

Reduction of Allenes and Acetylenes by Catalytic and Chemical Methods: 'Molecular Queueing' Effects in Competitive Hydrogenation

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Reductions of but-2-ynoic, but-3-ynoic, and buta-2,3-dienoic acid have been studied over the complete range, but with special attention to semi-reduction. Similar results are reported for but-2-yn-1-ol, but-3-yn-1-ol, and buta-2,3-dien-1-ol. Heterogeneous catalytic (Lindlar Pd, Pd-BaSO₄, Pt-C, Rh-C, and a Raney-type Ni), homogeneous catalytic [Rh(PPh₃)₃Cl and Pt-SnCl₂ complex], and chemical reductants (Zn-Cu couple, CrSO₄, and di-imide) have been employed for each of the six substrates: selectivities, stereoselectivities, and regioselectivities are reported and compared. Various competitive hydrogenations have been examined. In the case of a but-3-ynoic-but-2,3-dienoic acid system (Pd catalyst), 'molecular queueing' among five unsaturated species is observed.

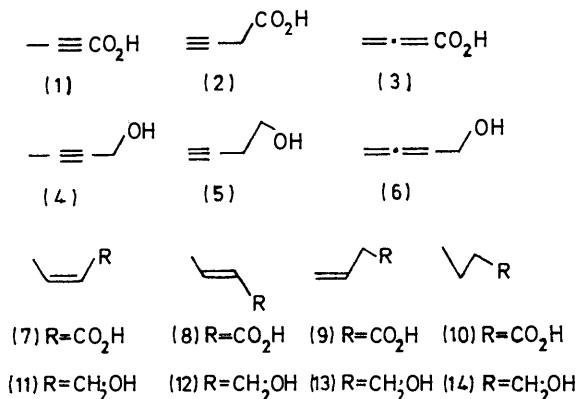
IN connection with work on allene hydrogenation,^{1,2} the catalytic and chemical reductions of six substrates have been investigated comparatively. These were the three isomeric acids (1)—(3) and the three isomeric alcohols (4)—(6). Each set consists of an internal and a terminal acetylene together with the related allene; the possible hydrogenation products are (7)—(14).

The hydrogenation systems involved heterogeneous catalysts (Lindlar Pd used without quinoline, Pd-BaSO₄, Pt-C, Rh-C, and a Raney-type Ni), homogeneous catalysts [Rh(PPh₃)₃Cl and Pt-SnCl₂ complex] and chemical systems (Zn-Cu couple, CrSO₄, and di-imide). The progress of each hydrogenation was followed by g.l.c. analysis throughout the reaction, and for each hydrogenation a full graphical presentation is available.† Tables 1 and 2 summarise the situation with regard to product composition at the end of the first stage (*i.e.* after absorption of 1 mol. equiv. of hydrogen). Also included are figures for selectivity, stereoselectivity, maximum *trans*-content attained in the second stage (an indicator of the stereomutating ability during reduction of the *cis*-olefins) and, for allenes, regioselectivity.

Of the five heterogeneous catalysts employed, the two palladium catalysts showed uniformly high selectivity, followed by nickel: the performance of the latter varies and it was rather poor when terminal acetylenes and α -acetylenic acids were substrates. Both platinum and rhodium were poor catalysts from a selectivity point of view. There has been some debate on the relative effectiveness of these two metals,^{3,4} but comparison

† These are obtainable for the reductions in Tables 1 and 2, as well as for the competitive hydrogenations mentioned, and are deposited as Supplementary Publication No. SUP 21326. For details of Supplementary Publications see Notice to Authors No. 7, in *J.C.S. Perkin I*, 1974, Index issue.

may not be very useful without close definition of substrate structure. Thus rhodium shows a poorer selectivity towards terminal acetylenes than towards di-substituted acetylenes and towards allenes. Lindlar palladium, followed by nickel, gave the best stereoselectivities, higher figures being generally obtained with the



alcohols than the acids. All the heterogeneous catalysts caused *cis*→*trans* stereomutation during the second stage: this was particularly marked in the case of palladium,⁵ and to a lesser extent, nickel, but small in the case of platinum. Some double bond migration during the second stage was also noted in the Lindlar-catalysed

¹ L. Crombie, P. A. Jenkins, and D. A. Mitchard, *J.C.S. Perkin I*, 1975, 1081.

