TRICYCLO[3.3.0.0^{2,8}]OCT-3-ENES: THEIR ACID CLEAVAGE REACTIONS AND CYCLOADDITIONS WITH DIENOPHILES

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Abstract – Tricyclo[3.3.0.0$^{2\ 8}$]oct-3-enes are conveniently obtained by the meta photocycloaddition of ethenes to benzenoid compounds. Acid catalyzed cleavage of the cyclopropane ring in the photoadduct affords bicyclo[3.3.0] and [3.2.1]octane derivatives and dienophiles undergo [2π+2π] and [2π+2σ+2π] cycloaddition to the ethene and ethenylcyclopropane moieties respectively. The preferred mode of reaction for both processes is controlled by the nature and position of the substituents in the meta cycloadduct.

The meta photocycloaddition of ethenes to benzenoid compounds directly yields tricyclo[3.3.0.0^{2,8}]oct-3-enes (dihydrosemibullvalenes) (1) and is potentially one of the most synthetically useful photochemical reactions that have been discovered.[1,2] Since the first reports of the process in 1966[3] numerous accounts concerning the mechanistic aspects and scope of the reaction have been published.[1,4] From data of the relative electron donor-acceptor properties of a benzene-ethene pair, the feasibility of the photoaddition proceeding preferentially by a meta or ortho reaction (see Scheme 1) can now be readily assessed.[5] Even in systems where the latter process has the higher quantum efficiency, the greater photolability of the ortho cycloadducts compared to the meta isomers under the conditions of their formation means that on prolonged irradiation the dihydrosemibullvalenes frequently predominate. Further, the factors which dictate the regio- and stereo-chemistries of the meta photocycloaddition have largely

Scheme 1
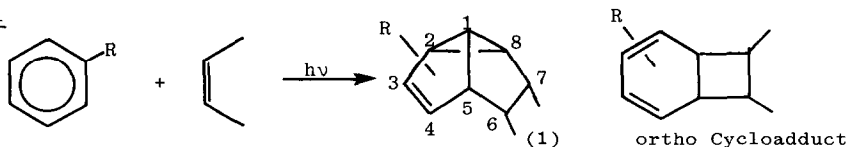
been elucidated,[6,7] although it must be admitted that control remains to be achieved over the isomer formation which in some cases results from the two directions of cyclopropane ring formation in the reaction intermediate (2) as shown in Scheme 2.[8] Nonetheless the combination of the applicability of the meta cycloaddition to a wide variety of ethene-benzene pairs, its occurrence as essentially the sole intramolecular reaction from 254 nm irradiation of 5-phenylpent-1-ene derivatives,[9] and the feasibility of obtaining multigram

quantities of the adducts with high isomer selectivity, render this photoprocess
most attractive as a synthetic step towards a variety of naturally occurring
compounds.[2]   Yet despite these features of the process, with the notable except-
ion of the elegant studies of Wender and co-workers principally with intra-
molecular systems,[2] the general synthetic usefulness of the meta photocyclo-
addition of ethenes to benzenoid compounds remains essentially unexploited.
Reports by ourselves[10] and others,[11,12] however, have indicated that chemical
transformations of meta photocycloadducts may have more general synthetic
potential than currently appreciated. Acidolysis of the cyclopropane ring to
give bicyclo[3.3.0] or [3.2.1] octane derivatives and thermal reaction of the
ethenylcyclopropane moiety of the meta adduct with dienophiles could be particu-
larly useful processes but the present sparse data does not allow reaction mode
predictability in either case. We now report on the features of the adducts
which influence and control their acidolysis and cycloaddition processes, and
thereby we demonstrate that these readily accessible ethenylcyclopropane systems

Scheme 2
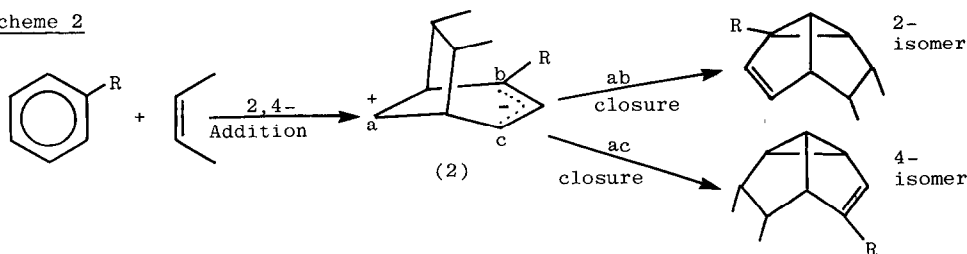
can be conveniently and selectively transformed to various commonly encountered
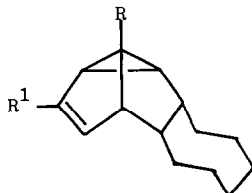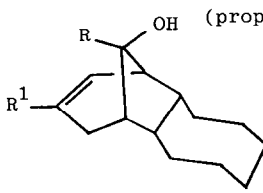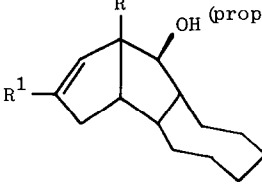ring systems.

Results and Discussion

i) Acidolysis of meta Photocycloadducts of Ethenes and Benzenoid Compounds.

