Photoadditions of 2-Cyclohexenone Derivatives to Cyclopentene. An Investigation of Stereochemistry

R. M. BOWMAN, C. CALVO, J. J. McCULLOUGH,* P. W. RASMUSSEN, AND F. F. SNYDER

Chemistry Department, McMaster University, Hamilton, Canada

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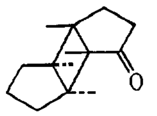
The photoaddition reactions of 4,4-dimethyl-2-cyclohexenone, 3-methyl-2-cyclohexenone, and 3-phenyl-2-cyclohexenone with cyclopentene have been studied. Trans-fused cyclobutanes are formed by the methylcyclohexenones but not by the phenyl derivative. The major product (47%) from 4,4-dimethyl-2-cyclohexenone and cyclopentene is the cis-anti-cis ketone. The latter was reduced by $LiAlH_4$ to the exo alcohol **6**, shown to have the anti configuration by an X-ray study. The details of the structure are described. The second product (38%) is a trans-fused cyclobutane **4** which equilibrates with base to a cis-fused isomer **7** assigned as the syn compound. The syn ketone **7** is reduced by $LiAlH_4$ to two isomeric alcohols. The addition of 3-methyl-2-cyclohexenone and cyclopentene appears to parallel the 4,4-dimethyl-2-cyclohexenone reaction. In contrast, 3-phenyl-2-cyclohexenone adds to afford only cis-fused compounds, the major one (93%) being tentatively assigned the cis-anti-cis structure. The factors controlling stereochemistry in the reactions are discussed. The excited state geometry, the nature of metastable and biradical intermediates, and the polarity of the substrate all appear to play a role. The timing of the bond formation is also considered, and it is concluded that trans-fused adducts may be formed by initial bonding of the olefin to C_2 of the cyclohexenone.

The stereochemistry of photocycloadditions of 2-cyclohexenones with alkenes,[1-3] and the factors controlling it, are among the most intriguing of stereochemical problems. Thus, while the triplet state additions of many cyclic unsaturated compounds, including cycloalkenes,[3] 2-cyclopentenone,[1,2] and aromatic compounds,[3] occur to afford cyclobutanes having cis ring fusions and anti stereochemistry, *e.g.*, **1**, simple 2-cyclohexenones can afford strained, trans-fused cyclobutanes.[1,2] Indeed, cycloaddition of 4,4-dimethyl-2-cyclohexenone and tetramethylethylene gives only trans-fused cyclobutane **2**, no cis-fused compound being detected.[4]



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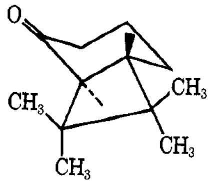

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The picture is further complicated in the cyclohexenone case by the observation that the trans-fused cyclobutanes are, in general, only formed whenever an electron-rich substrate is used.[2] Thus, the dimerization of cyclohexenone,[5,6] its reaction with acrylonitrile,[7,8] and the addition of 3-methyl-2-cyclohexenone and ethylene[9] all give little or no trans-fused compounds.[10] However, despite these synthetically important[11] and inherently interesting problems associated with enone photoannelation, very few careful studies of stereochemistry[12,13] have been reported, and these involved cyclopentenone. We are now describing our results on the reactions of cyclopentene with 4,4-dimethyl-2-cyclohexenone, 3-methyl-3-cyclohexenone, and 3-phenyl-2-cyclohexenone in this paper. This report includes the isolation of products, the assignment of their structures and stereochemistry, and a discussion of implications of the stereochemistry.

Results

Cyclopentene and 4,4-Dimethyl-2-cyclohexenone.— Irradiation of 4,4-dimethyl-2-cyclohexenone and 0.8 *M* cyclopentene in alcoholic solution, with a Hanovia 450 W, type L mercury vapor lamp using a Pyrex filter, resulted in disappearance of the enone carbonyl band at 6.00 μ and the formation of products giving two peaks on vpc (ratio 6:4), having two carbonyl bands at 5.83 and 5.91 μ. The nmr spectrum of the reaction mixture showed that three products were formed, since three pairs of methyl resonances in addition to that of the enone were observed. The per cent ratio of these three products was estimated to be 47:38:15 from the nmr spectrum, and the products will subsequently be referred to as **3**, **4**, and **5**, respectively. Samples of **3** and **4** were isolated by distillation and preparative vpc respectively and were identified as follows (Chart I).

Identification of 3.—The compound showed a molecular ion at *m/e* 192, showing that it was a 1:1 adduct of the enone and cyclopentene. The methyl resonances occurred at δ 0.87 and 0.88, and the carbonyl infrared absorption was at 5.91 μ, suggesting a cis-fused cyclobutane structure.[7] The adduct was unchanged by treatment with base, also suggesting that **3** is not a trans-fused adduct.[7] Further, this ketone readily formed a thiosemicarbazone, indicating that the carbonyl function is relatively unhindered. These observations all pointed to the cis-anti-cis structure for **3**

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[1] For a recent and particularly lucid review which covers the many facets of enone photoannelation, see P. de Mayo, *Accounts Chem. Res.*, **4**, 41 (1971).

[2] Earlier work was reviewed by P. E. Eaton, *ibid.*, **1**, 50 (1968).

[3] For a number of examples, see R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966, Chapters 5, 6.

[4] P. J. Nelson, D. Ostrem, J. D. Lassila, and O. L. Chapman, *J. Org. Chem.*, **34**, 811 (1969).

[5] E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 3482 (1967).

[6] (a) G. Mark, F. Mark, and O. E. Polansky, *Justus Liebigs Ann. Chem.*, **719**, 151 (1969); (b) P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, **91**, 5090 (1969).

[7] E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

[8] T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, **34**, 509 (1969).

[9] Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966).

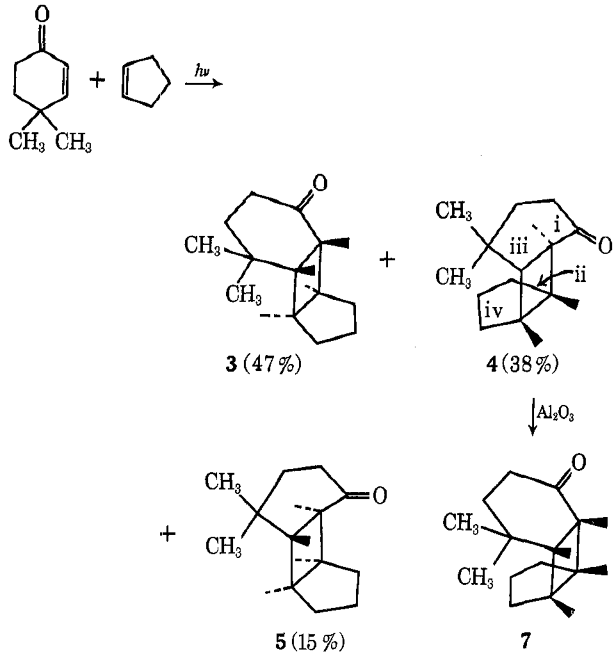
[10] See, however, P. Boyle, J. A. Edwards, and J. H. Fried, *J. Org. Chem.*, **35**, 2560 (1970). Note also ref 6b.

