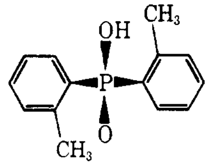


Figure 2.—Perspective view down the C_2 axis (assuming rapid proton transfer) of **4**.

groups on opposite sides of the tetrahedral phosphorus atom. Cyclization to Y would then clearly proceed through loss of a methyl. Therefore, the *o*-tolyl compounds we have studied appear to cyclize to biphenylphosphorus ions[17] in contrast to the conclusion for *o*-tolyl sulfones.[14]

Experimental Section

The compounds used in this study were mostly prepared by previously published procedures[18] during an investigation of the hydrolytic behavior of derivatives of diarylphosphinic acids. Their infrared, nmr, and mass spectra, melting points, and, where appropriate, elemental analyses, were in accord with their postulated structures.[5]

Diphenylphosphine oxide was prepared by an adaptation of Miller's[19] method. Diphenylchlorophosphine (11 g, 0.05 mol) was stirred under nitrogen in dry benzene (150 ml) at 25°, while a solution of water (0.9 ml, 0.05 mol) and triethylamine (5.05 g, 0.05 mol) in acetone (4 ml) was added dropwise over a 1-hr period. After stirring for a further 15 min, the solution was filtered, then extracted with 50 ml of 5% HCl, two 50-ml portions of 5% $NaHCO_3$, two 50-ml portions of H_2O, and finally dried over $MgSO_4$. Removal of benzene gave an oil which solidified after 3 hr at 0°. Two recrystallizations from dry ether at −40° gave white hygroscopic crystals (4.89 g, 48.4%), mp 49–51° (sealed tube) (lit.[20] mp 53–56°).

Diphenylphosphinic acid-O-d_1 was prepared with approximately 80% deuterium by dissolving the protonated acid in DMSO containing a large excess of D_2O and standing 24 hr at 25°. The solvent was removed and the partially deuterated acid dried over P_2O_5 at 100° *in vacuo*. Deuterium content was estimated from the ratio of the m/e 141 and 142 peaks ($PhPO_2H^+$ and $PhPO_2D^+$, respectively) present in the mass spectrum.

Mass spectra were determined with an A.E.I. MS9 mass spectrometer, using direct insertion technique, at a source temperature of 160° and electron beam energy 70 eV.

Registry No.—**1**, 1707-03-5; **2**, 18621-09-5; **3**, 18593-18-5; **4**, 18593-19-6; **5**, 18593-20-9; **6**, 1706-90-7; **7**, 1733-55-7; **8**, 1706-96-3; **9**, 5573-42-2; **10**, 18593-22-1; **11**, 18593-23-2; **12**, 18621-10-8; **13**, 4559-70-0; **14**, 2959-74-2; **15**, 18593-24-3; **16**, 18593-25-4; **17**, 18593-26-5; **18**, 18593-27-6.

Acknowledgment.—We thank Robert Marmor, Robert D. Cook, and Jean P. McNeal for assistance in preparation of some of the compounds, and Dr. David Lightner for help with the mass spectrometer.

---

(17) A spectrum was obtained for phenyl-*o*-tolylphosphinic acid with 85% OD. Although there is no evidence that clearly indicates which cyclic fragmentation is occurring, the data are consistent with $3^+ \rightarrow Y \rightarrow P$.

(18) K. Sasse in Houben-Weyl's "Methoden der organischen Chemie, Organische Phosphorverbindungen," Vol. 1 and 2, G. Thieme Verlag, Stuttgart, 1963.

(19) R. C. Miller, *J. Org. Chem.*, **24**, 2013 (1959).

(20) B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957).

Photochemical Cycloaddition. Some Applications of the Use of Enolized β-Diketones[1,2]

B. D. Challand, H. Hikino,[3a] G. Kornis, G. Lange[3b] and P. de Mayo

Department of Chemistry, University of Western Ontario, London, Ontario, Canada

Received July 31, 1968

Photochemical cycloaddition of the enol acetates of cyclic β-diketones to alkenes gives adducts which are β-acetoxy ketones. These accordingly undergo reverse aldol reactions under mild alkaline conditions to give cyclic 1,5-diketones. This sequence has been used for the synthesis of a number of systems containing seven- and eight-membered rings. Cyclopentane-1,3-dione enol acetate gives adducts with dichloroethylene. One of these, by the action of mild alkali, has been converted in one step and in 45% yield into γ-tropolone. Addition of the same enol acetate to chloromaleic ester gave an adduct which could be brominated, hydrolyzed, and oxidized to the α-diketone. This, on mild acid hydrolysis followed by mild alkaline hydrolysis, gave stipitatonic acid in 4% over-all yield. Cycloaddition of the enol acetate of 2-methyl-1,3-cyclopentanedione to cyclohex-2-enone ketal **42** gave a single adduct which could be reduced to the alcohol and thence to mesylate **45**. Mild treatment with base gave **46**, converted by reaction with methylmagnesium iodide, the Simmons–Smith reagent, methylation and hydrogenolysis to the ketone (**52**). Reduction gave a number of alcohols from the dehydration of which racemic β-himachalene (**36**) was obtained in a ten-step over-all synthesis. Also, the synthetic hydrocarbons could be converted into himachalene dihydrochloride (**60**) the racemate of the dihydrochloride obtained from natural himachalenes.

Some time ago we showed[4] that the process of photocycloaddition could be used for the synthesis of a δ-diketone. A typical example was the addition of acetylacetone to cyclohexene to give diketone **1**.[5,6]

A natural extension of this process appeared to be the use of cyclic β-diketones. Under these circum-

---

(1) Photochemical Synthesis. Part 25. Part 24: H. Izawa, P. de Mayo, and T. Tabata, *Can. J. Chem.*, **47**, 51 (1969).

