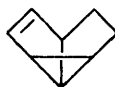


The Photo-cycloaddition of Vinyl Acetate to Benzene and its Simple Derivatives: Functionalisation of the Dihydrosemibullvalene Skeleton

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The photo-reaction of vinyl acetate with benzene yields both *ortho*- and *meta*-cycloadducts in an initial ratio of 1 : 7. The *ortho*-product has *endo*-stereochemistry but a mixture of regio- and stereo-isomers result from the *meta*-cycloaddition. Base-catalysed hydrolysis of the *meta*-adducts yields the corresponding alcohols, whereas acid treatment gives 2-substituted derivatives of bicyclo[3.3.0]octa-3,7-diene. The photo-reaction of vinyl acetate with toluene, anisole, fluorobenzene, and *p*-xylene also yields *meta*-cycloadducts: the results are discussed in terms of previously proposed reaction intermediates.

THE *meta*-photo-cycloaddition of ethylenes to benzene is, in principle, an excellent one-step route to the dihydrosemibullvalene system (1) but although the reaction has been described and discussed for several years,¹⁻⁶ prior to the preliminary account of the present work,⁷ the addition had been restricted to hydrocarbon ethylenes^{2,3,8} and vinyl ethers⁹⁻¹² which, furthermore, frequently give appreciable amounts of other 1 : 1 adducts with benzene. The objectives of the present study were to functionalise (1) and thence to investigate such compounds as a route



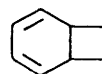
(1)

to semibullvalene,¹³ to assess if an ethylene substituted with a functional group, unlike vinyl ethers¹² and alkenes,^{8,14} displayed any regio-selectivity in *meta*-photo-addition to benzene, and to test further the proposal that this mode of reaction would be more efficient than the corresponding *ortho*-process for ethylenes with ionisation potential (I.P.) similar to that of benzene (I.P. 9.24 eV). The vinyl acetate-benzene system (Δ I.P. 0.05 eV) was an ideal one to study to achieve these objectives, and the present paper describes the detail of and extends and discusses the results briefly outlined in ref. 7. It should be noted that two years subsequent to our communication,⁷ the photo-addition of vinylene carbonate was reported to yield *meta*- and *ortho*-cycloadducts with benzene.¹⁵ Other ethylenes substituted with functional groups which have been reported to photo-add to benzene are all dienophiles and give exclusively *ortho*-cycloadducts (2),¹⁶⁻¹⁸ which, depending on the particular ethylene, either have specifically *exo*-stereochemistry or are a mixture of the *exo*- and *endo*-stereoisomers.^{19,20}

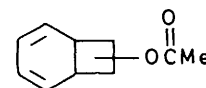
RESULTS AND DISCUSSION

Irradiation (254 nm) of equi-volume mixtures of benzene and vinyl acetate produced much polymer and four volatile products in an initial ratio of *ca.* 1.0 : 1.5 : 25.5 : 3.5 (g.l.c. elution Carbowax 20M). Continued irradiation rapidly changed this ratio to a steady value of *ca.* 1.0 : 1.5 : 90 : 1.0. The two shortest retention-time prod-

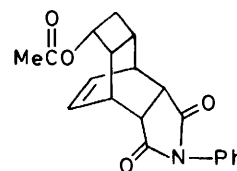
ucts had molecular weights of 134, whereas the two more major components were 1 : 1 adducts of the starting materials ($M^+ = 164$, m.s.-g.l.c.). The minor 1 : 1 adduct was thermally and photo-labile, fragmented readily to starting materials in the mass spectrometer (ratio of ions of *m/e* 164 : 104 : 78, 1 : 20 : 60, respectively), and was removed from chromatograms of the mixture by dienophiles. From these data it was concluded that the minor adduct has the *ortho*-cycloadduct structure (3). Because of the lability of (3) it proved impractical to isolate this 1 : 1 adduct, but from repeated short-duration irradiations of solutions of the addends in acetonitrile which increased the ratio of the minor to major adducts to *ca.* 1 : 6, a mixture enriched in (3) was obtained in sufficient amounts to allow the separation of the adduct as the 1 : 1 : 1 *N*-phenylmaleimide Diels-Alder adduct



(2)



(3)



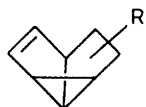
(4)