[11] P. G. Sammes, *Quart. Rev., Chem. Soc.*, **24**, 37 (1970), gives many examples of application in synthesis; see also ref 1.

[12] L. Duc, R. A. Mateer, L. Brassier, and G. W. Griffin, *Tetrahedron Lett.*, 6175 (1968).

[13] W. L. Dilling, T. E. Tabor, T. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, **92**, 1399 (1970).

Chart I



(Chart I), and there is ample precedent for this assignment.[14–16]

However, it was hoped to use **3** as a reference in assigning the stereochemistry to **4** and **5**, and X-ray work was undertaken to establish its structure. We were unable to obtain single crystals of the thiosemicarbazone of **3**. Therefore, the ketone was reduced with $LiAlH_4$ to an alcohol **6**, mp 51–56°, which reverted to **3** on chromic acid oxidation. This alcohol afforded a *p*-bromophenylurethane in good yield and this gave crystals suitable for an X-ray structure determination. The X-ray work is described in the Experimental Section. The structure of the *p*-bromophenylurethane is shown in Figure 1. It can be seen that the five- and six-membered rings have the anti relationship, and the two ring junctions are cis.

Also of interest is the exo configuration of the hydroxy group, a feature which would not have been predicted (see below).

Identification of 4.—This adduct had a molecular ion of *m/e* 192, and methyl group resonances at δ 0.98 and 1.19 in the nmr. The carbonyl band in the infrared was at 5.83 μ, and the compound isomerized on treatment with base to **7**, a ketone having the infrared absorption at 5.91 μ. This points to a trans-fused junction of the four- and six-membered rings, and its structure follows from that assigned to **7**.

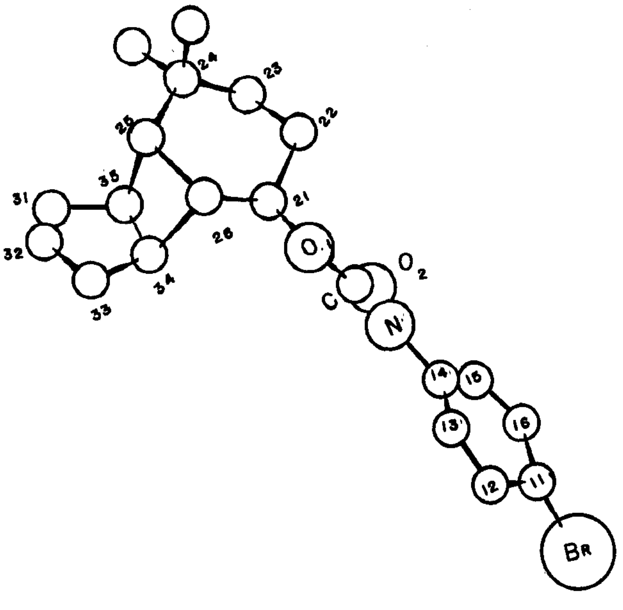


Figure 1.—Molecular structure of *p*-bromophenylurethane of **6**; numbering agrees with that used in Tables II and III.

Identification of 7.—This had carbonyl absorption typical[7] of cis-fused six–four ring junctions (5.91 μ). However, the compound was distinctly different from **3**, as shown by vpc and nmr (methyl group resonances at δ 0.95 and 1.02) and by the failure of attempts to prepare the thiosemicarbazone (*cf.* **3**, above). This indicates a hindered carbonyl group. Also, reduction of **7** with $LiAlH_4$ gave rise to two alcohols, **8** and **9**, quite different from **6**. Therefore, since **3** was shown to be the cis–anti–cis compound, **7** must have the cis–syn–cis configuration, and the compound is assigned the structure $1\beta,7\beta,2\beta,6\beta$-11,11-dimethyltricyclo[$5.4.0.0^{2,6}$]undecan-8-one.[19] It follows that **4** must be $1\beta,7\alpha,2\beta,6\beta$,11,11-dimethyltricyclo[$5.4.0.0^{2,6}$]undecan-8-one,[19] since the latter would be converted to **7** and not to **3** on equilibration with base.

Probable Identity of 5.—The unstable nature of this adduct precluded its isolation. Equilibration of the photolysis mixture, which shows three pairs of methyl group resonances, gives rise to a mixture of **3** and **7**, showing only two pairs of methyl resonances. Since **4** gives **7** on equilibration, **5** (15%, by nmr) should afford **3** when equilibrated and is assigned the $1\alpha,7\beta,2\beta,6\beta$ stereochemistry.[14]

The photoreaction and the equilibration are summarized in Chart I.

$LiAlH_4$ Reduction of Ketones 3 and 7.—The reductions of **3** and **7** are shown in Chart II. Ketone **3** gave a single alcohol **6** on $LiAlH_4$ reduction, as described above.

Ketone **7** was reduced with $LiAlH_4$ to afford two alcohols, **8** and **9**, which were separated by column chromatography. They both gave ketone **7** on chromic acid oxidation. They must be the exo and endo compounds, but we do not know which is which. Attempts to prepare crystalline derivatives were, as in the case of ketone **7**, unsuccessful.

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[14] The stereochemistry of the adducts is designated by α and β, as in steroid nomenclature; α or β refers to hydrogen, methyl, or phenyl substituents at the bridgehead positions. Thus, the cis–syn–cis compound **4** is the $1\beta,7\beta,2\beta,6\beta$ isomer.

[15] Some of these are as follows. (a) Cyclopentenone additions: P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344, 2454 (1962); see also ref 2. (b) Dimerization of coumarin: G. O. Schenck, I. von Wilucki, and C. H. Krauch, *Chem. Ber.*, **95**, 1409 (1962). (c) Dimerization of cyclohexenones: P. Yates, S. N. Ege, G. Buchi, and D. Knutsen, *Can. J. Chem.*, **45**, 2927 (1967); S. N. Ege and P. Yates, *ibid.*, 2933 (1967). See also ref 5 and 6.

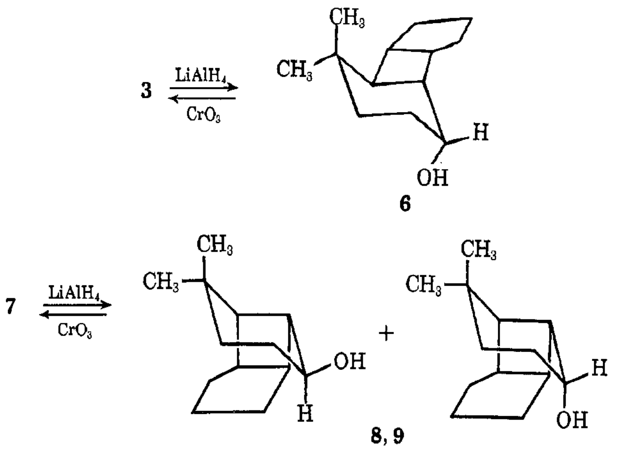
[16] The closest analogy to our reactions is the photolysis of 3-methyl-2-cyclohexenone and 4,4-dimethylcyclopentene, used by Corey and Nozoe[17] in the synthesis of α-caryophyllene alcohol. The adduct used had to be cis–anti–cis to afford the required alcohol, whose geometry is known from X-ray work.[18]

[17] E. J. Corey and S. Nozoe, *J. Amer. Chem. Soc.*, **87**, 5733 (1965).