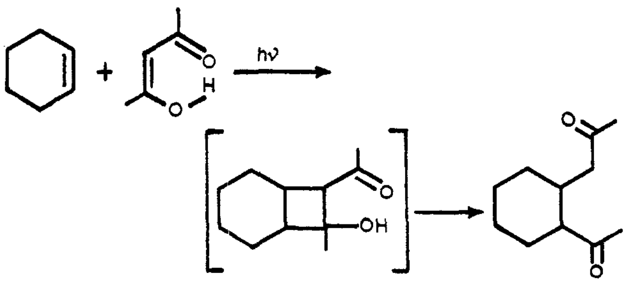
(2) Part of the material presented here has been reported in preliminary form: (a) H. Hikino and P. de Mayo, *J. Amer. Chem. Soc.*, **86**, 3582 (1964); (b) G. Lange and P. de Mayo, *Chem. Commun.*, **3**, 704 (1967); (c) B. D. Challand, G. Kornis, G. Lange, and P. de Mayo, *ibid.*, 704 (1967).

(3) (a) On leave from Tohoku University, Sendai, Japan; (b) Department of Chemistry, University of Guelph, Ontario, Canada.

(4) P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963).

(5) At that time no consideration was given to the detailed nature of the photochemical process. Very recently[6] in this and other applications of this type of synthesis, it has been shown that a triplet of the acetylacetone is most probably involved.

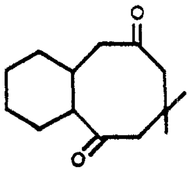
(6) H. Nozaki, M. Kurita, T. Mori, and R. Noyori, *Tetrahedron*, **24**, 1821 (1968).



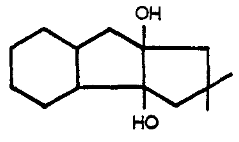
1

stances the resultant 1,5-diketone would be part of a ring, and, provided that the diketone did not undergo further chemical transformations under the conditions of generation, might provide a useful synthetic route to such rings.

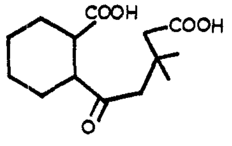
The first pair of reagents selected was cyclohexene and dimedone (5,5-dimethylcyclohexane-1,3-dione). Irradiation gave an adduct having appropriate carbonyl absorption and which appeared to be the desired substance, **2**. It was accompanied by a smaller amount of a more polar substance having no carbonyl absorption, but showing hydroxyl absorption in the infrared region.



2



3

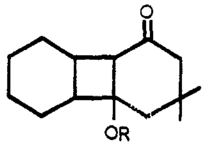


4

The correctness of the representation **2** for the ketonic substance was required to be very rigidly demonstrated in this, the first example of such a transformation. The substance was accordingly oxidized with potassium permanganate in aqueous acetone. A crystalline dicarboxylic acid was obtained, $C_{14}H_{22}O_5$, in which no carbon atoms had been lost. Further oxidation of the dimethyl ester of this with concentrated nitric acid gave a mixture of acids which was esterified. Chromatographic separation gave *trans*-cyclohexane-1,2-dicarboxylic acid dimethyl ester[7] and dimethyl α,α-dimethyl succinate. A small amount of material with exactly the same retention time as dimethyl β,β-dimethyl glutarate was observed. The two, *i.e.*, the cyclohexane dicarboxylate and the dimethyl succinate, former substances, together contain all of the carbon atoms of the original diketone, **2**, and, taking into account the nature of the starting materials, confirm the structure allocated to the adduct.

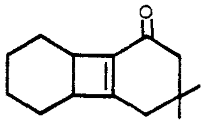
Further confirmation came from a study of the more polar substance accompanying **2**. The most probable structure for this substance, taking into account the fact that the empirical formula required two hydrogen atoms in addition to those found in **2**, was that shown in **3**. This could be formed by the normal reduction of the excited ketone to the ketyl radical, and further reaction in the same manner as in the classical photochemical reductions of benzophenone to benzpinacol and acetone to pinacol.[8] This was confirmed when it was found that cleavage of **3** with periodic acid regenerated **2**. It was also shown that irradiation of **2**, under the conditions of its formation, led to the production of **3**. The same transannular reduction was observed by the use of zinc and acetic acid.[9-11]

The occurrence of the secondary reduction and, more especially, the low solubility of enols in hydrocarbon solvents suggested the use of a derivative of the β-diketone, and of these the acetate seemed most suitable, being both easily prepared and not introducing a new chromophore absorbing at wavelengths longer than those absorbed by Pyrex. From cyclohexene and dimedone enol acetate adduct **5** was obtained and hydrolysis of the acetate attempted with base in aqueous dioxane. It appeared, however, that elimination to the cyclobutene preceded hydrolysis because product **7** was obtained. This was readily recognized by its ultraviolet absorption spectrum. Substitution of ethanol for the aqueous dioxane led to the desired diketone **2**. The use of methanol also gave **2**, but in addition another substance was formed, attributed structure **6**.



5 R = Ac

6 R = Me



7

The use of the enol acetate, while facilitating the cycloaddition introduced a limitation on the size of the ring which could be generated, since 1,5-diketones in a nine- or higher membered ring would be expected to cyclize under the conditions of the ester hydrolysis. While it was believed that this problem could be circumvented by a device such as used in the synthesis of β-himachalene (see below) the problem became irrelevant when it was later shown by other workers that cyclenones with seven-membered rings did not cycloadd,[12] and so imposed a limit on the utility of the method in any event.

That the method could be used on an open-chain substrate was shown by the cycloaddition of cyclohexane-1,3-dione to methyl acrylate. Two adducts were obtained, **8** and **9**, which were readily distinguishable. Diketone **9** although in the diketonic form as isolated, gradually enolized in chloroform or in methanol solution.

A final example involved the use of a different enol acetate, that of cyclopentane-1,3-dione. The product

---

(7) A small amount of the corresponding acid was crystallized directly out of the oxidation mixture.

