593. *Hydrogen Transfer. Part IX.* The Selective Dehydrogenation of Unsaturated Alcohols by High-potential Quinones.*

By E. A. Braude, R. P. Linstead, and K. R. Wooldridge.

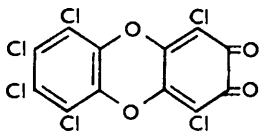
Allylic, benzylic, and propargylic alcohols are thermally dehydrogenated in good yields to the corresponding aldehydes or ketones by high-potential quinones. Thus cinnamyl alcohol and *o*-chloranil (tetrachloro-1 : 2-benzoquinone) give cinnamaldehyde and tetrachlorocatechol (which form a crystalline molecular compound) in quantitative yield at room temperature. The preparative uses of this mild and selective method of oxidation are illustrated.

The theoretical aspects of such reactions are discussed and it is suggested that the hydrogen-transfer proceeds in two steps, slow abstraction of a hydride anion from the C–H bond of the donor to give a resonance-stabilised oxonium ion and a quinol anion, followed by fast abstraction of a proton from the O–H bond :

$$C{=}C{-}CH{-}OH + Q \longrightarrow C{=}C{-}C{=}\overset{+}{O}H.Q\bar{H} \longleftrightarrow \overset{+}{C}{-}C{=}C{-}OH.Q\bar{H} \longrightarrow C{=}C{-}C{=}O + QH_2$$

The relations between the oxidation of alcohols by quinones and by other reagents are considered.

As part of a general study of hydrogen-transfer reactions,[1] we have been interested in the dehydrogenation of alcohols to aldehydes or ketones by quinones. Photochemical reactions of this type were first observed by Ciamician [2] and were later studied by several other investigators.[3,4,5] In unpublished investigations, we have observed that saturated alcohols do not undergo measurable oxidation in the dark, whereas primary and secondary allylic alcohols are thermally dehydrogenated by high-potential quinones such as *o*-chloranil (tetrachloro-1 : 2-benzoquinone). Thus, cinnamyl alcohol is readily converted at room temperature into cinnamaldehyde in almost quantitative yield. Thermal dehydrogenation also takes place with alcohols containing other types of unsaturated substituents on the carbon atom bearing the hydroxyl group, particularly with benzyl and propargyl alcohol. α-Keto-alcohols (*e.g.*, benzoin), on the other hand, do not react thus.



(I)

The interaction of benzyl alcohol and *o*-chloranil was first studied almost fifty years ago by Jackson and MacLaurin.[6] They used no solvent and did not isolate tetrachlorocatechol, but a derivative, later shown to have structure (I) and to be formed by the condensation of tetrachlorocatechol and *o*-chloranil with elimination of hydrogen chloride. The other product was first taken to be benzyl chloride, but was later [7] identified (by smell) as benzaldehyde.

For preparative purposes, it is convenient to carry out the oxidation in solvents, such as ether, carbon tetrachloride, or benzene; the reaction can be followed by observing the disappearance of the colour of the quinone. Under such conditions little of the derivative (I) is formed, and the catechol can be separated by adsorption on alumina, and the oxidation product isolated simply by evaporation of the residual solution. This procedure has been applied to a number of unsaturated alcohols of widely varied structures (see Table). Although large differences in reactivity are observed, good yields can generally be obtained without employing excess of the reagent.

Cinnamyl alcohol reacts quantitatively in 15 hr. at room temperature and, in this case,

* Part VIII, *J.*, 1954, 3595.