($M^+ 337$, m.p. 176–177 °C). The n.m.r. spectrum (Experimental section) was completely in accord with the assigned structure (4) and in particular allowed the assignment of *endo*-stereochemistry to the acetate group in (4) and hence in (3).† In particular the ethenyl protons resonated as a complex multiplet centred at δ 6.35; essentially the resonance was comprised of six lines each split further and coupling constants of 8, 6, and 2 Hz were determined in the multiplet. Thus the two ethenyl protons are non-equivalent. In similar *exo*-stereoisomers, the ethenyl protons have the same chemical shift

† It is a constant cause for concern that the stereoisomers of such *ortho*-cycloadducts may equilibrate thermally *via* the monocyclic triene;²¹ hence in all operations involving (3), including the Diels-Alder reaction, the temperature was maintained at <30 °C.

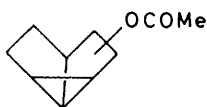
and resonate as an overlapping double doublet which generally appears as a triplet.²⁰ Yields of the Diels-Alder product based on the concentration of the minor 1 : 1 adduct were assessed to be *ca.* 80% but it is considered unlikely that the *exo*-isomer of (4) would have escaped detection as this stereoisomer may be expected to be the less soluble of the two and would have crystallised first from the reaction.¹² Hence we deduce that the *ortho*-cycloaddition of vinyl acetate to benzene is stereospecifically *endo*. This result is interesting in the context of other *ortho*-cycloadditions. At one time it appeared that such products from ethylenes with I.P.s less than that of benzene would yield exclusively the *endo*-stereoisomer^{3,22} and the vinyl acetate-benzene example fits nicely into this proposal,⁹ but recently it has been shown that *exo-ortho*-cycloadducts are formed from enol ethers and benzene and although 2,3-dihydrofuran does yield a mixture of the stereoisomers,¹² there now seems to be no relationship between donor/acceptor property of the ethylenes and the stereochemistry of *ortho*-cycloaddition.

The major product from irradiation of vinyl acetate and benzene could be obtained in gram quantities, in >95% purity by vacuum distillation of the irradiated product following treatment with a dienophile. The *meta*-cycloadduct structure (5) is assigned to this product from its spectroscopic properties (Experi-

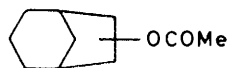


(5) R = OCOMe

(14) R = OH



(6)

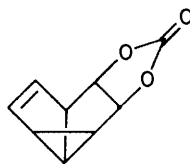
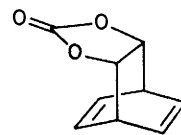


(7)

mental section) and comparison with those of benzene-ethylene photo-products of known structure.^{5,6,8} In the mass spectrometer the adduct fragmented readily with a base ion at *m/e* 43 but the $C_8H_8^+$ ion at *m/e* 104 was *ca.* 60% of this indicating a facile loss of CH_3CO_2H via a McLafferty rearrangement: fragmentation to starting materials was a minor process. In agreement with the structure, on catalytic hydrogenation (Pd-C) the 1 : 1 adduct consumed 2 mol hydrogen. Consumption of the first mol was rapid and gave one compound (M^+ 166) which had no ethenyl protons (n.m.r. spectrum) but the cyclopropane ring remained (i.r. spectrum) and hence structure (6) is assigned to this product. Continuation of the hydrogenation led to the slow conversion of (6) into a product of molecular weight 168 which is deduced to be a mixture of bicyclo[3.2.1]octane acetates (7).

Quantum yields for the *ortho*- and *meta*-cycloadditions of vinyl acetate (3.5M) to benzene (1.1M) in iso-octane were determined²³ to be 0.03 and 0.22 respectively.

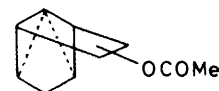
This ratio of efficiency of 1 : 7 for the two processes is approximately that which would be predicted for an ethylene which has an I.P. of *ca.* 9.19 eV.⁹ However, the photo-addition of vinylene carbonate (I.P. 10.1 eV) to benzene provides an exception to such predictions, for in this case where *ortho*-cycloadducts may be expected, only the *meta*- and *para*-adducts (8) and (9) were ob-

(8) 5:1 ratio of *endo* to *exo*

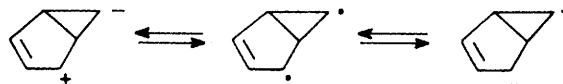
(9)

served.¹⁵ The experimental conditions of the present work and those involving vinylene carbonate were quite different, and those of the latter investigation were not conducive for the formation and stability of the *ortho*-cycloadduct.³ It could be that the *para*-adduct (9) is derived from a very photolabile *ortho*-isomer as noted in other systems.¹¹ Nevertheless, if this latter product had been formed with an efficiency, relative to that of the *meta*-process, approaching that predicted from the addend I.P.,⁹ there is little doubt that it would have been detected. The factors operating in the vinylene carbonate-benzene system, not present in others, which affect the efficiency of the modes of cycloaddition remain at present a matter for speculation.