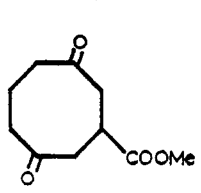
(8) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N.Y., 1965, p. 139.

(9) This reagent had previously been used[10] for the reduction of 2,6-diphenyl-1,5-cyclooctanedione to the pinacol. A recent example of such a reduction has been recorded by Agosta.[11]

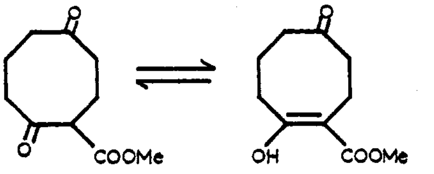
(10) S. Wawzonek, *J. Amer. Chem. Soc.*, **65**, 839 (1943).

(11) W. C. Agosta, *ibid.*, **89**, 3505 (1967).

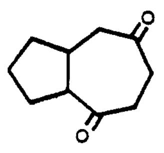
(12) P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965); E. J. Corey, M. Tada, R. Le Mahieu, and L. Libit, *ibid.*, **87**, 2051 (1965).



8



9

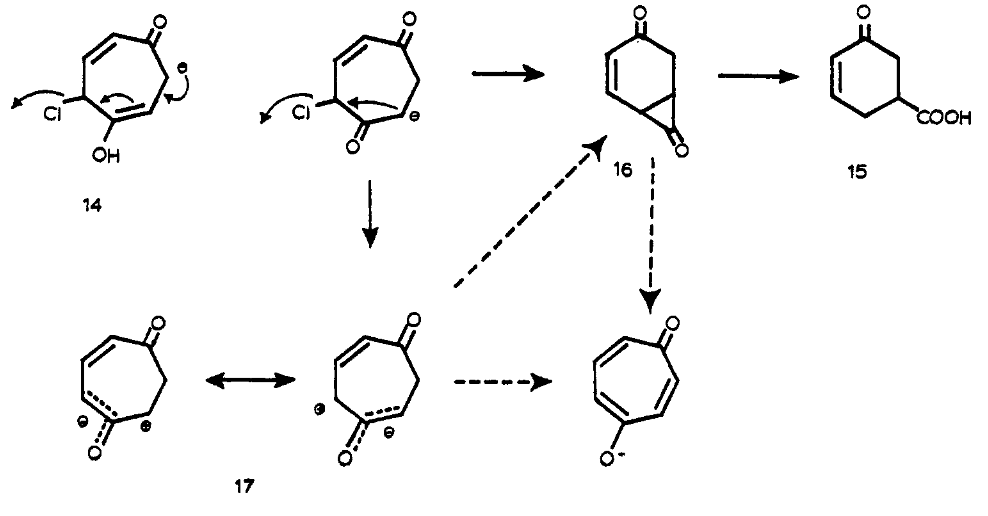


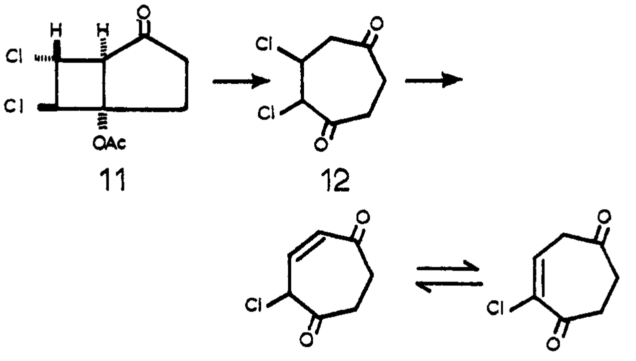
10

from cycloaddition to cyclopentene was diketone **10**, which has the carbon skeleton of a perhydroazulene. An attempt to demonstrate this by reduction to the diol followed by dehydrogenation was abortive; the only identified product was naphthalene. Presumably the facile generation of a cation adjacent to the junction permitted by the presence of the alcoholic function facilitated the rearrangement. The remainder of the present report concerns three specific applications of the cycloadditive process just described.

γ-Tropolone.—The construction of the seven-membered ring requires the use of cyclopentane-1,3-dione enol acetate and an ethylenic derivative. The diketonic product would then contain two double-bond equivalents against the four present in the tropolone. Since γ-tropolone contains no substituents the two extra double-bond equivalents were required to be introduced as eliminable substituents. It was simpler to incorporate these in the ethylene rather than in the ketone and 1,2-dichloroethylene appeared suitable. The cycloaddition went in good over-all yield, and the product consisted, as would follow for a nonconcerted process,[13] of at least three isomers which were separated by gas–liquid partition chromatography, although only two were properly characterized. The main product, mp 90–91°, was originally tentatively allocated the stereochemistry in **11** on the basis of nmr data, but we are now of the opinion that this is somewhat conjectural. The original[2a] procedure reported has been modified for the subsequent treatment of this substance. Although the yields are not better the process is quicker. Adduct **11** (or stereoisomer) was merely dissolved in methanolic alkali for 1 min. The yield of γ-tropolone formed, measured spectroscopically, was 45%. The tropolone itself was isolated by extraction of impurities at pH 4, isolation with ether, crystallization, and sublimation. The yield of material having mp 208–212° was 30%, a very considerable improvement on previous syntheses.[14]

Scheme I





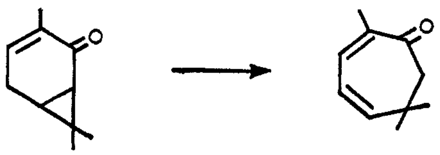
It is interesting to speculate on the mechanism of formation of the tropolone. The first step surely involves the usual hydrolysis and dealdolization to give **12**. A rapid β elimination of the halide to give **13** would then be reasonable. The two possible elimination products are tautomers and would be expected to be equilibrated. In principle only the loss of hydrogen chloride is required to give γ-tropolone. This might be represented through enol **14**, as a vinylogous β elimination. However **13** is an α-halo ketone and under these conditions a preferential Favorskii reaction might be expected leading to a carboxylic product of type **15**, and conceivably some of the material followed this pathway since carboxylic acids were certainly formed, but closer inspection reveals an interesting possibility. Among the mechanisms presently entertained as ex-

---

(13) (a) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964). (b) See also P. de Mayo, J.-P. Pete, and M. F. Tchiv, *Can. J. Chem.*, **46**, 2535 (1968); G. Mark, F. Mark, and O. E. Polansky, *Ann. Chem.*, **719**, 151 (1968).