[1] Braude and Linstead, *J.*, 1954, 3544 *et seq.*
[2] Ciamician, *Gazzetta*, 1886, **16**, 111; Ciamician and Silber, *Ber.*, 1901, **34**, 1531 *et seq.*
[3] Leighton and Forbes, *J. Amer. Chem. Soc.*, 1929, **51**, 3549; Leighton and Dresia, *ibid.*, 1930, **52**, 3556.
[4] Berthoud and Porret, *Helv. Chim. Acta*, 1934, **17**, 694.
[5] Bolland and Cooper, *Nature*, 1956, **177**, 483.
[6] Jackson and MacLaurin, *Amer. Chem. J.*, 1907, **38**, 127.
[7] Jackson and Kelly, *ibid.*, 1912, **47**, 197.

the products can be separated as a solid 1 : 1 molecular complex of cinnamaldehyde and tetrachlorocatechol, which readily dissociates into its components in dilute solution or in polar media. The spectral properties of this interesting substance indicate that it is a crystalline inclusion compound [8] and not a semiacetal. The solid shows a band near

Oxidation of unsaturated alcohols by tetrachloro-1 : 2-*benzoquinone.*

No.	Alcohol	Temp.	Time *	Yield (%)
1	$CHPh{=}CH{\cdot}CH_2{\cdot}OH$	20°	2 hr.	53
	,,	20	15 hr.	100
	,,	35	8 hr.	85
2	$CHPh{=}CMe{\cdot}CH_2{\cdot}OH$	20	2 hr.	67
3	$CPh_2{=}CMe{\cdot}CH_2{\cdot}OH$	20	4 days	47
4	$CHPh{=}CH{\cdot}CHMe{\cdot}OH$	20	2 days	72
5	$CPh{\equiv}C{\cdot}CHMe{\cdot}OH$	20	18 hr.	57
6	$CPh{\equiv}C{\cdot}CHPh{\cdot}OH$	20	16 hr.	63
7	$CPh{\equiv}C{\cdot}CH(OH){\cdot}CH{=}CHPh$	20	10 min.	91
8	$Ph{\cdot}CH_2{\cdot}OH$	20	3 days	39
	,,	35	3 hr.	67
9	$Ph_2CH{\cdot}OH$	20	7 days	42
10	$Ph{\cdot}CH(OH){\cdot}CH{=}CH_2$	20	6 days	66
11	$CHMe{=}CH{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH$	78	15 min.	39
12	$CHMe{=}CH{\cdot}CH(OH){\cdot}CH{=}CHMe$	20	15 hr.	87
13	Cholest-4-en-3β-ol	20	20 hr.	55

* For details, see experimental section.

1650 cm.$^{-1}$ ascribable to the conjugated-carbonyl stretching frequency, though slightly displaced with respect to the band (at 1657 cm.$^{-1}$) exhibited by cinnamaldehyde itself, while in dilute solution both the infrared and the ultraviolet light absorption are approximately additive with respect to the two components.

Benzyl alcohol is oxidised more slowly than cinnamyl alcohol, while 1 : 5-diphenylpent-1-en-4-yn-3-ol (no. 7) is oxidised considerably faster. In general, reactivity increases with the extent of conjugated unsaturation, but secondary react less readily than primary alcohols. Alicyclic alcohols appear to react more readily than do their acylic analogues, as shown by the oxidation of cholest-4-en-3-ol to cholest-4-en-3-one under conditions under which allyl alcohol is attacked only very slowly. In the case of compounds prone to anionotropic rearrangement, such as 1-phenylallyl alcohol (no. 10) and hepta-2 : 5-dien-4-ol (no. 12), acid-catalysed isomerisation appears to take place under the influence of tetrachlorocatechol, since mainly the oxidation products (cinnamaldehyde and hepta-3 : 5-dien-2-one) derived from the rearranged alcohols are obtained.

Although kinetic studies have not yet been carried out, the qualitative results show that these reactions have the characteristics of bimolecular, rather than chain, reactions and are comparable in this respect with the dehydrogenation of hydroaromatic compounds by quinones.[9,10] The latter process is considered to involve two steps, the slow abstraction of a hydride anion from the donor by the quinone, acting as electrophilic reagent, followed by a rapid transfer of a proton. The present observations can be rationalised in a similar fashion. The first step will be an electrophilic attack on the C–H bond of the $>CH{\cdot}OH$ group to give the conjugate acid of the corresponding aldehyde or ketone, and the quinol anion QH^-. In non-polar solvents these two intermediates will remain associated as an ion-pair and rapidly exchange a proton to give the products

$$R_2CH{\cdot}OH + Q \longrightarrow R_2C{=}\overset{+}{O}H.\overset{-}{Q}H \longrightarrow R_2C{=}O + QH_2$$