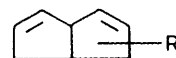
It was of importance from a mechanistic viewpoint to determine the degree of selectivity in the *meta*-cycloaddition of vinyl acetate to benzene. If the reaction proceeds *via* the *endo*-sandwich exciplex proposed as the intermediate in these photo-additions,^{5,6} then although *endo*-stereoisomers may be preferred, little regio-selec-



(10)



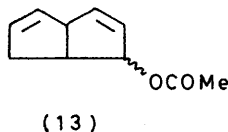
(11)



(12)

tivity is to be expected since formation of the vinyl-cyclopropane system in (5) from (10), the product of exciplex collapse, may proceed in two ways to yield the 6- and 7-regioisomers of (5). Small deviations from a unity ratio of the regio-isomers may be expected, since

some effect of the acetate group on the formation of the vinylcyclopropane system could be anticipated. On the other hand, a route involving prior rearrangement of the arene to such a species as the prefulvene intermediate (11)²⁴ which may be preferentially polarised to the left-hand side, would be expected to yield the 7-isomer selectively. It is well established that a convenient method of assessing the extent of the substitution in the *endo*-7-position of a mixture of *meta*-cycloadducts is by differential thermal pyrolysis.²⁵ The adduct with this position substituted, unlike its regio- and stereo-isomers, is prevented from yielding the bicyclo[3.3.0]octa-2,7-diene isomer (12) by a [1,5] sigmatropic shift and is hence thermally the most stable of the isomers, but at higher temperature may undergo a vinylcyclopropane-cyclopentene rearrangement which in the *meta*-cycloadducts simply results in change of the 7- to the 6-position and thus yields (12). Unfortunately on packed g.l.c. columns using a variety of liquid phases, the *meta*-adduct component could not be resolved into its isomers and liquid chromatograph or t.l.c. gave little better results. A Squalane S.C.O.T. column did, however, resolve the mixture into four components in a ratio of *ca.* 1 : 20 : 6 : 6 (g.l.c. elution sequence). These components were identified as the 1:1 *meta*-adducts from their mass spectra, which differed from each other only in the detail of the ratio of the parent-ion peak to those of *m/e* 104 and 43: in the most abundant adduct, the base ion was at *m/e* 104. Pyrolysis of the mixture in the injection port of the g.l.c. revealed that the major isomer was thermally the most stable, and this was substantiated by a similar procedure using packed-column g.l.c., when *ca.* 40% of the *meta*-adduct component was converted into an isomeric component at shorter retention time. In order to confirm that pyrolysis was occurring in the mode described above [*i.e.* (1)→(12)], gram quantities of the isomeric *meta*-adduct mixture were heated *in vacuo* for 30 min at 210 °C and the products isolated by preparative g.l.c. The major isomer was recovered unchanged (spectroscopic properties) and the pyrolysed product was isolated in an overall yield of 20%. The n.m.r. spectrum of this latter compound revealed a ratio of unsaturated: saturated: methyl protons of 4 : 5 : 3. Further detailed analysis of the spectrum was consistent with a mixture of the two stereoisomers of 4-acetoxycyclo[3.3.0]octa-2,7-diene (13). Small amounts of the 3-acetoxy-isomer of (12), resulting from pyrolysis of the 7-*exo*-acetoxy-*meta*-cycloadduct could have escaped detection, but clearly it is the 6-*exo*- and *endo*-acetoxy-*meta*-cycloadducts which yield (13). From the above data it is thus deduced that



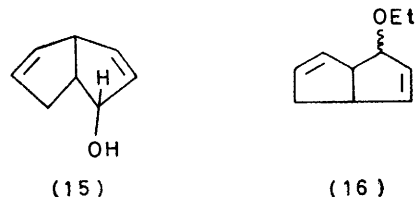
the 7-*endo*-, 7-*exo*-, 6-*endo*-, and 6-*exo*-isomers of (5) are formed in the ratio *ca.* 20 : 1 : 6 : 6, respectively.

