Photoisomerizations. X. The Photochemical Transformations of Alloocimene[1]

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The two previously unknown 4-cis-alloocimenes are described, together with two other new photoproducts of this terpene. Tentative configurational assignments are made to the two new alloocimenes, and those previously made to the 4-trans isomers are reviewed. The other photoproducts are the enallene (3) formed by 1,5-hydrogen migration, and the bicyclo[3.1.0]hexene (5a). The latter was degraded in four steps to 2,2-dimethylsuccinic acid; its structure has been confirmed by other chemical correlations and by spectral considerations. Acid-catalyzed isomerization gives the cyclopentene 18, and pyroysis gives the cyclopentene 16. Hydrogenation of these, to give two known 1,2-dimethyl-3-isopropylcyclopentanes, 17a and 17b, established the stereochemistry illustrated.

The photochemistry of acyclic trienes has been intensively examined in recent years, and several modes of photoisomerization have been observed. The reversible ring closure to a 1,3-cyclohexadiene is perhaps the most common of these, and alloocimene (1) afforded one of the early examples of this behavior. In 1962 Fonken[3] reported that this terpene is in photochemical equilibrium with the isomeric α-pyronene (2).

In the course of some work in this laboratory on the photoisomerizations of conjugated dienes it was observed that appropriately substituted acyclic dienes could undergo a photochemical 1,5-hydrogen shift.[4] The vapor phase photoisomerization of 1,3,5-hexatriene to 1,2,4-hexatriene[5] suggested that these 1,5 shifts might be extended to conjugated acyclic trienes in general, particularly since this type of reaction can be made photochemically irreversible by the choice of appropriate light sources and filters. Alloocimene appeared to be a suitable material with which to test this hypothesis.

Two geometrical isomers of this terpene have been known since 1944,[6] and Raman,[6] ultraviolet,[7-9] infrared,[7,9] and mass spectra[10] have been recorded.

Their stereochemistries are still questioned[11] although it is generally agreed that both isomers are trans at the 4,5 double bond (1a, 1b). Uncertainty about the configuration at the 6,7 double bond has been compounded by the use (sometimes overlooked) of two conflicting terminologies. In this paper the term alloocimene is applied to all four isomers, and, in accord with the IUPAC ruling,[12] 1a is referred to as the 4-trans-6-trans isomer. Some authors[8,13,14] use the IUPAC terminol-
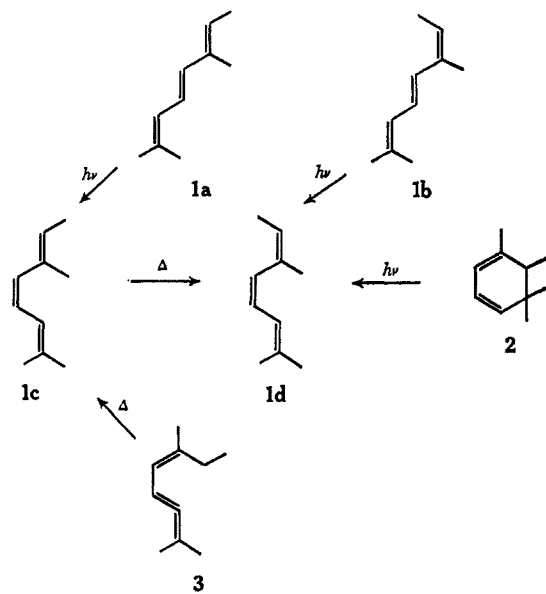
(1) (a) For paper IX, see K. J. Crowley, K. Erickson, A. Eckell, and J. Meinwald, manuscript in preparation. For preliminary communications, see (b) K. J. Crowley, Proc. Chem. Soc., 17 (1964); (c) K. J. Crowley, Tetrahedron Lett., 2863 (1965).
(2) University Chemical Laboratory, Trinity College, Dublin 2, Ireland.
(3) G. J. Fonken, ibid., 549 (1962).
(4) K. J. Crowley, Tetrahedron, 21, 1001 (1965).
(5) R. Srinivasan, J. Chem. Phys., 38, 1039 (1963), and earlier papers.
(6) J. J. Hopfield, S. A. Hall, and L. A. Goldblatt, J. Amer. Chem. Soc., 66, 115 (1944).
(7) R. T. O'Connor and L. A. Goldblatt, Anal. Chem., 26, 1726 (1954).
(8) K. Alder, A. Dreike, H. Erpenbach, and U. Wicker, Ann., 609, 1 (1957); cf. footnote b, Table I.
(9) C. Cappas, Ph.D. Thesis, University of Florida, 1962; Dissertation Abstr., 23, 846 (1962).
(10) A. F. Thomas and B. Willhalm, Helv. Chim. Acta, 47, 475 (1964).

(11) "Molecular Rearrangements," Vol. II, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 790.
(12) "Handbook for Chemical Society Authors," The Chemical Society, London, 1960, p 190.
(13) F. H. A. Rummens, Rec. Trav. Chim. Pays-Bas, 84, 1003 (1965).
(14) M. H. Klouwen and R. ter Heide, J. Chromatog., 7, 297 (1962).

TABLE I
LITERATURE ON 4-*trans*-ALLOOCIMENES

Trivial terminology	Bp, °C (mm)	Ultraviolet maxima,[a] mμ			Maleic anhydride adduct (mp, °C)	Structure given	Ref
Alloocimene A	89 (20)	267	277	288		*trans,trans*	} 6, 7
Heloocimene B	91 (20)	263	272	282	(84)	*trans,cis*	
Neoalloocimene	[89.1 (20)][b]	270	279	290	38	1b	} 8
Alloocimine	[88.1 (20)][b]	267	275	286	84	1a	
(A4)[c]	Low boiling[d]					1b	} 14
(A5)[c]	High boiling[d]					1a	
Alloocimene A	89 (20)	267	277	288		1b	} 9
Alloocimene B	91 (20)	263	272	282		1a	
Alloocimene I	Low boiling[d]					1a	} 13
Alloocimene II	High boiling[d]					1b	
	Low boiling[d]				36–42	1b	} 15
	High boiling[d]				80–82	1a	
	Low boiling[d]	268	277	287	37–40	1b	} This work
	High boiling[d]	264	273	282	82	1a	

[a] All in isooctane, except ref 8, where the solvent is not specified. [b] Alder, *et al.,*[8] would appear to have inadvertently exchanged boiling points, densities, and formation temperatures of the two isomers; other workers agree that the higher boiling[d] isomer has the higher density,[6,7,9] lower wavelength ultraviolet maxima,[7,9] higher-melting maleic anhydride adduct,[15] and higher temperature of formation.[9] [c] A4 and A5 are the trivial designations used by Klouwen.[14] [d] In agreement with other workers[9,14] it has been found that the lower boiling isomer has the lower retention time on all gas chromatographic columns examined.
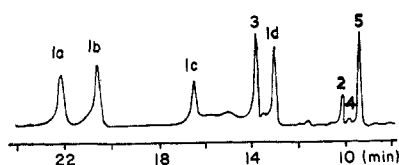

Figure 1.—Photoproducts of alloocimene (see Experimental Section); the glpc curve was obtained using a squalane capillary column at 101°. The higher base line between 1c and 1d is due to the progressive decomposition of the enallene (3) in the column to yield these two products.

ogy, others[9,15] the opposite, based on the relationship of like groups, and several investigators[6,7,10,16] do not clearly indicate which convention is followed.

