Heterogeneous Catalytic Hydrogenation of Allenes over Supported Palladium: Selectivity, Stereoselectivity, and Regioselectivity

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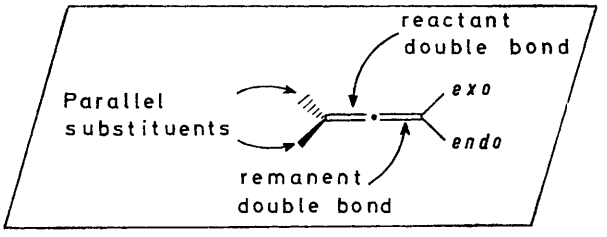
The palladium-catalysed hydrogenation of twelve allenes has been studied, from the point of view of product composition, over the complete range (0—2 mol. equiv.) of hydrogen absorption. Selectivity, stereoselectivity, and regioselectivity have been estimated with special reference to the semihydrogenation point. The relative haptophilicities of the four possible approaches of suitably substituted allenes to the catalyst surface show that steric effects play a major role in determining which orientations shall lead to product formation. In the case of conjugated allene esters and acids however, parallel orientation of the ester and acid groups is unexpectedly disfavoured: this may imply repulsive electronic contributions.

HETEROGENEOUS catalytic hydrogenation of olefins and acetylenes has been the subject of prolonged chemical interest,[1] but information on allenic systems is limited.[2] This study[3] was undertaken to examine the regioselectivity and stereochemistry of the semihydrogenation of substituted allenes under conditions of heterogeneous catalysis in the liquid phase, using palladium as the catalyst surface. Scheme 1 shows terminology



SCHEME 1 Allene orientation to a surface

useful in discussing simple overall 1,2-*cis*-hydrogen addition from a catalyst surface. Where appropriate for chiral allenes, attack at the reactant double bond may be specified by the *re*- and *si*-notation.

An allene of appropriate substitution can have four significant attitudes of presentation to a solid surface, designated (1; *endo*-A, *endo*-D) according to the atom or group pointing at the catalyst. These can lead, by 1,2-*cis*-addition of hydrogen, to four distinguishable olefins (2)—(5), and on further hydrogenation to (6) (Scheme 2). When structure (1) represents a chiral allene, the enantiomeric form, *ent*-(1) will similarly have four significant attitudes of presentation leading to the four enantiomers of (2)—(5), *e.g.* *ent*-(1; *endo*-D) generates *ent*-(2). This aspect is considered in the following paper. In this paper achiral allenes are mainly employed and the single chiral allene used is in (±)-form: in the latter example the symbolism (1)—(5) is taken to signify (±)-forms.

Much of the accumulated data on olefin hydrogenation can be explained, at least qualitatively, by the assumption that the structure of the olefin is largely retained in the transition state for adsorption.[1f] Steric effects occurring in the different modes of presentation of the allene to the hydrogenation catalyst might also be expected to play a significant part in determining the nature of the products of semihydrogenation. This would be so whether transition states for forming a rehybridised σ-bonded intermediate, or a π-complexed intermediate, are envisaged.

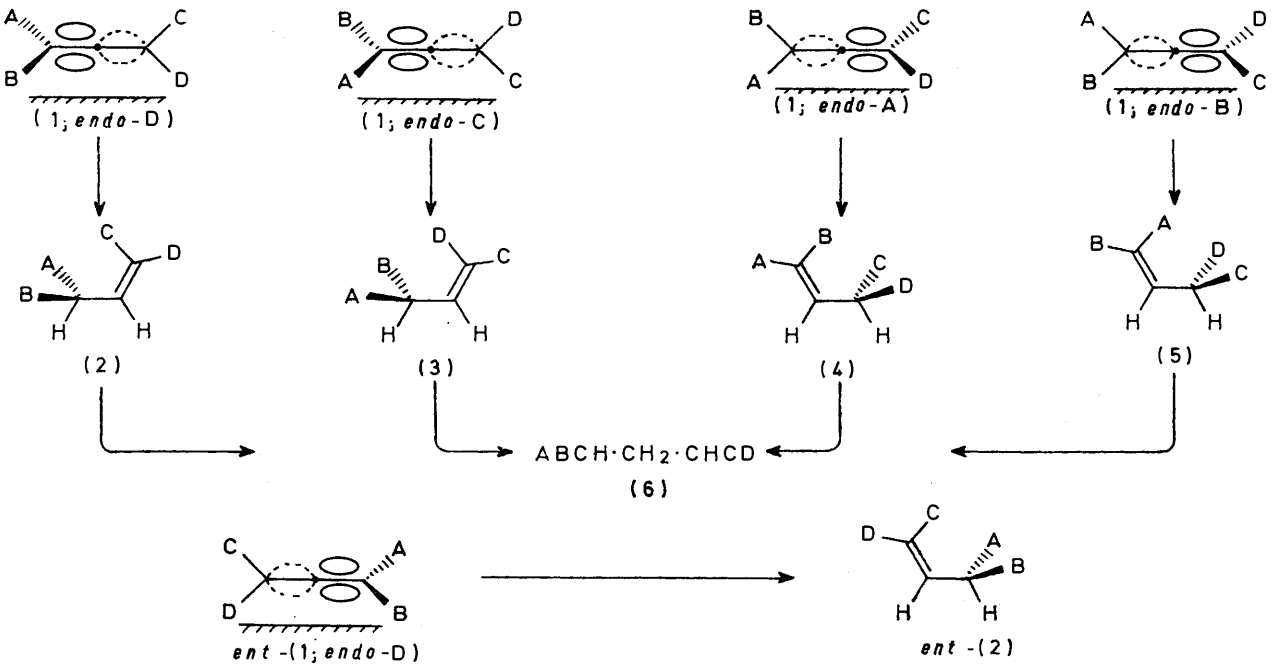
Addition of hydrogen to give a ' half-hydrogenated ' species has long been recognised as an important feature of the mechanism of catalytic hydrogenation.[1,4] In the

[1] *Inter alia* (*a*) R. L. Burwell, jun., *Chem. Rev.*, 1957, **57**, 895; *b*) T. I. Taylor in ' Catalysis,' ed. C. E. Schildknecht, Reinhold, New York, 1957, vol. V, ch. V; (*c*) H. A. Smith, *ibid.*, vol. V, ch. IV; (*d*) G. C. Bond in ' Catalysis by Metals,' Academic Press, London, 1962; (*e*) G. C. Bond and P. B. Wells, *Adv. Catalysis*, 1964, **15**, 91; (*f*) S. Siegel, *ibid.*, 1966, **16**, 123; (*g*) P. N. Rylander, ' Catalytic Hydrogenation over Platinum Metals,' Academic Press, London, 1967; (*h*) R. L. Burwell, jun., *Chem. Eng. News*, 1966, **56**; (*i*) R. L. Burwell, jun., *Accounts Chem. Res.*, 1969, **2**, 289; (*j*) J. J. Rooney, *Chem. in Britain*, 1966, 242.

[2] Kh. H. Balayan, A. A. Petrov, N. A. Borovikova, V. A. Kormer, and T. V. Yakovleva, *J. Gen. Chem. U.S.S.R.*, 1960, **30**, 3217; (*b*) G. F. Hennion and J. J. Sheehan, *J. Amer. Chem. Soc.*, 1949, **71**, 1964; (*c*) G. F. Hennion and C. V. DiGiovanna, *J. Org. Chem.*, 1965, **30**, 3696; (*d*) G. C. Bond and J. Sheridan, *Trans. Faraday Soc.*, 1952, **48**, 658; (*e*) J. H. Wotiz and H. E. Merrill, *J. Amer. Chem. Soc.*, 1958, **80**, 866; (*f*) L. I. Smith and J. S. Swenson, *ibid.*, 1957, **79**, 2962; (*g*) E. F. Meyer and R. L. Burwell, jun., *ibid.*, 1963, **85**, 2877, 2881; (*h*) A. Reiche, A. Grimm, and H. Albrech, *Brennstoff-Chem.*, 1961, **42**, 177.

[3] For a preliminary report see L. Crombie, P. A. Jenkins, D. A. Mitchard, and J. C. Williams, *Tetrahedron Letters*, 1967, 4297.