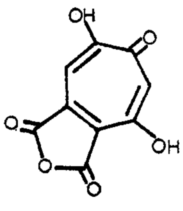
(14) Subsequent syntheses include O. L. Chapman and P. Fitton, *J. Amer. Chem. Soc.*, **85**, 41 (1963).

plaining much of the experimental data is that promulgated by Dewar[15] in which ionization of the halide in the enolate anion to a zwitterion, in this case **17**, precedes (or replaces) the more usual cyclopropanone intermediate (**16**). Loss of a proton from zwitterion **17** gives the tropolone anion directly (Scheme I). An alternative view is that collapse to the cyclopropanone does occur, but that rearrangement of the norcarenone proceeds faster than nucleophilic attack on the cyclopropanone carbonyl. The facility of such a rearrangement has been demonstrated in the conversion of carenone (**18**) into eucarvone (**19**).[16]

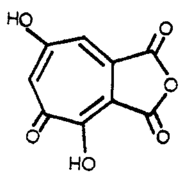


18 19

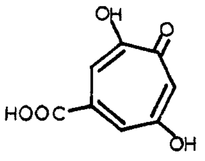
Stipitatonic Acid.—The mold metabolite, stipitatonic acid, **20**, was isolated by Segal[17] from *Penicillium stipitatum*. Structure **21** was proposed but later modified to **20**.[18,19] It was found[17] that this substance bore the same relationship to stipitatic acid **22** as puberulonic acid (**23**) does to puberulic acid (**24**), *i.e.*, by heating **20** in aqueous solution under reflux **22** is formed together with 1 equiv of carbon dioxide. Rather long syntheses of **22**,[20] **23**,[21] and **24**[22] had been reported, but not that of **20**. This therefore seemed a suitable object for our endeavors.[23]



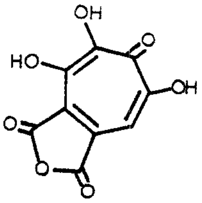
20



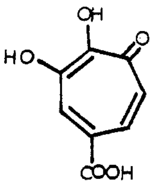
21



22

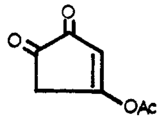


23

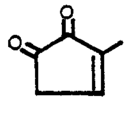


24

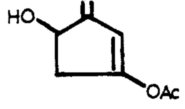
As in the case of γ-tropolone two double-bond equivalents were required to convert the normal cycloaddition product into the appropriate oxidation level. In addition, one more oxygen function was needed. Since, for simplicity, the carboxyl functions were best incorporated in the ethylenic moiety this oxygen function was required to be α to the carbonyl group of the β-diketone enol acetate, as in **25**, for example. However the use of a derivative such as **25** was precluded by the fact that other observations in these laboratories[24] had shown that ketone **26** did not undergo normal cycloadditive reactions. Instead it exhibited the photochemical properties of an unenolized α-diketone. Since alcohol **27** was not readily accessible it was decided to introduce the oxygen function and one double-bond equivalent of unsaturation after the cycloaddition step. There remained the selection of the mode of introduction of the remaining unit of unsaturation. Acetylene dicarboxylic ester seemed an obvious choice but in trial experiments using cyclopentadione enol acetate no desired adduct could be isolated. Instead there appeared to be some dimer of the enol ester and an adduct, in small yield, which seems best formulated as **28** and may have been formed by prior reduction of the acetylene. Substitution of chloromaleic anhydride for the acetylenic diester was not more successful and although no attempt was made to discover the cause a possible explanation is that energy transfer is effectively competing. In other systems both of these substances have undergone normal cycloadditive reactions.



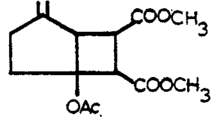
·25



26



27



28

Since it seemed likely that opening the anhydride would raise the triplet energy of the maleic derivative,[25–27] chloromaleic acid dimethyl ester was used as the addend. The cycloaddition proceeded well in dioxane solution by the use of light near 350 mμ. About 80–85% of distilled product was obtained, **29**, which probably consisted of a number of isomers. The mixture was, unfortunately, not stable to chromatographic treatment and when this was attempted elimination of hydrogen chloride occurred to give the crystalline ester **30** or its double-bond isomer.[28]

Since the next step was bromination, **30** was less suitable than **29**. The latter was brominated with pyridinium bromide perbromide in acetic acid and the product (**31**) treated with silver oxide in aqueous dioxane to give **32**. Hydrogen chloride was lost simultaneously. Finally, oxidation of the mixture of isomers

---

(15) (a) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954); (b) H. O. House and F. A. Richey, *J. Org. Chem.*, **32**, 2151 (1967); (c) A. Gaudemer, J. Parello, A. Skrobeck, and B. Tchoubar, *Bull. Soc. Chim. Fr.*, 2405 (1963); (d) A. S. Kende, *Org. Reactions*, **11**, 261 (1960).

(16) E. E. Van Tamelen, J. McNary, and F. A. Lornitzo, *J. Amer. Chem. Soc.*, **79**, 1231 (1957).

(17) W. Segal, *Chem. Ind.* (London), 1040 (1957).

(18) K. Doi and Y. Kitahara, *Bull. Chem. Soc. Jap.*, **31**, 794 (1958).

