

PHOTOADDITION REACTIONS OF TRANS DICHLOROETHYLENE WITH BENZENOID COMPOUNDS:  
FACILE FORMATION OF TETRACYCLO[3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>]OCTANES AND SEMIBULLVALENES

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Abstract: trans 1,2-Dichloroethylene undergoes a stereospecific photo-reaction with benzonitrile, the three tolunitriles,  $\alpha,\alpha,\alpha$ -trifluorotoluene, fluorobenzene, and chlorobenzene to give substituted 6-exo 7-endo dichloro-tricyclo[3.3.0.0<sup>2,8</sup>]oct-3-enes which on treatment with base yield cyclised products or semibullvalenes: phenol yields dichlorobicyclo[3.2.1]oct-2-en-8-one with this ethylene photochemically.

The inter- and intra-molecular meta photocycloaddition of ethylenes to benzenes<sup>1-3</sup> has been elegantly established by Wender and co-workers as a key step in the synthesis of several classes of polycyclic sesquiterpenes.<sup>4</sup> Wider acceptance of this photoreaction as a facile synthetic procedure has been limited by the low regio- and stereo-selectivities of the addition of many arene-ethylene systems and the restricted range of functionalised reactants which yield tricyclo[3.3.0.0<sup>2,8</sup>]oct-3-enes rather than the bicyclo[4.2.0]octa-2,4-dienes from the competing ortho photocycloaddition.<sup>1</sup> Recently we proposed that steric and electronic features of the arene and ethylene substituents may have a marked directing influence on the orientation and position of the reaction of the addends.<sup>5</sup> We now report that trans 1,2-dichloroethylene (TDE) is generally a most useful ethylene in this photoreaction as with certain benzenoid compounds it undergoes stereospecific and regioselective meta photocycloaddition and further, the adducts can be readily converted into tetracyclo[3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>]octanes or semibullvalenes.

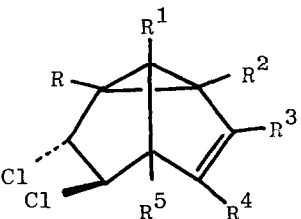
The photochemical experiments involved 254 nm irradiation of either equivolume mixtures of reactants or 1.0M arene and 3.5M TDE in cyclohexane, methanol, or acetonitrile. Solvent polarity had little effect on the efficiency of product formation but in some systems (e.g. C<sub>6</sub>H<sub>5</sub>Cl-TDE-C<sub>6</sub>H<sub>12</sub>) mixtures were complex as a result of solvent derived products. Nitrogen degassing of solutions led to "cleaner" reactions but did not appreciably influence the addition efficiency. The meta photocycloadducts from the arene-ethylene systems are presented in the Table. With the exception of the

phenol-TDE system, gram quantities of the adducts were readily obtained within 48 hours: periodic cleaning of the quartz irradiation tubes greatly increased yields. We had described in ref. 5 that the selectivity for formation of (1) was >50%. Subsequent studies have shown that at low reactant conversion (1) comprises >95% of the product mixture but is photolabile under the conditions of its formation and readily yields meta cycloadduct isomers.

Table. meta Photoadducts from 254 nm Irradiation of Benzenoid Compounds with TDE.<sup>6</sup>

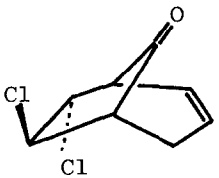
Benzene substituent(s)	CN	CN, <u>o</u> Me	CN, <u>m</u> Me	CN, <u>p</u> Me	CF <sub>3</sub>	F	Cl	OH
Product [respective ratio]	(1)	(2)	(3)	(4):(5) [1:1]	(6):(7) [3:1]	(8):(9) [2:1]	(10)	(11)



(1) R<sup>4</sup>=CN  
(2) R<sup>3</sup>=Me, R<sup>4</sup>=CN  
(3) R<sup>1</sup>=Me, R<sup>4</sup>=CN  
(4) R=Me, R<sup>4</sup>=CN  
(5) R<sup>2</sup>=CN, R<sup>5</sup>=Me  
(6) R<sup>4</sup>=CF<sub>3</sub>  
(7) R=CF<sub>3</sub>  
(8) R<sup>1</sup>=F  
(9) R<sup>3</sup>=F  
(10) R<sup>1</sup>=Cl  
(12) R<sup>1</sup>=OH