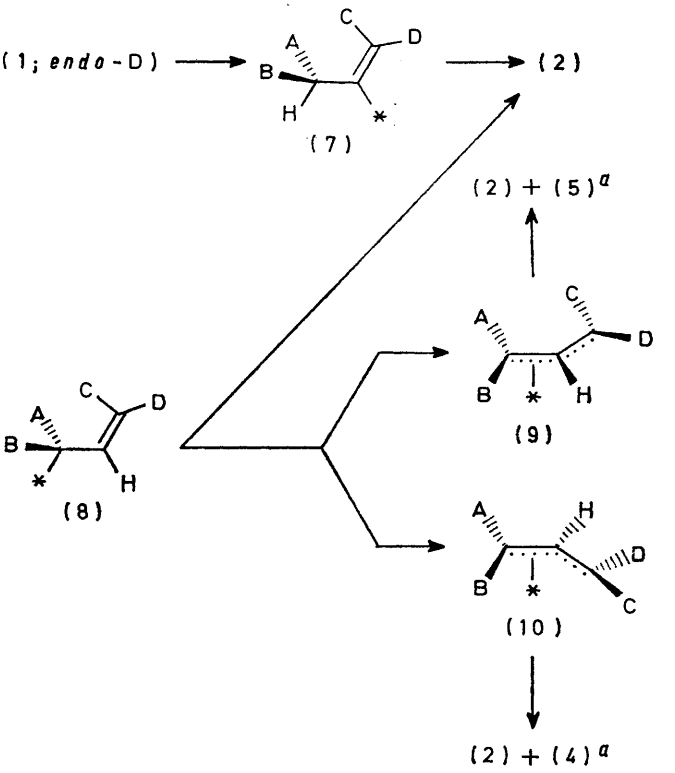
[4] I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 1164.



SCHEME 2 Attitudes of presentation of an allene to the catalyst surface, and their consequences

present case addition of hydrogen to (1; *endo*-D presentation) could lead to the half-hydrogenated species (7) and hence (2). On the other hand, addition to give the alternative (8), in which hydrogen addition has initially occurred at the central carbon, could lead, by flattening of the olefinic bond onto the catalyst surface, to the two π-allylic species [1] (9) and (10). Addition of a second hydrogen could then lead to (2) and the isomeric olefins (4) and (5) (Scheme 3).

In order to study experimentally the semihydrogenation of the allene system, a series of twelve allenes was synthesised: details are given in the Experimental section. Those selected had a variety of substitution patterns and were: 4-methylpenta-1,2-diene (11), buta-2,3-dien-1-ol (12), buta-2,3-dienyl acetate (13), 3-isobutyl-5-methylhexa-1,2-diene (14), 3-methylpenta-1,2-diene (15), 3,4-dimethylpenta-1,2-diene (16), 3,4,4-trimethylpenta-1,2-diene (17), 4-methylhexa-2,3-diene (18), buta-2,3-dienoic acid (19), methyl buta-2,3-dienoate (20), 2-methylbuta-2,3-dienoic acid (21), and methyl 2-methylbuta-2,3-dienoate (22). Consideration of the products formed at the end of the first phase † of catalytic hydrogenation gives only a limited perspective on the events taking place, and in all cases analysis was carried out throughout the reaction. The allenes were hydrogenated (5% Pd–$BaSO_4$) at atmospheric pressure in glass apparatus. Neat liquids were used or, in the case of solid allenes, n-pentane (pretreated with Raney nickel) was employed as solvent. Large samples (*ca.* 2 g) were used, and a few μl were withdrawn at intervals *via* a self-sealing cap and analysed by g.l.c. For each of the twelve allene systems, all the possible hydrogenation products were available in pure form by synthesis, purchase, or isolation from partially hydrogenated mixtures from the allene using preparative g.l.c., followed by identification and characterisation. This allowed



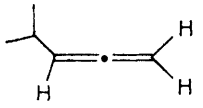
SCHEME 3 π-Allyl formation on the catalyst and its consequences

† The first phase, or stage, is the absorption of 1 mol. equiv. of hydrogen and the second phase the absorption of the second mol. equiv.

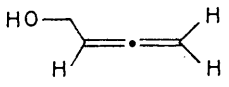
[a] In the chirality of (1) shown, (4) and (5) will be produced as enantiomers of those illustrated.

calibration and ready identification to be made in the analytical g.l.c. experiments. Satisfactory reproducibility was obtained in duplicate analytical tests using a second, different, batch of Pd–$BaSO_4$.

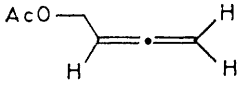
Figures 1—12 * show product-composition diagrams for the absorption of 0—2 mol. equiv. of hydrogen by the allenes mentioned above. Table 1 concentrates on the situation at the absorption of 1 mol. equiv. of hydrogen



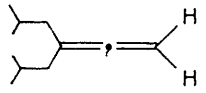
(11) (1; A = Pr^i, B = C = D = H)



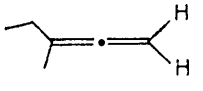
(12) (1; A = CH_2·OH, B = C = D = H)



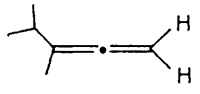
(13) (1; A = CH_2·OAc, B = C = D = H)



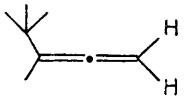
(14) (1; A = B = Bu^t, C = D = H)



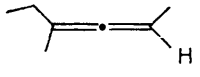
(15) (1; A = Et, B = Me, C = D = H)



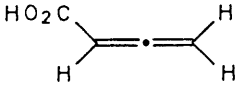
(16) (1; A = Pr^i, B = Me, C = D = H)



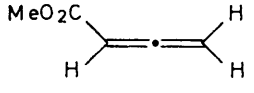
(17) (1; A = Bu^t, B = Me, C = D = H)



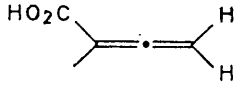
(18) (1; A = Et, B = C = Me, D = H)



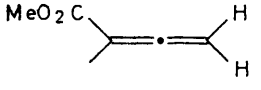
(19) (1; A = CO_2H, B = C = D = H)



(20) (1; A = CO_2Me, B = C = D = H)



(21) (1; A = CO_2H, B = Me, C = D = H)



(22) (1; A = CO_2Me, B = Me, C = D = H)

(end of first stage): the product composition is listed together with three parameters. Selectivity (Sel.) is a measure of the effectiveness of the system in producing olefins, without overhydrogenation giving saturated product, at the end of the first stage. Stereoselectively (Ss.) measures the *Z*/*E*-stereochemical purity of the major (or specified) geometrical isomer produced. Regiospecificity (Rs.) is a measure of the relative amount of hydrogenation occurring at the two double bonds of the allene system.

Figures 1—3 show that semihydrogenation of the three monosubstituted allenes (11)—(13) proceeds with high selectivity (97—100%). The favoured attitude of presentation for 1,2-hydrogenation, as indicated by the products, is the (1; *endo*-B) orientation which has the substituent in the *exo*-position and hydrogen substituents in the *endo*- and parallel positions. Thus the *cis*(*Z*)-olefins (5) are formed in 65—70% yield when A = Pr^i, CH_2·OH, or CH_2·OAc. [In the last case g.l.c. separation difficulties were encountered and (4) and (5) were measured together: the composition was determined at the end of the first stage by n.m.r. methods using the methylene doublets of *cis*- and *trans*-but-2-enyl acetates at τ 5·43 and 5·58, respectively.] The medium-hindered approach (Table 2) with the alkyl group in the parallel position is indicated by the formation of olefins [(2)/(3)] (Table 1) in 24—25% yield in the three examples. In each individual case only a single olefin can be formed by the two degenerate approaches (indicated by the

* Figures 1—18 are available as Supplementary Publication No. SUP 21325 (4 pp.). Figures 6—8 and 10 are also given here, as examples. For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

double numbering) and, from the product composition, taking the statistical factor into account, hydrogenation with the substituent in the parallel position is less than 20% as likely as hydrogenation with an *exo*-substituent. In the case of the 4-methylpenta-1,2-diene system (11), no product (4) from the hindered (1; *endo*-A) approach was observed (Ss. 100%) during the first stage. On the other hand some *trans*-but-2-en-1-ol (4) is formed in the first stage of the hydrogenation of buta-2,3-dien-1-ol and constitutes about 10% of the mixture at the semi-hydrogenation point. N.m.r. analysis shows *ca.* 3% *trans*-but-2-enyl acetate (4) in the corresponding buta-2,3-dienyl acetate system (see stereospecificity figures in Table 1). Formally the isomer (4), found in the first stage of the hydrogenation of these two monosubstituted allenes, could be a product of the hindered (1; *endo*-A) approach occurring to a restricted degree. On the other hand the origin of the *trans*(*E*)-isomers (4) may well be found in limited stereomutation of the thermodynamically less stable *cis*(*Z*)-isomers (5) during the first stage. This process often does not occur, or is very restrained, during the first stage. It sets in apace [5] during the second stage giving a maximum concentration of *trans*-isomer (4) (Table 1) which then declines through hydrogenation.