[18] K. W. Gemmell, W. Parker, J. S. Roberts, and G. A. Sim, *ibid.*, **86**, 1438 (1964).

[19] Implicit in these assignments is the assumption that the four- and five-membered rings are cis fused, as in **1**. While at least one case of trans fusion is known in photochemistry [H. D. Scharf, *Tetrahedron Lett.*, 4231 (1967)], enone additions have not been reported to give trans 5,4 ring junctions (*cf.* ref 12). If **3** and **5** were trans at the 5,4 junction, the adducts would be trans fused at *both* ring junctions, an extremely unlikely situation.

CHART II

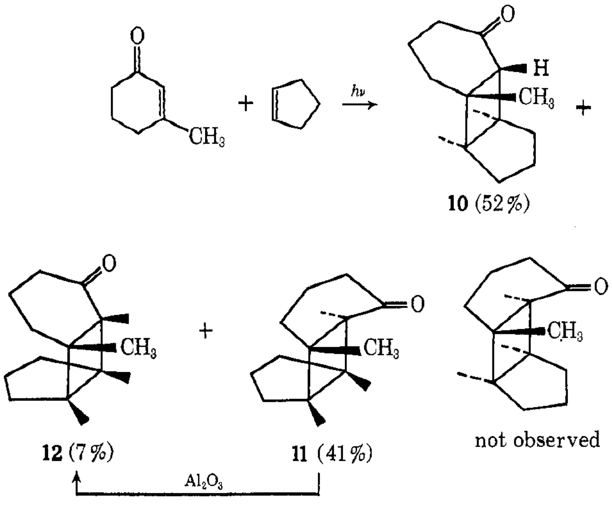


The formation of the exo alcohol from **3** is somewhat surprising. It is presumably the product of kinetically controlled reduction, in which the hydride approached along an equatorial path. In the reduction of **7**, this path may be hindered by the syn cyclopentane ring, and axial, exo approach apparently becomes competitive.

Cyclopentene and 3-Methyl-2-cyclohexenone.—This addition was studied to determine if an alkyl substituent at C_3 of the enone affects the stereochemistry of the addition.

The photolysis of 3-methyl-2-cyclohexenone and cyclopentene as described above gave rise to three mixed addition products, **10**, **11**, and **12**, separated by vpc. The reaction is shown in Chart III.

CHART III

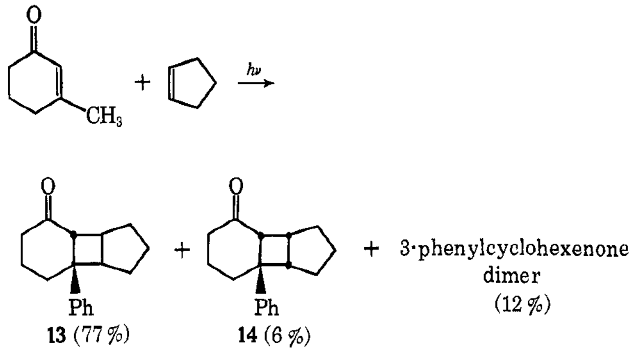


The major adduct **10** (52%) had carbonyl absorption at 5.91 μ and was stable to base treatment, indicating a cis six–four ring fusion. Note that the major adduct in the photoaddition of Corey and Nozoe[17] had the cis–anti–cis configuration,[16] and, by analogy with this, and with the 4,4-dimethyl-2-cyclohexenone addition described above, **10** is assigned the structure 1β-methyl-7β,2α,6α-tricyclo[5.4.0.0^{2,6}]undecan-8-one.

Isomer **11**, second in abundance (41%), had the carbonyl band at 5.82 μ, isomerized on base treatment, and was therefore a trans-fused cyclohexanone. The product of equilibration was not **10**, but **12**, the minor (7%) product of the photolysis. The latter had the carbonyl band at 5.91 μ and is assigned the cis–syn–cis structure, 1β-methyl-7β,2β,6β-tricyclo[5.4.0.0^{2,6}]undecan-8-one, by the same reasoning used above for **4** and **7**. Adduct **11** would therefore be 1β-methyl-7α,2β,6β-tricyclo[5.4.0.0^{2,6}]undecan-8-one. These findings agree with those of Cantrell, *et al.*,[8] whose results appeared while our work was in progress.

Cyclopentene and 3-Phenyl-2-cyclohexenone.—This reaction was also studied by Cantrell, *et al.*[8] Photolysis of 3-phenyl-2-cyclohexenone and cyclopentene in *tert*-butyl alcohol gave two mixed addition products, **13** and **14**, in the ratio of 90:7, respectively, by vpc. The reaction is shown in Chart IV.

CHART IV

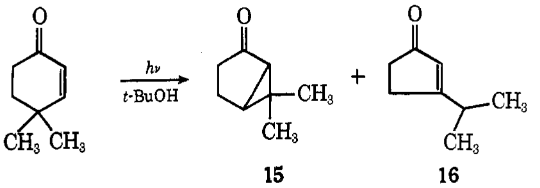


These were separated by column chromatography and preparative vpc, and gave molecular ions of *m/e* 240, with base peaks at *m/e* 173.

The major adduct **13** had mp 59.5–61°, was stable to base treatment, and had the carbonyl band at 5.91 μ. A cis-fused cyclohexanone system was indicated. The cis–anti–cis stereochemistry was tentatively assigned to **13** by analogy with the dimer of 3-phenyl-2-cyclohexenone.[15c] The minor adduct formed in this addition should therefore be the cis–syn–cis isomer.

2-Phenyl-2-cyclohexenone and Cyclopentene.—Irradiation of 2-phenyl-2-cyclohexenone and cyclopentene in the usual way for 45 hr resulted in no appreciable adduct formation, as indicated by vpc analysis and recovery of starting enone. The reason for this lack of reactivity is not apparent, but it should be noted that methyl substitution at C_2 of 2-cyclohexenone considerably retards the rate of addition.[7]

Multiplicity of 4,4-Dimethyl-2-cyclohexenone–Cyclopentene Addition.—While it is now well known that simple cyclic enone additions involve triplet states,[1] our method of establishing this in the case of 4,4-dimethylcyclohexenone differs from the standard methods. This enone[20] is known to undergo the "type A rearrangement"[21] on photolysis, to afford **15** together with the cyclopentenone **16**.[20]



15 **16**

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[20] O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

[21] H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **88**, 1965 (1966).

The "type A" enone rearrangement has been shown to be a triplet state reaction,[21] as also has the formation of **16**.[22] In the presence of a suitable concentration of cyclopentene, photolysis of 4,4-dimethyl-2-cyclohexenone gave a conveniently measurable ratio of rearrangement products (**15** and **16**) to adducts (**3**, **4**, **5**). It was found that this ratio was virtually unchanged by quenching with naphthalene, although a threefold retardation in rate was observed. The results of these experiments are given in Table I. The observation that the rearrangement product to adduct ratio does not change on quenching is good evidence that a triplet state of the enone adds to cyclopentene, and the following simple kinetic scheme can be used to describe the processes.