The contrast in behaviour between saturated alcohols, which are not oxidised under such conditions, and unsaturated alcohols undoubtedly arises because the positive ions derived from allylic and related systems are stabilised by charge-resonance (see summary) which will assist the removal of the hydride anion. In this respect there is a close parallelism with hydrocarbon donors which also undergo comparable dehydrogenation

[8] Cf. Powell, *J.*, 1948, 61; Schlenk, Sand, and Tillotson, *J. Amer. Chem. Soc.*, 1955, **77**, 3587.
[9] Braude, Jackman, and Linstead, *J.*, 1954, 3548, 3564.
[10] Braude, Brook, and Linstead, *J.*, 1954, 3569.

only at allylic or benzylic centres. Thus, the reaction succeeds in the formation of conjugated carbon–carbon double bonds in one case and of conjugated carbon–oxygen double bonds in the other. Oxygen-containing donors are, however, intrinsically much more reactive than hydrocarbon donors, as shown, for example, by comparing benzyl alcohol, which is oxidised rapidly at 35° by tetrachloro-1 : 2-quinone, with ethylbenzene which is dehydrogenated extremely slowly under such conditions.[11] Since the *overall* resonance-energy gains in the two cases are similar, the difference in reactivity must be ascribed to the effect of the OH group on the ease of fission of the C–H bond in H–CHPh–OH compared with that in H–CHPh–CH_3. The marked facilitation is indeed to be expected since the OH group, owing to its mesomeric effect, will increase the resonance stabilisation of the intermediate ion and provide a seat for the positive charge.

There is a close relation between the thermal dehydrogenation of unsaturated alcohols by quinones, and the Oppenauer oxidation [12] of alcohols in which quinones [13] or other carbonyl compounds are employed as hydrogen acceptors in the presence of aluminium alkoxides. Like the present reaction, the Oppenauer oxidation is thought to involve [14] the transfer of hydride anion but, unlike the present reaction, it succeeds even with saturated donors owing to the intervention of the catalyst which facilitates the fission of the C–H bond.

The only other reagents known to cause selective oxidation of allylic and related alcohols are activated manganese dioxide [15,16] and 2 : 4-dinitrophenylhydrazine.[17,18] The mechanism of oxidation by the former (carried out heterogeneously) has not been elucidated and the level of reduction reached by the oxide (which is used in large excess) in unknown. It is not unlikely, however, that one of the products is manganous hydroxide, $Mn(OH)_2$, and that the process closely resembles that described above, with manganese dioxide taking the place of a high-potential quinone. (The reduction potential [19] of manganese dioxide is about 1·25 v, which is considerably higher than that of *o*-chloranil, 0·87 v.) Support for this view comes from the interesting observation [11,20] that manganese dioxide, like high-potential quinones,[11,21] can induce aromatisations which entail migration of alkyl groups and almost certainly involve abstraction of hydride-ions.

The sequence of reactivity observed in the oxidation of allylic and related alcohols by 2 : 4-dinitrophenylhydrazine runs parallel, at least qualitatively, to that found with *o*-chloranil. Reactivity increases with increasing conjugated unsaturation in the alcohol, and this is to be expected since resonance stabilisation in the intermediate ion and in the product will increase likewise. Oxidation by 2 : 4-dinitrophenylhydrazine proceeds only under acidic conditions and the hydrazinium cation $R{\cdot}NH{\cdot}NH_3^+$ has been postulated as the reactive entity.[17] Such a cation will clearly be a powerful hydride-ion acceptor, although the hydrogen-transfer in this case is regarded as a cyclic rather than a two-step process.