[5] N. A. Dobson, G. Eglinton, N. Krishnamurti, R. A. Raphael, and R. G. Willis, *Tetrahedron*, 1961, **16**, 16.

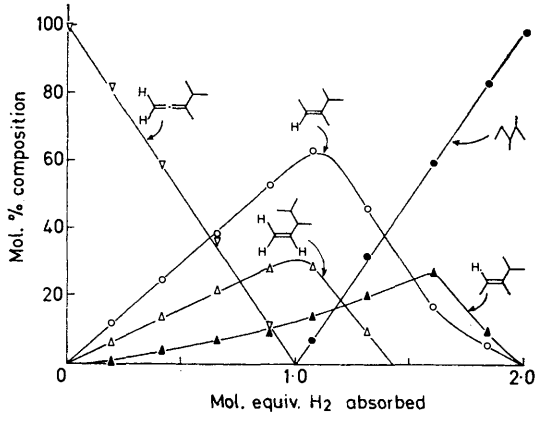


FIGURE 6 Hydrogenation of 3,4-dimethylpenta-1,2-diene (16)

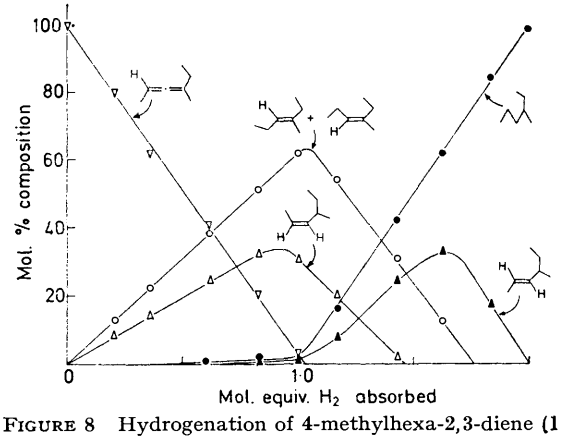


FIGURE 8 Hydrogenation of 4-methylhexa-2,3-diene (18)

Buta-2,3-dienoic acid (19) and its methyl ester (20) constitute two further monosubstituted allene examples (Figures 9 and 10). Selectivity (96 and 99%) and stereospecificity (98 and 97%) are high, and the earlier preparative observation [6] that the semihydrogenation of buta-2,3-dienoic acid gives nearly pure *cis*(*Z*)-crotonic acid is confirmed. Little *Z*–*E* isomerisation occurs until the second stage, when it becomes substantial (32—33% of *trans*-crotonic acid or ester at the maximum). The regiospecificities of the hydrogenations are 100% in each case, *i.e.* no but-3-enoic acid or ester [(2)/(3)] is found.

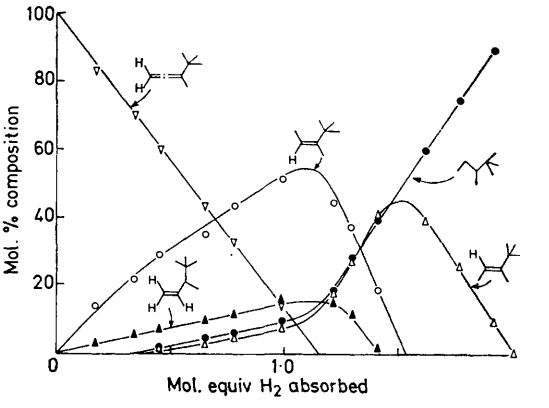


FIGURE 7 Hydrogenation of 3,4,4-trimethylpenta-1,2-diene (17)

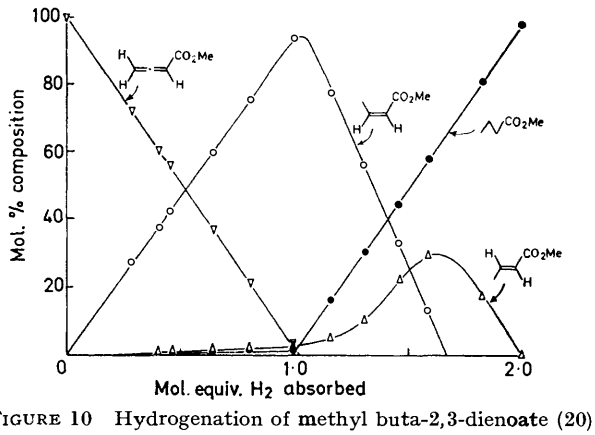


FIGURE 10 Hydrogenation of methyl buta-2,3-dienoate (20)

In view of the result from the three monosubstituted allenes discussed above, where products from a parallel orientation of the substituent are found, some further experiments were undertaken.

It was found that but-3-enoic acid is not hydrogenated preferentially in the presence of buta-2,3-dienoic acid (quite the contrary), so small amounts of the former are not being produced and converted into butanoic acid. The possibility that but-3-enoic acid and ester were rapidly isomerised by the catalyst system was examined. Hydrogenation of but-3-enoic acid alone showed that migration to the conjugated 2-enoic acid occurred but only *trans*-crotonic acid (maximum concentration 20%) and no *cis*-crotonic acid was formed. Since very little

[6] G. Eglinton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 1954, 3197.

TABLE 1

Product analyses at 1 mol. equiv. absorption of hydrogen (end of first stage) *

Allene hydrogenated	G.l.c.[a]	Products (%) at end of first stage: Allene (1)	Olefins (2) (3)	Olefins (4)	Olefins (5)	Sat. (6)	Max. % (4) in Stage 2	Sel.[b] (%)	Ss.[c] (%)	Rs.[d] (%)
(11) (1; A = Pr^i, B = C = D = H) [e]	A	3	←24→	0	70	3	31	97	100	74
(12) (1; A = CH_2·OH, B = C = D = H)	B	0	←25→	10	65	0	40	100	87	75
(13) (1; A = CH_2·OAc, B = C = D = H)	C	3	←24→	3	67	3		97	96	75
(14) (1; A = B = Bu^i, C = D = H)	D	3	←16→	←78→		3		97		83
(15) (1; A = Et, B = Me, C = D = H)	E	1	←17→	29 [f]	52 [f]	1	41	99	64	83
(16) (1; A = Pr^i, B = Me, C = D = H)	F	0	←30→	12 [g]	58 [g]	0	28	100	83	70
(17) (1; A = Bu^t, B = Me, C = D = H)	G	11	←16→	8 [h]	54	11	44	88	87	80
(18) (1; A = Et, B = C = Me, D = H)	H	3	30 2	←62→		3	33 [i]	97	94 [j]	66
(19) (1; A = CO_2H, B = C = D = H)	I	4	←0→	2	90	4	33	96	98	100
(20) (1; A = CO_2Me, B = C = D = H)	J	1	←0→	3	95	1	32	99	97	100
(21) (1; A = CO_2H, B = Me, C = D = H)	K	2	←4→	8	84	2	40	98	91	96
(22) (1; A = CO_2Me, B = Me, C = D = H)	L	2	←5→	6	85	2	51	98	93	95