Configurations have been assigned by various authors on the fallible basis of comparative physical and spectral properties (see Table I). After initially assigning 1b to the low boiling isomer,[17] Rummens[13] now considers this to be 1a, on the basis of infrared frequency shifts. Alder, *et al.,*[8] conclude, from extensive degradations of the maleic anhydride adducts, that the isomer giving the adduct of mp 84° is 1a and that giving the adduct of mp 38° is 1b. This is supported by the recent work of Milks and Lancaster,[15] who give nmr spectra of the two adducts and the dissociation constants of the corresponding diacids, both of which indicate that the higher melting adduct (from the higher boiling isomer) is of 1a, and the lower melting, of 1b. The results given below are in accord with these conclusions.

When a mixture of the two 4-*trans*-alloocimenes (10% 1a, 90% 1b) was irradiated, six main photoproducts (1c, 1d, 2–5) were observed (see Figure 1). Two of these (1c and 1d) disappeared, together with 1a and 1b, on prolonged irradiation.

Products 1c and 1d were obtained both from such an irradiation product mixture and by pyrolysis of the enallene (3) which is described below. Their nmr spectra are similar, and differ very little from those of

1a and 1b, and their infrared spectra suggest that the only double bonds present are trisubstituted and *cis* disubstituted. Their ultraviolet spectra suggest that they are both conjugated trienes, although that of 1d, in particular, is somewhat unusual,[18] perhaps because of a reduced hyperconjugative contribution from the nongeminal terminal methyl group, owing to lack of planarity of the triene system. Hydrogenation of a mixture of 1c (81%) and 1d (19%) gave only 2,6-dimethyloctane, and pyrolysis gave α-pyronene (see Table II).

These results indicate that both products are 4-*cis*-alloocimenes. This is confirmed by an analysis of the results given in Tables II and III, which also permits the tentative assignments of structure 1c to the less volatile of the two photoisomers and 1d to the more volatile.

These assignments are based on the consensus of earlier workers that, of the two 4-*trans* isomers of alloocimene, the higher boiling is 1a. The isomerizations 1a → 1c and 1b → 1d are one-step reactions, but 1a → 1d and 1b → 1c each require isomerization around two double bonds, and should thus be much slower. There is no reason to expect a large difference in the quantum yields of the two single-step reactions, and thus 1a → 1c and 1b → 1d should be the two main reactions in the early stages of the irradiation of a mixture of the two 4-*trans* isomers. It is then apparent from Table III that 1b gives rise to the more volatile photoproduct, which is thus 1d, and 1a, the highest boiling alloocimene, gives rise to the less volatile isomer, which is thus 1c. The relative rates of formation of these four isomers during the early stages of the irradiation of α-pyronene, which are shown in Table III, confirm these relationships.

The formation of a 4-*cis*-alloocimene on heating the enallene 3 should take place by a thermal (suprafacial[20])

(15) J. E. Milks and J. F. Lancaster, *J. Org. Chem.*, **30**, 888 (1965).
(16) Y.-R. Naves, *Helv. Chim. Acta*, **49**, 1029 (1966).
(17) F. H. A. Rummens, Diss. Techn. Hogeschool te Eindhoven 1963, p 123, as quoted in ref 16.

(18) The gas chromatographic behavior of 1d is also unusual[19] in that it is eluted more rapidly than would be expected for a conjugated triene, and in the large difference in retention index between 1d and 1c, compared with that between 1b and 1a (see Figure 1).
(19) Thanks are extended to Dr. M. Porter of the Natural Rubber Producers Research Association for this observation.
(20) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

TABLE II

THERMAL ISOMERIZATION OF THE ENALLENE (3)[a]

Temp, °C	Heating time, min	Product composition, % (by glpc)[b]							
		2	Unknown	Unknown	1d	Unknown[c]	3	1c	1a, b
112–114	1				6	0	72	22	d, e
	2				17	1	45	37	d, e
	4				16	2	29	53	d, e
	8				34	3	7	56	d, e
260–270	0.25	19	0	0	40	3	0	38	d, e
	1	57	5	1	18	2	0	17	d, e
	3	78	8	10	2	0	0	2	d, e

[a] The starting material was >93% 3 and contained no contaminants other than 1c and 1d; see footnote 23. [b] In order of elution from the capillary column (at 68°). [c] Its high retention time militates against this product being the isopropylidenecyclobutene which might be anticipated in the light of the results of Gil-Av. See E. Gil-Av and J. Herling, *Tetrahedron Lett.*, 1 (1967). The product was not isolated. [d] None detected. [e] 1a and 1b are slowly formed when the allene is kept at room temperature (50 and 30%, respectively, after 2 years). The more facile isomerization 1c → 1d may be explained by participation of the 2,3 double bond; it is also observed on glpc and is rapidly reversible at 130°: cf. E. M. Marvel, G. Caple, and B. Schatz, *ibid.*, 385 (1965).

TABLE III

IRRADIATION[a] OF ALLOOCIMENE AND OF α-PYRONENE. GAS CHROMATOGRAPHIC ANALYSIS[b] OF THE MAJOR INITIAL PRODUCTS

Irradiation time, min	Composition, %					
	5a	2	1d	1c	1b	1a
0	0	0[c]	0	0	73	27
2	0.13		4.0	1.2	67.3	29.8
3	0.24		5.0	1.7	64.1	28.9
4	0.4		6.3	2.0	62.7	28.7
6	1.1		8.9	2.4	59.4	28.1
16	2.0		11.3	4.2	53.3	29.3
40	10.4		16.3	7.8	40.6	25.2
0	0	87[d]	0	0	0	0
1	0.4	76.5	4.5	0.5	2.2	0.7
2	0.6	71.4	6.4	1.0	4.5	1.3
3	1.0	65.6	7.6	1.4	6.8	2.0
4	1.4	62.0	8.0	1.7	8.7	2.7
6	2.5	51.0	10.2	2.8	10.9	4.2
12	4.6	25.8	12.9	5.4	25.4	7.2

[a] As 1% (alloocimene) and 0.4% (α-pyronene) solutions in purified hexane (100 ml), under a slow stream of nitrogen. A Vycor filter was used. [b] A 150 ft × 0.01 in. capillary column, with squalane as stationary phase, was employed at 140 (alloocimene) and 120° (α-pyronene). Portions (1 ml) of the solutions were removed at the specified times, and most of the solvent was removed by evaporation before analysis. The products are listed in order of elution. [c] The amount of α-pyronene remained below 1% during the irradiation. When a Corex filter was used the proportion rose, but in no case did its proportion reach the value of 20% given by Fonken.[3] The yield of enallene (3) was also low under the conditions used. [d] An impurity (13%) remained unchanged throughout the irradiation.

1,5-hydrogen shift, a very general reaction.[21] Models indicate that steric factors favor the 4-cis-6-trans isomer (1c) rather than 1d as the immediate product of this isomerization. Since the less volatile new isomer is the main initial product (see Table II) this would appear to be 1c; the other should be 1d.

