The Reaction of *o*-Chloranil with Dimethylbutadiene: a Claisen Rearrangement Intermediate

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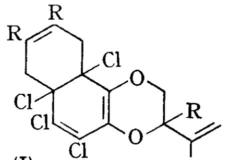
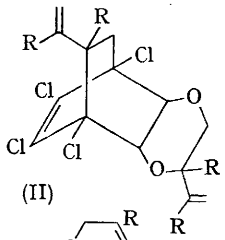
THE reaction of *o*-chloranil with dimethylbutadiene has been reported by Horner and Merz[1] to give a 1 : 2-adduct, which they suggested had either structure (I; R = Me) or structure (II; R = Me). We have repeated this reaction and obtained the same compound which cannot however have either of the structures suggested as it exhibits a non-conjugated carbonyl absorption at 1740 cm.$^{-1}$. We now present evidence that the adduct is a stereoisomer of either structure (III; R = Me) or (IV; R = Me).


(I)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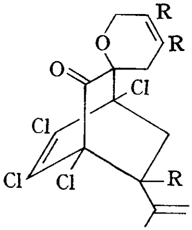
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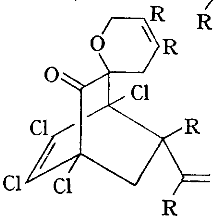
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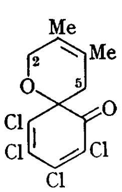
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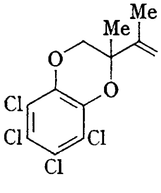
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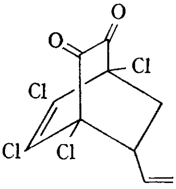
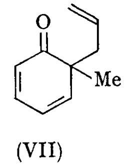

(VIII)


(VII)

When equimolecular amounts of dimethylbutadiene and *o*-chloranil react, a previously unreported yellow crystalline 1 : 1-adduct, m.p. 99—100°, is obtained, having structure (V) on the basis of its i.r. spectrum, which exhibits a single conjugated carbonyl absorption at 1700 cm.$^{-1}$, and its n.m.r. spectrum, which shows the presence of two vinyl-methyl groups (slightly broadened singlet τ 8·4), one methylene group (C-5) (a pair of doublets τ 7·97 and 7·42, J = 17 c./sec.) and another methylene group (C-2) (a pair of doublets τ 5·9 and 5·46, J = 14 c./sec.). This spirodihydropyran still retains the diene system of the *o*-quinone and will react with a second molecule of dimethylbutadiene, the latter acting as a dienophile, to give the 2 : 1-adduct (III or IV; R = Me), whose structure follows from its method of preparation and its n.m.r. spectrum, which shows the presence of a saturated methyl group (singlet τ 8·7), two identical vinyl-methyl groups (broadened singlet 8·38), another vinyl-methyl group (doublets τ 8·2,

J = 1·5 c./sec.), three methylene groups (a) (a pair of doublets τ 7·59 and 7·13, J = 13 c./sec.), (b) (a broad singlet τ 5·84), and (c) very broad singlets at τ 7·6 and 8·35 (hidden under methyl signal), and two vinyl-protons (singlet τ 5·08 and doublet τ 4·96, J = 1·5 c./sec.).

The adduct (V) possesses an allyl–*o*-dienone structure. Compounds of this type are known[2] to be intermediates in the Claisen rearrangement, and it is therefore consistent with the structure of the spirodihydropyran (V) that in boiling benzene solution (45 min.) it rearranges essentially quantitatively to the colourless crystalline benzodioxan (VI), m.p. 95—96°. A Claisen rearrangement intermediate (VII) has been previously synthesised[3] and shown to rearrange to a mixture of the allyl-ether and the *p*-allyl compound. However in the case of the compound (V) only migration of the allyl group from carbon to oxygen, to form the benzodioxan (VI), is possible. The structure of the benzodioxan (VI) follows readily from the absence of carbonyl absorption in its i.r. spectrum, and its n.m.r. spectrum which shows a saturated methyl group (singlet τ 8·54), a vinyl-methyl group (doublet τ 8·24, J = 1 c./sec.) a methylene group (a pair of doublets τ 6·05 and 5·62, J = 11·5) and two vinyl protons (τ 5·09 br, τ 5·01). The occurrence of this rearrangement strongly supports the structure assigned to the spirodihydropyran (V).

Although the photocatalysed addition of dimethylbutadiene to *p*-benzoquinone yields[4] a spirodihydropyran, the formation of (V) is the first reported case of such a reaction occurring non-photochemically in the quinone field. *o*-Chloranil is a "perhalogenated carbonyl compound" and such compounds are reported[5] to react with dienes to yield spirodihydropyrans. Although no spirodihydropyran has yet been isolated from the reaction of either cyclopentadiene or 1,4-diphenylbutadiene with *o*-chloranil, these reactions lead[1] to benzodioxans, and it is possible that unstable spirodihydropyrans may be intermediates.

Buta-1,3-diene reacts with *o*-chloranil to form a mono- and a bis-adduct. The latter compound had[1] been assigned structure (I or II; R = H) but from its spectral properties it is in fact a stereoisomer of (III or IV; R = H). The mono-adduct, not previously isolated, has the structure (VIII) as originally assigned.[1]

Results completely analogous to those described above have been obtained using *o*-bromanil and dimethylbutadiene.

All new compounds gave elemental analyses consistent with their structures.

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[1] L. Horner and H. Merz, *Annalen*, 1950, **570**, 89.
[2] S. J. Rhoads in "Molecular Rearrangements", Part 1, ed. P. de Mayo, Interscience, New York, 1963, p. 655.
[3] D. Y. Curtin and R. J. Crawford, *J. Amer. Chem. Soc.*, 1957, **79**, 3156.
[4] J. A. Barltrop and B. Hess, *J. Chem. Soc.*, 1965, 5182.
[5] J. Hamer and J. A. Turner in "1,4-Cycloaddition Reactions: The Diels–Alder Reaction in Heterocyclic Syntheses", ed. J. Hamer, Academic Press, New York, 1967, p. 205.