Photodimers of 3-Methylcyclohex-2-enone

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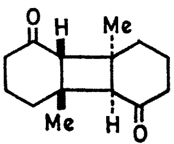
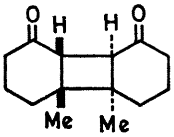
Summary The photodimerization of 3-methylcyclohex-2-enone yields two dimers whose structures have been determined as head-to-tail *anti,* (**1**) and head-to-head *anti,* (**2**).

RECENT studies[1,2] of the photodimerization of conjugated ketones including cyclohex-2-enone and cyclopent-2-enone[2] indicate that although the products in each case are the head-to-head (h–h) and heat-to-tail (h–t) dimers there are differences in the nature of the excited states. Several substituted cyclohex-2-enones[2c,3] have been reported to yield photodimers where the only product isolated was a h–h *anti*-dimer. In order to determine the effect of an alkyl substituent on the double bond we examined the products from the irradiation of 3-methylcyclohex-2-enone. Treibs[4] first examined the irradiation of this compound and isolated a single photodimer but was unable to determine its structure or stereochemistry.



(1)



(2)

The irradiation of 3-methylcyclohex-2-enone in aqueous alcohol yielded a dimer (m.p. 146—147°) as described by Treibs and its structure was determined in the following manner. An examination of its n.m.r. spectrum showed that the methyl group absorption had shifted from τ 8·03 in the starting ketone to 8·87 in the dimer. There was no absorption attributable to an olefinic proton and a new band appeared at τ 7·48 (singlet). The dimer no longer showed u.v. absorption characteristic of an unsaturated ketone and the carbonyl absorption in the i.r. occurred at 1720 cm^{-1}. These results along with the manner in which it formed are only compatible with structures in which the dimer contains a cyclobutane ring.

The configuration at the ring junction was determined by demonstrating the dimer's stability to alkali in D_2O under conditions in which the cyclobutane protons (τ 7·48) exchanged. Corey *et al.*[5] have shown that although both *cis* and *trans* six–four ring junctions form photochemically, the *trans*-compound isomerizes to the *cis* in the presence of alkali. An examination of the natural abundance ^{13}C–H satellite of the cyclobutane hydrogen ($J_{^{13}C-H}$ 132 ± 2 Hz) showed it to be a doublet with $J_{AA'}$ of 1·25 Hz. This coupling constant is too small for a vicinal coupling and therefore is due to a long-range coupling indicating that the dimer formed by h–t dimerization.[3] It has been possible to distinguish between an *anti*- and *syn*-stereochemistry about the cyclobutane ring as well as to confirm the above conclusions (h–t dimerization) by an *X*-ray analysis of crystals of the dimer. The unit cell dimensions and space group were obtained from oscillation and Weissenberg photographs. The crystals are orthorhombic, of space group, *Pbca,* with unit cell dimensions $a = 8{\cdot}0$, $b = 9{\cdot}9$, and $c = 14{\cdot}7$ Å. The number of molecules in the unit cell was obtained from a comparison of the calculated density; assuming four molecules per cell $D_c = 1{\cdot}25$ with $D_m = 1{\cdot}23$ g cm^{-3}. In the space group *Pbca* each unit cell has eight equal "asymmetric units" related in pairs by centres of symmetry.[6] Since there are only four molecules per cell it follows that each "asymmetric unit" is half a molecule and therefore each molecule has a centre of inversion. The h–t *anti*-dimer is the only dimer with *cis*-four ring junctions that has this property; thus its structure is established as h–t *anti,* (**1**).

An examination of the dimeric fraction produced in the irradiation revealed the presence of appreciable quantities of a second dimer along with small quantities of other dimeric materials. This second dimer (m.p. 69—70°) was purified *via* an intermediate diol. The solid dimer was pure by g.l.c. and showed the same retention time on several columns as a component present in the original irradiation mixture. The n.m.r. spectrum of this dimer was similar to that of the first showing a singlet at τ 8·88 (methyl) and 7·21 (cyclobutane). The six–four ring junction was shown to be *cis* since no isomerization occurred under conditions where the cyclobutane proton was exchanged. The ^{13}C—H satellite ($J_{^{13}C-H}$ 133±2Hz) of the cyclobutane proton was a doublet ($J_{AA'}$ 10 Hz) indicating h–h dimerization. The structure of the dimer was confirmed and the stereochemistry about the ring junction was determined as *anti,* (**2**), from a complete *X*-ray analysis.[7]

The presence of an alkyl substituent at the 3-position of a cyclohex-2-enone does not change the mode of dimerization from the unsubstituted case.

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