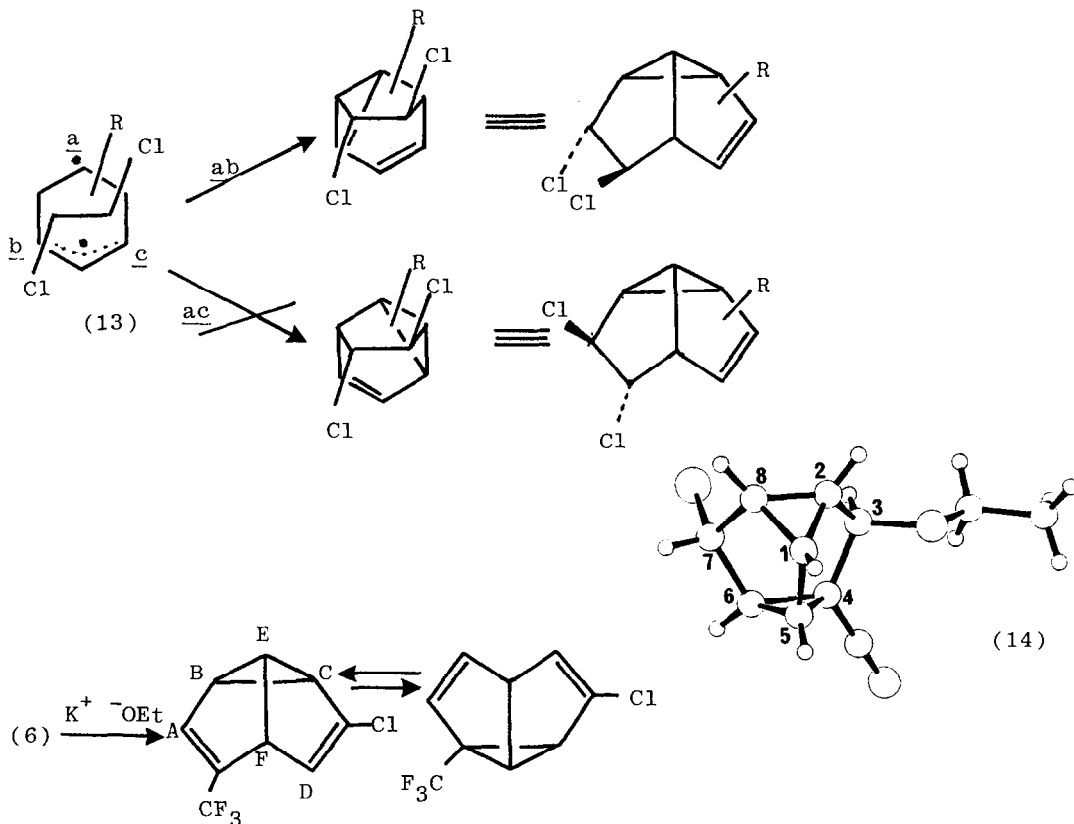
Other  
R's=H



(11)

Contrasted with these results, benzene,<sup>7</sup> alkylbenzenes and anisole on irradiation with TDE gave complex mixtures in which meta cycloadducts or products derived therefrom were minor components; the sole product from benzotrichloride was 1,1,2,3,3-pentachloro-1-phenylpropane and 1,2-dichloro-3-bromo-1-phenylethane was the major product from irradiation of bromobenzene and TDE.<sup>8</sup> It is, however, evident that for the systems in which the meta photocycloaddition is essentially the exclusive process, the reaction is stereospecific and also for four of the arenes examined is regiospecific. These observations not only encourage serious consideration of such reactions as synthetic procedures but also have important mechanistic implications. On the reasonable assumption that the pathway to products proceeds via the widely accepted route of ethylene addition followed by ethenyl cyclopropane formation,<sup>2</sup> then the observed 6-exo 7-endo dichloro specificity, regardless of the nature of the arene substituent or its position in the intermediate, is remarkable. It would seem that preferential and possibly exclusive cyclopropane formation in the intermediate (13) occurs between the a b rather than the a c positions. There appears to be

no obvious dictating effect for this closure other than it arises as a result of localisation of the radical (or charge) centre at the b position due to an interaction with the endo carbon-chlorine bond. The addition of TDE to phenol is apparently an exception to this directing influence.