(19) W. Segal, *Chem. Ind.* (London), 1726 (1958); *J. Chem. Soc.*, 2847 (1959).

(20) J. R. Bartels-Keith, A. W. Johnson, and W. I. Taylor, *ibid.*, 2352 (1951).

(21) T. Nozoe, K. Doi, and T. Hashimoto, *Bull. Chem. Soc. Jap.*, **33**, 1071 (1960).

(22) R. B. Johns, A. W. Johnson, and J. Murray, *J. Chem. Soc.*, 198 (1954).

(23) In view of the ready decarboxylation the present synthesis constitutes an alternative, shorter, route to stipitatic acid.

(24) We thank Dr. K. Endo for this information.

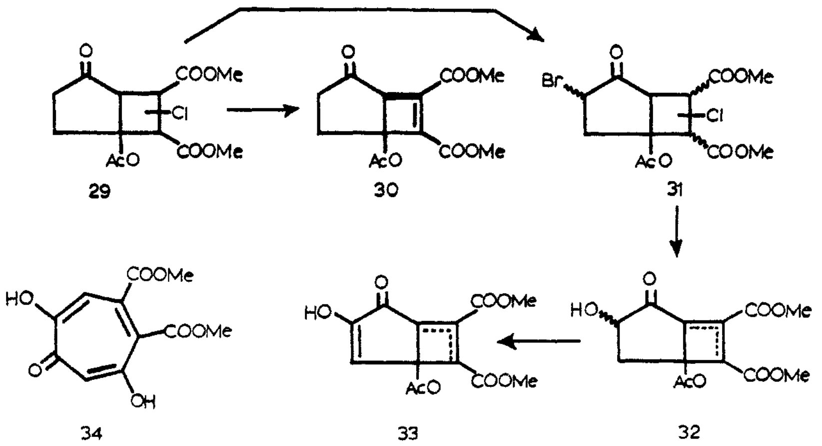
(25) There seems little doubt now that cyclopentenone cycloadditions proceed through a triplet,[26,27] though probably not the lowest energy triplet.[13b] Probably the same considerations apply to the enol acetate, but argument by analogy in photochemistry at the moment appears a mode of seppuku.

(26) P. E. Eaton and W. S. Hurt, *J. Amer. Chem. Soc.*, **88**, 5038 (1966).

(27) J. L. Ruhlen and P. A. Leermakers, *ibid.*, **89**, 4944 (1967).

(28) The wavelength of the absorption (255 mμ) is more in accord with the double bond lying between the ketone and the ester, but its extinction is very low, while the absorption at 204 mμ is much higher. Although having a sharp melting point and giving a single spot on thin layer chromatography, the substance may be a mixture of both isomers.

SCHEME II



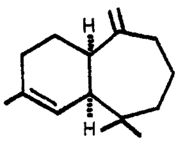
with bismuth oxide in acetic acid[29] gave the desired diketone at this stage; **33** proved too unstable for extended chromatographic treatment. (See Scheme II.)

Preliminary investigations showed that the mild base treatment previously employed for effecting hydrolysis and dealdolization would not serve in this instance. Tars appeared rapidly and a study of the ultraviolet absorption revealed that very little tropolone was being formed. This was not surprising since **33**, as a diosphenol, would be expected to be ionized in a basic medium, and the anion so produced could eliminate the β-acetoxyl group as acetate anion before nucleophilic attack could effect hydrolysis of this same acetate. Very mild treatment with hydrochloric acid, on the other hand, facilitated nucleophilic attack, which was now apparently able to compete with elimination. With subsequent dealdolization tropolone diester **43** was formed. The comparatively stable tropolone nucleus having been formed the substance was now sufficiently stable to survive mild basic hydrolysis of the ester functions. The over-all yield of stipitatonic acid by this route was near 4%, based on the starting enol acetate. No particular steps were necessary for anhydride formation which occurred spontaneously on isolation.

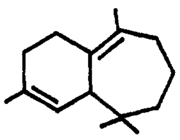
There appeared to be some confusion with regard to the ultraviolet spectrum of stipitatonic acid, particularly as to the longest wavelength band. The observed spectra are recorded in the Experimental Section. Although Bentley[30] recorded a change in the position of the maximum at 260 mμ in water, which in time moved to 250 mμ, the effects on the other bands are more dramatic. In particular the band at 432 mμ present immediately on dissolution disappears completely. No side reactions are involved since there are two well-defined isobestic points (at 320 and 392 mμ) and the simplest interpretation, as has already been suggested,[30] is that the process involves the hydrolysis of the anhydride and ionization of a carboxylic acid.

β-Himachalene.—The general synthesis, as so far developed, had a number of drawbacks. First, the direction of cycloaddition was not, and is not at present, under direct, predictable control. This aspect is being investigated. Second, within the restrictions implied by the cycloadditive process itself (ring rize), the resultant product was a diketone. Further manipulation then required a distinction to be made between these two functions which were placed in a rather similar environment. To avoid this situation alternative fragmentation processes were available and the following synthesis illustrates the use of one of these.

The isolation of α- (**35**) and β-himachalenes (**36**) was first recorded by Dev.[31] Subsequent work by Dev and by Erdtman[32] has established the structures here represented.[33] We chose to attempt the synthesis of β-himachalene, **36**, and the derived crystalline dihydrochloride.



35



36

The irradiation of 2-methylcyclopentane-1,3-dione enol acetate (**37**) in the presence of the ethylene ketal of cyclohexenone (**38**) could lead in principle to two modes of union, **39** and **40**, aside from the various stereochemical possibilities implied by each of these structures. Of the two, from models, **40** seemed stereochemically somewhat more favored, perhaps, than **39**, and, aside from other directing influences in cycloadditive processes which are not clearly understood yet, would be expected to be the more favored product. In any event, as was important, the undesired ketone **39** could be readily recognized. On treatment with acid or base the ketal and acetate would be expected to hydrolyze, and the hydroxy ketone dealdolize to give, for instance, substance **41**. This could β eliminate to give **42**, or, further, hydrolyze by addition-elimination to give **43**. These transformations would be readily detected by ultraviolet spectral changes, and, in the case of **43**, by the additional shift of the absorption with pH. No such pathway to a chromophore visible in the

---

(29) W. Rigby, *J. Chem. Soc.*, 793 (1951).