[a] G.l.c. analytical conditions: silanised Chromosorb W support (60—80 mesh) usually employed; A, silver nitrate (30%) in ethylene glycol (6 ft) in series with dimethylsulpholan (20%) (6 ft, 0°) (hydrogenation also at 0°); B, Carbowax 20M (6 ft), 90°; C, DEGS (5 ft, 56°); *cis*- and *trans*-but-2-enyl acetates could not be separated but n.m.r. analysis shows 67% (5) to 3% (4); D, didecyl phthalate (25%), (10 ft, 70°); E, didecyl phthalate (25%) (10 ft, 20°); F, didecyl phthalate (25%) (10 ft, 25°); G, didecyl phthalate (25%) (10 ft, 20°); H, dimethylsulpholan (20%) (10 ft, 25°) in series with Carbowax 20M (10%) (5 ft, 25°): the geometrical isomers (4) and (5) were not separated; I, converted into methyl esters (CH_2N_2) and analysed as J; J, polyethylene glycol adipate (10%) (5 ft, 50°); K, converted into methyl esters (CH_2N) and analysed as L; L, polyethylene glycol adipate (10%) (5 ft, 45°). For preparative g.l.c. to isolate products, the following systems were used: D, polymetaphenyl ether (30%) (100°); E, didecyl phthalate (40%) (20°); G, didecyl phthalate (50%) (20°); H, silver nitrate (30%) in ethylene glycol. [b] Selectivity (%) = (total yield of olefins/total yield of olefins + saturated product) × 100 (measured at the end of the first stage). [c] Stereoselectivity (%) = (yield of the major *Z*- or *E*-olefin/sum of the yields of the pair of corresponding *Z*- and *E*-olefins) × 100 (measured at the end of the first stage). [d] Regioselectivity (%) = [yield of major olefin structure (both *Z*- and *E*-isomers)/yield of major + minor olefin structures (*Z*- + *E*-isomers)] × 100 (measured at the end of the first stage). [e] Experimental accuracy (*cf.* Figure 1) less than for other allenes (early experiment). [f] Reference samples of (*Z*)- and (*E*)-3-methylpent-2-ene prepared by dehydration of 3-methylpentan-3-ol (toluene-*p*-sulphonic acid), followed by fractionation (spinning band). [g] Reference samples of (*Z*)- and (*E*)-3,4-dimethylpent-2-ene prepared by dehydration of 2,3-dimethylpentan-3-ol followed by fractionation (spinning band). [h] Specimen prepared by dehydrating 2,2,3-trimethylpentan-3-ol (toluene-*p*-sulphonic acid) which gave the *E*-isomer (4) only. [i] In this case maximum % of (3) reached during stage 2. [j] Refers to the formation of (2) in this case.

* The end of the first stage is taken as the cross-over, or meeting, point of the allene and fully saturated product curves on the graph. Theoretically this would be at exactly one mol. equiv. of hydrogen absorbed but imperfect experimental conditions lead to small deviations. Exact figures given deviate marginally from those in our preliminary communication [3] where they were read at the 1 mol. equiv. of hydrogen absorbed point on the graph scale.

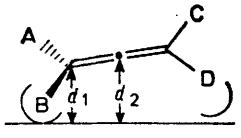
TABLE 2

Measured distances from a plane surface of the carbon termini of the reactant double bond in allenes [a]

Allene model	Orientation of allene to surface: (1; *endo*-D) [b] d_1	(1; *endo*-D) d_2	(1; *endo*-C) d_1	(1; *endo*-C) d_2	(1; *endo*-A) d_1	(1; *endo*-A) d_2	(1; *endo*-B) d_1	(1; *endo*-B) d_2
(11) (1; A = Pr^i, B = C = D = H)	1·55	1·75	1·55	1·75	1·50	2·05	1·35	1·60
(12) (1; A = CH_2·OH, B = C = D = H)	1·55	1·75	1·55	1·75	1·50	2·05	1·35	1·60
(13) (1; A = CH_2·OAc, B = C = D = H)	1·55	1·75	1·55	1·75	1·50	2·05	1·35	1·60
(14) (1; A = B = Bu^i, C = D = H)	1·80	1·90	1·80	1·90	1·45	1·90	1·45	1·90
(15) (1; A = Et, B = Me, C = D = H)	1·80	1·90	1·80	1·90	1·45	1·90	1·45	1·90
(16) (1; A = Pr^i, B = Me, C = D = H)	1·95	1·95	1·95	1·95	1·50	2·20	1·45	1·90
(17) (1; A = Bu^t, B = Me, C = D = H)	2·05	2·10	2·05	2·10	1·65	2·50	1·45	1·90
(18) (1; A = Et, B = C = Me, D = H)	1·80	1·90	2·05	2·40	1·60	2·05	1·60	2·05
(19) (1; A = CO_2H, B = C = D = H)	1·45	1·60	1·45	1·60	1·65	2·45	1·35	1·60
(20) (1; A = CO_2Me, B = C = D = H)	1·45	1·60	1·45	1·60	1·65	2·45	1·35	1·60
(21) (1; A = CO_2H, B = Me, C = D = H)	1·60	1·80	1·60	1·80	1·65	2·45	1·45	1·90
(22) (1; A = CO_2Me, B = Me, C = D = H)	1·60	1·80	1·60	1·80	1·65	2·45	1·45	1·90

[a] Measurements (Å) made using Crystal Structure models (allene double bond 1·31 Å) with inserted van der Waals spokes (hydrogen 1·2, methyl and methylene 2·0, oxygen 1·4 Å). The least hindered orientation at the surface is measured.

[b]



trans-crotonic acid is formed in the first stage, very little but-3-enoic acid could be formed and disposed of by this route. A possibility considered to explain the non-formation of but-3-enoic acid was that the simple 1,2-allene hydrogenation hypothesis was not valid and that a π-allyl species might intervene, ultimately to be hydrogenated giving no but-3-enoic acid (2), only the more stable but-2-enoic acid. However, as shown in Scheme 3, this process would give rise to both *cis*- and *trans*-crotonic acid [(5) and (4)]. Indeed, if the greater

thermodynamic stability of the *trans*-compound were reflected in the π-allyl complex, *trans*-crotonic acid would be the major product: this is contrary to the experimental findings.

The difficulty arises from the fact that the two orientations, (1; *endo*-D) and (1; *endo*-C), in which the carboxy-group occupies the parallel position, appear to involve less catalyst hindrance in the most favourable conformation than the other monosubstituted cases (11)—(13) in which there is a reasonable amount of product from this orientation (Tables 1 and 2). It may be that the crude measurement approach (in the most favourable carboxy-group orientation) underestimates the extent to which the carboxy- or ester group actually hinders the catalyst when in the parallel position. On the other hand, factors other than purely steric may be involved. Thus attempts have recently been made to set up a ' haptophilic series ' to assess the attractive (or repulsive) interactions of substituent groups towards an hydrogenation catalyst.[7] The haptophilicity, $H = f(E) - f(S)$ where E and S represent electronic and steric terms, respectively. It is relevant to the present case that the haptophilicity of $\cdot CH_2 \cdot OH$ is high whereas that of $\cdot CO_2Me$ is low. Nonetheless, the results from all the hydrogenations of monosubstituted allenes are generally explicable by a simple overall 1,2-hydrogenation with products controlled by the relative steric effects involved in the different approaches of the allenes to the catalyst surface.

The symmetrically substituted 1,1-di-isobutylallene (14) is semihydrogenated with high selectivity (97%) and higher regioselectivity (83%) (Figure 4) than the monosubstituted cases (11)—(13). The major olefinic product [(4)/(5)] (78%) is that from attack on the two identical orientations [(1; *endo*-A); (1; *endo*-B)] with the isobutyl groups occupying the *exo*- and *endo*-positions: these are the most sterically accessible orientations (Table 2). Attack involving the remaining two equivalent orientations [(1; *endo*-D); (1; *endo*-C)] with the two isobutyl groups in the parallel positions competes, but is less favoured [16% (2)/(3)].