This is in agreement with the above correlations. In contrast, a similar naive approach using the conrotatory photochemical ring opening of α-pyronene to a 4-cis-alloocimene leads to the opposite conclusion. Of the two conrotatory paths available, that leading to 1c appears to be sterically favored over that leading to 1d. This is because the secondary methyl group of 2 is compressed between the two geminal dimethyl groups in the transition state leading to 1d, but not in

that to 1c. The high 1d/1c ratio in the early stages of the irradiation of α-pyronene (see Table III) indicates that 1d, rather than the expected 1c, is the initial product. Such steric considerations are probably less reliable when applied to photochemical as opposed to thermal reactions.[22] The thermal (disrotatory) cyclization of 1c to α-pyronene should occur more readily than 1d → 2, but according to the results given in Table II the thermal interconversion of 1c and 1d takes place much more rapidly than cyclization; this reaction cannot be used to further clarify the identities of 1c and 1d.

The presence of the enallene (3) is readily observed by means of its characteristic infrared maximum at 5.12 μ. Its yield was improved when a Corex filter was used, and when the solution was kept cold (0°) during the irradiation, but beyond this no attempt was made to optimize the isomerization conditions. By careful fractional distillation at room temperature the enallene was isolated with little decomposition.

Gas chromatography indicated the absence of contaminants other than 1c and 1d,[23] and its ultraviolet absorption at 270 mμ showed it to contain less than 2% alloocimene; it gives one maximum, at 225 mμ (ϵ 24,600).[24] It gives a strong infrared band at 865 cm^{-1} attributed[25] to a cis-disubstituted double bond conjugated with an allenic grouping. Hydrogenation, with the uptake of 3 mol of hydrogen to yield only 2,6-dimethyloctane, showed that the enallene possesses the original carbon skeleton of alloocimene. Its nmr spectrum includes a nine-proton complex centered at δ 1.75, indicative of three vinyl methyl groups, and is in accord with two structures, of 2,6-dimethylocta-2,3,5-triene (3) and 2,6-dimethylocta-2,4,5-triene. The thermal behavior of the allene confirmed the prognosticated structure (3), the two 4-cis-alloocimenes being virtually the only products of mild pyrolysis (Table II). The formation of these can be explained readily as a 1,5-hydrogen shift,[21] whereas the transformation of the 2,4,5-triene to 1c or 1d requires a

(21) J. Wolinsky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, **84**, 2775 (1962).

(22) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(23) Owing to its thermal instability the purity of the enallene (3) cannot be determined by gas chromatography. It slowly decomposes even at 68°, yielding 1c and 1d; under optimum conditions, when only about 5% is decomposed, 1c/1d = 10, in agreement with the results in Table II.

(24) This is comparable with the maximum at 222 mμ (ϵ 18900) for an analogous triene of the type RCH=C=CH=CHR[25] (cis) since the enallene (3) shows only end absorption in the 250–300-mμ region; the maximum at 268 mμ (ϵ 3,800) reported by these workers for an analogous compound may be due to the presence of conjugated triene impurity.

(25) K. L. Mikolajczak, M. O. Bagby, R. B. Bates, and I. A. Wolff, *J. Org. Chem.*, **30**, 2983 (1965).
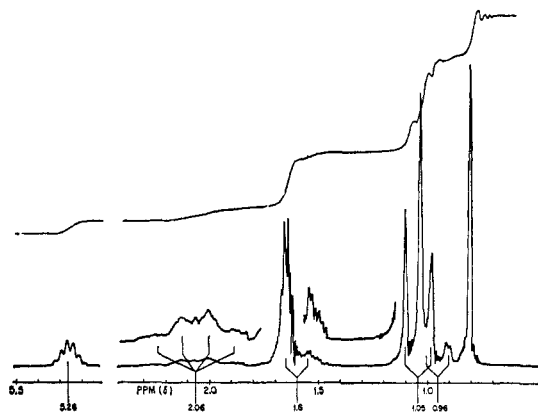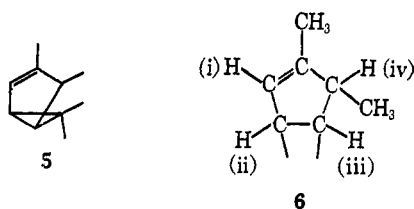
Figure 2.—Nuclear magnetic resonance spectrum of **5a** (without solvent).

thermal 1,3-hydrogen shift, for which there are no analogies, and which would not be expected to occur under such mild conditions.[20]

An analogous photoisomerization, of ethyl 1,3,5-hexatriene-2-carboxylate to the corresponding enallene,[26] has been reported; the product undergoes base-catalyzed isomerization to the conjugated enyne. Attempts to bring about a similar isomerization of hydrocarbon **3** using methanolic potassium hydroxide and a saturated solution of trimethylamine in pyridine, yielded only starting material.

The second main photoisomer obtained on prolonged irradiation is formed in about 14% yield, and was isolated in 98% purity by careful fractional distillation. It has the bicyclo[3.1.0]hexene structure **5**, which can be surmised solely on the basis of its nmr spectrum. This (Figure 2) shows four methyl groups [one vinyl (δ 1.67), one secondary (δ 1.05, $J = 7$ cps), and two tertiary (δ 1.04 and 0.82)[27]] and four one-proton resonances (located partly by spin decoupling), at δ 5.26 (i), 2.06 (iv), 1.6 (ii), and 0.96 (iii). Double irradiation experiments showed the vinyl proton (i) to be coupled with the vinyl methyl ($J < 1$ cps) and with the proton (ii) at δ 1.6 ($J < 1$ cps) and also showed the latter to be coupled ($J = 6$ cps) with the δ 0.96 proton (iii). This, in turn, is coupled ($J = 1.1$ cps) with the δ 2.06 proton (iv), while saturation of the latter also collapses the secondary methyl doublet and, to some extent, the vinyl methyl resonance. From this the partial structure **6** can be deduced, and **5** follows.

The photoproduct shows an ultraviolet maximum at 212 mμ, and infrared maxima at 3.29, 6.09, and 12.33 μ which are consistent with the presence of a trisubstituted double bond conjugated with a cyclopropane ring.

Ozonolysis, followed by oxidation of the ozonide with aqueous methanolic hydrogen peroxide, resulted in a 38% yield of the crystalline keto acid, **7**. The carbonyl group gives rise to maxima at 275 mμ (ϵ 45) and at 5.82 μ andt he carboxyl group at 5.92 μ. The nmr spectra of this acid and its methyl ester **8** are in
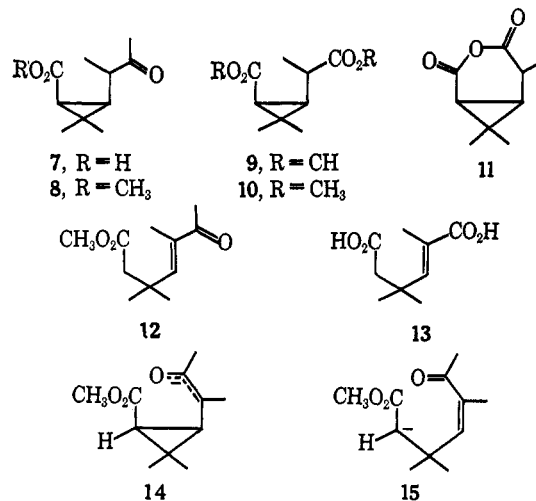
accord with the assigned structures. Sodium hypobromite oxidation of the keto acid to the crystalline dicarboxylic acid **9** further confirmed the presence of the methyl ketone group. The acid **9** yielded an anhydride (**11**), also crystalline, which showed infrared maxima at 5.57 and 5.71 μ, indicative of a glutaric, rather than a succinic, anhydride.