     There is a wealth of well-documented data concerning the acidolysis of
cyclopropane derivatives[13] but the reactions with the ethenylcyclopropane moiety
of meta photocycloadducts has attracted little attention. From initial studies
using the benzene-cyclopentene adduct and 84% aqueous acetone containing
4% v/v of concentrated hydrochloric acid, it was suggested that protonation at
the 4-position occurred and led to cleavage of the 2,8-bond giving hydroxy-
bicyclo[3.3.0]octene derivatives.[14] Subsequent X-ray data of similarly derived
products from other meta photocycloadducts discounted these structures and the
bicyclo[3.2.1]octene skeleton resulting from 1,2-cleavage was confirmed for the
acidolysis products.[11,15] The studies described below illustrate that the
product of acidolysis of meta adducts can be essentially controlled by the
position and nature of the substituent and further, since the yields from both
the photoaddition reaction and the facile cyclopropane ring opening are good,
the formation of bicyclo[3.3.0] and [3.2.1] octane derivatives by this route
becomes synthetically attractive.

     The influence of alkyl substituents on the mode of cyclopropane ring opening
under acidolysis conditions was investigated using the meta photocycloadducts of
a variety of alkylbenzenes with cis cyclo-octene. These systems were chosen
since they allow the selective formation of 1- and 3-substituted adduct isomers
as a result of the influence of substituent size on the positions of photo-
addition of the cycloalkene onto the arene.[7,16] The adducts were conveniently
synthesized by 254 nm irradiation of equivolume mixtures of the arene and ethene.
In order to eliminate decomposition and formation of chlorinated products during
acidolysis, the hydrochloric acid concentration was necessarily reduced from

4% to 0.75%. Under gentle reflux, the photoadducts were then converted essentially quantitatively within 3.5h into the bicyclic alcohols. In order to illustrate the main substituent effects on the course of acidolysis, representative examples of the results are presented in Table 1. The bicyclo[3.3.0] and

Table 1.   Acidolysis Products of Selected meta Photocycloadducts of
            cis Cyclo-octene and Alkylbenzenes

Photoadduct	Product of 1,2-Bond Cleavage	Product of 2,8-Bond Cleavage

	(proportion)	(proportion)
R=R^1=H (6)	R=R^1=H (50%) (18)*	R=R^1=H (50%) (19)*
R=Me,R^1=H	R=Me,R^1=H (100%) (17)	-
R=H, R^1=Bu^t	R=H,R^1=Bu^t (10%)	R=H, R^1=Bu^t (90%) (4)
R=Me,R^1=Pr^i	R=Me,R^1=Pr^i (100%) (3)	-

* Separated and identified as the corresponding ketones.

[3.2.1]octanol structures were proven by X-ray crystallographic analysis of derivatives in the case of (3) and (4). Structural assignments for the other products were achieved by comparison of their spectral characteristics with those of (3) and (4). Formation of the two bicyclo-octane systems is readily rationalised in terms of protonation at the 4-position of the photoadduct followed by cleavage of either the 1,2- or 2,8-cyclopropane bonds (see Scheme 3). Support

Scheme 3
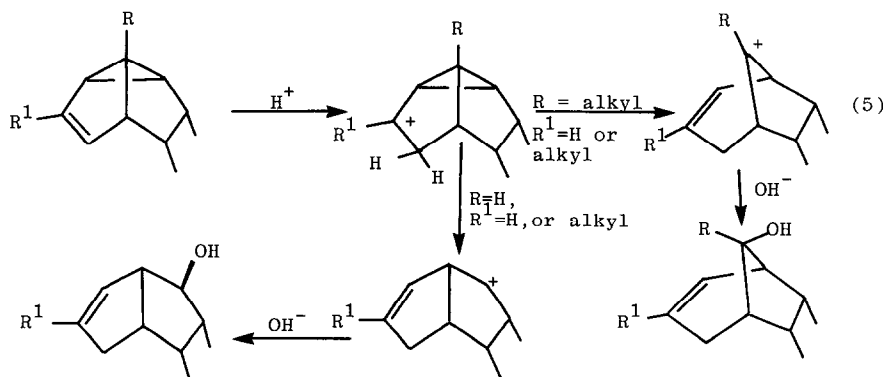
for this proposal is provided by the lack of reaction of the hydrogenated meta cycloadducts under the present acid conditions. It is evident that the position of the substituent markedly influences which bond of the cyclopropane ring is preferentially cleaved. Thus a 1-substituent results in specific breaking of the 1,2-bond to produce the tertiary carbocation (5) and thence the 8-hydroxy-bicyclo[3.2.1]oct-2-ene whereas 2,8-cleavage and formation of the bicyclo[3.3.0]

oct-2-ene skeleton requires a 3-substituent in the photoadduct. The 2,8-
cleavage is selective to 75-90% but for examples in which both 3- and 1-
substituents are present the latter controls the reaction and again breaking
of the 1,2-bond is the sole process. In contrast to these results, acidolysis
of the unsubstituted adduct (6) from benzene and cis cyclo-octene gives a
1:1 mixture of alcohols resulting from both 1,2- and 2,8- opening of the cyclo-
propane ring. This result is surprising since the reaction of the corresponding
benzene-cyclopentene adduct with acid yields only the bicyclo[3.2.1]oct-2-ene
skeleton[14] and hence it appears that the mode of cyclopropane cleavage in
unsubstituted dihydrosemibullvalene systems can be unexpectedly susceptible to
minor structural changes at remote sites. The presence of substituents does,
however, render the cleavage predictable but in contrast to the above directing
effects, the three examples of acidolysis of intramolecular meta photocyclo-
adducts which have been reported all occur by exclusive breaking of the 2,8-
bond regardless of the presence or absence of a 1-substituent:[17] this feature
in intramolecular systems remains to be explained.