(30) R. Bentley and C. P. Thiessen, *J. Biol. Chem.*, **238**, 1880 (1963).

(31) G. S. K. Rao, S. Dev, and P. C. Guha, *J. Indian Chem. Soc.*, **29**, 721 (1952).

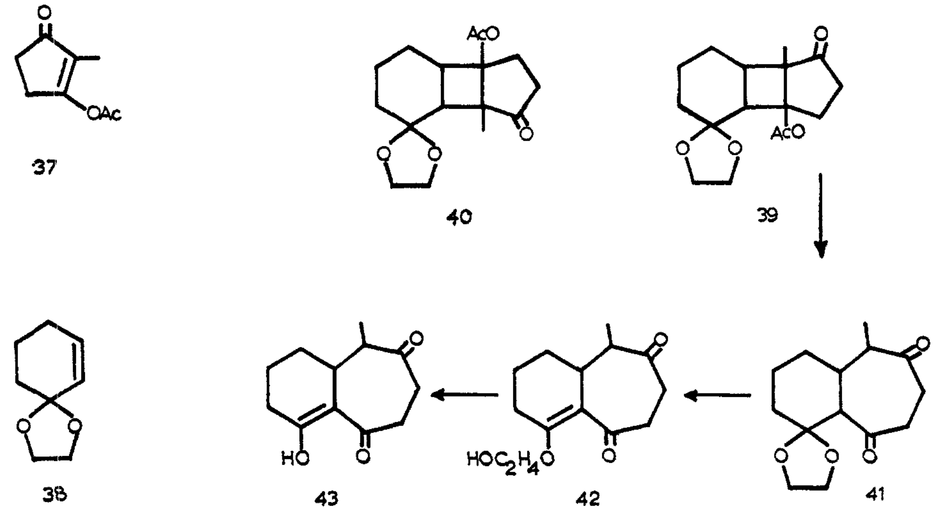
(32) (a) T. C. Joseph and S. Dev, *Tetrahedron Lett.*, 216 (1961); (b) J. B-Son Bredenberg and H. Erdtman, *Acta Chem. Scand.*, **15**, 685 (1961); (c) S. C. Bisarya and S. Dev, *Tetrahedron Lett.*, 3761 (1964); (d) T. C. Joseph and S. Dev, *Tetrahedron*, **24**, 3809 (1968).

(33) We are happy to acknowledge the assistance we have received from Dr. Dev and Professor Erdtman during this work in the way of spectra and specimens.

ultraviolet was possible for the desired ketone **40**. (See Scheme III.)

In the event essentially one adduct was obtained which, by the criterion just delineated, was the desired substance. It was estimated that less than 5% of isomer **39** could have been formed. This high degree of selectivity must have some other origin than the steric effect originally considered.[34]

SCHEME III



Corey has shown[13] that the polar character of the reactants has a strong influence on the stereochemistry of photochemical cycloaddition. The possibility that the double bond in the ketal could be polarized sufficiently to direct addition had to be considered. However, nmr spectra showed that the polarization is very small: the ^{1}H spectrum shows H_b downfield from H_a by only 0.29 ppm; the ^{13}C spectrum shows a negligible (*ca.* 3 ppm) difference between the C_a and C_b positions.[35] These figures correspond to an electron density difference[36] between C_a and C_b of only 0.03 electrons/C atom in contrast with truly polarized systems (*e.g.*, alkoxyethylenes, 0.3–0.4; dimethoxyethylene, 0.61). These results are indirectly confirmed by σ^* values.

Another interpretation of polar effects which has been offered has been to consider the over-all dipole interactions of the excited ketone and the olefin. The stereochemistry of the addition of maleic anhydride to *cis*-1,2-dichloroethylene, for example, has been well explained[37] by considering the dipolar interactions of the reactants and the enormous change in stereospecificity induced by changing the polarity of the solvent.[38] Similar rationalizations have been made for the dimerization of acenaphthylene[39] and cyclopentenone.[13b]

Preliminary calculations[40–43] suggest that the excited enone in the n,π^* state has a small over-all dipole in the direction of the acetate. The product is therefore probably formed by alignment of opposed dipoles if the reacting species is the n,π^* triplet. The situation is not interpretable easily in such a manner if the reactive species is the π,π^* triplet.

For the formation of the seven-membered ring, a fragmentation of the type used by Corey[44] and others was intended. For this purpose it was necessary that the leaving group selected should be *trans* to the quaternary methyl group. A substituent of the opposite configuration would necessitate the formation of *trans* double bond in a seven-membered ring as the result of the fragmentation. A consideration of a model of **38** indicated that the side *cis* to this methyl group was less hindered to attack (irrespective of the nature of the ring junction) and so sodium borohydride was chosen as the reducing agent. The required alcohol **44**, was obtained, and this was converted into methanesulfonate **45** *via* sulfene, conveniently generated *in situ* from methanesulfonyl chloride and triethylamine.[45]

The fragmentation was found to proceed under very mild conditions—*ca.* 2% alkali at 70°—and ketone **46** was obtained in 35% over-all yield from the enol acetate. Under these conditions equilibration of the

---

(34) This assumes that the excited state of the cyclopentenone concerned has approximately the same geometry as the ground-state molecule.

(35) We thank Mr. H. Brouwer and Dr. J. B. Stothers for this measurement.

(36) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, No. 14, 468 (1961); Gurudata, J. B. Stothers, and J. D. Talman, *Can. J. Chem.*, **45**, 731 (1967); K. S. Dhami and J. B. Stothers, *ibid.*, **43**, 510 (1965).