² L. Crombie, P. A. Jenkins, and J. Roblin, preceding paper.
³ G. C. Bond, G. Webb, P. B. Wells, and J. M. Winterbottom, *J. Catalysis*, 1962, **1**, 74.

⁴ L. K. Freidlin and Y. Y. Kaup, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1964, **12**, 2146 (*Chem. Abs.*, 1965, **62**, 766).

⁵ N. A. Dobson, G. Eglinton, M. Krishnamurti, R. A. Raphael, and R. G. Willis, *Tetrahedron*, 1961, **18**, 16.

hydrogenation of but-3-yn-1-ol where up to 9% of but-*trans*-2-en-1-ol was formed. It was absent at the semi-hydrogenation point and must arise from but-3-en-1-ol.

Towards buta-2,3-dienoic acid, the regioselectivity of Lindlar palladium is virtually exclusive for the production of but-2-enoic acid, and other heterogeneous systems

dienoic acid was hydrogenated much faster than but-2-ynoic acid (see Figure 1 for Pd-BaSO₄). For the platinum and rhodium catalysts the curves show much less restrained butyric acid production in the first stage, and some but-3-enoic acid also appeared and disappeared. When buta-2,3-dienoic acid and but-3-ynoic acid were

TABLE 1
Semi-reduction of but-2-ynoic, but-3-ynoic, and buta-2,3-dienoic acids

		Time	Residual substrate	(7) <i>cis</i>	(8) <i>trans</i>	(9) vinyl	(10) sat.	Sel. ^a	Ss. ^a	Rs. ^a	Max. <i>trans</i> (stage 2)
Lindlar Pd											
MeC≡C·CO ₂ H	(1)	<i>b</i>	1	96	2	0	1	99	98		16
HC≡C·CH ₂ ·CO ₂ H	(2)	<i>b</i>	2	96	0	0	2	98			0
H ₂ C=C=CH·CO ₂ H	(3)	<i>b</i>	1	93	5	0	1	99	95	100	27
10% Pt-C											
MeC≡C·CO ₂ H	(1)	<i>b</i>	21	54	4	0	21	73	93		8
HC≡C·CH ₂ ·CO ₂ H	(2)	<i>b</i>	15	0	0	70	15	82			0
H ₂ C=C=CH·CO ₂ H	(3)	<i>b</i>	21	49	4	7	21	74	92	88	6
10% Rh-C											
MeC≡C·CO ₂ H	(1)	<i>b</i>	28	39	4	0	28	61	91		6
HC≡C·CH ₂ ·CO ₂ H	(2)	<i>b</i>	29	0	0	42	29	59			0
H ₂ C=C=CH·CO ₂ H	(3)	<i>b</i>	20	53	4	3	20	75	93	95	9
Raney Ni (Nicat 101)											
MeC≡C·CO ₂ H	(1)	<i>b</i>	11	74	4	0	11	88	95		14
HC≡C·CH ₂ ·CO ₂ H	(2)	<i>b</i>	17	0	0	66	17	80			0
H ₂ C=C=CH·CO ₂ H	(3)	<i>b</i>	0	85	4	11	0	100	96	89	24
Rh(PPh ₃) ₃ Cl											
MeC≡C·CO ₂ H	(1)	<i>b</i>	21	58	0	0	21	73	100		0
HC≡C·CH ₂ ·CO ₂ H	(2) ^e	<i>b</i>	12	0	0	53	12	82			0
H ₂ C=C=CH·CO ₂ H	(3)		Complex formed								
Pt-SnCl ₂											
MeC≡C·CO ₂ H	(1)	<i>b</i>	24	46	6	0	24	68	88		10
HC≡C·CH ₂ ·CO ₂ H	(2)	<i>b</i>	14	0	6	66	14	84			6
H ₂ C=C=CH·CO ₂ H	(3)		Incomplete ^d								
Zn-Cu couple											
MeC≡C·CO ₂ H	(1)	4 h ^e	0	89	11	0	0	100	89 ^g		
		48 h	0	89	11	0	0	100	89 ^g		
HC≡C·CH ₂ ·CO ₂ H	(2)	1.1 h ^e	0	0	10	90	0	100	100 ^h		
		60 h	0	0	100	0	0	100	100 ^h		
H ₂ C=C=CH·CO ₂ H	(3)	1.9 h ^{e,f}	0	0	21	79	0	100	100 ^h	79	
		48 h	0	0	100	0	0	100	100 ^h	100	
		120 h	0	0	97	0	3	97	100 ^h	100	
Di-imide											
MeC≡C·CO ₂ H	(1)	2.7 h	40	20	0	0	40	33	100		
HC≡C·CH ₂ ·CO ₂ H	(2)	1.5 h	36	0	0	28	36	44			
H ₂ C=C=CH·CO ₂ H	(3)	0.25 h	22	20	6	31	22	83	77	54	