The 1,1-disubstituted allenes (15)—(17) form a set in which the gradually increasing bulk of one substituent is seen to have its effect on product composition (Figures 5—7). Selectivity was excellent for 3-methylpenta-1,2-diene and 3,4-dimethylpenta-1,2-diene, but was poor (88%) by usual standards for 3,4,4-trimethylpenta-1,2-diene. In the last case the more hindered allene presumably allows olefinic products to compete, to some extent, for catalyst sites during the first stage. An improvement in stereoselectivity could be effected by using Lindlar's catalyst system, but the hydrogenation then terminated when only 1·27 mol. equiv. of hydrogen had been absorbed. In regiospecificity, the hydrogenation of allene (15) is closely similar to that of (14), but in (15) the two major modes of attack [(1; *endo*-A); (1; *endo*-B)] can be differentiated. As might be expected, attack on the orientation with the ethyl group *endo* to the catalyst is less favoured [29% (4)] relative to that with an *endo*-methyl [52% (5)] (Table 1): each orientation has two parallel hydrogens. For allene (16), the product from the *endo*-methyl orientation is increased [58% (5)] whereas that from the *endo*-isopropyl orientation is now still more disfavoured [12% (4)]. The product from the orientation with two substituents in the parallel position [(2)/(3)] is also relatively larger in (16) than in (17). In the case of the 1-methyl-1-t-butylallene 54% of (5) is formed, and only 8% of (4). This trend is thus fully in line with the hypothesis that the relative catalyst hindrance towards the different orientations of the allene is reflected in the composition of the olefinic products. On the other hand, arguments based on olefin (4) carry with them some uncertainty because it constitutes the thermodynamically stable *E*-form in all three cases. The figures given are maximal and, especially for allene (17), could include material originating as (*Z*)-(5) and being stereomutated during the first stage. As seen earlier, this is not an important process in many allene hydrogenations, but the tendency may increase with more strained olefins such as (5) from allene (17). Indeed the low selectivity observed (88%) is evidence that in this case olefin is successfully competing for the catalyst surface. Once this happens, desorption of the ' half-hydrogenated ' olefin species[4] in the first stage brings about stereomutation [(5) ⟶ (4)]. A more thorough investigation of the position can be made by ^{14}C-labelling experiments as indicated in the accompanying paper.

As normally happens, there is substantial stereomutation of the less stable *Z*-olefins (5) to *E* (4) in the second stage (Figures 5—7). The behaviour of the olefins produced from the allene (15), under conditions of uncompeting adsorption onto the catalyst, was therefore studied. *cis*(*Z*)-3-Methylpent-2-ene isomerises to produce nearly 60% of the corresponding *trans*(*E*)-olefin (4) before 0·2 mol. equiv. of hydrogen has been absorbed (Figure 13). In the case of *trans*(*E*)-3-methylpent-2-ene (4) more than 20% of the corresponding *cis*(*Z*)-olefin (5) is formed before 0·2 mol. equiv. of hydrogen has been absorbed (Figure 14). It is clear that the two olefins equilibrate rapidly towards the thermodynamic mixture. In the case of the third olefin produced from the allene (15), 3-methylpent-1-ene, isomerisation occurs to both (*Z*)- and (*E*)-3-methylpent-2-ene, again towards the thermodynamic mixture (Figure 15). Thus the validity of arguments based on product composition reflecting the relative steric effects encountered by the different allene orientations, is contingent upon the hydrogenating allene competitively occupying the catalyst sites much more effectively than the olefinic products. A prerequisite for simple valid deductions is, therefore, that the reactions should have high selectivity. For the allene (17) serious doubts must arise though in this case the conclusions are unaffected even if the 8% of (4) is a stereomutation product arising from (5).

[7] H. W. Thompson and R. E. Naipawer, *J. Amer. Chem. Soc.*, 1973, **95**, 6379.

Figures 11 and 12 provide information on the hydrogenation of two further 1,1-disubstituted allenes, 2-methylbuta-2,3-dienoic acid (21) and its methyl ester (22). Selectivity is high, and the major product in each case is the angelate (5) from the (1; *endo*-B) form of attack (84—85%). A small amount of the product (6—8%) expected to arise from the (1; *endo*-A) attack, which is sterically less favoured (Table 2), is found: the latter mode of hydrogenation thus appears a little more favoured than in the unsubstituted buta-2,3-dienoic acid and ester cases. Small amounts (*ca.* 5%) of the products [(2)/(3)] expected from the (1; *endo*-C), (1; *endo*-D) degenerate approach were found. These were not represented at all in the buta-2,3-dienoic acid and ester cases, but in the present examples attack in this orientation is substantially disfavoured relative to other non-carboxylate 1,1-disubstituted cases such as (14)—(16). The vinyl ester (2)/(3) disappears rapidly after the end of the first stage. Figures 16—18 show the events occurring during the hydrogenation of 2-methylbut-3-enoic (2)/(3), angelic, and tiglic acids. It appears that the angelic ⟶ tiglic acid stereomutation proceeds still more rapidly in the second stage of the allene hydrogenation (Figure 12) than in the hydrogenation of angelic acid alone (Figure 17): this may be due to a catalyst conditioning effect.

One trisubstituted allene (18) was examined in the present work, but difficulty was encountered in separating the *Z*- and *E*-isomers of 3-methylhex-3-ene produced in the hydrogenation (Figure 8): they were therefore estimated together. Together, they represent the products of the (1; *endo*-A) and (1; *endo*-B) approaches of the allene and form 62% of the mixture at the end of the first stage. The (1; *endo*-D) approach, which appears little more hindered than the two approaches above, gives 30% of *cis*(*Z*)-4-methylhex-2-ene (2). Very little (*ca.* 2%) of the more stable *trans*(*E*)-isomer, which would come from the substantially more hindered (1; *endo*-C) approach, is formed. After the end of the first stage, however, large amounts of the latter olefin are formed by stereomutation of the *cis*(*Z*)-isomer. The system has good selectivity and the stereospecificity towards the formation of (2) is good. The results support the importance of allene-catalyst hindrance in determining the composition of the semihydrogenation products.

The allene hydrogenations studied in this work are thus, with one exception, highly selective processes. In other terms, the allene is considerably more strongly adsorbed by the catalyst than its hydrogenation products, which are desorbed from the surface and cannot be competitively readsorbed to any extent until the allene has disappeared. As mentioned earlier, it is assumed that the transition states leading to adsorbed molecules [(2)—(5) in Scheme 2, replacing the H atoms by *] reflect a good deal of the hindrance between unrehybridised allene and the catalyst. The form of the transition state may, however, vary with the different individual allenes and, if in an allene such as (17) it takes on more of the character of the dissociatively adsorbed and rehybridised structure [*cf.* (2*)—(5*)], the unfavourable intramolecular steric interactions of the t-butyl group (A) in (5*) may lead to a lowered population of adsorbed allene molecules, even though they eventually give product (5) in good yield. Such a diminished population would open the way for olefins to compete for hydrogenation sites and lead to lowered selectivity, as observed.

The broad picture reached in this work is thus that the products of the first stage of the hydrogenation are those which would be expected from a consideration of the relative hindrances of the different orientations of the allenes towards the catalyst surface. The conjugated allene acid and ester examples studied also indicate, however, that effects other than steric may become of additional importance in certain cases. Our results are consistent with the simple classical picture [4] of overall *cis*-1,2-hydrogenation, and, as in the following paper, no reasons for invoking π-allyl species as intermediates were found. (They have been invoked to explain the formation of *trans*-cyclononene, which is less stable than the *cis*-, during the hydrogenation of cyclonona-1,2-diene.[8])

EXPERIMENTAL

I.r. data refer to liquid films or paraffin mulls. N.m.r. data refer to solutions in deuteriochloroform.

Hydrogenations.—The allene [solid allene (1 g) in purified n-pentane (10 ml), or liquid allene (3 g) without solvent] and catalyst (0·1 or 0·3 g, respectively) were shaken at constant pressure with hydrogen in a glass hydrogenator. At intervals of *ca.* 0·2 mol. equiv. of hydrogen absorption samples (10 μl) were removed. The samples were diluted with carbon disulphide (100 μl) and used (1 μl) for g.l.c. analysis (flame ionisation detector) to construct the build-up–decline curves (Figures 1—12). Calibration factors were determined and applied for each component.

4-Methylpenta-1,2-diene System (Figure 1).—4-Methylpent-1-yn-3-ol with thionyl chloride gave a mixture (55% yield) of 3-chloro-4-methylpent-1-yne and 3-chloro-4-methylpenta-1,2-diene (Found: C, 61·55; H, 8·1. Calc. for C_6H_9Cl: C, 61·8; H, 7·8%), $\nu_{max.}$ 3322 (·C≡CH), 2347 and 2137 (·C≡C·), and 1965 cm^{-1} (·C=C=C). Treatment with zinc–copper couple [9,10] in ethylene glycol–cyclohexanol at 0°, raising the temperature slowly to 80°, refluxing the allene, and then distilling gave 4-methylpenta-1,2-diene contaminated with 4-methylpent-1-yne (4% by g.l.c.). The latter was removed by treatment with aqueous silver nitrate. Fractionation gave 4-methylpenta-1,2-diene (50 g, 47%), b.p. 65·2—65·5° at 758 mmHg, n_D^{20} 1·4230—1·4235 (Found: C, 87·45; H, 12·1. Calc. for C_6H_{10}: C, 87·75; H, 12·25%), $\nu_{max.}$ 1957 (·C=C=C·), 1692 (overtone), and 842 cm^{-1} (=CH_2) (lit.,[11] b.p. 70°, n_D^{22} 1·4232). Olefins and 2-methylpentane formed in the hydrogenation were obtained from commercial sources.

