

## Reaction of Diphenylketene with some Cyclohexa-3,5-diene-1,2-*cis*-diol Derivatives: Conversion of Chlorobenzene into Optically Active 2-Oxabicyclo[2.2.2]octen-3-one

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The dienes **11–15** react with diphenylketene to give mixtures of the corresponding [2 + 2]-adducts **16–20** and [4 + 2]-adducts **21–25**: the isomers **19/24** were converted into the optically active lactone **26** in two steps.

The microbial oxidation of benzene and derivatives **1–5** to furnish the corresponding optically pure<sup>1</sup> cyclohexadienediols **6–10** is well documented<sup>2</sup> (Scheme 1) and protected derivatives, such as **11–15**, have already been put to good use in synthetic organic chemistry.<sup>3</sup>

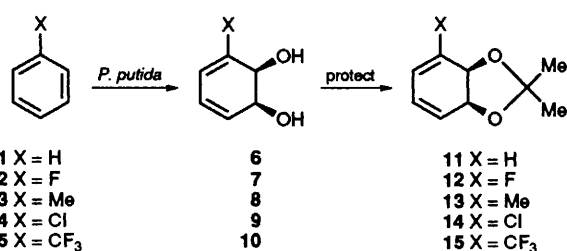
We report herein that all the dienes **11–15** react in an unexpected [4 + 2] fashion with diphenylketene, giving access to optically active 2-oxabicyclo[2.2.2]octen-3-one (a useful synthon previously described by Posner<sup>4</sup>) from the diene **14**.

Refluxing a solution of diphenylketene and the diene **11** in THF or hexane gave roughly equimolar amounts of the racemic compounds **16** and **21**, (Table 1).<sup>5</sup> The two products were isolated by column chromatography and shown to be stable in hot THF but equilibrated in refluxing *n*-octane (Table 2). Note that participation of the carbonyl group of a ketene in a [4 + 2] reaction is very rare.<sup>6</sup>

The fluoro compounds **12** and the toluene derivative **13** reacted with diphenylketene in a similar fashion. In both instances an excess of the [4 + 2] adducts **22–23** was obtained: in these cases the ratios of the products reflect thermodynamic preferences since the compounds **17/22** and **18/23** equilibrate on boiling in THF (Table 2)

The chlorodiene **14** and the trifluoromethyl diene **15** react with diphenylketene to give an excess of the corresponding [2 + 2] adducts **19** and **20**. The chloroisomers **19** and **24** equilibrate in hot THF; in contrast the trifluoromethyl system is stable in boiling THF but the compounds **20** and **25** interconvert in the higher-boiling solvents such as *n*-octane.

Treatment of the tricyclic compound **24** with excess tri-*n*-



Scheme 1

Table 1 Reaction of some cyclohexadienediol derivatives with diphenylketene

Diene	Solvent	<i>t</i> /h	Yields <sup>b</sup>		Ratio of adducts [4 + 2]:[2 + 2]
			% [4 + 2] adduct	% [2 + 2] adduct	
<b>11</b>	THF	20	27	32	1:1
	Hexane	48	33	52	1:1.5
<b>12<sup>a</sup></b>	THF	24	75	9	8:1
	Hexane	20	77	14	5.5:1
<b>13<sup>a</sup></b>	THF	20	71	11	7:1
	Hexane	20	75	13	6:1
<b>14<sup>a</sup></b>	THF	48	16	65	1:4
	Hexane	72	30	60	1:2
<b>15<sup>a</sup></b>	<i>n</i> -Octane	48	9	55	1:5

<sup>a</sup> Adducts interconverting at temperature of cycloaddition. <sup>b</sup> Yields refer to material isolated by chromatography over silica.

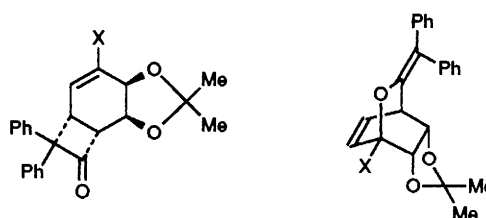
butyltin hydride in boiling THF gave the optically active compound **21** ( $[\alpha]_D^{25} -64.7$ , *c* 1.5, CHCl<sub>3</sub>) (Scheme 2). In fact the mixture **19/24** can be employed in this reduction reaction since, as mentioned above, the compounds **19/24** equilibrate in boiling THF. Only the chlorocompound **24** is reduced and the product obtained **21** does not equilibrate to the [2 + 2] product **16** under the conditions.

Oxidation of the enol ether **21** with excess dried *meta*-chloroperoxybenzoic acid gave the lactone **26** ( $[\alpha]_D^{25} -15.1$ , *c* 0.7, CHCl<sub>3</sub>) (70% yield) and benzophenone, presumably by the mechanism outlined in Scheme 3. It is noteworthy that the lactone **26**, a precursor of compounds of the shikimate type, is now available from chlorobenzene **1** in five steps.