In the above pyrolysis experiments, minor amounts of

two short-retention-time products with a molecular weight of 104 were also formed. At temperatures up to 350 °C, both in the injection port of the g.l.c. and in a flow system over alumina, the yields of these products increased but were not synthetically useful. Spectroscopic examination of the separated pyrolysis products revealed that they were styrene and cyclo-octatetraene: semibullvalene and the dihydro-pentalenes, the other possible C₈H₈ isomers, would not be expected to be stable under these pyrolysis conditions.²⁶

Several attempts to separate the isomers of (5) on a preparative scale were unsuccessful, but in anticipation that this problem could be resolved with the derived alcohols and also because dehydration of these latter products may provide a synthetically viable route to semibullvalene, (5) was hydrolysed. Much decomposition of the adduct was experienced and of the hydrolysis procedures, alcoholic potassium hydroxide gave the best results: nevertheless, yields were only *ca.* 40–50% and hence stereochemical deductions for the acetates could not be based on those of the alcohols. The trifluoroacetate of (5) may hydrolyse in better yields but since vinyl trifluoroacetate gave only trace amounts of photo-products with benzene, this aspect was not further pursued. The alcohols (*M*⁺ = 122) were, however, separated into four components which had a ratio of 70 : 5 : 5 : 15 and each showed facile loss of water in the mass spectrometer (base ion at *m/e* 104). The spectral properties of the mixture were consistent with the alcohol structure (14) but in practise it was only feasible to obtain the two major components as separated isomers. From an analysis of the n.m.r. spectra of these two isomers we deduce that the most abundant alcohol has the hydroxy-group in the 6-*endo*-position and that the other alcohol is the 7-*endo*-isomer. The minor components of the mixture which were present in equal amounts were thus assigned the 6- and 7-*exo*-hydroxy-structures. Consistent with these assignments, the alcohol produced in the major amounts was thermally isomerised at 250 °C (30 min) to an isomer, the spectroscopic properties of which were consistent with structure (15), whereas the isomer assigned the 7-*endo*-hydroxy-structure was essentially stable under these conditions.

It is known that *meta*-cycloadducts are acid-sensitive and undergo ring-cleavage in refluxing acetone in the presence of hydrochloric acid to give 2-hydroxybicyclo[3.3.0]oct-7-ene derivatives.²⁷ However, in view of the



unsatisfactory yields of the alcohols from base-catalysed hydrolysis of (5), it was decided to investigate conditions which may allow acid hydrolysis of the acetate with the minimum side reaction of cyclopropane ring-cleavage.

In all cases in which (5) gave reaction in the presence of acids, 2-substituted derivatives of bicyclo[3.3.0]octa-3,7-diene were obtained. For example (5) in refluxing aqueous ethanol was stable, but with trace amounts of acid a compound of molecular weight 150, and spectral data consistent with (16), was formed. Formation of (16) is interesting as it is the type of product obtained from acid treatment of semibullvalene.²⁸ Hence it appears that acid-catalysed elimination of the acetate from (5) and deprotonation yielded this C₈H₈ isomer, which under the experimental conditions gave (16). Despite several attempts, we were not able to promote the expulsion of the acetate under conditions which would not cause cleavage of the semibullvalene. Because of the acid-sensitivity of semibullvalene, all attempts to dehydrate the alcohol mixture were performed under basic or neutral conditions. A variety of procedures²⁹ were examined from simple heating in dimethyl sulphoxide to conversion into the xanthate and pyrolysis, but although on occasion minor amounts of a C₈H₈ compound were detected, no reaction gave reasonable conversions to semibullvalene.