[8] W. R. Moore, *J. Amer. Chem. Soc.*, 1962, **84**, 3788; G. V. Smith, *J. Catalysis*, 1966, **5**, 152.

[9] G. F. Hennion and J. J. Sheehan, *J. Amer. Chem. Soc.*, 1949, **71**, 1964.

[10] Y. I. Ginsburg, *J. Gen. Chem. U.S.S.R.*, 1945, **15**, 442 (*Chem. Abs.*, 1946, **40**, 4655).

[11] M. Bouis, *Ann. Chim.* (*France*), 1928, **9**, 442.

Buta-2,3-dien-1-ol System (Figure 2).—4-Chlorobut-2-yn-1-ol [12] (128 g) was added to stirred and cooled lithium aluminium hydride (98·4 g) in ether (3·4 l) and the mixture was refluxed (2 h). Work-up gave, on fractional distillation, buta-2,3-dien-1-ol (20 g, 25%), b.p. 57·5—58·5° at 45 mmHg, n_D^{19} 1·4780—1·4796, $\nu_{max.}$ 3344 (OH), 1961 (·C=C=C·), 1709 (overtone), and 851 cm^{-1} (=CH_2) (lit.,[13] b.p. 68—70° at 53 mmHg, n_D^{20} 1·4759). The *1-naphthylurethane* had m.p. 117—118° (Found: C, 75·15; H, 5·8, N, 6·0. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·5; N, 5·85%).

But-3-en-1-ol was made by Grignard reaction from allyl chloride,[14] *cis*-but-2-en-1-ol by semihydrogenation (Lindlar catalyst) of but-2-yn-1-ol, and *trans*-but-2-en-1-ol by reduction of crotonal (sodium borohydride).

Buta-2,3-dienyl Acetate System (Figure 3).—The allene, prepared by acetylation of the above alcohol (acetic anhydride–pyridine at 0°), had b.p. 65·5—66° at 43 mmHg, n_D^{20} 1·4482—1·4488, $\nu_{max.}$ 1692 (·C=C=C·) and 1741 cm^{-1} (C=O). The other components of the hydrogenation system were made similarly.

3-Isobutyl-5-methylhexa-1,2-diene System (Figure 4) (with J. C. Williams).—4-Ethynyl-2,6-dimethylheptan-4-ol, b.p. 83—83·5° at 18 mmHg, n_D^{21} 1·4420 (lit.,[15] b.p. 83—84° at 18 mmHg, n_D^{20} 1·4425), was made (40%) from sodium acetylide and di-isobutyl ketone; $\nu_{max.}$ 3440 (OH), 3300, 2105 (·C≡CH), 1380, and 1361 cm^{-1} (Me_2C). The alcohol was converted [16] into a mixture of 3-chloro-3-isobutyl-5-methylhex-1-yne and 1-chloro-3-isobutyl-5-methylhexa-1,2-diene (77%), b.p. 68—72° at 10 mmHg, n_D^{18} 1·4567, $\nu_{max.}$ 3300, 2090 (·C≡CH), 1940 (·C=C=C·), 1380, and 1360 cm^{-1} (Me_2C). Treatment with zinc–copper couple in ethanol [9] gave *3-isobutyl-5-methylhexa-1,2-diene* (24%), b.p. 63·5—65° at 16 mmHg, n_D^{21} 1·4420 (Found: C, 86·7; H, 13·3. $C_{11}H_{20}$ requires C, 86·7; H, 13·2%), purified by preparative g.l.c. (polymetaphenyl ether; 140°); n_D^{20} 1·4433, $\nu_{max.}$ 1963 and 844 (·C=C=CH_2), 1388, and 1371 cm^{-1} (Me_2C), τ 5·42 (2H, quintet, *J* 3 Hz), *ca.* 8·2 (6H, m), and 9·09 (12H, d, *J* 6 Hz).

The hydrogenation and partial hydrogenation products were separated by preparative g.l.c. on 30% polymetaphenyl ether on Chromosorb P (60—80 mesh) at 100° (10 ft × ⅜ in column), and identified by spectral means. 3-Isobutyl-5-methylhex-1-ene, $\nu_{max.}$ 1642, 992, and 907 cm^{-1} (vinyl), had τ 4·52 (1H, m, C=CH) and 5·10 (2H, m, $C=CH_2$): the remainder of the spectrum integrated for 19 protons. 3-Isobutyl-5-methylhex-2-ene had $\nu_{max.}$ 1655 and 844 cm^{-1} (trisubst. olefin) and τ 4·78 (1H, q of unresolved multiplets, *J* 6·5 Hz, =C*H*Me); the remainder of the spectrum integrated for 21 protons and the olefinic methyl group had τ 8·38 (3H, *J* 6·5 Hz).

3-Methylpenta-1,2-diene System (Figure 5).—Treatment of 3-methylpent-1-yn-3-ol (198 g), below 5°, with concentrated hydrochloric acid (860 ml), calcium chloride (112 g), copper(I) chloride (80 g), and copper bronze (0·7 g) [16] gave 3-chloro-3-methylpent-1-yne (54%), b.p. 53—54° at 130 mmHg, n_D^{20} 1·4319 (lit.,[16] b.p. 53—56° at 128 mmHg, n_D^{25} 1·4302), and 1-chloro-3-methylpenta-1,2-diene (14%), b.p. 74—75° at 130 mmHg, n_D^{20} 1·4762 (lit.,[17] b.p. 68—70° at 100 mmHg). Treatment of 3-chloro-3-methylpent-1-yne (58 g) with zinc–copper couple [from zinc (62 g)] gave 3-methylpenta-1,2-diene (70%), b.p. 70—70·5°, n_D^{24} 1·4438 (lit.,[18] b.p. 70—70·5°, n_D^{20} 1·4560), g.l.c. pure (didecyl phthalate; 35°), $\nu_{max.}$ 1964 and 850 cm^{-1}, τ 5·49 (2H, sextet, *J* 3·6 Hz), 8·08 (2H, triple quartet, *J* 6·6 Hz), 8·34 (3H, t, *J* 3·6 Hz), and 9·01 (3H, t, *J* 6·6 Hz).

Partial hydrogenation of the allene and preparative g.l.c. (40% didecyl phthalate; 20°) gave the four possible products. 3-Methylpent-1-ene, n_D^{18} 1·3846 (lit.,[19] 1·3842), had $\nu_{max.}$ 1642, 998, and 908 cm^{-1}, identical with an authentic spectrum (A.P.I.[20] No. 707); n.m.r. data confirmed the identity. 3-Methylpent-*cis*-2-ene, n_D^{20} 1·4018, had $\nu_{max.}$ 1675 and 826 cm^{-1} and the *trans*-isomer, n_D^{20} 1·4048, $\nu_{max.}$ 1670 and 828 cm^{-1}. The n.m.r. spectrum of each contained 1H multiplets, τ 4·5—5·0, with the remainder of the spectrum integrating for 11 protons. It has been reported [21] that *trans*-coupling constants for protons separated by more than three bonds are always greater than *cis*. The *cis*-olefin spectrum contained a quartet of triplets at τ 4·91 consistent with the olefinic proton being *trans* to a methylene (*cis*-coupling too small to be resolved). The *trans*-olefin spectrum contained a quartet of quartets indicating this to have the olefinic proton *trans* to a methyl. To confirm assignments 3-methylpentan-3-ol was dehydrated (toluene-*p*-sulphonic acid) and the 3-methylpent-2-enes were separated by spinning-band distillation. Stereospecific synthesis shows that the isomer of lower b.p. is the *cis*.[22] 3-Methylpent-*cis*-2-ene thus obtained had b.p. 67·8—68·1°, n_D^{20} 1·4022 (lit.,[19] 1·4016) and the *trans*-isomer, b.p. 70·0—70·5°, n_D^{20} 1·4048 (lit.,[19] 1·4050). These were identified (g.l.c. and spectroscopy) with the partial hydrogenation products. The i.r. spectrum of our 3-methylpent-*cis*-2-ene agreed with the A.P.I. spectrum (721) and that of our *trans*-isomer with A.P.I. 720 (*i.e.* with configurations on the A.P.I. spectra reversed as suggested by Cornforth *et al.*[22]).