Degradation of the photoproduct to a known compound was achieved by base-catalyzed fission of the cyclopropane ring of the keto ester **8**. This is an extention of the work of Widmark[28] and of Crombie and coworkers[29] on the base-catalyzed ring opening of *cis*- and *trans*-methyl homocaronates to 3,3-dimethylbutene-1,4-dicarboxylic acid. When the ester **8** was treated with methanolic potassium hydroxide and the resulting acid mixture was reesterified, gas chromatography indicated starting material (25%) and a new ester (73%) and yielded the latter in the pure state. In agreement with the anticipated structure (**12**), the product has ultraviolet absorption [λ_{max} 292 mμ (ϵ 83), 228 mμ (ϵ 13,900)] corresponding to a mono- or disubstituted α,β-unsaturated ketone, and infrared maxima indicative of the same group (5.99 μ), of a saturated ester (5.76 μ), and of a carbon–carbon double bond (6.10 μ). The structure (**12**) is completely confirmed by the nmr spectrum.

Ozonolysis of this unsaturated keto ester (**12**) followed by performic acid oxidation yielded the known 2,2-dimethylsuccinic acid. Hydrolysis of the same keto ester yielded the free acid; since this could not be crystallized, it was oxidized directly with sodium hypobromite and gave the crystalline dicarboxylic acid **13** which showed λ_{max} 212 mμ (ϵ 12,000) as expected[30] for a disubstituted α,β-unsaturated acid and gave infrared and nmr spectra in agreement with the structure **13**.

(26) H. Prinzbach and E. Druckrey, *Tetrahedron Lett.*, 2959 (1965).

(27) The chemical shifts for these two methyl groups are close to those (δ 0.8, 1.07) reported for the similar methyl groups in Δ^3-carene by S. P. Acharya, *ibid.*, 4117 (1966).

(28) G. Widmark, *Ark. Kemi*, **11**, 195 (1957).

(29) L. Crombie, J. Crossley, and D. A. Mitchard, *J. Chem. Soc.*, 4957 (1963).

(30) A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

In the alkaline ring fission of the keto ester **8**, the keto group stabilizes the intermediate anion (**14**), while the ester groupling stabilizes the resultant acyclic anion (**15**). That the free carboxylate ion is less efficient in stabilizing the corresponding anion is shown by the slower rate of fission when the keto acid **7** is subjected to the same alkaline conditions: the main product is the same, but is formed about twenty times more slowly. On the other hand similar treatment of the diester (**10**) resulted in no detectable amount of the acyclic diacid (**13**), while *cis*-homocaronic acid, the homologous diester without the α-methyl group, undergoes ring opening to the extent of 39% under the same conditions.[29] This illustrates the marked destabilizing effect of an α-methyl group on the intermediate anion.

With the structure of the photoproduct established as **5**, its stereochemistry can now be considered. The reversible formation of the anhydride **11** shows that the cyclopropane–cyclopentene ring fusion is *cis*; furthermore no example of a *trans*-fused bicyclo[3.1.0]-hexane is known. Of the two possible *cis*-fused structures, **5a** and **5b**, the former was favored,[1c] since $J_{4,5} = 1.1$ cps, which suggests[31] that the two protons are approximately at right angles. However, since the relevant bond angles are not close to tetrahedral, such a conclusion should be considered as very tentative; it was, nevertheless, confirmed by the following chemical correlations.

To determine the configuration of the 4-methyl group relative to the cyclopropane ring, reactions were sought in which the cyclopropane ring is opened without the risk of inversion of the resulting isopropenyl group, while the cyclopentene ring remains intact. This was achieved in two ways, by pyrolysis and by acid catalysis.

Thermal 1,5-homodienyl hydrogen shifts are now widely recognized,[32] and would be expected to occur in a structure such as **5a**. In fact, when heated at 330° for 1 hr, the photoproduct gave a distillate (59%) consisting of four main components. One of these was not identified, two were found to be 1,2,3- and 1,2,4-trimethylbenzenes, and the major component (54%) was new. That this has the structure **16** is indicated by its infrared, ultraviolet, and nmr spectra.
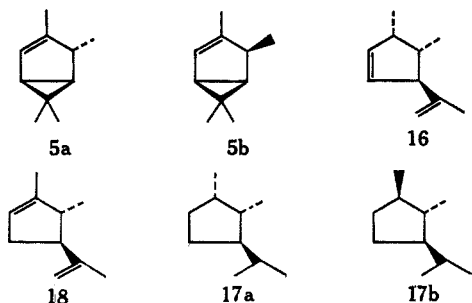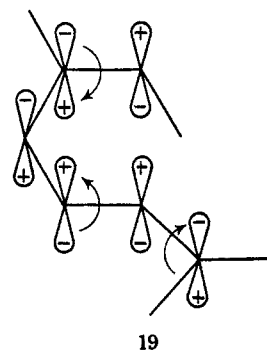
nmr[33a] and infrared[33b] spectra of authentic (±)-1-*cis*-2-dimethyl-*trans*-3-isopropylcyclopentane. Thus the stereochemistries of precursors **16** and **5a** are as shown.

This was confirmed by the acid-catalyzed isomerization of the photoproduct (**5a**) to the hydrocarbon **18**. The latter was the only significant isomer isolated (45%) when **5a** was left in contact with acid-washed alumina at room temperature for a short time. This cyclopentene (**18**) shows only end absorption in the ultraviolet spectrum, and gives infrared maxima indicative of >C=CH₂ and >C=CH— groups. Its nmr spectrum is in complete accord with the assigned structure.

Hydrogenation of this hydrocarbon (**18**) yielded two tetrahydro products (78 and 15%). The major component was identified as 1-*trans*-2-dimethyl-*cis*-3-isopropylcyclopentane (**17b**) by its infrared spectrum[33b] and the minor product was found to be **17a** by the same method.

The photoproduct **4**, which is formed in 2% yield, was not obtained in quantities sufficiently large to permit detailed examination. Its nmr and ultraviolet spectra suggest a structure similar to **5a**, but attempts to convert it into a degradation product of this have not yet given satisfactory results.

In contrast with the findings of Ullman's group[34] it seems improbable that the cyclohexadiene (**2**) is the principal direct precursor of **5a**.[35] If it were, the rate of formation of **5a** should be much greater on irradiation of α-pyronene than of alloocimene, but the results given in Table III show that this is not the case. The triene and the cyclohexadiene, which have qualitatively similar absorption spectra, were separately irradiated in the same apparatus; virtually all the <300-mμ light was absorbed in each experiment. Approximately the same amount of **5a** was formed in each irradiation, although in one case α-pyronene was absorbing over twice as much of the light as either 4-*cis*-alloocimene, whereas in the other it absorbed at least 50 times less than either (being present as less than 0.05% during this period). Since the formation of both **3** and **5a** takes place with sunlight, using Pyrex glass, the intermediacy of a higher singlet state is unlikely. By analogy with the related cyclization in the α-phellandrene series[1a] it is probable that the S1 state (**19**) of **1d** is the direct precursor of **5a**.

5a   **5b**   **16**

18   **17a**   **17b**

Hydrogenation of this pyrolysis product gave mainly (73%) the tetrahydro derivative **17a**, which gave the

19

(31) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); H. Conroy, *Advan. Org. Chem.*, **2**, 311 (1960).

