# The Photochemical Reaction of Benzene with Ethylenes: Studies with Allyl Compounds, Enamines, Vinyl Sulphide, and 5,6-Dichlorobicyclo[2.2.1]hept-2-ene

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Benzene undergoes regio- and stereo-selective *meta* photocycloaddition to methyl but-3-enoate and pent-1-en-4-ol but methyl allyl ketone and *NN*-dimethylallylamine yield only products of the addend: likewise irradiation of benzene with enamines or methyl vinyl sulphide at 254 nm does not yield photoadducts. The *meta* photocycloadducts of benzene with methyl but-3-enoate and vinyl acetate and the ketones obtained by oxidation of the adducts from pent-1-en-4-ol are all essentially photostable and do not undergo Norrish Type II eliminations. The dechlorination products of the *meta* photocycloaddition of 5,6-*trans*-dichlorobicyclo[2.2.1]hept-2-ene and benzene undergo a retro-Diels–Alder addition at high temperatures, but the C_8H_8 isomer formed is cyclo-octatetraene.

IT is about twenty years since the first photocyclo-addition reaction of benzene to an ethylene was reported,[1] but although numerous publications have appeared on particular systems,[2,3] there are still features concerning ethylenic structure and substituents whose effects on the reaction of the addend with photoexcited benzene remain largely undetermined.

It is well-established that in cases where photochemical reaction does occur between dienophilic ethylenes and benzene and its derivatives, the mode of cycloaddition observed is that arising from *ortho* attack:[2,3] in some cases photo-substitution products also result.[4] As part of studies into factors which affect the mode and
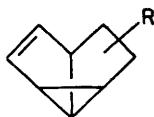

(1) R = OAc

(11) R = CH$_2$CH(OH)Me

(12) R = CH$_2$Ac

efficiency of photocycloaddition of ethylenes to benzenoid compounds, we have examined the reactions of cyclic and acyclic alkenes[5] and enol ethers[6] of differing structure and ionisation potential. From these investigations the formation of the *meta* cycloadducts (1) as the major volatile product from irradiation of mixtures of vinyl acetate and benzene could be predicted and hence by this reaction functionality can readily be introduced into the dihydrosemibullvalene skeleton.[7,8] These results prompted us to extend the studies of this reaction to a variety of other functionalised ethylenic systems in order to assess further the type of substituent which may promote or inhibit the photoreaction, and in particular to assess what effect, if any, functional groups not directly in conjugation with the ethylene would have on the overall process. It was also of interest that such a study could yield *meta* cycloadducts which may be suitable for an examination of the feasibility of this reaction as a step, which in principle would be con-

venient and versatile, in the synthesis of semibullvalene and its derivatives. Pyrolysis of the acetates (1) is quite unsuitable for this purpose as the temperatures required are too high and the derived alcohols are not amenable to high-yield dehydration.[8] Two further routes from *meta* cycloadducts to this C_8H_8 isomer which are plausible are the Norrish Type II elimination and the retro Diels–Alder reaction: to some extent the choice of ethylenes for the present study was made also with these approaches in mind.

We now report on the photochemical reactions of benzene with methyl but-3-enoate, methyl allyl ketone, *NN*-dimethylallylamine, pent-1-en-4-ol, 1-amino-*NN*-diethyl-2-methylpropene, 1-amino-*NN*-dimethylcyclopentene, methyl vinyl sulphide, and *trans*-5,6-dichlorobicyclo[2.2.1]hept-2-ene. The results are considered in this order and the reasons for examining these particular ethylenes in photoreaction with benzene are discussed in turn below.

RESULTS AND DISCUSSION

Ethylenes substituted with electron-withdrawing substituents (*e.g.* maleic anhydride, acrylonitrile, methyl-acrylate, and methyl vinyl ketone) are known to yield *ortho* photocycloadducts (2) exclusively with ben-
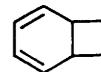

(2)

zene.[1,2,9,10] In the present study it was first of general interest to determine if a methylene group between the vinyl and functional group (*i.e.* allyl compounds) would be sufficient to insulate completely the chromophores in this particular type of process and thus cause a change in reaction mode to yield *meta* products as observed from propene and benzene.[11]

Irradiation (254 nm) of equivolume solutions of benzene with methyl but-3-enoate led to the rapid formation of two 1:1 adducts of the starting materials (m.s.–g.l.c., M^+ 178) in an approximate ratio of 7:3