3,4-Dimethylpenta-1,2-diene System (Figure 6).—3-Chloro-3,4-dimethylpent-1-yne (54%), b.p. 72—75° at 105 mmHg, n_D^{22} 1·4436 (lit.,[16] b.p. 66—68° at 100 mmHg, n_D^{25} 1·440), was prepared as in the previous example and converted by similar methods into 3,4-dimethylpenta-1,2-diene, b.p. 89—89·5°, n_D^{20} 1·4342 (lit.,[18] b.p. 90—91°, n_D^{20} 1·4560), $\nu_{max.}$ 1958, 845 (·C=C=CH_2), 1383, and 1370 cm^{-1} (Me_2C), τ 5·43 (2H, quintet, *J* 2·9 Hz, ·CHMe·C=C=CH_2), *ca.* 8·0 (1H, m, Me_2CH·C=C=CH_2), 8·30 (3H, t, *J* 2·9 Hz, CH_3·C=C=CH_2), and 8·97 (6H, d, *J* 6·0 Hz, Me_2CH).

Partial hydrogenation and preparative g.l.c. gave all the possible hydrogenation products, separated by a 50% silver nitrate–ethylene glycol column at 20°. 2,3-Dimethylpentane, n_D^{20} 1·3920 (lit.,[19] 1·39196), had i.r. data identical with those of an authentic sample (A.P.I. No. 658).[20] 3,4-Dimethylpent-1-ene, n_D^{20} 1·3998 (lit.,[19] 1·3995) was identified by i.r. (994 and 913 cm^{-1}) and n.m.r. [τ 5·10 (2H, m, vinyl) and 9·11 (6H, d, *J* 7·8 Hz, Me_2CH)] spectra. The two remaining olefinic samples, *cis*- and *trans*-3,4-

[12] W. J. Bailey and G. Fujiwara, *J. Amer. Chem. Soc.*, 1955, **77**, 165.
[13] W. J. Bailey and C. R. Pfeifers, *J. Org. Chem.*, 1955, **20**, 1337.
[14] M. G. Etlinger and J. E. Hogkins, *J. Amer. Chem. Soc.*, 1955, **77**, 1831.
[15] M. F. Ansell, J. W. Hancock, and W. J. Hickinbottom, *J. Chem. Soc.*, 1956, 911.
[16] G. F. Hennion and A. P. Boisselle, *J. Org. Chem.*, 1961, **26**, 725.
[17] T. Favorskaja and Z. Zakharova, *Zhur. obshchei Khim.*, 1940, **10**, 446; *Chem. Zentr. II*, 1940, 1567.
[18] M. Bertrand, *Bull. Soc. chim. France*, 1956, 461.
[19] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Brown, and G. L. Pimental, 'Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds,' American Petroleum Institute, Carnegie Press, Pittsburgh, 1953.
[20] American Petroleum Institute Research Project 44 (Catalogue of Infrared Spectral Data).
[21] R. R. Fraser, *Canad. J. Chem.*, 1960, **38**, 549.
[22] J. W. Cornforth, R. M. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 1959, 112.

dimethylpent-2-ene, were also prepared for reference by spinning-band fractionation of the mixture obtained by dehydrating 2,3-dimethylpentan-3-ol with toluene-*p*-sulphonic acid. N.m.r. data supported the structures but did not allow unequivocal assignment of geometry. The *cis*-isomer, b.p. 89·5°, n_D^{25} 1·4079 (lit.,[19] 1·4078), was identified by i.r. comparison with A.P.I. spectrum No. 1796 and the *trans*-isomer, b.p. 91·5°, n_D^{25} 1·4101 (lit.,[19] 1·4101), by comparison with A.P.I. spectrum No. 1904.[20] The correctness of the *cis*- and *trans*-assignments was tested by catalytic addition (Pd–$BaSO_4$) of *ca.* 0·5 mol. equiv. of hydrogen to each olefin. *cis*-3,4-Dimethylpent-2-ene gave *trans*- (40·5%), unchanged *cis*- (8·5%), and 2,3-dimethylpentane (51·0%). *trans*-3,4-Dimethylpent-2-ene gave unchanged *trans*- (41·7%), *cis*- (8·5%), and 2,3-dimethylpentane (50·8%). The olefins are thus correctly assigned with respect to their thermodynamic stabilities.

3,4,4-*Trimethylpenta*-1,2-*diene System* (Figure 7).—3,4,4-Trimethylpent-1-yn-3-ol [23] was treated with the hydrochloric acid reagent (above) to give 3-*chloro*-3,4,4-*trimethylpent*-1-*yne* (18%), glassy crystals, m.p. 92·5—94° (from methanol–water) (Found: C, 66·4; H, 9·15, Cl, 24·8. $C_8H_{13}Cl$ requires C, 66·4; H, 9·0; Cl, 24·6%), $\nu_{max.}$ (CCl_4) 3302, 2115, 1390, and 1365 cm^{-1}, τ 7·49 (1H, s), 8·22 (3H, s), and 8·84 (9H, s). The filtrate was distilled to give 1-chloro-3,4,4-trimethylpenta-1,2-diene (22%), b.p. 90—92°, n_D^{15} 1·4652 (lit.,[24] b.p. 91—92° at 110 mmHg), $\nu_{max.}$ 1963, 824, 1380, and 1368 cm^{-1}, τ 4·10 (1H, q, *J* 2·1 Hz), 8·22 (3H, d, *J* 2·1 Hz), and 8·89 (9H, s). Treatment of 1-chloro-3,4-trimethylpenta-1,2-diene with zinc–copper couple gave 3,4,4-*trimethylpenta*-1,2-*diene* (42%), b.p. 105—106°, n_D^{21} 1·4389 (Found: C, 87·25; H, 12·6. C_8H_{14} requires C, 87·2; H, 12·8%), $\nu_{max.}$ 1960, 840, 1392, and 1365 cm^{-1}, τ 5·44 (2H, q, *J* 3·1 Hz), 8·31 (3H, t, *J* 3·1 Hz), and 8·95 (9H, s). The same reaction, using 3-chloro-3,4,4-trimethylpent-1-yne, gave 3,4,4-trimethylpenta-1,2-diene (36%), b.p. 105—100°, n_D^{24} 1·4378, identical with the above.

The three olefinic semihydrogenation products were isolated by preparative g.l.c. (50% didecyl phthalate; 20°). 3,4,4-Trimethylpent-1-ene was recognised from spectral evidence: $\nu_{max.}$ 1642, 998, and 912 cm^{-1}, τ 5·15 (2H, m) and 4·38 (1H, m). It had n_D^{20} 1·4123 (lit.,[20] 1·4120). The n.m.r. spectra of the other two mono-olefins each had 1H multiplets at τ 4·5—5·0 with the remainder integrating for 15H. 3,4,4-Trimethylpent-*trans*-2-ene was recognised by the quartet of quartets at τ 4·76; the *cis*-isomer had a quartet at τ 4·95 (olefinic proton *trans* to t-butyl). Further evidence for the geometry is the *cis* ⟶ *trans* conversion occurring readily in the second stage of the hydrogenation reaction, the change being in the direction of thermodynamic stabilities (compression in models). Preparation of a comparison specimen of 3,4,4-trimethylpent-2-ene by dehydration of 2,2,3-trimethylpentan-3-ol [25] gave the *trans*-isomer only, b.p. 112°, identical with the above specimen. The following i.r. correlation was also noted. In 3-methylpent-*cis*-2-ene an absorption at 1021 is shifted to 998 cm^{-1} in the *trans*-isomer. A similar shift (1021 ⟶ 993 cm^{-1}) was observed for the *cis*- and *trans*-3,4-dimethylpent-2-enes. The 3,4,4-trimethylpent-2-enes, assigned *cis*- and *trans*-configurations above, showed the shift from 1011 to 994 cm^{-1}. The saturated product, 2,2,3-trimethylpentane, n_D^{20} 1·4031 (lit.,[20] 1·40295), had the expected i.r. spectrum (A.P.I. 576) and n.m.r. data.