(32) G. Ohloff, *Chem. Ber.*, **93**, 2673 (1960); D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966), and earlier papers; W. R. Roth, *Ann.*, **671**, 10 (1964); W. R. Roth and B. Peltzer, *ibid.*, **685**, 56 (1965); R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 5578 (1964).

(33) (a) K. Sisido, S. Kurozomi, K. Utimoto, and T. Isida, *J. Org. Chem.*, **31**, 2795 (1966). (b) Professor Sisido kindly supplied copies of the infrared spectra of all four isomers of 1,2-dimethyl-3-isopropylcyclopentane, which were synthesized by this group.

(34) E. F. Ullman, W. A. Henderson, and K. R. Huffman, *Tetrahedron Lett.*, 935 (1967).

(35) Direct photoisomerization of a 4-*trans*-alloocimene to **5a** would also appear highly improbable, particularly in the light of the results of J. Meinwald and P. Mazzocchi, *J. Amer. Chem. Soc.*, **89**, 1755 (1967).

Similar photoisomerizations of other trienes to bicyclo[3.1.0]hexenes are reviewed elsewhere.[1,36]

Experimental Section

All boiling points and melting points are uncorrected. Microanalyses were performed by A Bernhardt, Max Planck Institut, 433, Mülheim, Germany, and by F. Pascher, Bonn, Germany. Gas-liquid partition chromatography (glpc) was carried out on a Perkin-Elmer vapor fractometer, Model 154-D, using a 200-cm squalane column unless otherwise is specified: the capillary column used was 150 ft × 0.01 in. and contained polypropylene glycol as the stationary phase except for the experiments outlined in Table III. Infrared and ultraviolet (solvent, 2,2,4-trimethylpentane) spectra were recorded on Perkin-Elmer Model 127 and Unican Model S.P. 500 instruments, respectively, unless otherwise indicated. Nuclear magnetic resonance (nmr) spectra were taken on a Varian A-60 spectrometer, in carbon tetrachloride with tetramethylsilane as an internal standard, unless otherwise noted; double irradiation experiments were performed using a V-6058 spin-decoupler accessory. All irradiations were carried out using a 450-W Hanovia lamp no. 679A-36, in a water-cooled quartz immersion well.

Alloocimene (L. Light and Co.), after careful fractionation through a 36-in. spinning-band column, had bp 92–93° (22 mm); glpc showed 10% **1a** and 90% **1b**, and the infrared spectrum corresponded to that reported[7] for "4-*trans*-6-*trans*-alloocimene." Separation by glpc gave **1a** and **1b**, which, on following the procedure described,[8] yielded the maleic anhydride adducts, mp 37–40° and mp 82°, respectively.[37]

α-Pyronene, prepared as described,[38] had bp 51.5–53° (21 mm) and was identified by its infrared spectrum.[7] For use in the experiment described in Table III it was purified by glpc.[39]

Irradiation of Alloocimene.—To obtain the enallene (**3**), the triene (12 g) in dry ether (500 ml) was irradiated at 0–5°, using a Corex filter, until the absorption at 270 mμ was reduced to less than 1% of its original value (40 hr). The composition of a sample removed after 21-hr irradiation is shown in Figure 1. At the end of the irradiation two main photoproducts were evident on glpc; that which was eluted more slowly (**3**) was partly decomposed in the capillary column even at 68°. The ether solution was cooled to −25° and evaporated on a rotary evaporator under reduced pressure. The residue was distilled at 0.2 mm in a short-path still, the receiver of which was cooled to −100°. The distillate (5.7 g) contained 77.5% enallene, according to glpc using the capillary column (*i.e.*, 37% yield). Fractionation of the distillate through an 18-in. spinning-band column gave the enallene as a colorless oil [bp 23.8–24.1° (0.45 mm) n^{25}D 1.4989] which appeared, on separation through the capillary column at 69°, to be at least 96% homogeneous. The product showed uv absorptions at 225 mμ (ϵ_{max} 24,600), and at 280 (270), 270 (540), 260 (1250), 200 (7500), and 190 (23,600). It showed infrared maxima (neat) at 3.32, 3.38–3.5 (s) 5.12, 6.09 (w), 6.89 (s), 7.12, 7.27, 7.35, 8.12 (s), 8.4, 9.25 (s), 9.43, 9.78, 9.93, 11.55, and 12.22 μ (s), Its nmr spectrum showed a triplet at δ 1.00 (J = 7 cps, 3 H), a quartet at 2.12 (J = 7 cps, 2 H), and a complex series of bands at 1.65–1.8 (9 H) and at 5.2–6.2 (2 H).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.00; H, 11.74.

To obtain the other photoisomers a solution of alloocimene (150 g) in purified hexane (3 l.) was irradiated in three portions, for a total of 620 hr. During the irradiation, which was carried out as described above except that the temperature of the solution was maintained at 50°, the ultraviolet absorption at 280 mμ decreased to 7% of its original value. Removal of the solvent and rapid distillation of the photoproducts gave the volatile products (53.1 g), bp 40–93° (20 mm), a dimer fraction (79.4 g), bp 50–130° (0.25 mm), and a residue (17.5 g). Careful distillation of the volatile product mixture through a 36-in. spinning-band column, and glpc of the fractions obtained, indicated yields of the two chief photoproducts of 13.5% (**5a**) and 2.0% (**4**). The higher-boiling components were principally the four isomers

of alloocimene. The chief photoisomer (**5a**) was obtained in 98% purity and had the following properties: bp 61.2° (37 mm), 51° (20 mm); n^{21}D 1.4543; λ_{max} 212 mμ (ϵ 5080), end absorption at 188 mμ (ϵ 4770); ν_{max} (neat) 3.29, 3.32, 3.39 (s), 3.42 (s), 3.49, 6.09, 6.9 (s), 7.27 (s), 7.51, 7.75 (w) 8.02 (w), 8.32, 8,89, 9.01, 9.25, 9.37, 9.53, 9.81, 10.04, 10.26, 10.51, 10.87 (w), 11.88 (s), 12.33 (s), 12.7 (w), and 13.65 μ (w). Its nmr spectrum is shown in Figure 2.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.05; H, 11.61.

The minor photoisomer has a boiling point of *ca.* 55° (120 mm). By glpc it was obtained in 80% purity, with one main contaminant detectable only with the capillary column. This fraction showed λ_{max} 215 mμ (ϵ 4500), and 280 (220), 270 (340), 260 (460), 250 (670), 240 (1350), 230 (2700), 220, (4000), 210 (4400), and 200 (4400). It showed infrared maxima (neat) (Perkin-Elmer Model 337) at 3005, 2980, 2850 (s), 2810, 2710 (w), 1640 (w), 1445, 1365, 1320 (w), 1285 (w), 1200, 1124, 1110 (w), 1080 (w), 1044 (w), 1010, 1000, 993, 962 (w), 945 (w), 837 (s), 800, and 724 cm^{-1}. Its nmr spectrum (CDCl$_3$) showed a singlet at δ 0.98 (6 H), a doublet (J = 7 cps) at 1.04 (3 H), a rough quartet (J = 7 cps) at 2.8 (1 H), broad singlets at 5.26 (1 H), and 1.62 (3 H), and a complex series of peaks at 0.7–2.2 (2 or 3 H). By double irradiation the doublet methyl resonance at δ 1.04 was found to be coupled with the quartet at 2.8. The latter does not appear to be appreciably coupled with the olefinic proton, but coupling with the unsaturated methyl at δ 1.62 was observed. The vinyl methyl and vinyl hydrogen resonances are also coupled.