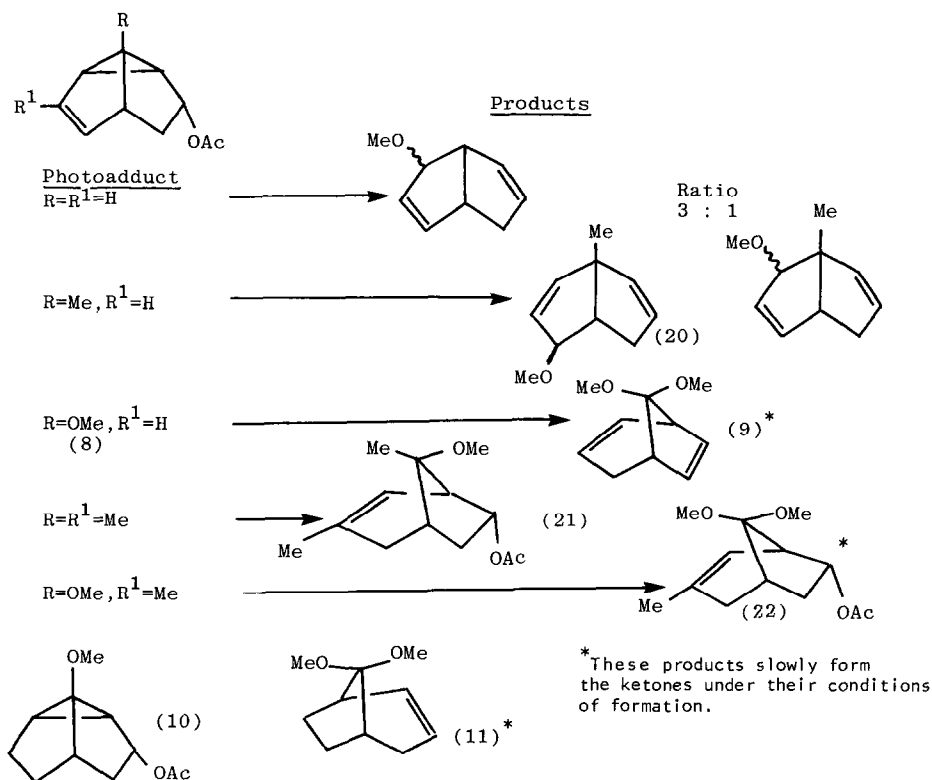   Irradiation of benzenoid compounds in the presence of vinyl acetate
conveniently yields dihydrosemibullvalenes having a 7-endo acetate substituent
as the major products.[18] We have previously noted that the meta cycloadduct
derived from benzene can readily be transformed on refluxing in weakly acidic
methanol into the bicyclo[3.3.0]octadiene (7).[10] This specific 2,8-ring opening
of the cyclopropane ring is accounted for by protonation at the acetate function
and ethenylcyclopropane assisted elimination of acetic acid as shown in
Scheme 4. Wender and co-workers have used arene-vinyl acetate meta photocyclo-

Scheme 4
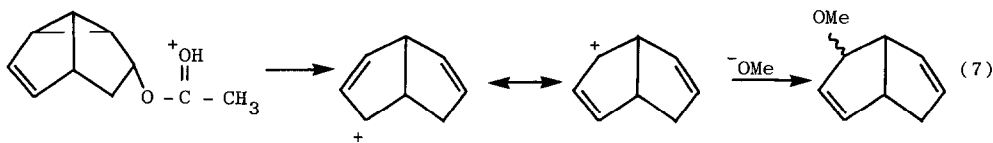
adducts as key intermediates in synthetic routes to modhephene[19] and isoirido-
myrmecin[20] and in view of such synthetic potential of these readily accessible
photoproducts, the possibility of controlling the methanolysis-elimination
reaction by substitution on the ethenylcyclopropane system has been investigated.
The results presented in Table 2 are to illustrate particular directing effects
of substituents which, from a study of a variety of vinyl acetate derived
adducts, appear to be general.   It is evident that the presence of 1-alkyl
groups has little or no effect on the reaction of these meta adducts in acidified
methanol and for the mono-substituted compounds acetate protonation and 2-8 bond
cleavage is, as for the unsubstituted adduct, the exclusive pathway. Treatment
of the 1-methoxy compound (8) under the present conditions again appears to
involve acetate protonation but now cleavage of the 1,8- rather than the 2,8-
bond of the dihydrosemibullvalene accompanies elimination of the acetic acid.
Consistent with this interpretation for the formation of (9) rather than a route
involving 4-protonation and breaking of the 1,2-bond with subsequent acetic acid
elimination, the hydrogenated adduct (10) underwent ready methanolysis and elimin-
ation to give (11).   Hydrogenation of (9) and (11) followed by further hydrolysis
gave the common product, bicyclo[3.2.1]octan-8-one. The presence of a 3-alkyl
substituent for both the 1-alkyl- and 1-methoxy-dihydrosemibullvalene acetates
has a pronounced effect on the methanolysis reaction. The products now evidently

Table 2.   Products from Treatment of _meta_ Photocycloadducts of
          Vinyl Acetate and Substituted Benzenes with MeOH/H$^+$

R

R^1

OAc

Photoadduct
R=R^1=H

Products

MeO

Ratio
3 : 1   Me

MeO

Me

R=Me,R^1=H

(20)

MeO   MeO   OMe

Me   OMe

MeO

R=OMe,R^1=H
(8)

(9)*

Me   OMe

R=R^1=Me

(21)   MeO   OMe

Me   *

OAc

MeO   OMe

R=OMe,R^1=Me

Me   (22)   OAc

OMe

MeO   OMe

*These products slowly form
the ketones under their conditions
of formation.