^a For definitions see ref. 1. ^b Data measured at the cross-over or junction point of the substrate and saturated product curves (normally very close to '1 mol equiv. of hydrogen absorbed' on the scale). An alternative presentation, analysing the situation at the disappearance point of the substrate, does not lead to differences in the broad interpretation. ^c Buta-2,3-dienoic acid (23%) found and hydrogenation ceased at 0.8 mol. equiv. H₂ uptake. ^d But-3-ynoic acid noted in early stages with lesser amounts of but-*cis*-2-, but-*trans*-2-, and but-3-enoic acids and a little butyric acid. ^e Substrate just disappeared. ^f But-3-ynoic acid noted in first few min.; all disappeared after 0.5 h. ^g Stereospecificity towards production of *cis*-olefin. ^h Stereospecificity towards production of *trans*-olefin.

also show high regioselectivity. In the case of buta-2,3-dien-1-ol however, the regioselectivity is diminished (64—72%), rhodium giving the highest figure (83%) (*cf.* ref. 1).

Sequential catalytic hydrogenation of the unsaturated functions in undeca-1,7-diyne has been reported earlier⁵ and some competitive hydrogenations were undertaken to see if useful intermolecular selectivity could be attained among compounds (1)—(6). Buta-2,3-dienoic acid and but-3-ynoic acid in admixture were hydrogenated at fairly comparable rates over platinum on carbon. On the same catalyst, or over Rh-C or Pd-BaSO₄, buta-2,3-

hydrogenated together over palladium on barium sulphate however, a remarkable pattern of selectivity emerged, which may be described as 'molecular queueing';⁶ it is illustrated in Figure 2. But-3-ynoic acid is hydrogenated to but-3-enoic acid with buta-2,3-dienoic acid surviving largely unchanged: only limited amounts of but-*cis*-2-enoic acid are formed. As soon as all the terminal acetylene has hydrogenated, the allenic acid is hydrogenated mainly to but-*cis*-2-enoic acid: meanwhile but-3-enoic acid competes poorly for catalyst sites and remains largely unchanged. With disappearance of the allene, but-3-enoic acid is rapidly hydrogenated whilst but-*cis*-2-enoic acid remains largely unchanged.

⁵ L. Crombie and P. A. Jenkins, *Chem. Comm.*, 1969, 394.

On hydrogenation of the last of the but-3-enoic acid, the but-*cis*-2-enoic acid is hydrogenated rapidly, and much more rapid stereomutation, hitherto a subdued process, begins. But-*cis*-2-enoic acid is more rapidly hydrogenated than the *trans*-acid and the latter is the last unsaturated species to be hydrogenated. The 'molecular queue' thus involves a sequence of five unsaturated

was encountered in initiating reaction with the butynoic acids in benzene. Both towards the acetylenic acids and alcohols selectivities were poor, although *cis*-stereospecificity was excellent. Poor selectivities have been noted with this catalyst in benzene with respect to other systems.⁹ The hydrogenation of but-3-ynoic acid was accompanied by isomerisation to buta-2,3-dienoic acid