When a 2% hexane solution of alloocimene was left for 4 months in a stoppered Pyrex flask in sunlight, gas chromatography showed the formation of small amounts (*ca.* 10% each) of the enallene (**3**) and the bicyclo[3.1.0]hexene (**5a**).

When the irradiation was carried out in quartz with a low pressure 400-W, 2537-Å source, the absorption at 280 mμ decreased five to ten times more slowly than when the high pressure lamp was used.

Hydrogenations. A.—The enallene (**3**, 120 mg) in olefin-free hexane (5 ml) was added to a prereduced mixture of hexane (10 ml) and 5% platinum on charcoal (180 mg). Hydrogen uptake ceased after 20 min, when 3.02 equiv had been absorbed. Filtration and evaporation of the solvent left 2,6-dimethyloctane (98% pure by glpc) which was identified by its glpc retention time and its infrared spectrum.[40]

B.—A mixture of 4-*cis*-alloocimenes (81% **1c** and 19% **1d**, 143 mg) was treated in the same manner and yielded the same product (97% pure), similarly identified. In this case uptake of hydrogen (2.99 equiv) ceased after 3 hr.

C.—The photoproduct **5a** (399 mg) was added to a prereduced, stirred suspension of 5% platinized charcoal (400 mg) in purified hexane (10 ml). Hydrogen absorption ceased after 80 min when 129 ml (1.49 equiv) had been absorbed. Glpc using a squalane column indicated the presence of one major product (82%) which was isolated by glpc.

Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.88; H, 13.20.

In fact this was probably a mixture of the two expected dihydro products, since glpc on the capillary column indicated two components in a 2:1 ratio. Several unsuccessful attempts were made under varying conditions, to achieve reduction of **5a** without the accompanying hydrogenolysis.

Pyrolysis of the Enallene (3).—The photoproduct **3**, in 30-μl portions, was sealed in small glass tubes with the minimum air space and heated in a metal bath under the conditions given in Table II. The product obtained on heating for 3 min at 270° was a pale yellow liquid, 78% homogenous, which had the infrared and ultraviolet spectra[7] of α-pyronene (**2**).

4-*cis*-Alloocimenes.—In an early experiment, an attempt to isolate the enallene by distillation resulted in thermal isomerization to a mixture of **1c** (81%) and **1d** (19%): bp 68–68.5° (10 mm); λ_{max}^{ether} 268 mμ (ϵ 21.500). The two 4-*cis*-alloocimenes were later isolated from a product obtained by irradiation, and having a composition similar to that shown in Figure 1. This was subjected to a flash distillation, decomposing the enallene, and the distillate was separated[37] on a Varian Aerogaph Autoprep

(36) K. J. Crowley and P. H. Mazzocchi in "The Chemistry of Alkenes," part II, J. Zabicky, Ed., Interscience Publishers, Inc., New York, N. Y., in press.

(37) The author thanks Mr. A. Fröhlich for this experiment.

(38) L. A. Goldblatt and S. Palkin, *J. Amer. Chem. Soc.*, **66**, 655 (1944).

(39) The author thanks Mrs. M. A. Tamers for this purification.

(40) Authentic 2,6-dimethyloctane was obtained by reducing a mixture of 4-*trans*-alloocimenes. Its infrared spectrum showed no peak near 12.2 μ, but is otherwise very similar to that published by V. I. Komarewsky and C. C. Shin, *ibid.*, **72**, 1562 (1950).

gas chromatograph (20 ft × 0.375 in. column of 30% Carbowax at 100°).

4-*cis*-6-*trans*-Alloocimene (77%, with 23% 1d) had the following spectral data: λ_{max} 264 mμ (ϵ 18,900) and 273 (20,200) and a shoulder at 282 (14,400); ν_{max} (neat) at 3015, 2965 (s), 2929 (s), 2855, 1648 (s), 1450, 1375, 1075 (w), 1050 (sh), 1039, 983 (w), 853, 831, 816, 770 (sh) and 754 cm^{-1} (s). This and the following infrared spectrum were obtained on a Perkin-Elmer Model 337 spectrometer.

4-*cis*-6-*cis*-Alloocimene (77%, with 23% 1c) had the following spectral data: λ_{max} 257 mμ (ϵ 15,300) and 263.5 (16,100) and a shoulder at 271 (14,900); ν_{max} (neat) 3015, 2968 (s), 2920 (s), 2855, 1650, 1453, 1380, 1195 (w), 1076, 1049, 1040, 985 (w), 958 (w), 876, 853, 832 (s), and 750 cm^{-1} (s).

The nmr spectra of all four alloocimenes have complex olefin resonances, differing only in detailed structure, at δ 5.0–6.3 (four protons) and vinyl methyl resonances at 1.78 (12 protons); in every case the latter includes a high-field resonance (1–2 H) which is a single peak for 1a (δ 1.69), 1b (δ 1.66), and 1c (δ 1.66), whereas for 1d it is two peaks (δ 1.60, 1.50).

Isomerization of 1c and 1d to 1a and 1b.—A mixture of 1c and 1d (81% 1c, 19% 1d; 190 μl), together with iodine (5 mg) and dry ether (25 ml) was irradiated for 8 hr in a Pyrex flask cooled in running water with a 200-W tungsten filament lamp. The solution was filtered through alumina and evaporated, and the residue was distilled at 18 mm (bath temperature, 130°). Glpc showed the distillate to be 59% 1a and 39% 1b; its infrared is in agreement.

Oxidation of the Bicyclo[3.1.0]hexene (5a).—The photoproduct (52.5 g, 93%), in a mixture of chloroform (25 ml) and methanol (25 ml), was cooled to −80° and treated with ozonized oxygen until the solution was pale blue. The solvents were removed under reduced pressure, and 30% hydrogen peroxide (30 ml) and methanol (30 ml) were added.[41] After the solution had been refluxed for 30 min the methanol was removed and 10% aqueous sodium carbonate (50 ml) was added. The solution was washed with two 40-ml portions of ether, brought to pH 2 with dilute sulfuric acid, and rapidly extracted with two 50-ml portions of ether. The combined extracts were washed with two 20-ml portions of water, dried (Na$_2$SO$_4$), and evaporated. Crystallization of the residue from pentane and then from ethyl acetate gave the keto acid 7 (1.45 g, 21%), mp 89–91°. The mother liquors, in aqueous methanol, yielded a further quantity (1.2 g, 17%) of keto acid. After sublimation the product had mp 91–92°; λ_{max} 275 mμ (ϵ 45), end absorption at 200 mμ (ϵ 1100) (in 95% ethanol). Its nmr spectrum (CDCl$_3$) showed a composite nine-proton peak consisting mainly of a singlet at δ 1.25 together with a doublet (J = 6 cps) at 1.2, a broad three-proton singlet at 2.14, and broad multiplets centered at 1.5 (two protons) and 3.1 (one proton); the carboxyl proton gave a broad singlet at δ 10.0.