TABLE I

PHOTOREARRANGEMENT AND ADDITION OF 4,4-DIMETHYL-2-CYCLOHEXENONE AND CYCLOPENTENE

Naphthalene, M^b	Conversion of enone, %	Product composition, mol %[a] Rearrangement products **15**	**16**	Addition products **3, 4, 5**
	73	11	8[c]	81
	83	10	6	84
	76	10	7	83
0.050	80	10	11	79
0.050	74	11	11	79
0.050	83	11	11	78

[a] Analysis by vpc on a 10 ft × 0.125 in. 12% QF-1 at 175°. [b] Methanol as solvent. Molar concentrations were 0.0143 and 0.0858 for 4,4-dimethylcyclohexenone and cyclopentene, respectively. [c] Estimated maximum error ±4%.

$$\text{enone } T_1 \xrightarrow{k_r} \text{rearrangement}$$

$$\text{enone } T_1 + \text{cyclopentene} \xrightarrow{k_a} \text{adducts}$$

$$\text{enone } T_1 + \text{naphthalene} \xrightarrow{k_q} \text{enone} + \text{naphthalene } T_1$$

The "type A" addition ratio is therefore given by the expression

$$\text{rearrangement/addition} = k_r/k_a[\text{cyclopentene}]$$

Since k_r for this rearrangement (in a different enone) was found[21] to have a value of 2.9×10^5 sec^{-1}, the above expression allows an estimate of k_a to be made. A cyclopentene concentration of 0.086 M gives a product ratio of 1/8, and from this a value of 2.7×10^7 l. mol^{-1} sec^{-1} for k_a is derived, which is similar to the rate constants for 2-cyclohexenone–cyclohexene additions.[1]

The additions of 3-phenyl-2-cyclohexenone and alkenes may occur *via* the singlet or triplet states to afford the same products in both cases. Our work on the multiplicity of this reaction will be described elsewhere.

Discussion

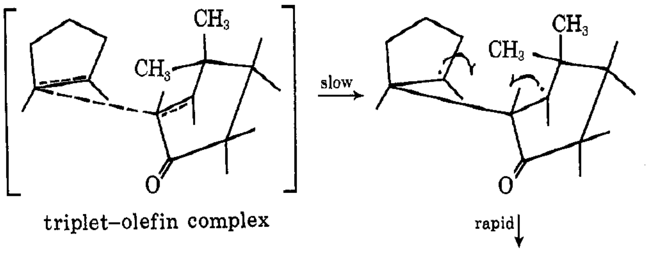
In general, the formation of cyclobutanes by addition of triplets is sensitive to steric effects, and the adduct with cis–anti–cis stereochemistry predominates in a number of structurally different cases.[5,6,15,16] Therefore, the assignment of the cis–anti–cis configuration to **3** is no surprise, but does show that mixed additions of 2-cyclohexenones conform to the above general rule.

The trans-fused adducts formed in these 2-cyclohexenone additions are particularly interesting. The structure of the major, trans-fused compound **4** can be rationalized in terms of a mechanism comprising the following steps: (a) attack by a nonplanar triplet T_1 of the enone on ground state alkene (it is proposed that initial bonding occurs at C_2 of the enone), and (b) rapid formation of the second bond of the cyclobutane ring, before the enone residue can relax to its equilibrium configuration. This sequence has been considered previously, notably by de Mayo,[1] and can be used to explain the stereochemistry of **4**.

There is now ample evidence[1] that additions of cyclic enones occur from the triplet manifold, generally T_1, and our experiments confirm this in the case of 4,4-dimethyl-2-cyclohexenone. There are also strong indications that unconstrained enones should resemble ethylene in being twisted about the carbon–carbon double bond in state T_1. This inference derives from spectroscopic studies on model compounds,[23] and from calculations.[24] Thus, in general, the trans-fused adducts could arise from a twisted cyclohexenone, if the geometry of the latter can be preserved throughout the reaction.

Consider now the geometry of adduct **4**. It can be seen that the bonds of the five- and six-membered rings are mutually anti in the region of the carbonyl group (bonds i and ii are anti and bonds iii and iv are syn). This could mean that initial bonding to cyclopentene occurs close to the carbonyl group in the enone triplet state, and steric interactions are causing a preference for anti attack in this bonding process. That steric effects are generally important in this type of addition is evidenced by the predominance of cis–anti–cis adducts in many cases.[5,6,15,16] Once the steric relationship of bonds i and ii has been fixed, then the shape of the trans-fused molecule is determined (assuming only cis fusion at the 5–4 ring junction).[19]

As pointed out above, it is difficult to see why an equilibrated 1,4 biradical should close to give adducts, *e.g.*, **5**, which are considerably less stable than other possible products. Since it is probable that biradicals are intermediates in this type of cyclobutane formation,[7,25] it is therefore necessary to propose that the second bond-forming step is a rapid one. This is reasonable in the case of 2-cyclohexenones and cyclopentene, since the radical centers are not effectively stabilized. One might therefore envisage the formation of **4** as follows.



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(22) O. L. Chapman, Abstracts, 20th National Organic Symposium, Burlington, Vt., June 18–22, 1967, p 133.

(23) R. L. Cargill, P. de Mayo, A. C. Miller, K. R. Neuberger, D. M. Pond, J. Saltiel, and M. F. Tchir, *Mol. Photochem.*, **1**, 301 (1969).

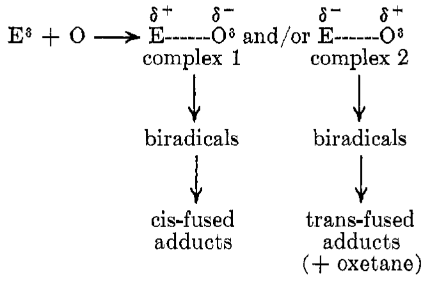
(24) (a) J. J. McCullough, H. O. Ohorodnyk, and D. P. Santry, *Chem. Commun.*, 570 (1969); (b) A. Devaquet and L. Salem, *Can. J. Chem.*, **49**, 977 (1971); (c) also work by Professor N. C. Baird and by Dr. J. S. Wasson, cited in footnote 19 of ref 1.

(25) J. J. McCullough, J. M. Kelly, and P. W. Rasmussen, *J. Org. Chem.*, **34**, 2933 (1969).

While this sequence is reasonable and explains the trans-fused structures, it is certainly not a complete picture. First of all it does not explain why the only cyclobutane found in the addition of 4,4-dimethyl-2-cyclohexenone and tetramethylethylene is trans fused. Second, it does not account for the absence of these strained systems from additions of 2-cyclohexenones and electron-deficient substrates (see, however, ref 6b, 10). These last two facts may be related and could be due to charge-transfer interactions in the triplet olefin encounter complex. There is evidence that the latter are intermediates[26,27] in these additions and selective quenching of cis- and trans-fused product formation can be ascribed to them.[28] It is possible that the twisted geometry of the cyclohexenone triplet is generally only preserved, to give trans-fused products, if the cyclohexenone reacts with an electron-rich substrate, *e.g.*, tetramethylethylene,[4] 1,1-dimethoxyethylene,[7,8] and norbornadiene,[25] but not when the substrate is acrylonitrile,[7,8] 2-cyclohexenone,[6b] or even ethylene.[9] It seems that oxetane formation frequently parallels that of trans-fused cyclobutanes[4,28] and this suggests that the latter are formed by attack near the carbonyl group of the enone triplet (*cf.* formation of **2**).