TABLE 2
Semi-reduction of but-2-yn-1-ol, but-3-yn-1-ol, and buta-2,3-dien-1-ol

		Time	Residual substrate	(11) <i>cis</i>	(12) <i>trans</i>	(13) vinyl	(14) sat.	Sel. ^a	Ss. ^a	Rs. ^a	Max. <i>trans</i> (stage 2) ^a
Lindlar Pd											
	MeC≡C·CH ₂ ·OH	(4)	<i>b</i>	0	100	0	0	100	100		40
	HC≡C·CH ₂ ·CH ₂ ·OH	(5)	<i>b</i>	0	100	0	0	100			
	H ₂ C=C=CH·CH ₂ ·OH	(6)	<i>b</i>	0	63	4	33	100	94	67	26
10% Pd-BaSO ₄											
	MeC≡C·CH ₂ ·OH	(4)	<i>b</i>	0	94	6	0	100	94		45
	HC≡C·CH ₂ ·CH ₂ ·OH	(5)	<i>b</i>	0	0	0	100	0	100		9
	H ₂ C=C=CH·CH ₂ ·OH	(6)	<i>b</i>	0.5	67	5	27	0.5	100	93	72
10% Pt-C											
	MeC≡C·CH ₂ ·OH	(4)	<i>b</i>	13	69	3	0	13	85	96	6
	HC≡C·CH ₂ ·CH ₂ ·OH	(5)	<i>b</i>	14	0	0	72	14	84		0
	H ₂ C=C=CH·CH ₂ ·OH	(6)	<i>b</i>	17	34	8	24	17	80	81	64
10% Rh-C											
	MeC≡C·CH ₂ ·OH	(4)	<i>b</i>	14	64	2	0	14	83	97	18
	HC≡C·CH ₂ ·CH ₂ ·OH	(5)	<i>b</i>	25	0	0	50	25	66		0
	H ₂ C=C=CH·CH ₂ ·OH	(6)	<i>b</i>	14	55	5	12	14	84	92	83
Raney Ni (Nicat 101)											
	MeC≡C·CH ₂ ·OH	(4)	<i>b</i>	6	88	0	0	6	94	100	27
	HC≡C·CH ₂ ·CH ₂ ·OH	(5)	<i>b</i>	16	0	0	68	16	81		0
	H ₂ C=C=CH·CH ₂ ·OH	(6)	<i>b</i>	3	58	2	34	3	87	97	64
Rh(PPh ₃)Cl											
	MeC≡C·CH ₂ ·OH	(4)	<i>b</i>	21	58	0	0	21	73	100	0
	HC≡C·CH ₂ ·CH ₂ ·OH	(5)	<i>b</i>	17	0	0	66	17	80		0
	H ₂ C=C=CH·CH ₂ ·OH	(6)		Unchanged							
Pt-SnCl ₂											
	MeC≡C·CH ₂ ·OH	(4)		Incomplete ^c							
	HC≡C·CH ₂ ·CH ₂ ·OH	(5)	<i>b</i>	10	0	6	74	10	89		6
	H ₂ C=C=CH·CH ₂ ·OH	(6)		Unchanged							
Zn-Cu couple											
	MeC≡C·CH ₂ ·OH	(4)	200 h ^d	0	98	2	0	0	100	98	
	HC≡C·CH ₂ ·CH ₂ ·OH	(5)	120 h ^d	0	0	0	100	0	100		
	H ₂ C=C=CH·CH ₂ ·OH	(6)	72 h ^d	0	36	12	52	0	100	75	52
Di-imide											
	MeC≡C·CH ₂ ·OH	(4)	27 h ^e	41	18	0	0	41	31	100	0
	HC≡C·CH ₂ ·CH ₂ ·OH	(5)	15 h ^e	45	0	0	10	45	18		0
	H ₂ C=C=CH·CH ₂ ·OH	(6)	8.2 h ^e	33	28	6	0	33	51	82	100
CrSO ₄											
	MeC≡C·CH ₂ ·OH	(4)	100 h ^d	0	0	100	0	0	100	100	
	HC≡C·CH ₂ ·CH ₂ ·OH	(5)	3 h ^d	0	0	0	100	0	100		
	H ₂ C=C=CH·CH ₂ ·OH	(6)	35 min ^d	0	5	7	88	0	100	58 ^f	88

^{a, b} See Table 1. ^c With 55% but-2-yn-1-ol remaining, 36% but-*cis*-2-en-1-ol and 9% of its *trans*-isomer had been formed. ^d Further treatment over a reasonable period does not alter the composition. ^e No break in the reaction which proceeds to give butan-1-ol. ^f Refers to *trans*.

species. But-3-yn-1-ol and buta-2,3-dien-1-ol were competitively hydrogenated at comparable rates over both palladium-barium sulphate and rhodium-carbon: buta-2,3-dien-1-ol was hydrogenated more rapidly than but-2-yn-1-ol.