(g.l.c. elution sequence, Carbowax 20M). The ratio was time invariant, and addition of dienophiles to the adduct mixture had no detectable effect, but whereas the major component was stable up to temperatures of 350 °C for 1.5 min, the minor product was converted into a mixture of isomers. The adducts were separated by preparative g.l.c. and from detailed analysis of the 220-MHz ^{1}H n.m.r. spectrum of the major 1 : 1 adduct, this product was assigned the 7-*endo-meta* cycloadduct structure (3)


(3) R^1 = CH$_2$CO$_2$Me, R^2= H
(4) R^1= H, R^2= Me
(5) R^1= Me, R^2= H
(6) R^1= OAc, R^2= H

(7) R = OAc
(8) R = CH$_2$CO$_2$Me
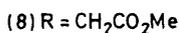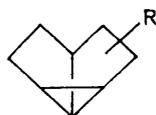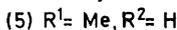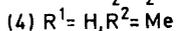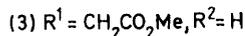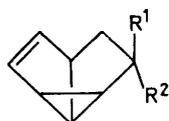
whereas the minor component was judged to be a mixture of the 7-*exo*-, the 6-*exo*-, and the 6-*endo*-isomers: these assignments are consistent with the relative thermal stabilities of the two components.[12] The photoaddition of propene to benzene is reported to yield only equal amounts of 7-*exo*- and -*endo*-methyl isomers (4) and (5) respectively.[11] It proved impractical to assess the isomer composition of the minor adduct component from benzene and methyl but-3-enoate, but the ^{1}H n.m.r. spectrum of this product revealed the presence of three isomers in an approximate ratio of 1 : 4 : 6, hence the maximum ratio of the 7-*exo*- to the 7-*endo*-isomer is 1 : 4 and of the 6- to the 7-regioisomers is 1 : 3. Thus in this example of *meta* cycloaddition, there is a selectivity greater than that previously observed from any other benzene–ethylene system [6,8] and this again raises the possibility that this feature of the addition may reflect the involvement of the two mechanistic pathways of *meta* addition followed by vinyl cyclopropane formation and prior arene rearrangement to the prefulvene intermediate followed by ethylene addition.[13,14]

Norrish Type II elimination of esters to give ethylenes and acids is a well documented process and frequently the yields are synthetically useful.[15] Reports of the alternative mode of elimination to form ethylenes and esters are, however, comparatively rare but did appear as early as 1958.[16] The *meta* cycloadducts from benzene and methyl but-3-enoate could in principle undergo photoelimination of methyl acetate to give semibullvalene, and those from vinyl acetate and benzene [*i.e.* (1)] may yield this C$_8$H$_8$ isomer and acetic acid. Although semibullvalene is known to be acid sensitive,[17] both processes were examined, originally to assess the relative efficiencies of the two types of elimination as well as to investigate the synthetic potential of the reaction. In the event, however, both adducts proved to be remarkably photostable to both 254 and 206 nm radiation in polar and non-polar solvents, and in the absence and presence of benzene. In particular, from no experiment

was there evidence for even 0.1% conversion into semibullvalene: minor amounts of polymeric materials were the only photoproducts. With respect to which type of elimination may have been favoured, it is worth noting here that in the mass spectrometer the two 7-*endo*-isomers (3) and (6) showed quite differing fragmentation behaviour. Thus the ratios of abundances of the parent ion and those of the C$_8$H$_8$$^+$ and C$_6$H$_6$$^+$ ions for (3) were 1 : 2 : 4 (base ion) respectively, whereas those of (6) were 1 : 20 (base ion) : 8 respectively. It therefore appears that in the latter case a facile McLafferty rearrangement-elimination of acetic acid occurs but with (3) the parent ion is relatively stable and reversion to starting materials under electron impact is a more favoured process. The lack of photoelimination from (1) and (3) suggested that the vinyl cyclopropane chromophore may act as an efficient energy sink but this was discounted to some extent as the initially formed products (7) and (8) respectively from catalytic hydrogenation of these *meta* cycloadducts were also essentially photostable. Further discussion here of the lack of photoelimination from these compounds would merely be speculation but experiments are in process to attempt to determine the reason for the observed stability.