(10)

OAc

(11)*

result from protonation at the 4-position and cleavage of the 1,2-cyclopropane
bond leaving the acetate function in the product. Thus the reactions of vinyl
acetate _meta_ photocycloadducts in acidic methanol may be specifically controlled
by substituents on the ethenylcyclopropane moiety to yield bicyclo[3.3.0]octa-
2,6-dienes by 2,8-bond cleavage and acetate elimination or bicyclo[3.2.1]oct-ene
or -diene derivatives by breaking of the 1,2- or 1,8-cyclopropane bond and
retention or elimination of the acetate respectively.

ii) Reactions of _meta_ Photocycloadducts of Ethenes and Benzenoid Compounds
     with Dienophiles.

     There is a limited literature concerning the reactions of ethenylcyclopro-
pane systems with dienophiles. Products of (2π+2π)[21] and (2π+2σ+2π) (homo Diels
Alder) cycloadditions,[22] and of "ene"[22] and "pseudo ene"[12] additions (Scheme 5)
have all been reported and from the sparse available data it appears that which
pathway is preferred is dependent on the substitution on the ethenyl cyclopropane[23]
and the nature of the dienophile.[22] Further, the formation of (2π+2π) cyclo-
adducts can be markedly influenced by the polarity of the solvent,[21] and in some
systems the reaction is apparently complicated by the thermal rearrangement of
the cyclobutane to a cycloheptene, the homo Diels Alder product.[24]

     Despite the versatile and convenient synthesis of ethenyl cyclopropane
systems by the _meta_ photocycloaddition of ethenes to benzenoid compounds, there
has been very scant interest shown over the years in the reaction of these
adducts with dienophiles. We reported the (2π+2π) cycloaddition of tetracyano-
ethene (TCNE) to the _meta_ cycloadduct (6) in 1966[3b] and Subrahmanyam described
the homo Diels Alder adduct of the anisole-cyclopentene adduct with TCNE and
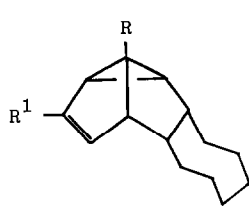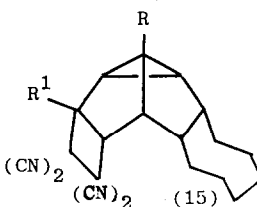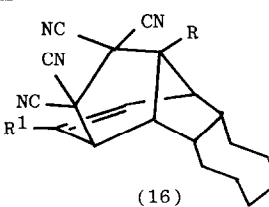
Scheme 5
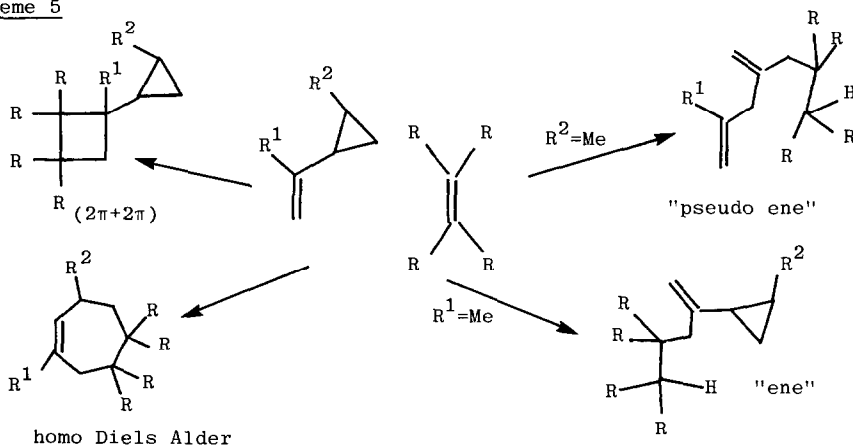
homo Diels Alder

4-phenyl-1,2,4-triazoline-3,5-dione ten years later.[25] More recently Sheridan
has observed "ene", "pseudo ene" and homo Diels Alder products between the
4-methyltriazoline dione and the meta photoadduct of m-xylene and cyclopentene,[12]
and we have reported that (2π+2σ+2π) cycloaddition with acetylenic dienophiles
and these photoproducts can be promoted under 11k bar pressure.[26]

    In view of the paucity of information concerning the reactions of dienophiles
with ethenylcyclopropane systems, and in order to widen the scope of the chemical
transformations of meta photocycloadducts particularly in their use as intermedi-
ates to polycyclic systems, the reactions of a variety of these arene-ethene
photoadducts with a range of ethenes, acetylenes, and azo compounds has been
studied. Only known powerful dienophiles such as TCNE and triazoline diones were
reactive under ambient pressure and in these cases with arene-cycloalkene meta
cycloadducts, complete conversion of the starting materials was evident within
2h for most systems at room temperature. Reactions with chlorosulphonyl isocyan-
ate (CSI) as the dienophile were complete at 0°C in 16h. Progress of the reaction
was readily assessed in most cases by monitoring the fading of the colouration
(violet through to yellow) produced immediately on mixing the reactants in
dichloromethane solution. The results of the reactions for the meta cycloadducts
of cis cyclo-octene and benzenoid compounds with TCNE are summarised in Table 3
and are typical of those observed with CSI as dienophile and with vinyl acetate
photoadducts: in the latter systems, however, reaction times at room temperature
were generally two days. Triazolines in general did not undergo (2π+2π) cyclo-
addition with the meta cycloadducts and wherever feasible gave "ene" and/or
"pseudo ene" products as well as the homo Diels Alder adduct. The principal
conclusions from the present study are that meta photocycloadducts having
a substituent at the 1-position undergo a facile homo Diels Alder reaction but
the presence of a 3-substituent results in the (2π+2π) cycloaddition being the
sole process except in cases where a 1-methoxy substituent is present when again
the (2π+2σ+2π) reaction is exclusive. These observations are readily accounted
for in terms of electrophilic attack of the dienophile at the 4-position of the
photoadduct to form (13) which may either ring close to yield the cyclobutane
product or rearrange to the precursor (14) of the homo Diels Alder adduct.
Which route is followed is clearly dictated by the substituent stabilisation at
the charge/radical centres and this feature predictably results in specific
reaction to give good yields of (2π+2π) or (2π+2σ+2π) cycloadducts (15) and (16).