These processes are summarized in Chart V, where

CHART V



E^3 = enone triplet and O = unsaturated substrate. It is clear that the polarity of complex 1 should be favored by electron-deficient substrates, while complex 2 will be more important with those which are electron rich.

A second factor which must be important in determining stereochemistry is the stability of the proposed biradical intermediates. If these possessed considerable stability, then formation of trans-fused systems might be precluded by the relatively long lifetimes of the biradicals. In the case of 3-phenyl-2-cyclohexenone additions, both Cantrell[8] and the authors found no evidence for trans-fused products. This may be due to radical stability. However, the tendency for twisting about the C=C double bond in the excited states of this enone is probably considerably less than in simple enones.[29] Both these factors could be important. It should be mentioned that the above considerations do not counter the results of Dilling[13] on 2-cyclopentenone and 1,2-dichloroethylene, and their interpretation. Obviously, restrictions are imposed on the geometry of T_1 by the five-membered ring. Also, the biradicals formed in this case should be more stable owing to the chloro substituents. Therefore, the situation is rather different from 2-cyclohexenone–olefin reactions.

Finally, we would point out that an explanation of the trans-fused compounds cannot be derived from the arguments of Stephenson and Brauman.[30] They attributed the stereospecificity of 1,4-biradical ring closures to an energetic biradical, resulting in very rapid closure. This situation obtains when the biradicals are formed, for example, by loss of nitrogen from an azo compound.[31] However, the 1,4 biradicals from enone–olefin additions have about 17 kcal of excess energy.[32,33] This would not be sufficient to provide the strain energy of even cis-fused cyclobutanes (26.4 kcal), and an alternative explanation must be sought.

Experimental Section

Materials.—All solvents and reagents for photoaddition reactions were distilled before use. The cyclohexenones used were 3-methyl-2-cyclohexenone (Aldrich reagent) and 4,4-dimethyl-2-cyclohexenone,[34] bp 53–55° (2.5 mm). The method of Gannon and House[35] was used in preparing 3-ethoxy-2-cyclohexenone, bp 110–113° (3 mm). From this 3-phenyl-2-cyclohexenone was prepared by the method of Woods and Tucker[36] and Allen and Converse:[37] mp 63.5–64° (lit. mp 64–65° [15c]); λ_{max} (EtOH) 222 mμ (ϵ 14,200) and 284 (17,200).[15c] The compound was obtained as colorless crystals by chromatography on silica gel and repeated crystallization from ethanol.

Cyclopentene (Aldrich reagent) was distilled at atmospheric pressure, bp 44°.

tert-Butyl alcohol was Baker Analyzed reagent, bp 82°. Methanol was Mallinckrodt Analytical Reagent, bp 64.5–65°. Benzene for column chromatography was Mallinckrodt Analytical Reagent. Naphthalene, mp 80° (Fisher, purified), was recrystallized from ethanol.

Photolyses.—All photolyses were run under nitrogen, Canadian Liquid Air certified grade, further purified by successive passage through vanadous sulfate solution[38] and concentrated sulfuric acid, and over potassium hydroxide pellets. The lamp used was a Hanovia Type L450W, fitted with a Pyrex sleeve in a water-cooled quartz immersion apparatus.

Chromatography.—Column chromatography was on silica gel, Grace, grade 923 (100–200 mesh), except where stated otherwise. Analytical vapor phase chromatography (vpc) was performed on a Varian Aerograph Model 204-B dual column instrument, having flame ionization detectors, with a helium flow rate of 30 ml/min.

Preparative vpc was conducted on a Varian Aerograph dual column instrument with thermal conductivity detectors, with a helium flow rate of 60–80 ml/min.

Spectra.—Nuclear magnetic resonance (nmr) spectra were run on a Varian A-60, T-60, or HA-100 instrument, in spectral grade CCl_4 or CS_2, using tetramethylsilane as internal standard, and chemical shifts are given in parts per million downfield from this standard. Infrared spectra were recorded with a Beckman IR-5 or a Perkin-Elmer Model 337 instrument, using CS_2 (Fischer spectroanalyzed) as solvent. Mass spectra were obtained using an Hitachi Perkin-Elmer RMU 6A instrument.

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Melting points were taken on a Reichert hot stage and are reported uncorrected. Elemental analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich., or by A. B. Gygli, Toronto.

Synthesis of 2-Phenyl-2-cyclohexenone.—A modification of the method of Warnhoff, Martin, and Johnson[39] was used in the synthesis of 2-phenyl-2-cyclohexenone. To 15.50 g (0.089 mol) of 2-phenylcyclohexanone, mp 50–52° (Aldrich reagent) in dry carbon tetrachloride (100 ml), with 1 drop of concentrated HCl, was added during 90 min sulfuryl chloride (12.03 g, 0.0891 mol) in dry CCl_4 (15 ml). The reaction was stirred for an additional 3 hr and maintained at 25° throughout. After successive washings with 2 × 25 ml of distilled water, 2 × 20 ml of saturated $NaHCO_3$ solution, and 25 ml of saturated sodium chloride solution, the solution was dried ($MgSO_4$) and the ether was distilled.

To this residue, *N*,*N*-dimethylformamide (25 ml) and lithium chloride (2.34 g) was added. After flushing with nitrogen, the reaction flask was heated to 100° for 40 min with stirring. The mixture was then cooled, ether (100 ml) and 3% H_2SO_4 (100 ml) were added, and the mixture was stirred for 4 hr. The aqueous layer was separated and extracted with 2 × 50 ml of ether. The combined ether fractions were washed with 40 ml of saturated NaCl solution and 40 ml of saturated $NaHCO_3$ solution, and dried ($MgSO_4$). Crystallization of the residue after solvent removal from hexane gave 2-phenyl-2-cyclohexenone (6.78 g, 44%) as pale yellow needles, mp 91–94° (lit.[39] mp 94–94.5°).

Photoaddition of 4,4-Dimethyl-2-cyclohexenone and Cyclopentene.—4,4-Dimethyl-2-cyclohexenone (7.300 g, 0.059 mol) and cyclopentene (22.1 g, 0.324 mol) in methanol (400 ml) were irradiated with the Hanovia lamp fitted with a Pyrex sleeve under nitrogen for 4 hr. Monitoring by vpc (5 ft × 0.125 in. of 5% QF-1 on 60–70 Chromosorb W at 160°) showed products of retention times of 4 and 5 min, and that 85% of the enone had reacted. The solution was evaporated to afford 11.0 g of yellow oil showing carbonyl bonds in the infrared at 5.84 and 5.91 μ. The oil was distilled without fractionation to yield 9.948 g of ketone mixture, bp 115–120° (4.0 mm), consisting of ketones **3** and **4**, according to vpc, infrared, and nmr spectra. A sample of this mixture was distilled in a Nester-Faust Auto-annular spinning band column (Teflon band), at a reflux ratio of 30:1. From 8.6 g of mixture, 4.0 g of **3** was obtained, bp 124° (8 mm). This had infrared absorption at 5.91 μ, and methyl resonances at δ 0.87 and 0.88. It showed one peak on columns of QF-1, Carbowax, and FFAP. It is assigned the cis–anti–cis structure **3**, 1α,7α,2β,6β-11,11-dimethyltricyclo[5.4.0.0.^{2,6}]undecan-8-one, on the basis of the X-ray work described below. *Anal.* Calcd for $C_{13}H_{20}O$: C, 81.25; H, 10.42. Found: C, 81.02; H, 10.40.