It may appear from the methyl but-3-enoate–benzene system that allyl compounds would behave as alkenes and react with photoexcited benzene to yield only *meta* cycloadducts. In order to gain further information concerning the effect of this aspect of ethylene structure on the reaction and to assess the reactivity of bichromophoric addends in this process, we examined the systems methyl allyl ketone–benzene and *NN*-dimethylallylamine–benzene at concentrations such that the arene absorbed >80% of the radiation. Neither system, however, yielded 1 : 1 adducts. Methyl allyl ketone gave low yields of oxetan and cyclobutane dimers, the detailed structures of which were not investigated and the *NN*-dimethylallylamine–benzene system produced small amounts of products which were also formed from irradiation of the amine alone.[18] We have previously
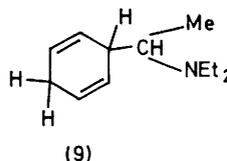
(9)

(10)

reported that irradiation of solutions of tertiary aliphatic amines and benzene yields acyclic *para* photoadducts (9) and that the reaction is greatly accelerated in the presence of methanol.[19] In the present amine system, however, the presence of methanol did not noticeably affect the photoreaction and formation of adducts of type (9) was not observed. To account for the above lack of photoaddition in the systems we suggest that interaction between photoexcited benzene and the above allyl compounds results in dissipation of the energy by a radiationless conversion involving intramolecular interaction between the vinyl and the other functional group

of the bichromophoric addend. From these results it seems that if the allyl substituent has a relatively low-lying excited state then energy is dissipated from its interaction with photoexcited benzene by other processes than arene addition: this argues more for the involvement of an excited state complex intermediate [14] in these addition reactions than for formation of the *meta* cyclo-adducts by ethylene trapping of a ground-state diradical (10) formed by prior arene rearrangement.[13] In agreement with these considerations, pent-1-en-4-ol did undergo photoaddition to benzene to give four 1 : 1 adducts (m.s.–g.l.c., M^+ 164) in a time-independent ratio of approximately 14 : 1 : 1 : 6 (elution sequence on Carbowax 20M). The spectroscopic data of the mixture and those of the two major adducts separated by preparative g.l.c. were consistent with the *meta* cycloadduct structure (11) and again the major isomer is assigned to the 7-*endo*-isomer on the basis of its thermal stability.[12] The mixture of alcohols was oxidised with Jones chromic acid which gave a yield of *ca.* 80% of four products (ratio 2 : 1 : 40 : 25 elution sequence Carbowax 20M) which all had M^+ 162 (m.s.–g.l.c.) and other spectroscopic data consistent with their being a mixture of the ketones (12), which are formally the products of *meta* cyclo-addition of methyl allyl ketone and benzene. However, despite ready fragmentation of the four ketones under electron impact to ions of mass 104 (base ion) and 58, irradiation of (12) at wavelengths between 250 and 300 nm in hydrocarbon or acetonitrile solution caused only very minor changes in the mixture. Thus traces of an isomer which may conceivably have been a cyclo-butanol type II cyclisation product were formed, but specifically there was no evidence for photoelimination of acetone and formation of semibullvalene. Hence the potential Norrish Type II elimination compounds (1), (3), and (12) are all essentially photostable under the variety of conditions employed in the present study.

The efficiency and mode of photocyclisation of arenes to enol ethers is very dependent on the structure of the addend.[6] Analogous investigations with enamines and vinyl sulphides have not apparently been undertaken. We have examined the photoreaction of benzene with 1-amino-*NN*-diethyl-2-methylpropene, 1-amino-*NN*-di-methylcyclopentene, and methyl vinyl sulphide. It should, however, be noted that both enamines and vinyl sulphides have appreciable absorptions in the 254-nm region and for this reason it was necessary to use in the present experiments relatively high concentrations of benzene (*i.e.* 10% solution of the ethylene in the arene), a situation which is known to increase the concentration of T_1 benzene *via* decay of the excimer,[20] and T_1 benzene does not result in adduct formation.[21]

Hence it may not be surprising that the products from these experiments were only those obtained by irradiation of the ethylene alone or in inert solvents. 1,1-Dimethylethylenes yield 'ene'-type acyclic adducts (13) with benzene *via*, it is proposed, a mechanism involving electron and proton transfer.[5] No products of this type were observed from the former amine even in the pre-

sence of methanol, which is surprising as it may have been expected that in such a system the primary step of electron transfer would have readily occurred.