    To summarise, the reactions reported here illustrate that the dihydrosemi-
bullvalene derivatives, readily and predictably obtained by the meta photocyclo-

Table 3   Products of the Reaction of TCNE with _meta_ Photocycloadducts

of _cis_ Cyclo-octene and Benzenoid Compounds

(CN)$_2$

(CN)$_2$ (15)

(2π+2π)

NC   CN   R

CN

NC

R^1

(16)

homo Diels Alder

(2π+2σ+2π)

R=R^1=H (6)	R=R^1=H	–
R=Me,R^1=H	–	R=Me,R^1=H
R=OMe,R^1=H	–	R=OMe,R^1=H
R=R^1=Me	R=R^1=Me	–
R=OMe,R^1=Me	–	R=OMe,R^1=Me
R=Me,R^1=Pr$^{\underline{i}}$	R=Me,R^1=Pr$^{\underline{i}}$	–

addition of ethenes to benzenoid compounds, undergo highly selective or specific chemical transformations in good yields and under mild conditions. Bicyclo[3.3.0] and [3.2.1]octanes are conveniently accessible from the photoadducts under acidic conditions and reactions of the ethenylcyclopropane moiety with dienophiles leads to cyclobutane formation or homo Diels Alder adducts. The course of these transformations is controlled by the nature and the position of the substituent(s) on the photoadduct. The latter in a particular ethene-arene photosystem can be predicted from the factors which are known to influence the orientation of the _meta_ photocycloaddition reaction.

(13)

(14)

(15)

(16)

(23)
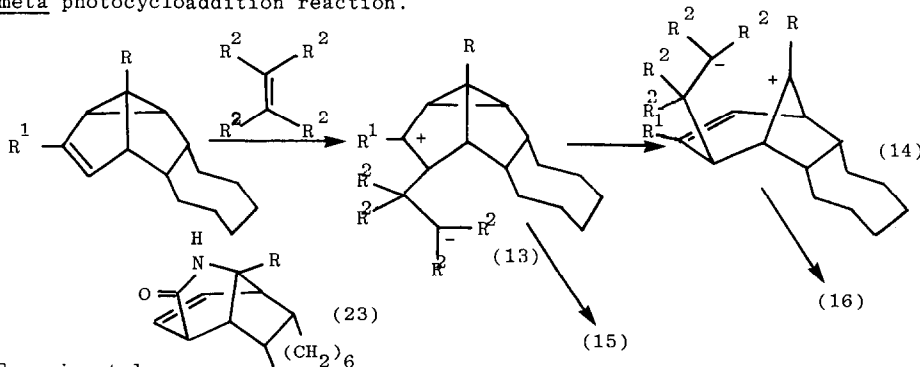
Experimental

The _meta_ photocycloadducts were prepared by 254 nm irradiation (two 60 cm 30w low pressure mercury arc lamps) of equivolume mixtures of the benzenoid compound and the ethene contained in four 50x1 cm silica tubes. Radiation absorbing polymer was periodically removed from the inner surface of the reaction tubes. Reactants were recovered by rotary evaporation and the crude adducts were purified by vacuum distillation at 0.05 mm Hg. By such means quantities in excess of 5g of distilled adducts were obtained from 24h irradiation. Where necessary (e.g. for the products of _t_-butylbenzene and _cis_ cyclo-octene) further adduct purification

and isomer separation was achieved by preparative GC or flash chromatography. The adducts were identified by comparison of their spectral properties with those reported in the literature (see refs. 1-6).

The acidolysis reactions of the photoadducts of alkylbenzenes were achieved by the addition of concentrated hydrochloric acid (0.56 ml) to a solution of the photoproduct (0.5g) in 84% aqueous acetone (75 ml). The mixture was gently refluxed and the reaction was monitored by TLC.   On complete disappearance of the photoadduct (ca. 0.5-3.5h), the reaction mixture was neutralised with a saturated solution of sodium bicarbonate and extracted with dichloromethane (2×25 ml). The combined dichloromethane extracts were dried over anhydrous sodium sulphate and the solvent removed to give yields of the unpurified alcohols of the order of 90%. Further purification of the product was achieved where necessary by flash chromatography (4:1, 40-60 b.p. petroleum ether:diethyl ether). The acid catalysed reactions of the vinyl acetate-arene meta photocycloadducts involved the addition of concentrated hydrochloric acid (40μl) to a solution of the adduct (1.0g) in methanol (50 ml) and gentle refluxing the mixture. The reaction as judged by GC was essentially complete within 30 min. but the adduct derived from anisole was only 40% converted at this time and the product from both this system and that from the p-methylanisole adduct underwent slow hydrolysis under the conditions of their formation to give the corresponding ketone: these reactions were quenched at 80% conversion of the starting material. Work up of these reactions was the same as that outlined above for the cis cyclo-octene adducts and gave yields of the crude product between 80 and 90%. The products derived from the toluene and anisole adducts could only be obtained in purities satisfactory for analytical data by preparative GC.