The homogeneous catalyst tris(triphenylphosphine)rhodium chloride^{7,8} was used in ethyl acetate as difficulty

⁷ J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1711.

⁸ F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 1574.

and it was found in separate experiments that the acetylene-allene conversion was brought about by tris(triphenylphosphine)rhodium chloride in ethyl acetate in the absence of hydrogen: but-3-yn-1-ol was not isomerised, and was hydrogenated normally. Buta-2,3-dienoic acid and buta-2,3-dien-1-ol could not be successfully hydrogenated in this homogeneous system; in the former case an insoluble yellow complex, m.p. 173°, was formed.

⁹ A. J. Birch and K. A. M. Walker, *J. Chem. Soc. (C)*, 1966, 1894.

It was not further investigated, but allene-rhodium complexes have been reported.^{10,11} Experiments with another homogeneous catalyst, platinum-tin(II) chloride complex,^{12,13} also showed unattractive selectivities and in the case of but-2-ynoic acid the stereoselectivity was not high.

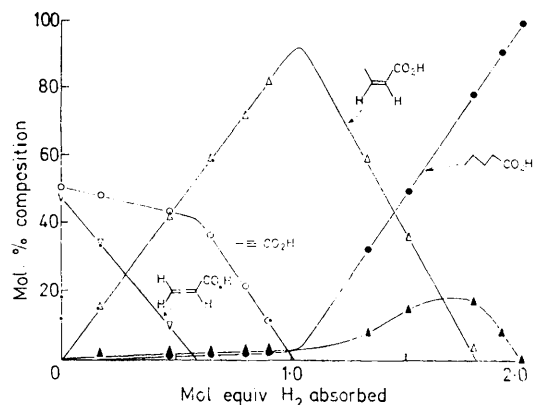


FIGURE 1 Competitive hydrogenation (Pd) of buta-2,3-dienoic acid and but-2-ynoic acid

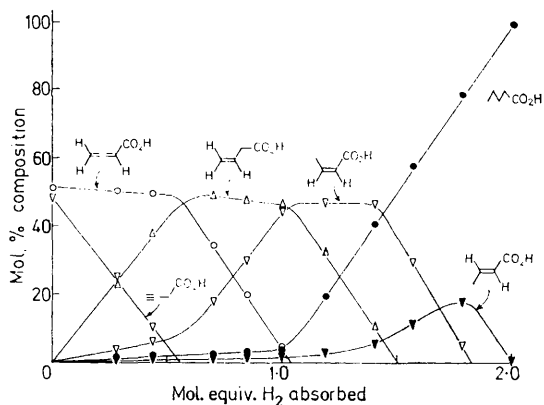
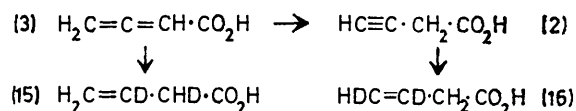


FIGURE 2 Competitive hydrogenation (Pd) of buta-2,3-dienoic acid and but-3-ynoic acid

The 'chemical' system, zinc-copper couple in refluxing ethanol^{14,15} was highly selective for the production of olefins from acetylenes in all examples, and in the case of but-2-ynol it was also highly stereospecific. On the other hand but-2-ynoic acid was reduced to a mixture of but-*cis*- and but-*trans*-2-enoic acids (89 : 11) in under 4 h: the composition remained unchanged after 48 h. But-3-ynoic acid gave a mixture of but-3-enoic and but-*trans*-2-enoic acids (90 : 10) after a little over 1 h, but as refluxing with the couple continued progressive isomerisation to but-*trans*-2-enoic acid ensued and after 60 h this was the sole product. Buta-2,3-dienoic acid showed related behaviour. At the disappearance point of the allene (1.9 h) the product was but-3-enoic acid (79%) and but-*trans*-2-enoic acid (21%), and in the very early stages of the reaction small amounts of but-3-ynoic acid were

detected. After 48 h refluxing the product was entirely but-*trans*-2-enoic acid, again showing the 3-ene \rightarrow *trans*-2-ene isomerising tendency of the zinc-copper couple in this system. On the other hand the selectivity of the reagent is impressive: even after boiling for 120 h only 3% of butyric acid had been formed. The complete lack of formation of but-*cis*-2-enoic acid on Zn-Cu reduction of buta-2,3-dienoic acid contrasts sharply with heterogeneous catalysis over platinum metals and nickel.