Experimental

Analytical data were determined in the organic microanalytical (Mr. F. H. Oliver and staff) and spectroanalytical (Mr. R. L. Erskine and Mrs. A. I. Boston) laboratories of this Department.

General Procedure.—Except where otherwise noted, the oxidations were carried out as follows: A solution approximately 0·2M with respect to the alcohol and the quinone, and

[11] Braude, Linstead, and Lowe, unpublished work.
[12] For a review, see Djerassi, *Org. Reactions*, 1951, **6**, 207.
[13] *Inter al.*, Wettstein, *Helv. Chim. Acta*, 1940, **23**, 388; Adkins and Franklin, *J. Amer. Chem. Soc.*, 1941, **63**, 2381; Ruzicka and Rey, *Helv. Chim. Acta*, 1941, **24**, 529; Ruzicka Rey, Spillmann, and Baumgartner, *ibid.*, 1943, **26**, 1653; Heilbron, Jones, and Robins, *J.*, 1949, 444; Djerassi, *J. Amer. Chem. Soc.*, 1949, **71**, 1003; Braude and Timmons, *J.*, 1950, 2007.
[14] Jackman and Macbeth, *J.*, 1952, 3252; Doering and Aschner, *J. Amer. Chem. Soc.*, 1953, **75**, 393; Williams, Krieger, and Day, *ibid.*, p. 2404.
[15] Weedon, *Ann. Reports*, 1953, **50**, 169.
[16] Harfenist, Bavley, and Lazier, *J. Org. Chem.*, 1954, **19**, 1608; Highet and Wildmann, *J. Amer. Chem. Soc.*, 1955, 4399.
[17] Braude and Forbes, *J.*, 1951, 1762.
[18] Franzen, *Chem. Ber.*, 1955, **88**, 717.
[19] Maxwell and Thirsk, *J.*, 1955, 4054, 4057.
[20] Bächli and Karrer, *Helv. Chim. Acta*, 1955, **38**, 1863.
[21] Beames, Braude, Jackman, and Linstead, *Chem. and Ind.*, 1954, 1174.

containing a slight excess of the latter, was kept in the dark or heated under nitrogen. It was then passed through a short column of alumina, and the oxidation product was eluted with chloroform and isolated or converted into a derivative in the usual way.

Oxidation of Cinnamyl Alcohol (No. 1).—(*a*) The alcohol (0·5 g.) and quinone (0·94 g.) in carbon tetrachloride (70 ml.) were kept at room temperature for 15 hr. Most of the solvent was removed at 20 mm., and the residue crystallised from carbon tetrachloride, giving the cinnamaldehyde–tetrachlorocatechol complex (1·4 g.) as colourless needles, m. p. 90°, undepressed on admixture with the sample described below.

Treatment of the complex with Brady's reagent gave cinnamaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 253°. Dissolution of the complex in acetic acid, followed by addition of water, gave tetrachlorocatechol which after sublimation under reduced pressure had m. p. and mixed m. p. 193°.

(*b*) A solution of the alcohol (0·5 g.) and quinone (0·9 g.) in chloroform was kept for 2 hr. at room temperature. Working up gave cinnamaldehyde 2 : 4-dinitrophenylhydrazone (0·62 g., 53%), m. p. 253°.

(*c*) A similar experiment in refluxing ether (150 ml.) gave, after 8 hr., 0·98 g. (85%) of cinnamaldehyde 2 : 4-dinitrophenylhydrazone.

(*d*) The alcohol (0·13 g.) and 2 : 3-dichloro-5 : 6-dicyano-1 : 4-benzoquinone (0·22 g.) in chloroform after 24 hr. gave 0·30 g. (26%) of cinnamaldehyde 2 : 4-dinitrophenylhydrazone.