The reactions of the meta photocycloadducts with TCNE were performed in the following manner. The adduct (1.0g) was dissolved in dichloromethane (40 ml) and TCNE (2% mol excess) was added. The reaction was monitored by TLC and fading of the colouration produced on mixing the reactants. On complete conversion of the starting materials (0.5-2h), the solvent was removed by rotary evaporation and diethyl ether (40 ml) added. The off-white solid product was filtered and recrystallised from n-hexane: yields of 65-75% of product having satisfactory analytical data were obtained. The reactions of the adduct (0.5g) in dichloromethane (20 ml) with CSI (equimolar amount) in dichloromethane (1 ml) were maintained at 0°C for 16h. A saturated sodium bicarbonate solution (20 ml) was then added, the mixture was shaken, and the organic layer separated and dried over anhydrous sodium bicarbonate. The solvent was removed by rotary evaporation and the products purified by flash chromatography (4:1, 40-60 b.p. petroleum ether: ethyl acetate). The data which allowed structural assignments to be made for the products described above from the reactions under acid conditions and in the presence of dienophiles are given below. The [1]H n.m.r. spectra were recorded on a Perkin Elmer R-34 Spectrometer and structural assignments were confirmed by extensive decoupling experiments and, where appropriate, the effects of addition of shift reagents and shaking the samples with D_2O. Satisfactory purity of samples for accurate mass determination was assured by TLC and GC.

Products from acidolysis   i) meta Photocycloadducts of cis cyclo-octene and benzenoid compounds. (3) δ(CDCl₃) 6.65(1H,br s), 5.44(1H,br d), 2.71(1H,m), 2.58(1H,m), 2.26(4H,overlapping m's), 1.69(3H,s), 1.01(6H,d), and 1.7-1.0 (13H, overlapping signals); v_{max} (CHCl₃) 3400 cm⁻¹. M^+ calc. found m/z 262.2307. The phenyl urethane derivative (m.p. 189.5-191°C from ethanol) had C, 78.93; H, 9.45; and N, 3.25%; $C_{25}H_{35}NO_2$ requires C, 78.74; H, 9.19; and N, 3.67%. (4) δ(CDCl₃) 5.47(1H,m), 4.15(1H,s), 3.37(1H, dd), 2.96(1H,m), 2.35(3H,m), 2.0-1.3(14H,overlapping m's), and 1.00(9H,s); v_{max} (CHCl₃)3450cm⁻¹; M^+ calc. 262.2297, found m/z 262.2313. The p-bromophenyl urethane (m.p.165-7°C from ethyl acetate) had C, 65.15; H, 7.51; and N, 3.07; $C_{28}H_{34}O_2NBr$ requires C, 65.22; H, 7.39; and N, 3.03%. The minor acidolysis product from the t-butylbenzene-cis cyclo-octene adduct had δ(CDCl₃) 5.30(1H,br s), 3.71(1H,dd), 2.96(2H,m), 2.32(3H,m), 1.04(9H,s) and 2.0-1.0(14H,overlapping m's), v_{max} (CHCl₃) 3370 cm⁻¹; M^+ calc. 262.2297, found m/z 262.2330. (17), δ(CDCl₃) 5.67(1H,q of q), 5.38(1H,16 lines), 2.42(2H overlapping m's), 2.27(1H,m), 2.20(1H,m), 2.01(1H,br t), 1.83(1H,m), 1.41(3H,s), and 1.8-1.2(5H, overlapping m's); v_{max} (CHCl₃) 3370 cm⁻¹; M^+ calc. 220.1788, found m/z 220.1821. The alcohols (1:1 mixture by GC) from acidolysis of the meta photocycloadducts of benzene and cis cyclo-octene could not be satisfactorily freed from each other and the waxy crystalline mixture (0.4g) in acetone (10 ml) was oxidised with Jones' chromic acid to give the mixture of ketones (0.3g 1:1 mixture by GC) which were separated by flash chromatography (20:1, 40-60 b.p. petroleum ether:ethyl acetate).(18) δ(CDCl₃) 5.51(1H, q of q), 5.40(1H,m), 2.60(2H, overlapping m's), 2.13(4H, overlapping m's) and 2.0-1.0(12H, overlapping m's). v_{max} (CHCl₃) 1750 cm⁻¹; M^+ calc. 204.1514, found m/z 204.1540. (19) δ(CDCl₃) 5.68(2H,overlapping m's), 3.30(1H,m), 3.08(1H,m), 2.50-2.20(4H,overlapping m's), and 2.0-1.20(12H,overlapping m's); v_{max} (CHCl₃) 1740 cm⁻¹; M^+ calc. 204.1514, found m/z 204.1533.
ii) meta Photocycloadducts of vinyl acetate and benzenoid compounds
(20) δ(CDCl₃) 5.96(1H,d + fine splitting), 5.75(1H,dd), 5.62(1H,m), 5.54(1H,m),