The observation of a little but-3-ynoic acid in the early part of the allene reduction led to suspicion that hydrogenation might proceed *via* an initial isomerisation to the former. The Zn-Cu couple reduction was therefore studied in [²H]methanol. The two routes entertained are illustrated in the Scheme. Progress was followed by



SCHEME

g.l.c., and when all the allene had just reacted, the but-3-enoic and but-*trans*-2-enoic acids were isolated by preparative g.l.c. (diethylene glycol succinate; 130°). The but-3-enoic acid showed a broad singlet at τ 4.8 (2H, H₂C=) and a singlet at 6.9 (1H, CHD), and comparison with the n.m.r. spectrum of the undeuteriated acid showed it to be the 2,3-dideuterio-acid (15), which must be produced directly from the allene. Small amounts of (16) might not be easily detected but it is clear that hydrogenation after isomerisation to (2) is not a major pathway. Reduction of the ester, methyl buta-2,3-dienoate, was slow and no methyl but-3-ynoate was detected in this experiment. Competitive reduction of a mixture of but-3-ynoic and but-2-ynoic acids with Zn-Cu couple in refluxing ethanol did not reveal pronounced intermolecular selectivities, though the terminal acetylene is reduced distinctly faster than the disubstituted acetylene. The corresponding butynols gave a similar result.

Acetylenic and allenic alcohols were reduced more slowly than the corresponding acids. The very high selectivity and stereospecificity, and the stability of the olefinic alcohols to further boiling with the reagent, make this an attractive method for semi-hydrogenation of the acetylenic alcohols. Reduction of buta-2,3-dien-1-ol with Zn-Cu couple gave comparable amounts of 2,3- and 3,4-reduction products, the latter having a 3 : 1 *cis*-*trans* ratio. The view that hydrogenations by Zn-Cu couple take place on the metal surface seems reasonable when the products from the two acetylenic alcohols are considered. The results with the allenic alcohol differ quantitatively from those obtained by heterogeneous

¹⁰ T. Kashiwagi, N. Yasuoka, N. Kasai, and M. Kukudo, *Chem. Comm.*, 1969, 317.

¹¹ P. Racanelli, G. Pantini, A. Immirzi, G. Allegra, and L. Porri, *Chem. Comm.*, 1969, 361.

¹² R. D. Cramer, E. L. Jenner, R. V. Lindsey, jun., and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1963, **85**, 1691.

¹³ H. van Bekkum, J. van Gogh, and G. van Minnen-Pathius, *J. Catalysis*, 1967, **7**, 292; L. P. van't Hoff and B. G. Linsen, *ibid.*, p. 295; G. C. Bond and M. Hellier, *Chem. and Ind.*, 1965, 35.

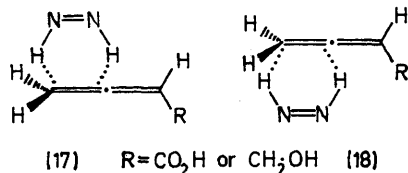
¹⁴ F. Strauss, *Annalen*, 1905, **342**, 190; B. S. Rabinovitch and F. S. Looney, *J. Amer. Chem. Soc.*, 1953, **75**, 2652.