Finally we have examined a reverse Diels–Alder reaction of a *meta* photocycloadduct as a route to semi-bullvalene. The conditions under which the thermal process occurs in practice vary considerably and it has also been observed to result from electron impact [22] and on ultraviolet irradiation.[22,23] We decided to study the elimination of cyclopentadiene from the compound of structure (14) which is formally the *meta* cycloadduct of
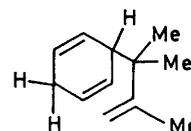

(13)

benzene and bicyclo[2.2.1]hepta-2,5-diene but since we were aware that (14) cannot be obtained by such a direct route [24] and that the mono-ene does undergo addition to benzene,[25] we have examined the synthesis of (14) by the addition of *trans* 5,6-dichlorobicyclo[2.2.1]-hept-2-ene (15) to benzene followed by dechlorination. Irradiation of a 15% solution of benzene in (15) gave after removal of the reactants, a viscous brown oil which from mass-spectral analysis consisted of 1 : 1 adducts of the starting materials and dimers of the ethylene: the relative yields of the products showed the same variation
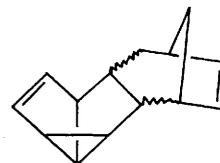

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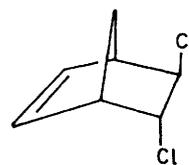
(15)

with reactant concentration as the system with the hydro-carbon ethylene.[25] The ^{1}H n.m.r. spectrum of the distilled product mixture was very similar in proton resonance position and multiplicity of signal to that described for the *meta* cycloadducts of benzene and bicyclo[2.2.1]hept-2-ene,[25] and the integration of the spectrum was consistent with the presence of *ca.* 12% of the ethylene cyclobutane dimer. The presence of chlorine in the ethylene appeared, therefore, to have little effect on its photoaddition to benzene. As the product mixture was somewhat intractable, it was considered that separation of adduct and dimers may be better achieved on the

dechlorinated products. The crude irradiation product was treated with sodium anthracenide in tetrahydrofuran,[26] which gave good yields of hydrocarbons separable by preparative g.l.c. Two compounds of molecular weight 170 ($C_{13}H_{14}$) were obtained in a ratio of 2 : 1 and although their stereochemistries were not determined in the present work, by analogy with the benzene–bicyclo-[2.2.1]hept-2-ene addition, the similarity of the ^{1}H n.m.r. spectra and the thermal behaviour of the adducts,[25] we assign structures (16) and (17) to the major and minor

(16)   (17)
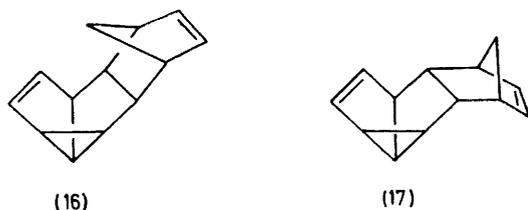
products respectively. In the mass spectrum of both (16) and (17) the base ion occurred at 104, thus indicating a ready retro-Diels–Alder reaction under electron impact but again, however, both products were essentially photostable and only polymeric material was formed on prolonged irradiation under a variety of conditions. The compounds were also surprisingly thermally stable and not until 320 °C did significant decomposition occur to yield a C_8H_8 compound. This compound was isolated by preparative g.l.c. and was found, as expected at these temperatures,[27] to be cyclo-octatetraene.

Thus we have shown that with simple allyl compounds, the success or failure of the photoaddition process with benzene is very dependent upon the type of substituent even though this is, of course, not in direct conjugation with the ethylene. Substituents which inhibit addition have lower-lying energy levels than those which have no apparent effect on the reaction, and we propose that in the former case energy is lost possibly from an excited state complex of the addends by interaction between the groups of the bichromophoric addend. As has been observed with the bicyclo-octane (18), through-bond

Ph—⟨ ⟩—NMe₂

(18)
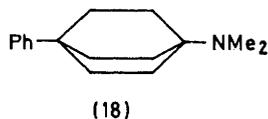
interaction in bichromophoric systems can occur over appreciable distances.[28] The interaction prevents reaction of either chromophore for not only is the ethylene addition inhibited in NN-dimethylallylamine but so also is that of the tertiary amino-grouping. Attempts to use the *meta* cycloaddition as a route to semibullvalene have failed since the Norrish Type II process did not occur with either the esters (1) and (3) or ketone (6) and the temperatures required for the retro-Diels–Alder reaction would cause rearrangement of this C_8H_8 isomer.