On treatment with thiosemicarbazide, sodium acetate, and HCl in aqueous methanol, **3** readily formed a thiosemicarbazone, mp 160–162°. *Anal.* Calcd for $C_{14}H_{23}N_3S$: C, 63.37; H, 8.74; N, 15.84; S, 12.06. Found: C, 63.11; H, 8.94; N, 16.01; S, 12.00. The other fractions (total 4.0 g) from the spinning band distillation were mixtures of **3** and **4**. These were separated by preparative vpc on 10 ft × 0.375 in. of 20% QF-1 on 45–60 Chromosorb W at 215°. By making several injections, 300 mg of **3** and 200 mg of **4** were obtained from 1.0 g of mixture (recovery 50%). **4** was homogeneous by VPC (QF-1 and FFAP columns) and had carbonyl absorption at 5.84 μ and methyl resonances at δ 0.98 and 1.19. It is assigned the structure 1β,7α,2β,6β,11,11-dimethyltricyclo[5.4.0.0^{2,6}]undecan-8-one.

Base-Catalyzed Equilibration of 4.—The trans-fused cyclobutane adduct (**4**, *ca.* 50 mg) isolated from the photolysis was stirred at ambient temperature with Fisher basic alumina (10 g), in ether (50 ml), until the infrared spectrum showed complete disappearance of the carbonyl band at 5.83 μ, with appearance of a new band at 5.91 μ. The alumina was filtered and the ether was evaporated to yield a compound (*ca.* 50 mg) identical by vpc, nmr, and infrared spectra with the 1β,7β,2β,6β isomer **7** isolated from the equilibrated photolysis product.

Equilibration of the Photolysis Mixture of 3 and 4.—A sample of distilled photolysis mixture consisting of ketones **3** and **4** (9.257 g) was heated under reflux for 3 hr with a 5% solution of potassium hydroxide in aqueous methanol, 1:1 (100 ml). The mixture was poured into water and worked up with ether. The residue which remained on evaporation of the ether was distilled to afford 5.55 g of ketone mixture. This mixture showed only one carbonyl band at 5.91 μ, and one peak on vpc (10 ft × 0.125 in. of 12% QF-1 on 60–70 Chromosorb W at 218°). Also, the methyl resonances at δ 0.98 and 1.19 were replaced by resonances at δ 0.95 and 1.10. On columns of FFAP or Carbowax (5 ft × 0.125 in. at 180°) the mixture showed two peaks, ratio 6:4. The compounds were separated by preparative vpc on 10 ft × 0.375 in. of 10% Carbowax on 60–80 Chromosorb W at 210°. By making repeated injections, 2.8 g of mixture was resolved to yield 933 mg of **3** and 329 mg of **5** (46% recovery). The latter ketone had infrared absorption at 5.91 μ and methyl singlets at δ 0.95 and 1.02, and gave one peak on vpc (columns FFAP, QF-1 and Carbowax). It is assigned the cis-syn-cis configuration **7** and is 1β,7β,2β,6β,11,11-dimethyltricyclo[5.4.0.0^{2,6}]undecan-8-one.

Reduction of Ketone 3 with LiAlH$_4$.—Ketone **3**, from the above fractional distillation (2.177 g, 0.011 mol) in ether (20 ml) was added dropwise to a stirred slurry of lithium aluminum hydride (0.50 g, 0.013 mol) in ether (40 ml), and the mixture was refluxed for 5 hr. The residual hydride was decomposed with water and the aluminum compounds were filtered. The ether was dried (Na_2SO_4) and evaporated to afford 1.794 g (80α) of alcohol as an oil which solidified on standing. Sublimation at 50° (1 mm) gave waxy crystals, mp 51–56°. *Anal.* Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.00; H, 11.39. The alcohol readily formed a *p*-bromophenylurethane on treatment with *p*-bromophenylisocyanate in refluxing cyclohexane. The derivative was formed in 71% yield, mp 130–132° (from ethanol). *Anal.* Calcd for $C_{20}H_{26}O_2NBr$: C, 61.22; H, 6.68; N, 3.56; Br, 20.37. Found: C, 61.37; H, 6.57; N, 3.69; Br, 20.26. The X-ray structure determination described below was performed on this derivative, showing the alcohol **6** to be *exo*-1α,7α,2β,6β-11,11-dimethyltricyclo[5.4.0.0.^{2,6}]undecan-8-ol.

Description of X-Ray Work.—The *p*-bromophenylurethane derivative of **6** crystallized from aqueous ethanol as needles. The crystals had surface irregularities which caused them to be translucent rather than transparent. The lattice parameters were determined from a least squares refinement of 15 values of 2 θ measured with monochromatic Mo Kα radiation utilizing a Syntex automatic diffractometer. The values obtained were a = 13.00(1), b = 5.597(5), c = 27.20(3) Å and β = 109.46(5)°. The space group was established as $P2_1/c$ since Weissenberg photographs indicated that l odd and k odd reflections were extinct for the $h0l$ and $0k0$ sets, respectively. The calculated density is 1.36 g/cm^3 for z = 4, while the value measured using a solution of potassium tartrate in water is 1.40 g/cm^3.

A crystal with dimensions of 0.03 × 0.03 × 0.05 mm was used to record data. Graphite monochromatized Mo Kα radiation was used in conjunction with a Syntex automatic diffractometer. All the data in a hemisphere with a maximum radius defined by $2\theta \leq 35°$ were recorded using a θ–2θ scan with a scan rate determined by the intensity at the peak and a scan range dependent upon the value of θ. Backgrounds were recorded on either side of the peak and used to determine the integrated intensity together with an estimated standard deviation based upon counting statistics. Those reflections whose intensity were less than 3σ were regarded as unobserved with the maximum possible intensity set at 3σ. Reflections whose intensity calculated < 0 were left out of the refinement. Of the total 1025 reflections in the data set, 610 had observable intensities. The data were corrected for Lorentz and polarization but not absorption.

