (210 mg), $n_D^{25}$ 1·4950, isolated with ether, and hydrogenated ($PtO_2$) in ethyl acetate. Chromatography in ether on alumina (Grade I) furnished n-docosane (70 mg, 23%), m.p. 45° from ethanol.

### *Hydrogenation of undec-4-yne*

Hydrogenation with several catalysts under closely parallel conditions furnished undec-4-ene containing various amounts of the *trans*-isomer (estimated by measurements of the 968 $cm^{-1}$ band of the *trans*-isomer) (see Table 1). In all cases absorption slowed when 1 molar equivalent of hydrogen had been absorbed (the experiment was then stopped) but ceased spontaneously only with the Lindlar catalyst. The Lindlar–quinoline catalyst was employed in either ethyl acetate or cyclohexane. After removal of the catalyst the filtrate was washed successively with dil hydrochloric acid and water, dried ($Na_2SO_4$) and distilled.

In similar experiments, the olefins hept-2-ene (59%), b.p. 100–101°/735 mm, $n_D^{20}$ 1·4100, and dec-5-ene (87%), b.p. 63–64°/6 mm, $n_D^{19}$ 1·4245, obtained by reduction of hept-2-yne and dec-5-yne in the presence of the Lindlar catalyst were estimated to contain 1% and 5% of the *trans*-isomers respectively; with 10% palladium–charcoal–acetic acid the amounts were 7% and 10%. A high percentage (>50%) of the *trans*-isomer was present in dec-4-ene, b.p. 70–71°/14 mm, $n_D^{25}$ 1·4233, resulting from the hydrogenation (10% palladium-charcoal) of dec-4-yne; undec-5-ene, b.p. 72–73°/10 mm, $n_D^{25}$ 1·4271, similarly prepared, contained a smaller, though still substantial, proportion.

### cis-*Undec-4-ene*

Dry chlorine was passed into a solution of antimony pentachloride (1·5 g) and *trans*-undec-4-ene (24·9 g) in chloroform (35 cc) at −70° and in diffuse light, until 95% (10·9 g) of the theoretical amount

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[22] W. Chodkiewicz, Thesis, Paris (1957).

[23] P. A. McCusker and R. R. Vogt, *J. Amer. Chem. Soc.* **59**, 1307 (1937).

had been added. After stirring for a further 15 min at −70°, the mixture was poured into water (50 cc) and 4,5-*dichloroundecane* (24·5 g, 70%) b.p. 126–129°/10 mm, $n_D^{25}$ 1·4574, (Found: C, 58·7; H, 9·35. $C_{11}H_{22}Cl_2$ requires: C, 58·7; H, 9·8%) isolated by steam distillation.

The dichloride (17 g) was added during 90 min to a solution of potassium hydroxide (8·5 g) in n-propyl alcohol (20 cc) at 85–90° and the reaction mixture stirred for a further 18 hr at this temp. The mixture was poured into water and the organic phase steam distilled. The 5(?)-*chloroundec-4-ene* (11·7 g, 88%) was obtained as a colourless oil, b.p. 97–101°/9 mm, $n_D^{25}$ 1·4498. (Found: C, 70·3; H, 10·8. $C_{11}H_{21}Cl$ requires: C, 70·0; H, 11·1%).

A solution of the chloride (10·3 g) in ether (25 cc) was added dropwise to a solution of sodium (7·5 g) in liquid ammonia (100 cc) at −40°. After a further hour the mixture was decomposed with ammonium chloride, most of the ammonia evaporated and the product isolated with ether. cis-*Undec-4-ene* (6·3 g, 75%) b.p. 73°/9 mm, $n_D^{25}$ 1·4288 (Found: C, 85·55; H, 14·2. $C_{11}H_{22}$ requires: C, 85·6; H, 14·4%) exhibited the expected medium absorption at approximately 700 cm$^{-1}$ and no absorption at ca. 970 cm$^{-1}$ and adsorbed 1·05 double-bond equivalents of hydrogen on microhydrogenation.

### *Stereomutation experiments*

These experiments were carried out in a conventional hydrogenation apparatus using a flask (250 ml) fitted with a side arm carrying a serum cap. Cyclohexane was used as solvent and Baker[24] 10% palladium–charcoal as catalyst. Aliquots (5 ml) were removed at intervals by means of a hypodermic syringe, filtered through celite and the intensity of the *trans*-band at 968 cm$^{-1}$ measured using a Unicam S.P. 130 prism-grating infra-red spectrometer. A standard solution of pure *trans*-undec-4-ene absorbed at $\nu_{max}^{cyclohexane}$ 968 cm$^{-1}$, $\Delta\nu_{\frac{1}{2}}{}^{a}$ 12 cm$^{-1}$, $\varepsilon = 124$.

(i) Substantially pure *cis*-undec-4-ene (490 mg) in cyclohexane (39 ml) was shaken in an atmosphere of nitrogen and air with prehydrogenated catalyst (43 mg) for 2 hr. No stereomutation was observed. A similar result was obtained in an exactly similar experiment using catalyst which had just been used in a hydrogenation (oct-1-yne to oct-1-ene).

(ii) The results in table 2 were obtained using the following conditions.

(case *i*) Undec-4-ene (IV) (905 mg) in cyclohexane (30 ml) using 10% catalyst (22 mg).
(case *j*) Undec-4-ene (IV) (990 mg) in cyclohexane (42 ml) using catalyst (17 mg).
(case *k*) Undec-4-ene (IV) (1036 mg) in cyclohexane (35 ml) using calalyst (22 mg).
(case *l*) Undec-4-ene (IV) (1524 mg) in cyclohexane (32 ml) using catalyst (128 mg).

(iii) Hydrogenation of substantially pure *cis*-undeca-1,7-diene (III) (1194 mg) in cyclohexane (35 ml) using catalyst (27 mg) resulted in concurrent hydrogenation of the terminal double bond and stereomutation of the central double bond as shown by the following table.

| Time (min) | 0 | 17 | 27 | 43 | 72 |
|---|---|---|---|---|---|
| Molar hydrogen absorption | 0 | 0·32 | 0·5 | 1·0 | 1·25 |
| % *trans* in ethylene product | 11 | 63 | 79 | 76 | ca. 75 |

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[24] Messrs. Engelhard Industries Ltd., Baker Platinum Division.