EXPERIMENTAL

The radiation source used for investigation of the addition reactions was a bank of Hanovia 15-W low-pressure mercury-arc lamps. Other sources used in the Norrish Type II experiments were a 500-W Hanovia medium-pressure mercury arc, an argon–iodine lamp powered by a microwave generator,[29] and a 200-W super-pressure mercury arc fitted in a Bausch and Lomb high intensity grating monochromator. Irradiation experiments were carried out both under air and following nitrogen degassing but this had little effect except in the studies with the amines when the latter condition was necessary to prevent rapid formation of a brown colouration.

Photoaddition of Methyl But-3-enoate to Benzene.— Irradiation of an equivolume solution (200 ml) of the reactants gave, after 24 h and removal of the starting materials at water-pump vacuum, *ca.* 2 g of a colourless oil which was comprised of the two 1 : 1 adducts. The components were separated by preparative g.l.c. with *ca.* 95% purity. The major 1 : 1 adduct had $\nu_{max.}$ (liquid smear) 3 050m, 3 030w, 3 000w, 2 940s, 2 860w, 1 740s, 1 600w, 1 436m, 1 420m, 1 370m, 1 350m, 1 300—1 270s, 1 150—1 000m, 720m, and 655m cm^{-1}, δ (220 MHz, CCl_4) 1.4—1.5 (1 H, d, J_{gem} 13 Hz, *endo* 6-H), 1.65—1.75 (1 H, t, $J_{1,2} = J_{2,8} = J_{2,3} = 2$ Hz, 2-H), 1.8—1.9 (1 H, q, $J_{2,8} = J_{1,8} = J_{7,8} = 7$ Hz, 8-H), 2.40—2.48 (1 H, m, $J_{exo-6,5}$ 6, $J_{exo-6,exo-7} = 11$, J_{gem} 13 Hz, *exo*-6-H), 2.5 (2 H, d, $J_{CH_2,exo-7}$ 8 Hz, –CH$_2$–), 2.6—2.7 (1 H, q, $J_{1,7}$ 6, $J_{1,2} = J_{6,7} = 7$ Hz, 1-H), 2.9—3.0 (1 H, m, $J_{exo-7,exo-6}$ 11 Hz, *exo*-7-H), 3.1 (1 H, t, $J_{1,3}$ 1, $J_{1,5} = J_{5,exo-6} = 6$ Hz, 5-H), 3.6 (3 H, s, Me), 5.4 (1 H, AB q, $J_{4,5}$ 1.5 Hz, $J_{3,4}$ 5.5 Hz, 4-H), and 5.6 (1 H, AB q, $J_{3,4}$ 5.5, $J_{2,3}$ 2 Hz, 3-H). The spectral data for the minor component were very similar to those reported above but the ^{1}H n.m.r. signals were not so clearly resolved and the CO$_2$Me resonance was now three very close singlets of approximate intensity 1 : 4 : 6

Attempted Norrish Type II Elimination of (1) *and* (3).— The adducts (0.1 g) were dissolved in pentane or aceto-nitrile (1 ml) and irradiated with the sources described above following nitrogen degassing. The experiments were monitored by g.l.c. and n.m.r. spectroscopy and also repeated in benzene solution. In no case was evidence obtained for the formation of semibullvalene which would have been detected by g.l.c. at very low concentrations.

Photoaddition of Pent-1-en-4-ol to Benzene.—Mixtures of benzene (30 ml) and pent-1-en-4-ol (50 ml) were irradiated for periods of 24 h and the starting materials recycled. Each experiment produced *ca.* 1 g of a mixture of 1 : 1 adducts. The distilled mixture (95—110 °C at 0.5 mmHg) had $\nu_{max.}$ (liquid smear) 3 500—3 200s, 3 050m, 3 020w, 2 960s, 2 920s, 2 850m, 1 600w, 1 455—1 445m, 1 370m, 1 350m, 1 125m, 1 080m, 720m, and 680m cm^{-1}. The two major products separated by preparative g.l.c. had similar i.r. spectra to that outlined above. The major isomer of the two had δ (60 MHz, CCl_4), 1.0—1.2 (3 H, d, J 6 Hz), 1.2—1.9 (5 H, m), 2.3 (1 H, br s), 2.2—2.6 (2 H, m), 2.4—2.8 (1 H, q, J 6 Hz), 2.9—3.2 (1 H, t of t, J 6 Hz), 3.4—4.0 (1 H, m, J 6 Hz), and 5.3—5.7 (2 H, 2 × AB q, J 5.5 and 2 Hz); the minor isomer had δ (60 MHz, CCl_4), 1.1 (3 H, d, J 6 Hz), 1.2—1.9 (5 H, m), 1.9 (1 H, s), 2.0—2.5 (2 H, m), 2.5—2.8 (1 H, q, J 6 Hz), 2.9—3.1 (1 H, m), 3.4—3.9 (1 H, m), and 5.3—5.7 (2 H, 2 × AB q, J 5.5 and 2 Hz).