¹⁵ A. J. Clark and L. Crombie, *Chem. and Ind.*, 1957, 143.

catalytic hydrogenation with palladium, but are generally similar.¹ On the other hand palladium-catalysed reduction of buta-2,3-dienoic acid gives no but-3-enoic acid, only but-*cis*-2-enoic acid.¹ It may be that, in the same reduction with Zn-Cu, which gives 79% of but-3-enoic acid and no *cis*- Δ^2 -acid, the carboxylate anion interacts attractively with the zinc surface. This would account for the preponderance of product from allene orientation with a 'parallel' carboxylic function.¹

The reactions of but-2- and -3-ynoic acids, as well as buta-2,3-dienoic acid, with chromium(II) sulphate¹⁶ resulted in immediate conversion into olefins, and no saturated product was detected. But-2-ynoic acid gave but-*trans*-2-enoic acid and the 3-ynoic isomer gave the 3-enoic acid. The product from buta-2,3-dienoic acid was exclusively but-3-enoic acid. This result agrees with findings that the reduction is greatly accelerated in olefins possessing co-ordination sites and electron-withdrawing groups.¹⁶ The reduction of but-3-yn-1-ol and but-2-yn-1-ol by chromium(II) sulphate was, as expected, considerably slower but gave but-3-en-1-ol and but-*trans*-2-en-1-ol, respectively, with excellent selectivity and stereospecificity as has been reported earlier.¹⁶ Reduction of the allenic alcohol, although producing mainly (88%) but-3-en-1-ol, gave significant amounts of but-*cis*- and but-*trans*-2-en-1-ols.

Reduction of the acetylenic acids and alcohols with di-imide¹⁷ showed extremely low selectivity for the production of olefins, though it was stereoselective.¹⁸ This is in keeping with general views on this reagent¹⁹ for olefin production: it was the least suitable reductant examined. A recent report states that nona-1,2-diene yields 17% of non-*cis*-2-ene and 3-ethylpenta-1,2-diene yields 16% of 3-ethylpent-2-ene, with no formation of saturated hydrocarbon, when reduction is carried out with di-imide.²⁰ In our work the two allenes examined both showed low selectivity and saturated material was present from the earliest stage: furthermore stereospecificity was poor. More *cis*- than *trans*- Δ^2 -acid or alcohol was however formed in each case. There is evidence that di-imide



does not induce *cis*→*trans* stereomutation¹⁸ and it appears that di-imide can attack the 3,4-linkage of the allene molecule from either side, the less hindered (17)

¹⁶ C. E. Castro and R. D. Stephens, *J. Amer. Chem. Soc.*, 1964, **86**, 4358; C. E. Castro, R. D. Stephens, and S. Mojé, *ibid.*, 1966, **88**, 4964.

¹⁷ E. J. Corey, D. J. Pasto, and W. L. Mock, *Tetrahedron Letters*, 1961, 347; E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *J. Amer. Chem. Soc.*, 1961, **83**, 3725; F. Aylward and M. Sawistowska, *Chem. and Ind.*, 1962, 484.

¹⁸ S. Hunig, H. R. Müller, and W. Thier, *Angew. Chem. Internat. Edn.*, 1965, **4**, 271.

¹⁹ C. E. Miller, *J. Chem. Educ.*, 1965, **42**, 254.

²⁰ G. Nagendrappa and D. Devaprabhakar, *Tetrahedron Letters*, 1970, 4243.

being preferred [*cf.* (18)]. Rather surprisingly regioselectivity was 100% in the case of buta-2,3-dien-1-ol but poor for buta-2,3-dienoic acid. Competitive hydrogenations of but-*trans*-2-enoic and but-*trans*-3-enoic acid show that di-imide reduces them at comparable rates.

EXPERIMENTAL

Materials.—But-3-yn-1-ol,²¹ b.p. 129°, n_D^{20} 1.4407, was oxidised²² to but-3-ynoic acid, m.p. 83–84°. Isomerisation with potassium carbonate²³ gave buta-2,3-dienoic acid, m.p. 64–65°. Carboxylation of prop-2-ynylmagnesium bromide gave but-2-ynoic acid,²⁴ m.p. 75–76°. But-*cis*-2-enoic acid was obtained (b.p. 64° at 8 mmHg, n_D^{20} 1.4455) by catalytic hydrogenation over palladium. Methyl esters were prepared with diazomethane (in ether at –60° with exactly 1 mol. equiv. for methyl buta-2,3-dienoate). But-*cis*-2-en-1-ol, b.p. 120°, n_D^{20} 1.4341 was made by semi-reduction of the corresponding acetylene. Treatment of 4-chlorobut-2-yn-1-ol²⁵ with lithium aluminium hydride gave buta-2,3-dienol,²⁶ b.p. 60° at 60 mmHg, n_D^{20} 1.4760. Purities were checked by g.l.c.