4.18(1H,br s), 3.50(3H,s), 2.84(1H,q of t), 2.40-2.0(2H,overlapping m's), and
1.24(3H,s); M^+ calc. 150.1045, found m/z 150.1054. The minor product from
treatment of the toluene-vinyl acetate adduct with acidic methanol was a mixture
of isomers (M^+ = 150) and had δ(CDCl₃) 5.86(1H,m), 5.60(1H,m), 5.55(2H,m's),
4.02(1H,br s), 3.41(3H,s), 3.00(1H,m), 2.62(1H,m),2.30(1H,m's), and 1.18(3H,s).
(9) δ(CDCl₃) 6.38(1H,q), 6.02(1H,m), 5.75(1H,q), 5.45(1H,m), 3.28(3H,s),
3.25(3H,s), 2.77(2H,m), 2.48(1H,d of m), and 1.98(1H,d of m); M^+ calc. 166.0994,
found m/z 166.1008. The hydrogenated product (10) had δ(CDCl₃) 5.64(1H,q of d),
3.38(3H,s), 3.31(1H,m), 2.89(1H,dd), 2.68(1H,12 lines), 2.05(3H,s), and
2.0-1.2(6H,overlapping m's); ν$_{max}$ (smear) 1738 cm⁻¹; M^+ calc. 196.1099,
found m/z 196.1115. Treatment of the hydrogenated product with acidified methanol
gave (11) δ(CDCl₃) 5.86(1H,16 lines), 5.60(1H,16 lines), 3.29(3H,s), 3.25(3H,s),
2.56(1H,d of m's), 2.44(1H,br t), 2.28(1H,m), and 2.1-1.4(5H overlapping m's);
M^+ calc. 168.1146, found m/z 168.1141. Product from hydrogenation of (9) and
(11) had δ(CDCl₃) 3.27(3H,s), 3.20(3H,s), 2.16(2H,m), and 1.9-1.3(10H, over-
lapping m's); M^+ calc. 170.1302, found m/z 170.1328; treatment of this product
(0.3g) with hydrochloric acid (0.2ml) in 80% aqueous acetone (50 ml) gave
bicyclo[3.2.1]octan-8-one as the sole product. (21) δ(C₆D₆) 5.47(1H,m),
5.33(1H,br d), 3.20(1H,m), 3.01(3H,s), 2.76(1H,overlapping q of d), 2.59(1H,m),
2.16(1H,d of m), 1.85(1H,m), 1.77(3H,s), 1.52(3H,s), 1.38(1H,dd), and 1.13(3H,s);
ν$_{max}$(smear) 1745 cm⁻¹; M^+ calc. 224.1412, found m/z 224.1433. (22)δ(CDCl₃)
5.50(1H,br d), 5.15(1H,overlapping d of t), 3.25(3H,s), 3.24(3H,s), 2.85(1H,dd),
2.5-2.3(4H,overlapping m's), 2.04(3H,s), 1.72(3H,br s), and 1.39(1H,dd);
ν$_{max}$(smear) 1742 cm⁻¹; M^+ calc. 240.1356, found m/z 240.1371.

Products from reaction of <u>meta</u> photocycloadducts with TCNE

(15) (R=R¹=H) m.p. 214°C (ref. 3b); δ(CDCl₃) 3.66(2H,m),2.95(1H,m),
2.55(4H,overlapping m's), 2.08(1H,m), and 2.0-1.0(12H,overlapping m's);
ν$_{max}$ (nujol mull) 2255cm⁻¹; C, 75.50; H, 6.44; and N, 17.64%; C₂₀H₂₀N₄ requires
C, 75.95; H, 6.33; and N, 17.72%. (16) (R=Me,R¹=H), m.p. 217-218°C;
δ(CDCl₃) 6.25(1H,dd), 5.86(1H,dd + fine splitting), 3.31(1H,overlapping dd),
3.07(1H,m), 2.46(3H,m), 1.63(3H,m), and 2.0-1.0(12H,m); ν$_{max}$ (nujol mull)
2245cm⁻¹; C, 76.12; H, 6.82; and N, 17.11%; C₂₁H₂₂N₄ requires C, 76.36;
H, 6.67; and N, 16.97%. (16) (R=OMe,R¹=H), m.p. 195-8°C; δ(CDCl₃) 6.19(1H,
d of d), 5.94(1H, d of m), 3.54(3H,s), 3.31(2H,m), 3.10(1H, t of d), 2.55(1H,m),
2.28(1H,m), and 2.0-1.0(12H,overlapping m's); ν$_{max}$ (nujol mull) 2225cm⁻¹;
C, 72.58; H, 6.72; and N, 16.55%; C₂₁H₂₂N₄O requires C, 72.83; H, 6.36; and
N, 16.18%. (15) (R=R¹=Me), m.p. 145-147°C, δ(CDCl₃) 2.99(1H,s), 2.67(3H,m),
1.83(3H,s), 1.55(3H,s), and 2.0-1.0(14H,overlapping m's); ν$_{max}$(nujol mull)
2250cm⁻¹; C, 76.74; H, 7.06; and N, 16.54%; C₂₂H₂₄N₄ requires C, 76.74;
H, 6.98, and N, 16.28%. (16) (R=OMe,R¹=Me), m.p. 226-9°C, δ(CDCl₃) 5.90(1H,br d),
3.58(3H,s), 3.34(1H,q of d), 3.08(1H,d), 3.02(1H,br dd), 2.53(1H,m), 2.26(1H,m),
2.00(3H,s), and 2.0-1.0(12H,overlapping m's); ν$_{max}$ (nujol mull) 2245 cm⁻¹;
C, 73.82; H, 6.95; and N, 15.81%; C₂₂H₂₄N₄O requires C, 73.33; H, 6.67; and
N, 15.56%. (15) (R=Me,R¹=i-Pr), m.p. 123-5°C, δ(CDCl₃) 3.35(1H,br s),
2.61(4H,overlapping m's); 1.87(6H,d), 1.49(3H,s), and2.0-1.0(14H,overlapping m's);
ν$_{max}$(nujol mull) 2262cm⁻¹; C, 77.83;H, 7.62; and N, 14.93%; C₂₄H₂₈N₄ requires
C, 77.42; H. 7.53; and N, 15.05%.