Oxidation of (11).—The distilled adduct (11) (0.6 g) in acetone (10 ml) was cooled in an ice-bath and the mixture

stirred continuously during the dropwise addition of Jones chromic acid reagent. When all the alcohol had been converted into the ketone (12) (colour change, g.l.c.) the mixture was allowed to stand for 10 h and the acetone solution was decanted from the green solid. The acetone was evaporated under nitrogen to give 0.45 g of a mixture of ketones. The combined product from several experiments was distilled at 70—80 ° and 0.2 mmHg and had $v_{max.}$ (liquid smear) 1 710 cm^{-1} and $\lambda_{max.}$ (cyclohexane) 280 nm. The ^{1}H n.m.r. spectrum was very similar to that outlined for (3). The irradiation of (12) was carried out as for (1) and (3).

Irradiation of 1-*Amino*-NN-*diethyl*-2-*methylpropene,* 1-*Amino*-NN-*dimethylcyclopentene, and Methyl Vinyl Sulphide in Benzene Solution.*—A solution of each of the above ethylenes (5 ml) in benzene (45 ml) was degassed under nitrogen and irradiated for 24 h. The starting materials were removed at water-pump vacuum. Analysis of the oily residues (*ca.* 0.5 g) by combined g.l.c.–m.s. alongside the products from irradiation of the neat ethylene (1.0 ml) or in hydrocarbon solvent (1.0 ml of a 10% solution) revealed that 95% of the mixture from the benzene–ethylene reaction was derived from photolysis of the ethylene alone. The products from methyl vinyl sulphide all had abundant ions at m/e values of 89 ($EtSCH_2CH_2$), 75 ($EtSCH_2$), and 61 (EtS).

Photoaddition of (15) *to Benzene.—*The dichloroethylene (15) was prepared by heating cyclopentadiene (129 ml), (*E*)-1,2-dichloroethylene (123 ml), and quinol (0.5 g) in an autoclave at 208 °C for 60 h.

The solution of benzene (30 ml) in (15) (170 ml) was irradiated for 24 h, and the starting materials removed from the brown solution to give *ca.* 3 g of a viscous oil which comprised the adduct–ethylene dimer mixture. The mixture was distilled (210—230 °C at 0.02 mmHg) and the ^{1}H n.m.r. spectrum was very similar to those reported for the benzene–bicyclo[2.2.1]hept-2-ene adducts.[25] The resonances centred at δ 4.1 and 3.5 (each 1 H) in the present case were assigned to the protons geminal to the chlorine substituents.

Dechlorination of the Products from Benzene and (15).—Sodium (1 g) was added to a solution of anthracene (4 g) in dry tetrahydrofuran (175 ml) under nitrogen. The blue solution was cooled in an ice-bath and the photoproduct (2 g) was added dropwise while the solution was vigorously stirred. Work-up of the solution with water (1 ml) and extraction of the mixture with pentane following removal of the tetrahydrofuran gave *ca.* 1 g of the dechlorinated mixture. The dechlorinated adducts had δ (60 MHz, CCl$_4$), 1.04—1.35 (2 H, m), 1.55 (1 H, t, *J* 6 Hz), 1.6 (1 H, t, *J* 6 Hz), 1.8 (1 H, d, *J* 6 Hz), 2.2 (1 H, d, *J* 6 Hz), 2.3—2.6 (1 H, q, *J* 6 Hz), 2.4—2.8 (2 H, m), 2.9 (1 H, d, *J* 6 and 2 Hz), 5.45 (2 H, s), and 5.95 (2 H, AB q, *J* 6 and 2 Hz); the ethylene dimers had δ (60 MHz, CCl$_4$), 1.05—1.4 (4 H, m), 2.0—2.4 (4 H, m), 2.60 (4 H, m), and 6.05 (4 H, m). Photolysis of (14) was carried out under the conditions described above for the esters and ketones and although the solutions turned bright yellow no evidence was obtained for the formation of C_8H_8 isomers.

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