The bromine atom position was determined from the Patterson function. The signs determined from the subsequent structure factor calculation were used to calculate an electron density map from which the remaining atoms were found. The structure was refined utilizing a full matrix least squares program written by Stephens for the CDC-6400. The atomic scattering curves, dispersion corrected where necessary, were taken from the International Tables for X-Ray Crystallography.[40] Weights, w, were chosen so that $w|F_o - F_o|^2$ would locally be independent of the F_o, observed structure factor, and the function obtained was

$$W = [25 + 0.2|F_o| + 0.04\, F_o|^2]^{-1}$$

Unobserved reflections whose calculated structure factor was less than the minimum observable value were given zero weight in the refinement. The final R value is 0.10, while the least squares residual is 0.13. The refinement was terminated when

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TABLE II

BOND DISTANCES AND ANGLES IN *p*-BROMOPHENYLURETHANE WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atoms	Bond length, Å	Atoms	Bond angle, deg	Atoms	Bond angle, deg
Br–C11	1.90 (3)				
C11–C12	1.51 (4)	C16–C11–C12	112 (2)	C13–C14–C15	117 (4)
C12–C13	1.39 (5)	C11–C12–C13	113 (2)	C14–C15–C16	115 (4)
C13–C14	1.36 (5)	C12–C13–C14	123 (4)	C15–C16–C11	136 (4)
C14–C15	1.43 (5)	Br–C11–C12	110 (2)	Br–C11–C16	136 (4)
C15–C16	1.27 (5)	N–C14–C13	121 (4)	N–C14–C15	122 (4)
C16–C11	1.24 (6)				
C14–N	1.40 (4)	C14–N–C	117 (3)	C21–O1–C	102 (2)
N–C	1.57 (5)	N–C–O1	92 (3)	O1–C21–C22	113 (4)
C–O2	1.04 (4)	N–C–O2	133 (4)	O1–C21–C26	97 (4)
C–O1	1.48 (4)	O1–C–O2	134 (3)		
O1–C21	1.51 (4)				
C21–C22	1.58 (5)	C26–C21–C22	109 (4)	C23–C24–C25	112 (4)
C22–C23	1.62 (6)	C21–C22–C23	102 (4)	C24–C25–C26	116 (4)
C23–C24	1.53 (4)	C22–C23–C24	106 (4)	C25–C26–C21	107 (3)
C24–C25	1.52 (4)	C23–C24–C24a	101 (3)	C23–C24–C24b	117 (3)
C25–C26	1.64 (5)	C25–C24–C24a	106 (3)	C25–C24–C24b	113 (3)
C26–C21	1.66 (5)				
C24–C24a	1.71 (6)	C24a–C24–C24b	107 (3)		
C24–C24b	1.46 (6)				
C25–C35	1.54 (6)	C35–C25–C24	127 (4)	C34–C26–C21	105 (4)
C26–C34	1.64 (5)	C35–C25–C26	88 (4)		
C31–C32	1.44 (6)	C31–C32–C33	113 (4)	C33–C26–C21	109 (3)
C32–C33	1.60 (6)	C32–C33–C34	99 (4)	C34–C35–C31	109 (3)
C33–C34	1.67 (5)	C35–C31–C32	104 (4)		
C34–C35	1.48 (5)				

the calculated shifts were less than $^1/_3$ of the estimated standard deviations. A final difference synthesis showed no missing structural features, although peaks as high as $^1/_4$ of a carbon atom were noted.

Table II contains a list of pertinent bond lengths and angles. Tables III, containing the parameters, and Table IV, comparing the observed and calculated structure factors, will appear in the microfilm edition.[41] The structure is shown in Figure 1.

Reduction of Ketone 7 with $LiAlH_4$.—Ketone **7** (201 mg, 0.0011 mol) in ether (10 ml) was added to a stirred suspension of lithium aluminum hydride (51.0 mg, 0.0013 mol) in ether (5.0 ml). The mixture was heated at reflux for 6 hr, and the excess hydride was decomposed with water (20 ml). The alumina was filtered and the ether layer was separated and dried (Na_2SO_4). The residue on evaporation of the ether was an oil (123 mg, 58%) which showed two peaks on vpc (5 ft × 0.125 in. 5% QF-1 on 60–80 Chromosorb W at 150°) in the ratio of about 2:1. The mixture was chromatographed on 80 g of silica gel for tlc (E. Merck, A. G.; grain size, 10–40) packed in a column 2.5 × 50 cm. Elution was with benzene–ether (4:1) and 20-ml fractions were collected. A pressure of 5 psi was applied to obtain a reasonable flow rate. Fractions 1–6 contained fast-moving material (vpc), 38 mg; fractions 7–9 contained 36 mg of alcohol **8**, mp 74–78°, obtained as needles from pentane, mp 78–79°. *Anal.* Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.47; H, 11.27. Fractions 10–13 contained 56 mg of alcohol **9**, mp 89–91°, recrystallized from pentane, mp 90–91°. *Anal.* Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.44; H, 11.38.

Oxidation of Alcohols 6, 8, and 9 to the Corresponding Ketones.—The alcohol (20 mg) in ether (5 ml) was stirred at ambient temperature for 5 hr with 1.5 ml of a solution containing 1.19 g of sodium dichromate dihydrate and 1.31 g of H_2SO_4 in 98 ml of water. The ether layer was separated and dried ($MgSO_4$) and the ketonic product was subjected to vpc analysis (5 ft × 0.125 in. 10% QF-1 at 140°). When oxidized in this way alcohol **6** gave product of identical retention time with that of **3**. Alcohols **8** and **9** were oxidized to a compound with the same retention time as **7**.

Quenching of the Addition of 4,4-Dimethyl-2-cyclohexenone and Cyclopentene.—Six solutions (80 ml) of 4,4-dimethyl-2-cyclohexenone (0.0143 *M*) and cyclopentene (0.0858 *M*), three of which contained naphthalene (0.050 *M*), were cooled in Dry Ice–acetone, flushed with purified nitrogen for 0.5 hr, and irradiated. The unquenched solutions were photolyzed for 190 min; those containing naphthalene for 570 min. The products (rearrangement and 1:1 addition products) were analyzed by vpc (10 ft × 0.125 in. 12% QF-1 on 60–70 Chromosorb W at 175°) without removal of the solvent. The products ratios obtained are given in Table I. The vpc was calibrated for this work with prepared mixtures of purified adduct and rearrangement product.

Photoaddition of 3-Methyl-2-cyclohexenone and Cyclopentene.—Irradiation of 3-methyl-2-cyclohexenone (2.374 g, 0.0133 mol) and cyclopentene (24.52 g, 0.360 mol) in *tert*-butyl alcohol (375 ml) and methanol (20 ml) for 5.5 hr resulted in reaction of about 99% of the enone. The solvent was distilled *in vacuo* at 30° into a receiver at −78°. Infrared bands in the residual oil (2.50 g) at 5.82 (trans 6–4 ring fusion) and 5.91 μ (cis 6–4 ring fusion) indicated a near equimolar ratio of cis and trans 6–4 fused rings. A flash distillation afforded 2.05 g of liquid, bp 110° (5 mm) (10 ft × 0.125 in. 12% QF-1 at 194°). Analysis of the photolysis mixture by vpc showed three products with retention times of 8.3, 9.5, and 10.5 min.

The nmr of the photolysis mixture showed the disappearance of the methyl signal at δ 1.97 of 3-methyl-2-cyclohexenone and the appearance of three methyl singlets. By measuring the area of the methyl peaks, product ratios were established and are given following the chemical shift: δ 0.95, 51.6% (**10**); 1.06, 41.3% (**11**); 1.31, 7.1% (**12**). The isomers were separated by preparative vpc on 10 ft × 0.375 in. of 20% QF-1 at 183°. Recovery from this separation was poor owing to the similar retention times of the products.

The following fractions were collected. (a) A peak, retention time 38 min, had carbonyl absorption at 5.91 μ (cis-fused 6–4 junction) and a methyl singlet at δ 0.95. This, the major product, is assigned the cis–anti–cis configuration **10**. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.84; H, 10.14. (b) A sample of the product of retention time 42 min had carbonyl absorption at 5.82 μ (trans 6–4 ring fusion) and a methyl singlet at δ 1.06. On the basis of this data and of the equilibration of the compound to **12** with base, it is assigned structure **11**.