Anal. Calcd for C$_9$H$_{15}$O (CO$_2$H): C, 65.19; H, 8.75; neut equiv, 184. Found: C, 65.46, 65.58; H, 8.42, 8.56; neut equiv, 177.

Treatment of a methanolic solution of this acid with excess ethereal diazomethane gave the keto ester 8: ν_{max} (neat) 3.39, 3.48, 5.8 (s), 6.94, 7.21, 7.29, 7.37, 7.58, 7.9 (w), 8.1, 8.3–8.5, 8.53, 8.73, 8.86, 9.05, 9.2, 9.5, (w), 9.78 (w), 10.2, 10.7, 11.73 (s), 12.15, 12.85, and 13.5 μ. Its nmr spectrum (CDCl$_3$) showed broad singlets at δ 1.2 (6 H), 2.1 (3 H), and 3.58 (3 H), a doublet (J = 6 cps) at 1.13 (3 H), and multiplets at 1.5 (2 H) and 3.05 (H).

Anal. Calcd for C$_{11}$H$_{18}$O$_3$: C, 66.64; H, 9.15. Found: C, 65.54; H, 9.30.

In one experiment, ozonolysis of the photoproduct (93.6% containing two less volatile components of 1.9 and 4.5%) and working up in the usual manner gave another acid in 2.9% yield. After crystallization from ethyl acetate this had mp 147–148° (rapid heating) and 133–135° (slow heating); no ultraviolet maximum was apparent [λ 210 mμ (ϵ 340), 205 (520), 200 (1000), 195 (2050) in 95% EtOH]. The ir spectrum showed ν_{max} (KCl disk) at 5.88 and 6.01 μ. Its nmr spectrum (acetone-d_6) showed complex multiplets at δ 0.9–1.4 (14 or 15 H), 1.4–1.6 (1 or 2 H), 1.8–2.2 (2 H), and 2.6–3.0 (H).

Anal. Calcd for C$_9$H$_{17}$O$_5$ (CO$_2$H): C, 51.27; H, 7.75; neut equiv, 234. Found: C, 51.14; H, 7.90; neut equiv, 225.

Hypobromite Oxidation of the Keto Acid (7).—A cold colution of sodium hypobromite, prepared from bromine (0.7 ml) and 20%

aqueous sodium hydroxide (10 ml), was added to a solution of the keto acid (0.31 g) in 10% aqueous sodium hydroxide (5 ml), and the mixture was kept at −15° for 1 hr. After being decolorized with sodium metabisulfite the mixture was acidified, extracted with two 15-ml portions of ethyl acetate, washed with two 10-ml portions of saturated aqueous sodium chloride, dried, and evaporated. Crystallization of the residue from ether gave the diacid 9 (0.24 g, 78%) which, after a further crystallization from ethyl acetate–hexane, had mp 160–162°; no ultraviolet maxima [194 mμ (ϵ 2000) in 95% ethanol] was apparent; ν_{max} (KCl disk) 5.84–5.92 (s), 6.9 (s), 7.08, 7.17, 7.22, 7.39 (w), 7.61, 8.0–8.1 (s), 8.62, 8.91, 9.01, 9.23, 9.5, 9.96 (w), 10.24, 10.8–10.95, 11.6, 12.04, 12.58, and 13.45 μ.

Anal. Calcd for C$_7$H$_{12}$ (CO$_2$H)$_2$: C, 58.05; H, 7.58%; neut equiv, 93. Found: C, 58.66; H, 7.74; neut equiv, 103.

The same acid (mixture melting point, infrared spectrum) was also obtained directly from the hydrocarbon, although in only 2.2% yield when the ozonolysis product was worked up according to the method of Corey and Burke.[41] In this experiment the keto acid was not obtained crystalline, and the diacid (9) had to be purified through the preparation, sublimation, and subsequent hydrolysis with hot water of the anhydride. This compound, which sublimed as an oil after the crude acid was refluxed for 0.5 hr with excess acetic anhydride, was obtained as crystals, mp 34–41°, after being crystallized from ether–pentane at −80°.

Anal. Calcd for C$_9$H$_{12}$O$_3$: C, 64.27; H, 7.19. Found: C, 64.32; H, 7.18.

Ring Opening of the Keto Ester (8).—The keto ester (61 mg, 96.6%; contaminated with solvents) in 10% methanolic potassium hydroxide (6 ml) was refluxed for 3 hr. The solution was diluted with water, concentrated under reduced pressure, acidified to pH 2, and extracted with two 10-ml portions of ether. The combined extracts were washed with saturated aqueous sodium chloride, dried, and treated with excess ethereal diazomethane. This yielded a mixture (57 mg) which was found by glpc to contain the starting material (25.3%) and one main product (73.3%). This unsaturated keto ester (12), when purified by glpc, had the following spectral properties: $\lambda_{max}^{95\% \text{ EtOH}}$ 292 mμ (ϵ 83), 228 mμ (ϵ 13,900); ν_{max} (neat) 3.39, 5.76 (s), 5.99 (s), 6.10, 6.95, 7.30, 7.40, 8.1, 8.6, 8.85, 9.12 (w), 9.72, and 11.27 μ (w). Its nmr spectrum showed a six-proton singlet at δ 1.3, a three-proton doublet (J = 1.3 cps) at 1.83, singlets at 2.23 (three protons), 2.43 (two protons), and 3.61 (three protons), and a one-proton quartet (J = 1.3 cps) at 6.66.

Anal. Calcd for C$_{11}$H$_{18}$O$_3$: C, 66.64; H, 9.15. Found: C, 65.98; H, 8.28.

Attempts to crystallize the corresponding unsaturated keto acid, obtained by hydrolysis of the gas chromatographically purified ester (12) were fruitless.

When the free keto acid (7, 98 mg) was treated for 24 hr with boiling 10% methanolic potassium hydroxide (10 ml) an oil (91 mg) was obtained. After esterification this was found by glpc to consist of the cyclopropane keto ester (66%) and the unsaturated keto ester (12, 24%) (together with two minor products); this was confirmed by the infrared and ultraviolet spectra of the ester mixture. The diester 10 was prepared with diazomethane in the usual way (83 mg, 98%, containing 2% volatile solvents) and was treated similarly (3-hr reflux). The infrared spectrum of the product indicated only starting material, but glpc showed 97% 10 and two new compounds, neither of which had the same retention time as the dimethyl ester of 13.

Oxiation of 12. A. To 2,2-Dimethylsuccinic Acid.—A solution of the unsaturated keto ester (44 mg, <99% purified by glpc) in methanol (10 ml) was cooled to −80° and treated with ozonized oxygen until the solution became blue. The solvent was evaporated, formic acid (1.0 g) and 30% hydrogen peroxide (1.0 g) were added, and the mixture was refluxed for 0.5 hr. The nonvolatile acidic product was isolated by extraction with ether in the usual way. The resulting solid (13 mg) was recrystallized from ether–hexane and proved to be 2,2-dimethylsuccinic acid (9.5 mg, 30%): mp 141–142°; mmp 140–141° with an authentic sample (Aldrich Chemical Co.). The two samples had identical infrared spectra.

B. To 4,4-Dimethylpent-2-ene-2,5-dicarboxylic Acid (13).—The unsaturated keto acid was obtained as a liquid (165 mg) on saponification of the corresponding ester (175 mg, <99% pure, purified by glpc) by refluxing in 10% potsssium hydroxide in methanol. After dissolving in 10% aqueous sodium hydroxide (10 ml), it was treated with aqueous sodium hypobromite (from 0.7 g of bromine), and the solution was maintained at 0–5° for

(41) *Cf.* E. J. Corey and H. J. Burke, *J. Amer. Chem. Soc.*, **78**, 174 (1956).

