The Crystal and Molecular Structure of α-3-*p*-Bromobenzoyloxy-(cyclopentadiene dimer)

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THE α- and β-isomers of 3-hydroxy(cyclopentadiene dimer) are particularly interesting in view of the Cope rearrangement, which leads to *syn*- and *anti*-10-hydroxy(cyclopentadiene dimer), respectively. This rearrangement takes place with remarkable ease;[1] the reason for such a behaviour must be connected with the favourable pre-orientation of the diallylic system.[2]

To elucidate this situation, a *X*-ray determination of the molecular structure of α-3-hydroxy(cyclopentadiene dimer) has been undertaken. Since the alcohol has a low m.p. (37°), the *p*-bromobenzoate† (racemic; 91°) was used. This compound is triclinic, space group $P\bar{1}$, with $a = 10{\cdot}11$, $b = 11{\cdot}39$, $c = 6{\cdot}78$ Å, $\alpha = 76{\cdot}9°$, $\beta = 80{\cdot}4°$, $\gamma = 73{\cdot}1°$ and two molecules per unit cell. The structure was solved by three-dimensional Patterson and Fourier synthesis. After a least-squares refinement the R index is 0·068 on 2244 measured independent reflexions, out of 3285 present (Cu-K_α, multiple-film Weissenberg technique).

The most salient details of the molecular geometry are shown in the Figure. The bridgehead

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† The systematic name for this compound is tricyclo[5,2,1,$0^{2,6}$]deca-4,8-dien-3-yl *p*-bromobenzoate.

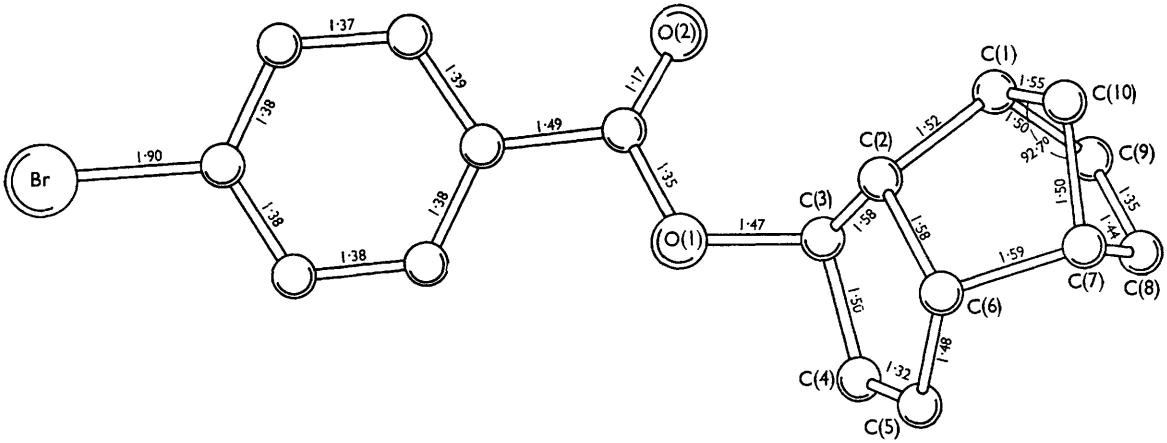

FIGURE. *Most significant bond distances and angles in α-3-*p*-bromobenzoyloxy(cyclopentadiene dimer).*

angle C(1)–C(10)–C(7) can be compared with a value of 97° and 96°, as found in the tricyclo-[3,2,1,$0^{2,4}$]octane[3] and norbornene[4] nuclei and the double bonds C(4)–C(5) and C(8)–C(9), show normal lengths. The distance C(6)–C(7) (1·59 ± 0·015 Å) seems particularly important, because this is the bond broken during the Cope rearrangement; the ease of this reaction is therefore understandable. The favourable pre-orientation of the di-allylic system seems to be of minor importance, because the two double bonds are situated rather far from each other [C(4)–C(9) 3·35; C(5)–C(8) 2·84 Å]. The overlap integral between the π-orbitals involved in the formation of the new bond amounts only to $S \simeq 0{\cdot}02$, as compared with $S \simeq 0{\cdot}06$ in "boat-like" and $S \simeq 0{\cdot}05$ in "chair-like" reaction paths for 1,5-hexadiene.

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