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[41] Listings of structure factors, coordinates, and anisotropic temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-2084. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.64; H, 10.11. (c) A fraction at 33 min had carbonyl absorption at 5.91 μ (cis 6-4 fusion) and a methyl singlet at δ 1.31. It was the minor compound, and was identical with the product of equilibrium of **11**. It is assigned the cis-syn-cis structure **12**. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.97; H, 10.20.

Equilibration of 11.—The photoadduct **11** (30 mg) was dissolved in 30 ml of ether, basic alumina was (2.0 g) added, and the solution was stirred for 3.5 hr. After filtration and evaporation of the ether, the infrared showed a band at 5.91 μ and the nmr had a methyl singlet at δ 1.30, characteristic of isomer **12** (see below). Analysis on a 10 ft × 0.125 in. 12% QF-1 at 194° showed the disappearance of a peak of retention time 10.5 min and the appearance of a peak at 8.3 min corresponding to **12**.

Photolyses with 2-Phenyl-2-cyclohexenone.—Irradiation of 2-phenyl-2-cyclohexenone (1.779 g, 0.0103 mol) and cyclopentene (16.87 g, 0.248 mol) for 45 hr in *tert*-butyl alcohol (380 ml) and methanol (20 ml) gave less than 5% cross-addition products as indicated by vpc and recovery of starting enone.

Photoaddition of 3-Phenyl-2-cyclohexenone and Cyclopentene.—Irradiation of 3-phenyl-2-cyclohexenone (1.663 g, 0.0097 mol) and cyclopentene (11.06 g, 0.163 mol) in *tert*-butyl alcohol (375 ml) and methanol (20 ml) for 7 hr resulted in reaction of 97% of 3-phenyl-2-cyclohexenone, determined by vpc analysis on 3 ft × 0.125 in. of 10% FFAP at 245°. The vpc analysis showed that two products were formed having retention times of 7.4 (**13**) and 12.3 min (**14**), in the ratio 90:7 as measured from vpc peak areas. After removing the solvent by distillation, the residue (1.873 g) was chromatographed on a 3 × 28 cm column of silica gel slurry packed in benzene, and 200-ml fractions were collected. Fractions 1–5 were eluted with benzene, 6–10 with 0.5% ethyl acetate–benzene, 11–20 with 1%, 21–25 with 2%, 26 and 27 with 4%, 28 with 8%, and 29–30 with 15% ethyl acetate–benzene. Fractions 14–16 contained the major photoadduct **13** (959 mg). This gave colorless prisms, mp 59.5–61°, from aqueous ethanol. *Anal.* Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.93 Found: C, 84.99; H, 8.30. The compound had infrared absorption at 5.91 μ and was stable to base, strongly suggesting cis fusion of the cyclohexanone ring. It is assigned the cis–syn–cis structure **13**.

Fractions 29–30 contained the photodimer of 3-phenyl-2-cyclohexanone (500 mg), which had mp 199–200° from ether–light petroleum (lit.[15c] mp 204–205°).

Registry No.—**3**, 34404-88-1; **3** thiosemicarbazone, 34404-89-2; **4**, 34404-90-5; **6**, 34404-91-6; **6** *p*-bromophenylurethane, 34404-92-7; **7**, 34404-93-8; **8**, 34404-94-9; **9**, 34404-95-0; **10**, 34404-96-1; **11**, 34404-97-2; **12**, 34404-98-3; **13**, 34404-99-4; cyclopentene, 142-29-0; 4,4-dimethyl-2-cyclohexenone, 1073-13-8; 3-methyl-2-cyclohexenone, 1193-18-6; 2-phenyl-2-cyclohexenone, 4556-09-6; 3-phenyl-2-cyclohexenone, 10345-87-6.

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Stereochemistry and Mechanism of Thermal and Base-Catalyzed Rearrangements of α-Hydroxy Ketones

CALVIN L. STEVENS,* THEODORE A. TREAT,[1] AND P. MADHAVAN PILLAI

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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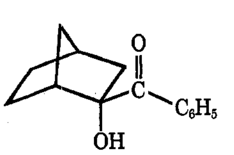
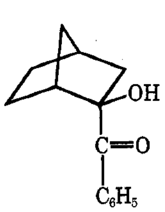
A pair of diastereomeric α-hydroxy ketones, *exo*-2-benzoyl-*endo*-2-hydroxybicyclo[2.2.1]heptane (**1**) and *endo*-2-benzoyl-*exo*-2-hydroxybicyclo[2.2.1]heptane (**2**), were prepared starting from 2-benzoylbicyclo[2.2.1]heptane (**3**). Rearrangement of these hydroxy ketones under pyrolytic conditions yielded products predicted by a cyclic concerted mechanism, **1** giving exclusively *endo*-2-hydroxy-*exo*-2-phenyl-3-bicyclo[3.2.1]octanone (**8**) and **2** yielding an equilibrium mixture of *exo*-3-hydroxy-*endo*-3-phenyl-2-bicyclo[3.2.1]octanone (**9**) and *exo*-2-hydroxy-*endo*-2-phenyl-3-bicyclo[3.2.1]octanone (**10**). On the other hand, treatment of hydroxy ketone **1** with sodium hydroxide in a water–dioxane system yielded **10** while compound **2** rearranged to give **8** under more severe alkaline conditions. The proof of structure for all the rearrangement products is presented and mechanisms are discussed for the transformations.

The rearrangements of 17-hydroxy-20-keto steroids have been studied extensively as a method for D-homoannulation.[2] Outside the steroidal field, the only investigation in this area appears to be that of Elphimoff-Felkin and coworkers, who extended this reaction for the preparation of a few cyclic acyloins.[3] The present work was undertaken to investigate the stereochemistry of this rearrangement in simpler systems where diastereomeric hydroxy ketones (**1** and **2**) could be prepared. The norbornane ring system was chosen, as it has the additional advantage of undergoing carbon skeletal rearrangements with great facility.



1



2

Results

Hydroxy ketone **1** was prepared by a series of reactions starting from the known 2-benzoylbicyclo[2.2.1]heptane[4] (**3**). Treatment of **3** with bromine in CCl_4 at room temperature yielded a single crystalline bromo ketone, *exo*-2-bromo-*endo*-2-benzoylbicyclo[2.2.1]heptane (**4**). That the bromine and benzoyl groups were attached to the same carbon in **4** was indicated by the nmr spectrum, which showed no downfield protons characteristic of hydrogen on a carbon bearing a bromine or a benzoyl group. The exo configuration of

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[1] Taken in part from the Ph.D. Dissertation of T. A. Treat, Wayne State University, 1969; Ethyl Corporation Fellow, 1968–1969.

[2] For a review, see N. L. Wendler in "Molecular Rearrangements," Part II, P. de Mayo, Ed., Interscience, New York, N. Y., 1964, p 1114.

[3] I. Elphimoff-Felkin, G. LeNy, and B. Tschoubar, *Bull. Soc. Chim. Fr.*, 522, 581 (1958).

[4] N. K. Kochetkov and A. Y. Khorlin, *Zh. Obshch. Khim.*, **27**, 3182 (1957); *Chem. Abstr.*, **52**, 8984*g* (1958).