The regio-selectivity observed with the present *meta*-cycloaddition of some 60% for formation of the 7-*endo*-isomer of (5) is noteworthy, but is of the same order as that observed in the addition of ethyl vinyl ether to benzene where again the 7-*exo*-ethoxy-isomer is the minor product.¹² It is possible that even this small degree of regio-selectivity reflects the involvement to some extent of a mechanistic pathway which does not include the sandwich exciplex^{5,6} as an important intermediate and it is not obvious why, if an intermediate such as (10) is formed from the exciplex, the 6-regio-isomer yields equal amounts of its stereoisomers whereas the 7-isomer has essentially *endo*-stereochemistry. The postulation of the sandwich exciplex in *meta*-cycloaddition was made from the observed remarkable specificity of *endo*-2,6-attack of several alkenes to methyl- and methoxy-benzenes.^{5,6} The alkenes were, however, 1,2-symmetrically disubstituted, and hence the question of regio-isomers did not arise. In an attempt to obtain further information on the involvement of such excited-state complexes in the present reaction, we have examined the photo-addition of vinyl acetate to several benzene derivatives and determined the orientation of attack and regio-selectivity of the formation of the *meta*-cycloadducts. The arenes examined were toluene, anisole, fluorobenzene and *p*-xylene. All systems gave increased yields of polymer compared to that involving benzene, but *meta*-cycloadducts were the major volatile reaction products. In contrast with the addition of cyclopentene to fluorobenzene,³⁰ the adducts from vinyl acetate and this arene were relatively stable, but from ¹⁹F n.m.r. spectra the *meta*-attack appeared non-selective and three positional isomers of the adduct were formed. The ¹H n.m.r. spectra of the adducts from the other arenes, however, showed that the 1-position of (1) was substituted and hence the mode of attack was exclusively 2,6. From thermolysis studies, we assess that the 7-

endo-isomer was again *ca.* 60% of the total *meta*-adduct mixture. Thus the present results are consistent with the intermediacy of a species in which the addends are oriented with respect to each other to give specifically 2,6-attack. There was no evidence for interaction between the addends in the ground state, and hence the proposal that this specific orientation occurs in the excited state seems reasonable. In other cases, however, where the arene is substituted with bulky groups, then participation of a different mechanistic pathway appears to be involved to some extent.³¹

EXPERIMENTAL

The irradiation source comprised Hanovia 15-W low-pressure mercury-arc lamps. Degassing solutions caused negligible effects on the efficiency of product formation. In preparative experiments, it was desirable to remove the polymer from the walls of the quartz tube periodically in order to obtain gram quantities of the 1:1 adducts. Quantum-yield measurements were made on solutions of 1.1M benzene, 3.5M vinyl acetate in iso-octane, and product formation was followed and determined by g.l.c.

Irradiation of Benzene and Vinyl Acetate.—The starting materials from an equi-volume (400 ml) irradiation (24 h) of vinyl acetate and benzene were removed at water pump pressure to give *ca.* 15 g of a viscous orange-yellow oil. The oil was shaken with diethyl ether (150 ml) for 30 min and the ethereal layer decanted from the polymeric material. Removal of the diethyl ether and distillation of the oil (85–90 °C at 0.1 mmHg) gave *ca.* 8 g of the adduct mixture containing *ca.* 90% of (5). By repeated irradiation (2 h duration) of an equi-volume mixture (400 ml) of vinyl acetate, benzene, and acetonitrile, and following the above work-up procedure, (3) and (5) were obtained in a 1:6 ratio.

Formation of (4). The sample (2 g) of the adduct mixture used in this experiment was not distilled but was simply the ether extract of the crude product. *N*-Phenylmaleimide (0.3 g) was added to the adduct mixture in diethyl ether (20 ml). Over a period of 4 d at room temperature, crystals of (4) separated with concomitant decrease (g.l.c.) in the proportion of (3). The product (0.45 g), m.p. 176–177 °C, had the following spectral features: ν_{max} (Nujol mull) 1 775m, 1 735s, 1 710s, 1 600w, 1 500m, 1 260m, 1 245m, 1 230m, 1 220m, 1 195s, 755m, 735m, 695m, and 675m cm⁻¹; δ (100 MHz, CDCl₃) 1.6–3.0 (1 H, m), 3.01 (3 H, s), 2.37–2.67 (2 H, m), 2.85–3.10 (3 H, m), 3.20–3.45 (2 H, v br m), 4.92–5.2 (1 H, q with minor splittings), 6.15–6.55 (2 H, six-line multiplet further split, *J* 8, 6, and 2 Hz), 7.12–7.3 (2 H, m) and 7.3–7.56 (3 H, m) (Found: C, 71.05; H, 5.85; N, 4.55. C₂₀H₁₉O₄N requires C, 71.22; H, 5.64; N, 4.15%).