(37) R. Steinmetz, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **98**, 3854 (1965).

(38) J. A. Berson, Z. Hamlet, and W. A. Müller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).

(39) I-M. Hartmann, W. Hartmann and G. O. Schenck, *Chem. Ber.*, **100**, 3146 (1967).

(40) The change in magnitude in a component of a dipole in going from a ground state to an excited state[41] (*e.g.*, the energy of a n,π^* transition) can be expressed as a function of the dielectric constant of the medium. For cyclopentenone a linear relationship was found, from which the dipole moment of the n,π^* singlet was deduced to be very small. The dipole moment of the enol acetate in the ground state may be computed to be about 2.5 ± 0.6 D inclined at *ca.* 30° to the C_1–O axis. Excitation then leads to a dipole change such that the component along the C_1–C_2 axis is reversed.[42] These computations refer only to n,π^* singlets but Zimmerman has made calculations[43] which suggest that the π-electron distributions of n,π^* enone singlet and triplet states are very similar. If these conclusions apply to substituted cyclopentenones also, their dipoles may also be similar.

(41) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957); A. Balasubramanian and C. N. R. Rao, *Spectrochim. Acta*, **18**, 1337 (1962); E. M. Kosower, G-S. Wu, and T. S. Sorensen, *J. Amer. Chem. Soc.*, **83**, 3147 (1961); M. B. Ledger and P. Suppan, *Spectrochim. Acta*, **23A**, 641 (1967).

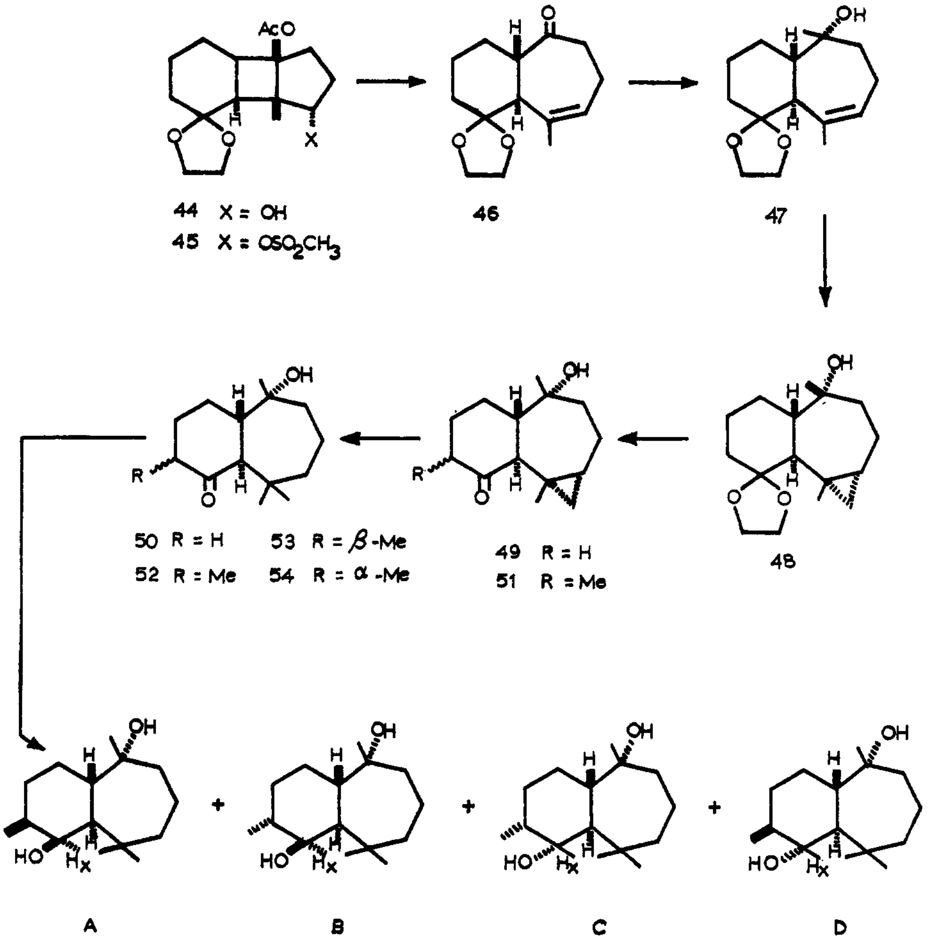
(42) B. D. Challand, Thesis, University of Western Ontario, 1968.

(43) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

(44) E. J. Corey, R. B. Mitra, and H. Uda, *ibid.*, **86**, 485 (1964).

(45) T. Durst and J. F. King, *Can. J. Chem.*, **44**, 1869 (1966); *J. Amer. Chem. Soc.*, **87**, 5684 (1965).

SCHEME IV



stereochemistry of the ring junction could be expected. The fusion was now expected to be *trans* and subsequent results confirmed this.[46,47]

Ketone **46** was converted into carbinol **47** in high yield with methylmagnesium iodide. The stereochemistry is allocated on the basis of models which indicate that the introduced methyl group is *cis* to the adjacent ring junction proton irrespective of the nature of the ring junction assuming approach from the less hindered side. (See Scheme IV.)

Treatment of **47** under Simmons-Smith conditions[48] gave a mixture of **48** and **49**. It was not unexpected that the dioxolan ring was cleaved in the rather long reaction times involved since Blanchard and Simmons[49] report that even diethyl ether was attacked by their reagent. To simplify the isolation the crude mixture was treated with dilute aqueous methanolic acid to complete the removal of the ketal and **49** only was isolated. The stereochemistry allocated is assigned on the basis of other studies of this reaction[50] which have indicated that the methylene is inserted *cis* to the nearby hydroxyl group.