Analytical G.l.c.—Mixtures were analysed by on-column injection with a Pye 104 instrument and flame ionisation detector. The acids were chromatographed on polyethylene glycol adipate (5%) on chloro(dimethyl)silane-treated Chromosorb W at 50° (nitrogen at 80 ml min⁻¹) and retention times (min) were: methyl butyrate 5.4, methyl but-*cis*-2-enoate 7.6, methyl but-3-enoate 7.9, methyl but-*trans*-2-enoate 12, methyl buta-2,3-dienoate 26.6, methyl but-3-ynoate 40, methyl but-2-ynoate 72.0. Calibration factors were applied for each component. Diethylene glycol succinate and dinonyl phthalate (the latter at 70°) also gave satisfactory separations.

The alcohols were separated on 5% polyethylene glycol adipate at 50° and had the following retention times (min): butan-1-ol 8.5, but-3-en-1-ol 11.0, but-*trans*-2-en-1-ol 15, but-*cis*-2-en-1-ol 17.5, buta-2,3-dien-1-ol 30.0, but-3-yn-1-ol 40.0, and but-2-yn-1-ol 70.0; calibration factors were applied for quantitative estimation.

Reduction Techniques.—Hydrogenations over heterogeneous catalysts were carried out in glass apparatus with Raney nickel-treated pentane as solvent: analytical samples were withdrawn at intervals. Palladium (5%) on barium sulphate, platinum (10%) on carbon, and rhodium (10%) on carbon were supplied by Engelhard Industries Ltd.; Nicat 101 was a gift from Crosfield Chemicals, and Lindlar catalyst was used without quinoline. Nicat 101, supplied under water, was transferred to ethanol and then n-pentane before use.

Chlorotriphenylphosphinerhodium was supplied by Engelhard Industries. Catalyst (one-fifth the weight of substrate) was shaken in ethyl acetate with hydrogen until dissolution was effected: the sample was then injected.

Platinum-tin chloride complex was made under nitrogen from tin(II) chloride dihydrate (10 mmol) in methanol

²¹ A. G. Henne and K. W. Greenlee, *J. Amer. Chem. Soc.*, 1945, **67**, 484.

²² I. Heilbron, E. R. H. Jones, and F. Sondheimer, *J. Chem. Soc.*, 1949, 604.

²³ G. Eglinton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 1954, 3197.

²⁴ I. N. Nazarov, S. N. Ananchenko, and I. V. Torgov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk.*, 1959, 95 (*Chem. Abs.*, 1959, **58**, 16,085f).

²⁵ W. J. Bailey and E. Fujiwara, *J. Amer. Chem. Soc.*, 1955, **77**, 165.

²⁶ W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, 1955, **20**, 1337.

through which nitrogen had been bubbled for 2 days (120 ml). Chloroplatinic acid (1.0 mmol) was added and the red complex formed was stored under nitrogen. For 300 mg of substrate, 25 ml of catalyst solution was employed. Samples removed during the hydrogenation were diluted with water, acidified (2N-HCl), and extracted with ether.

Zinc-copper couple was supplied by Metal Hydrides Inc. For 300 mg of substrate in alcohol (20 ml), 0.5 g of couple was used. Activity was lost after about 1 day in the refluxing mixture and if necessary more was then added: work-up was as above.

Reductions with di-imide of substrate (300 mg) in ethanol (15 ml) were performed by bubbling air through the mixture after adding hydrazine hydrate (100%; 4 mol. equiv.) in ethanol (5 ml), followed by a trace of copper sulphate.

Chromium(II) sulphate was prepared by stirring (18 h) chromium(III) sulphate pentadecahydrate (100 g) in water (700 ml) under nitrogen with zinc dust (26 g). The blue solution was filtered under nitrogen. Chromium(II) sulphate solution (5 ml) was used to reduce substrate (200 mg) in water (*ca.* 1 ml), all operations and transfers being conducted under nitrogen. Addition produced immediate colour changes to green (alcohols) or brown to blue-black (acids). Samples were removed at intervals, saturated with ammonium sulphate, and extracted with ether.

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