Spectroscopic properties of (5). Following removal of (3) as (4), the adduct mixture was >95% (g.l.c.) (5) and this sample had the following spectroscopic properties: ν_{max} (liquid film) 3 060m, 3 040m, 3 020m, 2 940s, 2 860s, 1 740s, 1 605w, 1 455s, 1 380s, 1 365s, 1 245s, 1 040s, 1 020–1 000m, 865m, 725m, and 690m cm⁻¹; λ_{max} (cyclohexane) 209 nm; δ (60 MHz, CDCl₃) 1.6–1.9 (1 H, m), 1.9 (3 H, s), 2.0–2.6 (4 H, m), 2.6–2.9 (1 H, m), 3.0–3.2 (1 H, m), and 5.3–5.8 (2 H, AB quartet with minor splitting, *J* 5.5 and 2 Hz).

Pyrolysis of (5). Samples (1.0 g) of (5) were sealed under vacuum (0.1 mmHg) in a tube of capacity 5 ml. The tube

was then immersed in a paraffin bath at 210 °C for 30 min. Preparative g.l.c. of the pyrolysed mixture was achieved on 10% Carbowax 20M columns. The major product had spectroscopic properties very similar to those reported above while the minor component (200 mg) had ν_{\max} (liquid film) 3 050m, 2 920s, 2 850s, 1 730s, 1 600m, 1 430m, 1 372—1 360m, 1 240s, 1 020—1 050m, 720m, and 690m cm^{-1} ; δ (60MHz, CDCl_3) 2.0 (3 H, s), 1.9—3.0 (3 H, m), 3.0—3.5 (1 H, q with further splitting, J 8 and 2 Hz), 3.5—3.9 (1 H, v br s), and 5.5—6.0 (4 H, m).

Base hydrolysis of (5). The distilled mixture of (5) (1 g) was treated with 5% aqueous ethanolic potassium hydroxide (20 ml). A brown colouration appeared immediately. The mixture was allowed to stand for 2 d with occasional shaking, and was then continuously extracted with diethyl ether for 15 h. Evaporation of the resulting yellow solution gave a viscous yellow oil (0.5 g). Combined yields from several experiments were distilled at 150—170 °C and 0.05 mmHg. The alcohol mixture had ν_{\max} (liquid smear) 3 620—3 300s, 3 050m, 3 030s, 2 940s, 2 860m, 1 600m, 1 440—1 350m, 1 070—1 055s, 1 020—1 000m, and 720m cm^{-1} ; λ_{\max} (cyclohexane) 220 nm; δ (60 MHz, CDCl_3) 1.1—3.3 (7 H, series of multiplets with singlet at 2.25, removed by D_2O), 4.35—4.8 (1 H, br m), and 5.55—5.95 (2 H, m). The two major alcohols were separated by preparative g.l.c. (Carbowax 20M), and had the following n.m.r. spectra (60 MHz, CDCl_3): 6-*endo*-isomer, δ 1.4—2.5 (5 H, m), 2.5—2.9 (1 H, q, J 6 Hz), 3.0—3.2 (1 H, t of t, J 6 Hz), 4.35—4.8 (1 H, m), and 5.6—5.95 (2 H, AB q with minor splitting); 7-*endo*-isomer, δ 1.1—2.0 (5 H, m), 2.0—2.2 (1 H, q), 2.9—3.2 (1 H, t of t), 4.2—4.6 (1 H, m, J 5 and 6 Hz), and 5.5—5.8 p.p.m. (2 H, AB q with minor splitting, J 5.5 Hz). The mixture of alcohols was pyrolysed in a manner similar to that described for the acetates and the products separated by preparative g.l.c. The major product gave an isomer with δ (60 MHz, CDCl_3) 1.1 (1 H, s, signal removed by D_2O), 2.0—2.7 (2 H, m), 2.8—3.2 (1 H, m), 3.4—3.7 (1 H, br m), 4.5 (1 H, split d, J 8 Hz), and 5.6—6.0 (4 H, m, J 5.5 Hz). Methods attempted for the dehydration of the alcohols were those outlined in standard texts and in ref. 29.