4-*Methylhexa*-2,3-*diene System* (Figure 8).—3-Bromo-3-methylpent-1-yne, b.p. 47·5—48° at 43 mmHg, n_D^{22} 1·4718 (lit.,[26] b.p. 22° at 12 mmHg, n_D^{19} 1·4695) was prepared (47%) by treating 3-methylpent-1-yn-3-ol with phosphorus tribromide. The bromo-compound with methylmagnesium bromide gave 4-methylhexa-2,3-diene, b.p. 35—35·5° at 75 mmHg, n_D^{17} 1·4414 (lit.,[27] b.p. 35° at 75 mmHg, n_D^{18} 1·4410). The allene showed a single peak on g.l.c. (10% didecyl phthalate; 60°) and had $\nu_{max.}$ 1968 and 890 cm^{-1}, τ 4·99 (1H, m), 8·07 (2H, dq, *J* 2·4 and 7·2 Hz), 8·32 (3H, d, *J* 2·4 Hz), 8·48 (3H, d, *J* 6·6 Hz), and 9·01 (3H, t, *J* 7·2 Hz).

The partial hydrogenation products were separated by preparative g.l.c. on 30% silver nitrate–ethylene glycol. 4-Methylhex-*cis*-2-ene, n_D^{20} 1·4024 (lit.,[20] 1·4024) was recognised spectrally ($\nu_{max.}$ 715 cm^{-1}; olefinic 2H signal near τ 4·8). Its i.r. spectrum was identical with A.P.I. spectrum No. 2666.[20] 4-Methylhex-*trans*-2-ene, n_D^{20} 1·4021 (lit.,[20] 1·4023), $\nu_{max.}$ 1678 and 970 cm^{-1}, with an olefinic 2H signal near τ 4·6, had an i.r. spectrum identical with A.P.I. No. 1897. Two unresolved components were present in the third mono-olefinic fraction, $\nu_{max.}$ 1670 and 855 cm^{-1}. Comparison with i.r. spectra, A.P.I. Nos. 1816 and 1898 showed that the fraction was a mixture of 3-methylhex-*cis*- and -*trans*-3-enes. The 1H triplet of partly resolved multiplets near τ 4·88 accords with this conclusion. The mixture had n_D^{20} 1·4112 (lit.,[20] *cis*-isomer 1·4123, *trans*- 1·410).

Buta-2,3-*dienoic Acid System* (Figure 9).—But-3-ynoic acid (prepared by chromic acid oxidation of but-3-yn-1-ol) had m.p. 83—84° (lit.,[28] 83—83·5°). Treatment with 18% potassium carbonate solution at 40° for 2·5 h, gave buta-2,3-dienoic acid (71%), m.p. 63—64° (lit.,[6] 65—66°), $\nu_{max.}$ 1958, 1926, 865 (·C=C=CH_2), and 1690 cm^{-1} (CO_2H). But-3-enoic acid, b.p. 71—72° at 14 mmHg, n_D^{20} 1·4320 (lit.,[29] b.p. 77·5° at 19 mmHg, n_D^{20} 1·42386), was made by carboxylation of allylmagnesium bromide (cyclic reactor);[30] $\nu_{max.}$ 1710 (CO_2H), 1640, 992, and 925 cm^{-1} (·CH=CH_2). But-*cis*-2-enoic acid was prepared from but-2-ynoic acid by semihydrogenation (5% Pd–$BaSO_4$) and had b.p. 69° at 14 mmHg, n_D^{20} 1·4450, $\nu_{max.}$ 1700 (CO_2H), 1651, and 715 cm^{-1} (*cis*-CH=CH·). But-2-ynoic acid was prepared from prop-2-ynylmagnesium bromide (cyclic reactor) [30] by carboxylation and had m.p. 75—76° (lit.,[6] 75—76°), $\nu_{max.}$ 2250 (·C≡C·) and 1700 cm^{-1} (CO_2H). But-*trans*-2-enoic acid was commercial material.

Methyl Buta-2,3-*dienoate System* (Figure 10).—Despite reports of failure,[6] buta-2,3-dienoic acid can be esterified with ethereal diazomethane if the latter is standardised and used in stoicheiometric amount at −80°. *Methyl buta*-2,3-*dienoate* had b.p. 61·5—62·5° at 56 mmHg, n_D^{18} 1·4639 (Found: C, 61·0; H, 6·35. $C_5H_6O_2$ requires C, 61·2; H, 6·15%), $\nu_{max.}$ 1970, 1945, 860 (·CH=C=CH_2), and 1715 cm^{-1} (CO_2Me). The other esters required were prepared by esterification with diazomethane.

[23] R. A. Raphael, 'Acetylenic Compounds in Organic Synthesis,' Butterworth, London, 1957; W. J. Hickinbottom, A. A. Hyatt, and M. B. Sparke, *J. Chem. Soc.*, 1954, 2529.
[24] I. A. Favorskaja, *Zhur. obshchei Khim.*, 1948, **18**, 52 (*Chem. Abs.*, 1948, **42**, 4905d).
[25] F. C. Whitmore and K. C. Laughlin, *J. Amer. Chem. Soc.*, 1932, **54**, 4011.
[26] Y. Pasternak, *Bull. Soc. chim. France*, 1963, 1719.
[27] Y. Pasternak and M. Delepine, *Compt. rend.*, 1962, **255**, 3429.
[28] I. Heilbron, E. R. M. Jones, and F. Sondheimer, *J. Chem. Soc.*, 1949, 604.
[29] G. H. Jeffrey and A. I. Vogel, *J. Chem. Soc.*, 1948, 658.
[30] J. H. Wotiz and R. J. Palchak, *J. Amer. Chem. Soc.*, 1951, **73**, 1971; K. W. Greenlee, personal communication.

2-Methylbuta-2,3-dienoic Acid System (Figure 11). (with J. C. WILLIAMS).—The Grignard reagent from 1-bromobut-2-yne (cyclic reactor), on carboxylation, gave *2-methylbuta-2,3-dienoic acid* (22%), m.p. 70—70·5° (Found: C, 61·0; H, 6·1. $C_5H_6O_2$ requires C, 61·2; H, 6·15%), $\nu_{max.}$ 1918, 870 (·C=C=CH_2), and 1695 cm^{-1} (unsat. acid). 2-Methylbut-*trans*(*E*)-2-enoic (tiglic) acid was of commercial origin. Addition of bromine and dehydrohalogenation gave 3-bromo-2-methylbut-*cis*(*E*)-2-enoic acid (3-bromoangelic acid), m.p. 91—93° (lit.,[31] 92—94·5°), $\nu_{max.}$ 1710 and 1660 cm^{-1}, which on treatment with 9% sodium amalgam gave 2-methylbut-*cis*(*Z*)-2-enoic (angelic) acid (48%), m.p. 43—44° (lit.,[31] 44—46°), $\nu_{max.}$ 1695, 1660, and 798 cm^{-1}. Carboxylation of but-2-enylmagnesium bromide (cyclic reactor) gave 2-methylbut-3-enoic acid (34%), b.p. 82—84° at 25 mmHg, n_D^{24} 1·4244 (lit.,[32] b.p. 94° at 30 mmHg, n_D^{20} 1·4226), $\nu_{max.}$ 1700, 1642, 995, and 930 cm^{-1}. The sample of 2-methylbutyric acid was made by hydrogenation of the latter.

Methyl 2-Methylbuta-2,3-dienoate System (Figure 12).—Esters were made by esterification with diazomethane. Methyl 2-methylbut-2,3-dienoate had b.p. 47·5—50° at 22 mmHg, $n_D^{24\cdot5}$ 1·4631, $\nu_{max.}$ 1960, 1920, 850 (·C=C=CH_2), and 1700 cm^{-1} (CO_2Me).

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[31] R. E. Buckles and G. V. Mock, *J. Org. Chem.*, 1950, **15**, 680.
[32] J. F. Lane, J. D. Roberts, and W. G. Young, *J. Amer. Chem. Soc.*, 1944, **66**, 543.