Cinnamaldehyde–Tetrachlorocatechol Complex.—An authentic sample was prepared by adding cinnamaldehyde (0·68 g.) to a suspension of tetrachlorocatechol (1·38 g.) in carbon tetrachloride. When the mixture was heated to the b. p., nearly all the catechol went into solution. After filtering and cooling, the *complex* was deposited as colourless needles, m. p. 89°, smelling faintly of cinnamaldehyde (Found : C, 46·8; H, 3·0; Cl, 36·9. $C_9H_8O,C_6H_2O_2Cl_4$ requires C, 47·3; H, 2·6; Cl, 37·4%). Infrared absorption (paraffin mull) : Medium-intensity bands at 3140 (O–H stretching), 1650 (conjugated C=O stretching), 1623 (C=C stretching), 1590, 1563, 1399, 1311, 1292, 1261, 1202, 1268, 1160, 1140, 1017, 983, 809, 756, 741, 679, and 670 cm.$^{-1}$; in CCl_4, medium and strong bands at 3515 (H-bonded O–H stretching), 1683 (C=O stretching), 1626 (C=C stretching), 1456, 1393, 1316, 1285, 1205, 1178, 1120, 987, and 911 cm.$^{-1}$. Ultraviolet light absorption in hexane (0·01%) : $\lambda_{max.}$ 2160 Å (ε 32,000) and 2800 Å (ε 27,000).

Other Oxidations.—Reactions were carried out at room temperature unless otherwise stated. Yields are given in the Table. Some of the lower yields are based on the results of single experiments and could undoubtedly be increased by varying the conditions.

No. 2. α-Methylcinnamyl alcohol (0·5 g.) and *o*-chloranil (0·83 g.) in chloroform after 2 hr. gave α-methylcinnamaldehyde isolated as the 2 : 4-*dinitrophenylhydrazone* (0·74 g.) which crystallised from ethyl acetate–light petroleum (b. p. 60—80°) in red plates, m. p. 209—210°, $\lambda_{max.}$ 3900 Å (ε 42,000 in $CHCl_3$) (Found : C, 59·0; H, 4·5; N, 16·9. $C_{16}H_{14}O_4N_4$ requires C, 58·9; H, 4·3; N, 17·2%).

No. 3. α-Methyl-β-phenylcinnamyl alcohol (0·49 g.; m. p. 59°) and *o*-chloranil (0·54 g.) in ethanol (20 ml.) after 4 days gave α-methyl-β-phenylcinnamaldehyde (2-methyl-3 : 3-diphenylprop-2-enal) isolated as the 2 : 4-*dinitrophenylhydrazone* (0·41 g.), m. p. 242—243°, $\lambda_{max.}$ 3950 Å (ε 36,000 in chloroform) (Found : N, 14·2. $C_{22}H_{18}O_4N_4$ requires N, 13·9%).

No. 4. 1-Methyl-3-phenylallyl alcohol (0·62 g.) and *o*-chloranil (1·6 g.) in chloroform after 48 hr. gave benzylideneacetone 2 : 4-dinitrophenylhydrazone (1·0 g.), m. p. and mixed m. p. 223°.

No. 5. 4-Phenylbut-3-yn-2-ol (0·5 g.) and *o*-chloranil (0·85 g.) after 18 hr. in chloroform gave 4-phenylbut-3-yn-2-one isolated as the 2 : 4-dinitrophenylhydrazone (0·63 g.), m. p. 188—190°.

No. 6. 1 : 3-Diphenylprop-2-yn-1-ol (0·5 g.) and *o*-chloranil (0·6 g.) in ethanol (20 ml.) after 16 hr. gave 1 : 3-diphenylprop-2-yn-1-one isolated as the 2 : 4-*dinitrophenylhydrazone* (0·61 g.), m. p. 216—218° (Found : N, 14·9. $C_{21}H_{14}O_4N_4$ requires N, 14·5%).

No. 7. 1 : 5-Diphenylpent-1-en-4-yn-3-ol (1 g.; m. p. 69°) and *o*-chloranil (1·1 g.) in ethanol (20 ml.) after 10 min. gave 1 : 5-diphenylpent-1-en-4-yn-3-one isolated as the 2 : 4-*dinitrophenylhydrazone* (1·61 g.) which crystallised from ethyl acetate–light petroleum (b. p. 60—80°) in needles, m. p. 231—232°, λ_{max} 4100 Å (ε 29,000 in $CHCl_3$) (Found : N, 14·0. $C_{23}H_{16}O_4N_4$ requires N, 13·6%).