The reaction of CSI with the <u>meta</u> photocycloadduct of anisole and
<u>cis</u> cyclo-octene illustrates the homo Diels Alder addition observed with other
systems not specifically described in the text. The product (23) was purified
by flash chromatography, isolated in a non-optimised overall yield of 60%,
(purity assured by TLC only) and had m.p. 130-131°C; δ(CDCl₃) 6.22(1H,q),
5.70(1H,br q), 3.31(1H,t), 3.19(1H,br t), 2.86(1H,br t), 2.60(1H,m), 2.24(1H,m),
3.52(3H,s), and 2.0-1.0 (13H,overlapping m's); ν$_{max}$(nujol mull) 3155 and 1700 cm⁻¹;
M^+ calc. 261.1723, found m/z 261.1744.

References

1.   See references in D.Bryce-Smith and A.Gilbert, <u>Tetrahedron</u>,1977,<u>33</u>,2459;
      A.Gilbert, <u>Pure Appl.Chem.</u>, 1980,<u>52</u>,2669; "Aromatic Photochemistry" in
      "Photochemistry" (Specialist Periodical Report), ed. D.Bryce-Smith,
      The Royal Society of Chemistry, London, Vols.1-18.
2.   P.A.Wender and T.W.von Geldern, "Aromatic Compounds: Isomerisation and
      Cycloaddition" in <u>Photochemistry in Organic Synthesis</u>, ed. J.D.Coyle,
      The Royal Society of Chemistry Special Publication No. 57, 1986, 226,
      and references therein.
3.   (a) K.E.Wilzbach and L.Kaplan, <u>J.Amer.Chem.Soc.</u>, 1966, <u>88</u>, 2066;
      (b) D.Bryce-Smith, A.Gilbert, and B.H.Orger, <u>Chem.Commun.</u>, 1966, 512.
4.   J.Mattay, J.Runsink, J.A.Piccirilli, A.W.H.Jans, and J.Cornelisse,
      <u>J.Chem.Soc.Perkin I</u>, 1987, 15; J.A.van der Hart, J.J.C.Mulder, and
      J.Cornelisse, <u>J.Molecular Structure</u>, 1987, <u>151</u>,1 and references therein.

5. J.Mattay, Tetrahedron, 1985, 41, 2405; D.Bryce-Smith, A.Gilbert, and
    J.Mattay, Tetrahedron, 1986, 21,6011.
6. E.M.Osselton, E.L.M.Lempers, C.P.Eyken, and J.Cornelisse,
    Rec.Trav.Chim.Pays-Bas,1986,105,171.
7. D.Bryce-Smith, M.G.B.Drew, G.A.Fenton, and A.Gilbert,
    J.Chem.Soc.Chem.Commun., 1985, 607.
8. M.G.B.Drew, A.Gilbert, P.Heath, A.J.Mitchell, and P.W.Rodwell,
    J.Chem.Soc.Chem.Commun., 1983, 750; M.G.B.Drew, A.Gilbert, and
    P.W.Rodwell, Tetrahedron Letters, 1985,26,949.
9. G.C.R.Ellis-Davies, A.Gilbert, P.Heath, J.C.Lane, J.V.Warrington, and
    D.L.Westover, J.Chem.Soc.Perkin II, 1984, 1833.
10. A.Gilbert and P.Yianni, Tetrahedron, 1981, 37,3275.
11. R.Srinivasan, V.Y.Merritt, and G.Subrahmanyam, Tetrahedron Letters,
    1974, 15, 2715.
12. R.S.Sheridan, J.Am.Chem.Soc., 1983, 105,5141.
13. See for example C.H.de Puy, Fortschr.Chem.Forsch., 1973,40,73
    and references therein.
14. V.Y.Merritt, J.Cornelisse, and R.Srinivasan, J.Amer.Chem.Soc., 1973,95,8250
15. G.Subrahmanyam, R.Srinivasan, S.L.La Placa, and J.E.Weidenborner,
    J.Chem.Soc.Chem.Commun., 1975,231; V.Y.Merritt, J.Cornelisse, and
    R.Srinivasan, J.Amer.Chem.Soc., 1975,97,1987.
16. R.S.Sheridan, Tetrahedron Letters, 1982, 23, 267; D.Bryce-Smith,
    G.A.Fenton, and A.Gilbert, Tetrahedron Letters, 1982, 23, 2697.
17. P.A.Wender and J.J.Howbert, Tetrahedron Letters, 1983,24,5325;
    J.Mani, J.H.Cho, R.R.Astik, E.Stamm, P.Bigler, V.Meyer, and R.Keese,
    Helv.Chim.Acta., 1984, 67, 1930.
18. A.Gilbert and M.W.bin Samsudin, J.Chem.Soc.Perkin I, 1980, 1118.
19. P.A.Wender and G.B.Dryer, J.Amer.Chem.Soc., 1982, 104, 5805.
20. P.A.Wender and G.B.Dryer, Tetrahedron Letters, 1983, 24, 4543.
21. S.Nishida, I.Moritani, and T.Teraji, J.Org.Chem., 1973, 38, 1878.
22. S.Sarel, A.Felzenstein, and J.Yovell, J.Chem.Soc.Chem.Commun.,1973, 859.
23. D.J.Pasto and A.Fu-Chen, Tetrahedron Letters, 1973, 14, 713;
    T.J.Barton and R.J.Rogido, J.Chem.Soc.Chem.Commun., 1972, 878.
24. S.Sarel, A.Felzenstein, and J.Yovell, J.Chem.Soc.Chem.Commun.,1974,753.
25. G.Subrahmanyam, Ind.J.Chem., 1976, 14B, 365.
26. G.A.Fenton, N.S.Isaacs, and A.Gilbert, Tetrahedron Letters,1985,26,1597.