Direct Oxidation of Hydrocarbons to Unsaturated Aldehydes using 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ)

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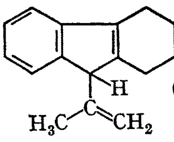
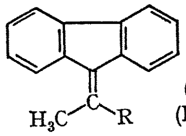
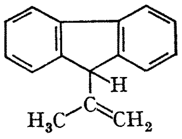
Summary Treatment of β-methylstyrene, allylbenzene, and related hydrocarbons with an excess of DDQ in benzene yields unsaturated aldehydes.

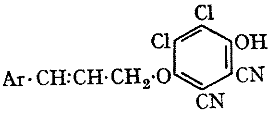
The reactions of DDQ with hydroaromatic compounds are well documented[1] and recently the dehydrogenation of a simple alkene has been reported.[2] However there is no previous report that certain hydrocarbon dehydrogenation reactions may result in the formation of carbonyl compounds in addition to, or instead of, the desired product.

In attempting the dehydrogenation of 9-isopropenyl-1,2,3,4-tetrahydrofluorene (I) with DDQ (3 molar equiv.) in benzene at room temperature we obtained the aldehyde (II) (45%) together with the expected product 9-isopropenylfluorene (IV) (30%). In refluxing benzene, (II) only was formed (64%). The structure of (II), m.p. 131°, was established by elemental composition and spectroscopic data [u.v. λ_{max} (EtOH) 270, 260 nm. (ϵ 22,350, 16,050); i.r. ν_{max} (CCl_4) 1670, 2710 cm.$^{-1}$; n.m.r. τ $-0{\cdot}74$ (s, 1H, C*H*O), 2·1—3·0 (m, 8H, Ar–*H*), 7·55 (s, 3H, C*H*$_3$)]. We believe that (II) is formed from (IV) since the same ratio of products is obtained when (IV) is similarly treated with DDQ. 9-Isopropylidinefluorene (III) also reacts with DDQ to give (II) (50%).


(I)


(II) R=CHO
(III) R=CH_3


(IV)


(V)

No attempt was made to adjust the reaction conditions to give optimum yields. Indene and α-methylstyrene failed to react, starting material only being recovered.

The applicability of the reaction is indicated in the Table. Addition of an excess of DDQ to a solution of the hydrocarbon in benzene immediately gave a deep green colouration which faded to a pale yellow solution. The solution was washed with dilute mineral acid, the solvent removed, and the residue chromatographed on alumina.

A competitive reaction between *trans*-β-methylstyrene

Table

Hydrocarbon	DDQ (molar equiv.)	Time† (hr.)	Product‡ (% yield)
$Ph\cdot CH_2\cdot CH{:}CH_2$	1·5	12[a]	$Ph\cdot CH\underset{t}{=}CH\cdot CHO$ (50)
$Ph\cdot CH\overset{c}{=}CH\cdot Me$	9	30[b]	,, (27)
$Ph\cdot CH\overset{t}{=}CH\cdot Me$	3	4[b]	,, (55)
$4\text{-}MeO\text{-}C_6H_4\cdot CH\overset{t}{=}CH\cdot Me$	1·5	2[a]	$4\text{-}MeO\cdot C_6H_4\cdot CH\overset{t}{=}CH\cdot CHO$ (50)
$Ph\cdot CMe\overset{c}{=}CHMe$	2	30[b]	$Ph\cdot CMe{=}CH\cdot CHO$ (20)

† [a] Stirred at room temperature. [b] Under reflux.
‡ Identified by n.m.r. spectra and comparison with authentic samples.

and 4-methoxy-*trans*-β-methylstyrene showed that the reaction of the latter with DDQ was virtually complete before any of the former was consumed. Thus the 4-methoxy-derivative must be at least 100 times more reactive than the parent hydrocarbon. This observation, together with the observation that allylbenzene, and *cis*- and *trans*-β-methylstyrene all yield *trans*-cinnamaldehyde indicates that the reaction involves hydride-ion transfer from the olefin to the quinone to form a resonance stabilised carbonium ion, *viz.*: $\mathrm{Ar{\cdot}CH\!:\!CH{\cdot}\overset{+}{C}H_2} \longleftrightarrow \mathrm{Ar{\cdot}\overset{+}{C}H{\cdot}CH\!:\!CH_2}$, which probably reacts with the semiquinone ion also formed to give the quinol ether (V). Quinol ethers have previously been isolated[3] in reactions of DDQ. Further hydride-ion abstraction and coupling would lead to an acetal which would readily decompose to give an aldehyde. The mechanistic details are at present being studied.

o- and *p*-Chloranil do not react in the above manner and therefore their use is preferred when dehydrogenation only is required.

We thank the S.R.C. for a maintenance grant (to J.A.G.S.).

(*Received, May 23rd,* 1969; *Com.* 727.)

[1] D. Walker and J. D. Hiebert, *Chem. Rev.*, 1967, **67**, 153.

[2] A. E. Asato and E. F. Kiefer, *Chem. Comm.*, 1968, 1684.

[3] E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *J. Chem. Soc.*, 1960, 3133.