No. 8. Benzyl alcohol (1 g.) and *o*-chloranil (2·3 g.) in refluxing ether (50 ml.) after 3 hr. gave benzaldehyde, isolated as the 2 : 4-dinitrophenylhydrazone (1·76 g.), m. p. and mixed m. p. 239—240°. A similar experiment with the alcohol (0·5 g.) and quinone (41·1 g.) in chloroform at room temperature for 3 days gave 0·52 g. of 2 : 4-dinitrophenylhydrazone.

No. 9. Diphenylmethanol (0·92 g.) and *o*-chloranil (1·2 g.) in chloroform after 7 days gave benzophenone, isolated as 2 : 4-dinitrophenylhydrazone (0·45 g.), m. p. and mixed m. p. 245°.

No. 10. 1-Phenylallyl alcohol (1 g.) and *o*-chloranil (1·8 g.) in carbon tetrachloride were shaken for 6 days at room temperature until the mixture was colourless. After filtration, the solution was passed through an alumina column, and the column was eluted with chloroform. The combined eluates were evaporated and the residue was treated with Brady's reagent. The precipitate was crystallised from ethyl acetate, giving cinnamaldehyde 2 : 4-dinitrophenylhydrazone (1·1 g., 47%), m. p. and mixed m. p. 251°, and a more soluble *derivative* (0·45 g., 19%), m. p. 159—160°, $\lambda_{max.}$ 3860 Å (ε 26,000 in $CHCl_3$) (Found : N, 18·1. $C_{15}H_{12}O_4N_4$ requires N, 17·9%). This is probably another form of phenyl vinyl ketone 2 : 4-dinitrophenylhydrazone for which Ramirez and Kirby [22] report m. p. 195—196°, $\lambda_{max.}$ 3830 (ε 27,800).

No. 11. Sorbyl alcohol (1·15 g.) and *o*-chloranil (2·9 g.) in refluxing ethanol (25 ml.) after 15 min. gave sorbaldehyde, isolated as the 2 : 4-dinitrophenylhydrazone (1·25 g.), red needles, m. p. and mixed m. p. 193°.

No. 12. Hepta-2 : 5-dien-4-ol [23] (1 g.) and *o*-chloranil (2·2 g.) in chloroform (30 ml.) after 15 hr. gave hepta-3 : 5-dien-2-one, isolated as the 2 : 4-dinitrophenylhydrazone (2·26 g.), m. p. 204°, $\lambda_{max.}$ 3980 Å (ε 30,000 in $CHCl_3$) (Found : C, 53·4; H, 5·0; N, 19·3. Calc. for $C_{13}H_{14}O_4N_4$: C, 53·8; H, 4·8; N, 19·3%). Ahmad and Weedon [24] give m. p. 205—206°.

No. 13. Cholest-4-en-3β-ol (78 mg.; m. p. 125°; kindly supplied by Dr. W. Klyne) and *o*-chloranil (50 mg.) in chloroform after 20 hr. gave cholest-4-en-3-one isolated as 2 : 4-dinitrophenylhydrazone (65 mg.), m. p. and mixed m. p. 225—226°.

The work described in this paper was presented, in part, at the XIVth International Congress of Pure and Applied Chemistry in Zürich on July 25th, 1955. The award of a Beit Research Fellowship (to K. R. H. W.) is gratefully acknowledged.

Department of Chemistry, Imperial College of Science and Technology,
South Kensington, London, S.W.7. [*Received, March 24th*, 1956.]

[22] Ramirez and Kirby, *J. Amer. Chem. Soc.*, 1953, **75**, 6026.
[23] Braude and Coles, *J.*, 1951, 2078.
[24] Ahmad and Weedon, *J.*, 1953, 3815.