90 min. Working up in the usual way gave an oil (136 mg) which slowly crystallized. This, after being crystallized three times from ethyl acetate–hexane, then once from benzene–hexane, gave fat needles (53 mg, 32%): mp 122–122.5°; $\lambda_{max}^{95\% \ EtOH}$ 212 mμ (ϵ 12,000); ν_{max} (KCl disk) 3.35, 5.9, 6.13, and 12.0 μ. Its nmr spectrum (acetone-d_6) showed broad singlets at δ 1.32 (6 H), 1.96 (3 H), 2.52 (2 H), 6.97 (H), and 9.7 (2 H).

Anal. Calcd for C_7H_{12} $(CO_2H)_2$: C, 58.05; H, 7.58; neut equiv, 93. Found: C, 58.12; H, 7.39; neut equiv, 96.

Isomerization of 5a. A. By Heat.—The photoproduct (1.26 g, 97%, containing two main impurities) was sealed in a thick-walled glass tube and kept at 330° for 1 hr. Distillation of the product yielded an oil (739 mg, 59%) which was found, by glpc, to contain mainly one new isomer (16, 54%), an unidentified component (10%), and two compounds identified as 1,2,4-tri-methylbenzene (8%) and 1,2,3-trimethylbenzene (8%). The latter two, isolated by glpc (squalane column), gave nmr spectra in agreement with these assignments, and gave the reported infrared spectra.[42] The main pyrolysis product, which was partly separated by glpc, using the capillary column, into two components (*ca.* 9:1), had λ 190 mμ (ϵ 14,000), 211 mμ (ϵ 2000); it also showed λ_{max} 258 mμ (ϵ 850) which can be attributed to the minor component. It gave infrared maxima at 3.24, 3.28, 3.39 (s), 3.42, 3.48, 5.6, 5.87 (s), 6.09 (s), 6.20, 6.09 (s), 7.3, 7.51, 7.78, 8.15, 8.7 (w), 8.91 (w), 9.21, 9.4, 9.59, 9.7, 9.86, 10.13, 10.33, 10.83, 11.3 (s), 11.7, 12.1, 12.7, 13.3, 13.8–14.0, and 14.9 μ (s). Its nmr spectrum (CDCl$_3$) showed one three-proton doublet (J = 7.2 cps) at δ 0.87 and another (J = 7.1 cps) at 0.96, singlets with fine splitting at 1.65 (3 H) and 4.73 (2 H), a two-proton complex at 5.64, and additional one-proton resonances located by double irradiation at 2.1 and 2.8. A singlet at δ 0.95 (0.7 H) is attributed to the contaminant. A one-proton resonance at δ 2.0–2.8 was not localized.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.15; H, 11.60.

When refluxed for 4 hr under nitrogen with 5% platinized charcoal, the photoproduct was partly (50%) isomerized to the same cyclopentene (16); this was the only major product and was identified by its infrared spectrum after being isolated by glpc.

(42) "Documentation of Molecular Spectroscopy," Verlag Chemie, Weinheim, 1958, infrared spectra cards no. 212 and 215.

The cyclopentene (16, 83 mg) was hydrogenated in pentane in the usual way. It absorbed 2.3 equiv of hydrogen and gave two main products (73 and 15%). After purification by glpc the major product (98% pure) gave infrared and nmr spectra virtually identical with those obtained by Sisido[33] for 17a.

Anal. Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.74; H, 14.16.

The second tetrahydro product was found by glpc and infrared spectrum, to be 17b. It probably resulted from the impurity present in the pyrolysis product.

B. With Acid.—The photoproduct (3.9 g, *ca.* 94%) was intimately mixed with dry, acid-washed alumina (Woelm, grade I, 43 g) which rapidly became warm. The next day the product was extracted with ether in a Soxhlet extractor and fractionated through an 18-in. spinning-band column. This yielded a small amount of starting material, but the main product was the isopropenylcyclopentene (18) (45% yield). The best fraction (95% by capillary column analysis) had bp 86–87° (82 mm). Spectral properties are as follows: λ_{max} 227 mμ (ϵ 435) impurity, 210 (2000), 190 (14,000); ν_{max} 3.25, 3.29, 3.38–3.5 (s), 5.62 (w), 6.10 (s), 6.89 (s), 7.26, 7.55, 7.78, 8.6 (w), 9.3, 9.82, 10.2 (w), 10.4 (w), 10.75, 11.25 (s), and 12.5 μ. Its nmr spectrum showed a three-proton doublet (J = 6.5 cps) at δ 1.05 and finely split singlets at 1.74 (6 H) 2.4 (1 H), 4.86 (2 H), and 5.43 (H), and uncharacterized multiplets (2 H) in the 2.1–2.8 region.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.21; H, 11.68.

The cyclopentene (18, 112 mg) was added to a prereduced suspension of 5% platinized charcoal (200 mg) in pentane (10 ml) and stirred overnight under hydrogen, of which 2.03 equiv were absorbed. The main tetrahydro product (78%), separated by glpc, gave an infrared spectrum virtually identical with that[33b] of 17b.

Anal. Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.68; H, 14.26.

The second component (15%), on isolation by glpc, gave the infrared spectrum of 17a.

Registry No.—1a, 17202-17-4; 1b, 17202-18-5; 1c, 17202-19-6; 1d, 17202-20-9; 3, 17202-21-0; 5a, 3742-45-8; 7, 3742-46-9; 8, 17202-24-3; 9, 3742-47-0; 11, 4779-85-5; 12, 17202-15-2; 13, 17202-16-3; 16, 3739-75-1; 17a, 17202-27-6; 17b, 17202-28-7; 18, 3739-77-3.

The Reactions of Triphenylphosphine with α-Haloisobutyrophenones and with α-Mesyloxyisobutyrophenone[1]

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α-Bromoisobutyrophenone 7 reacts with triphenylphosphine in aprotic solvents *via* elimination of hydrogen bromide to give methacrylophenone 11 and the β-ketophosphonium bromide which results from the addition of hydrogen bromide and triphenylphosphine to 11. Debromination of 7 to isobutyrophenone occurs with triphenylphosphine in the presence of methanol. α-Chloro- and α-mesyloxyisobutyrophenone give the corresponding β-ketophosphonium salt upon reaction with triphenylphosphine. The reaction of isopropylidenetriphenyl-phosphorane with benzoyl chloride gives an α-ketophosphonium bromide which can be distinguished from the above-mentioned β-ketophosphonium bromide *via* its nmr spectrum. The relationships of these elimination reactions to other reactions of α-bromo ketones with triphenylphosphine are discussed.

We have previously described the reactions of triphenylphosphine with α-bromoacetophenone 1 and with α-bromopropiophenone 2[3,4] which give the cor-

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responding α-ketophosphonium bromides. We have shown that the Hammett ρ value for the second-order reactions of a series of *meta*- and *para*-substituted α-bromoacetophenones with triphenylphosphine is +0.44 in nitromethane.[5] Such a small positive ρ value is similar to values obtained by us and by previous workers[6,7] for the pyridine–bromoacetophenone system.

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