The seemingly "reversed" stereochemistry of the isolated product (11) can, however, be accommodated in terms of prior formation of the meta cycloadduct (12) of expected stereochemistry which undergoes protonation at the 4-position and cleavage of the 1,2-cyclopropane bond to give (11) [ $\nu_{\max}$  1770  $\text{cm}^{-1}$ ]; HCl is formed during the reaction. Precedent for this rationalisation lies in our recent observation that protonation of meta cycloadducts of alkylbenzenes and hydrocarbon ethylenes occurs exclusively at the 4-position.<sup>9</sup>

Treatment of the TDE-arene adducts (0.1M) with 1% alcoholic potassium hydroxide solution brought about their high yield (>80%) conversion to either tetracyclo[3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>]octanes or semibullvalenes dependent on the nature or position of the substituent. Adducts with a nitrile group on the 4-position underwent attack of  $\text{EtO}^-$ , eliminated chloride, and cyclised to the tetracyclic compound. The detailed structure of the product (mp.= 91-92<sup>o</sup>) from (1) was determined by x-ray crystallography and is represented by (14). The crystals are orthorhombic, space group  $P2_12_12_1$  with cell dimensions

$a = 6.240$  (8),  $b = 10.275$  (8),  $c = 16.296$  (11) Å,  $U = 1045.0$  Å<sup>3</sup>,  
 $d_m = 1.29$  (2),  $d_c = 1.31$  g cm<sup>-3</sup>,  $\mu = 3.33$  Å. The two three-membered cyclopropane rings intersect each other at an angle of 40.1°. The two five-membered rings have the envelope conformation. Thus C(1), C(2), C(4), C(5) are coplanar to within 0.02 Å with C(3) 0.3 Å from the plane. Similarly C(1), C(5), C(6), and C(8) are coplanar to within 0.02 Å with C(7) 0.33 Å away. Both C(3) and C(7) are folded out of the rings in directions away from the cyclopropane rings.<sup>10</sup>

Base treatment of the adducts with no 4-conjugative substituent produced semibullvalenes. For example (6) gave (15) [ $M^+$  = 206.0106 and 208.0075 calculated for C<sub>9</sub>H<sub>6</sub>ClF<sub>3</sub>. 206.0109 and 208.0079] which had the following n.m.r. spectroscopic properties: <sup>1</sup>H spectrum (220 MHz, CDCl<sub>3</sub>)  $\delta$  values of 5.64 (H<sub>A</sub>, d, J<sub>A,B</sub> = 4.4 Hz), 4.76 (H<sub>B</sub>, br.m), 4.62 (H<sub>C</sub>, J<sub>C,B</sub> = 2.4 Hz), 4.08 (H<sub>D</sub>, d, J<sub>D,F</sub> = 5.2 Hz), 3.32 (H<sub>E</sub>, m, J<sub>E,F</sub> = 3.2, J<sub>E,B</sub> = 2.6 Hz) and 3.21 p.p.m. (H<sub>F</sub>, dd); <sup>13</sup>C spectrum (22.5 MHz, CDCl<sub>3</sub>) relative to T.M.S.,  $\delta$  values of 124.168 (q, J<sub>carbon-fluorine</sub> 271 Hz), 121.120 (q, J<sub>carbon-fluorine</sub> 3.1 Hz), 101.143, 99.030, 75.356, 51.628, and 48.770 p.p.m. (q, J<sub>carbon-fluorine</sub> 1.8 Hz). <sup>19</sup>F spectrum (84.3 MHz, CDCl<sub>3</sub>)  $\delta$  value of -63.4 p.p.m. (s) relative to CFC1<sub>3</sub>.

Thus the meta photoadditions of TDE to benzenoid compounds offer a facile route to a variety of compounds: the origin of the stereospecificity of the reaction is under investigation.

#### References and Notes

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8. See D. Bryce-Smith, W.M. Dadson, and A. Gilbert, J. Chem. Soc. Chem. Comm., 1980, 112, for other examples of photoinsertion of an ethylene into a carbon-halogen bond.
9. G.A. Fenton and A. Gilbert, unpublished observations.
10. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW.

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