Acid treatment of (5). The distilled adduct mixture of (5) (5 g) was refluxed in 10% aqueous ethanol (200 ml) for 2 h. Little change occurred as judged by g.l.c. Two drops of concentrated hydrochloric acid were added and immediately the concentration of (5) decreased and a shorter-retention-time product was produced. After 3 h reflux, when no (5) remained, the mixture was cooled, water (50 ml) added, and the solution extracted with light petroleum (b.p. 40—60 °C) (2 \times 100 ml). The petroleum extract was washed with water, dried (anhydrous MgSO_4), solvent removed, and the residue distilled at 60—70 °C (1 mmHg). This distillate, essentially one component by g.l.c., had δ (100 MHz, CDCl_3) 1.1—1.3 (3 H, overlapping Me triplets), 2.1—2.9 (2 H, m), 3.2—3.7 (4 H, m), 4.15—4.35 (1 H, br s), and 5.4—6.05 (4 H, m).²⁸

Irradiation of Substituted Benzenes with Vinyl Acetate.—Equi-volume solutions (400 ml) of vinyl acetate and the substituted benzene (toluene, *p*-xylene, anisole, or fluorobenzene) were irradiated for 24 h, with periodic removal of the sticky heavy polymer deposits from the cell walls. The starting materials were removed at water-pump pressure and the viscous yellow or orange residue (10—15 g) was digested with diethyl ether (150 ml). The ethereal layer was decanted from the polymeric material and the residues pro-

duced after removal of the diethyl ether were distilled at 0.05 mmHg to give pale yellow oils (4—6 g). The oils were subjected to g.l.c. (Carbowax 20M) and combined m.s.-g.l.c. analysis and their ^1H n.m.r. (100 MHz, CDCl_3) and i.r. (liquid film) spectra recorded. From these data and their comparison with adducts of known structure,^{5,6,8} the major components in all cases were assigned the *meta*-cycloadduct structure. Substitution at the 1-position of (1) was deduced for the major component of the adducts from vinyl acetate with toluene, *p*-xylene, and anisole from their ^1H n.m.r. spectra.⁵

(a) *Toluene*. ca. 95% one component, $M^+ = 178$; δ 1.39 (3 H, s), 1.6—2.6 (5 H, overlapping m), 1.92 (3 H, s), 2.72—2.86 (1 H d of t, J 2 Hz), and 5.42—5.78 (2 H, AB q, J 5.5 and 2 Hz with minor splittings); ν_{\max} 3 050sh, 3 020m, 2 940s, 2 929s, 2 855m, 1 730s, 1 600w, 1 245s, 1 185m, 1 030s, 980s, 725m, and 690m cm^{-1} .

(b) *p-Xylene*. ca. 90% one component, $M^+ = 192$; δ 1.36 (3 H, s), 1.4—2.5 (5 H, overlapping m), 1.78 (3 H, s), 1.94 (3 H, s), 2.6—2.8 (1 H, br d), and 5.03 (1 H, br s); ν_{\max} 3 020w, 2 950(sh), 2 920m, 2 850w, 1 730s, 1 645w, 1 245s, 1 190m, 1 045—1 015m, 805m and 755w cm^{-1} .

(c) *Anisole*. ca. 95% one component, $M^+ = 194$; δ 1.7—2.7 (5 H, overlapping m), 1.92 (3 H, s), 3.2—3.4 (1 H, d of t), 3.36 (3 H, s) and 5.55—5.78 (2 H, AB q, J 5.5 and 2 Hz with minor splittings); ν_{\max} 3 050w, 2 980(sh), 2 930m, 2 850w, 2 820w, 1 730s, 1 595w, 1 245s, 1 140m, 1 030m, 1 005m, 720m, and 685m cm^{-1} .

(d) *Fluorobenzene*. Two resolved components in the ratio ca. 4 : 1, M^+ of each = 182; ^{19}F n.m.r. signals (upfield of CFCl_3 at δ 119.4 (m), 120.5 (t), and 189.7 (q. of q) in the ratio ca. 1 : 4 : 16 respectively; the former two resonances are assigned to F on an ethylenic bond, and the latter to F on saturated carbon. That the sample was a mixture was also reflected in the fractional integration values of the ^1H n.m.r. spectrum; δ 1.6—3.0 (ca. 5 H, m), 1.91 and 2.00 (2 s, ratio ca. 4 : 1, respectively, total integral 3 H), 3.25—3.55 (ca. 1 H, d of d J 6 Hz), and 5.6—5.75 (ca. 2 H, m); ν_{\max} 3 060w, 2 945m, 2 850w, 1 730s, 1 665w, 1 595w, 1 240s, 1 120m, 1 100m, 1 030s, and 715m cm^{-1} .

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