In addition to the potential utility in organic synthesis this study raises a number of mechanistic issues which are of interest. For instance the [4 + 2]  $\rightleftharpoons$  [2 + 2] equilibration process seems to take place principally by an intramolecular process since pure optically active enol ether **21** ( $[\alpha]_D^{25} -64.7$ , *c* 1.5, CHCl<sub>3</sub>) furnishes optically active **16** ( $[\alpha]_D^{25} -159.6$ , *c* 0.7, CHCl<sub>3</sub>) and recovered enol ether on refluxing in octane. Heating the above optically active ketone **16** in octane for 48 h produced compound **21** ( $[\alpha]_D^{25} -59.7$ , *c* 0.5, CHCl<sub>3</sub>) (44%) and recovered **16** ( $[\alpha]_D^{25} -147.4$ , *c* 0.6, CHCl<sub>3</sub>) indicating the probable involvement of the dipolar species **27** in the rearrangement. However prolonged (one week) heating of **21**

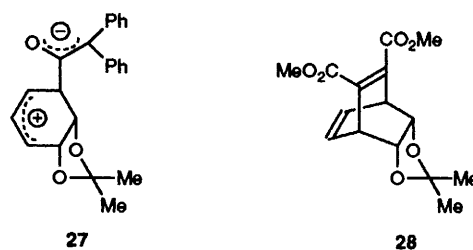
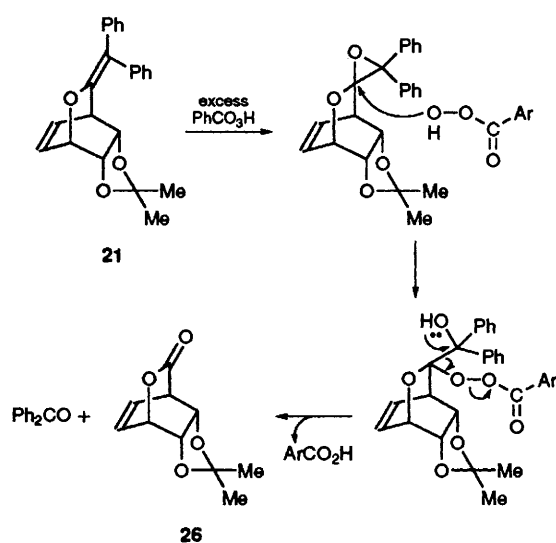
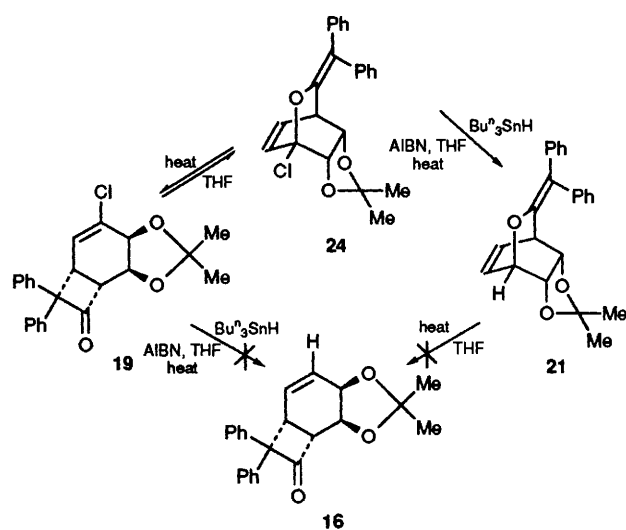
Table 2 Thermolysis of [4 + 2]- and [2 + 2]-adducts formed from diphenylketene and various cyclohexadienediols

Compound	Solvent	[4 + 2] adduct %	[2 + 2] adduct %	Ratio [4 + 2]:[2 + 2]
<b>16</b>	THF	0	100	—
<b>21</b>	THF	100	0	—
<b>16</b>	<i>n</i> -Octane	30	50	1:1.5
<b>21</b>	<i>n</i> -Octane	37	55	1:1.5
<b>17</b>	THF	87	9	10:1
<b>22</b>	THF	96	0	—
<b>18</b>	THF	89	11	8:1
<b>23</b>	THF	72	9	8:1
<b>19</b>	THF	19	66	1:3.5
<b>24</b>	THF	14	41	1:3
<b>20</b>	THF	0	100	—
<b>25</b>	THF	100	0	—
<b>20</b>	<i>n</i> -Octane	16	80	1:5
<b>25</b>	<i>n</i> -Octane	8	56	1:7



**16** X = H  
**17** X = F  
**18** X = Me  
**19** X = Cl  
**20** X = CF<sub>3</sub>

**21**  
**22**  
**23**  
**24**  
**25**



in octane containing excess dimethyl acetylene dicarboxylate produced the 'cross-over' product **28** suggesting retro [2 + 2] and/or retro [4 + 2] reactions take place slowly. The propensity of the dienediol derivatives **11–15** to promote, more or less, [4 + 2] reactions with a ketene such as diphenylketene warrants further investigation.

We thank the SERC (Biotechnology Directorate) and Pebec for a post-graduate research assistantship (to P. S.) and Professor Doug. Ribbons for supply of the compound **8**.

Received, 31st December 1993; Com. 3/07663F

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- 6 For one of the rare examples see H. Mayr and U. W. Heigl, *J. Chem. Soc., Chem. Commun.*, 1987, 1804.