The conversion of a cyclopropane ring into a methyl group by hydrogenolysis had ample analogy[51] and an apparently suitable case was tested prior to a study of **49** itself. 1-Methylcyclohexene was converted into 1-methylnorcarane by the Simmons-Smith reaction; hydrogenation of this with platinum oxide in acetic acid at room temperature and atmospheric pressure gave 1,1-dimethylcyclohexane in high yield.

Hydrogenation of **49** under these same conditions did not give the desired product **50**. Mixtures were produced in which the cyclic bond of the cyclopropane had been cleaved (to give an eight-membered ring) and in which the tertiary hydroxyl group had been hydrogenolyzed. The nature of the products was indicated in the nmr spectrum by, among other things, the number and splitting of the methyl groups. After joyless and extended experimentation it was found, happily, that the platinum-rhodium catalyst, prepared according to the method of Nishimura,[52] cleaved the cyclopropane ring in the desired direction. When sodium acetate was incorporated into the medium there was, in addition, very little hydrogenolysis of the tertiary alcohol.

A change in the direction of cleavage during the hy-

---

(46) Fragmentation reactions are facilitated by the breaking of parallel bonds,[47] but in the present system such a conformation would be highly strained. That the reaction occurs so readily emphasizes the strength of the driving force. The epimeric mesylate would be better oriented, but the product would contain the *trans* double bond.

(47) C. A. Grob, H. K. Kieter, H. Lutz, and H. Wilkens, *Tetrahedron Lett.*, 2901 (1964); C. A. Grob, *Bull. Soc. Chim. Fr.*, 1360 (1960).

(48) E. P. Blanchard, H. E. Simmons, and R. D. Smith, *J. Amer. Chem. Soc.*, **86**, 1347 (1964).

(49) E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964).

(50) See, for instance, W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

(51) For example, E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

(52) S. Nishimura and H. Taguchi, *Bull. Chem. Soc. Jap.*, **35**, 1625 (1962), and earlier papers.

drocracking of neohexane has been observed between platinum and tungsten on the one hand, and nickel and rhodium on the other. The latter cleaved the least highly substituted bond by, it was suggested,[53] initial adsorption of a 1,2 diradical while the former cleaved the most substituted linkage.

The stereochemistry of **50** was allocated, as shown, at the position α to the carbonyl, because of the low-field position (τ 7.3) of this methine proton ($J = 7$ Hz). It is about 0.3 ppm toward lower field than the analogous proton in **57** (τ *ca.* 7.6). This is attributed to the close proximity of the proton and hydroxyl group, requiring a *cis* orientation of these functions.

The methylation of **49** proceeded easily, but that of **50**, in contrast, did not occur under the same conditions to any appreciable extent, although the time of reaction was prolonged by a factor of 10.[54] The methylation of **49** gave a mixture of monomethylated compounds together with a small amount of dimethyl derivative. Separation of monomethylated derivatives **51** was not achieved; so the mixture was hydrogenated to give **52**, again as a nonseparated mixture. This mixture showed two carbonyl peaks in the infrared spectrum (at 1690 and 1708 cm^{-1}) indicating that the most hindered[55] ketone was present to three times the extent of the other. The former is assigned stereochemistry **53** on the assumption that no inversion at the bridgehead has taken place under the conditions of the hydrogenolysis. The cyclohexanone is then a slightly flattened chair with the methyl group equatorial. The other epimer (**54**) would then be in a twist boat conformation, and in this arrangement the geminal methyl groups are twisted away from the carbonyl function, which is now free and should have a normal carbonyl absorption. As an analogy 2-*t*-butyl-5-methylcyclohexanone has been reported to exist preferentially as twist boat with the methyl group equatorial.[56]

Two methods of reduction of the carbonyl group were employed. Lithium aluminum hydride gave a mixture of diol A and diol B. The stereochemistry was assigned on the basis of attack by the reagent from the less hindered side and was substantiated by dehydration experiments (see below). The ratio of the diols was, roughly at least, that of the ketones.

Reduction of the ketone mixture, **52**, with sodium in isopropyl alcohol–toluene gave diols B, C, and D; no A was detected. Now while diols A and B show the methine proton H_x as a narrow multiplet with half-height widths of 4 and 5 Hz, respectively, both at τ 6.07, diol D shows this proton as a very broad multiplet with half-height width of about 20 Hz. Such extensive splitting requires two diaxial couplings. By exclusion diol C must be the remaining isomer (half-height width = 5 Hz). Isomerization and the formation of a *cis*-fused product is considered unlikely since severe nonbonded interactions would be introduced in the ketone, nor is there any obvious reason why a very small equilibrium population of *cis* ketone isomer should be reduced so much more rapidly than the other isomers to make the alcohol a product in sensible amount. Finally, since all the isomers were dehydrated separately and in no case was α-himachalene, **35**, produced, the absence of any substance with a *cis* fusion seems an acceptable conclusion.

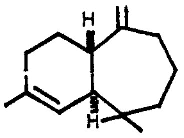
Dehydration of all four diols with phosphorus oxychloride and pyridine gave mixtures of dienes; these results are summarized in Table I. Compound **36** was found to be identical with naturally occurring β-himachalene in every respect except optical activity. The structure of **55**, *trans*-α-himachalene, and **56**, *trans*-γ-himachalene, were assigned after consideration of their spectra and chemical properties (see below). This completed the synthesis of racemic β-himachalene (ten steps).

TABLE I

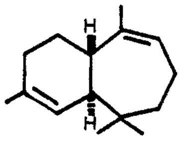
DEHYDRATION PRODUCTS OF DIOLS A–D

Diol	Amount (%) of diene products[a]			Others
	36	55	56	
A	2	4	2.5	90
B	*b*	*b*	*b*	98
C	8	30	41	20
D	8	25	29	36

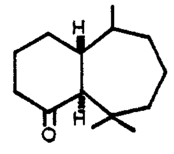
[a] Analyzed by glpc (±1%). [b] Less than 0.5%.



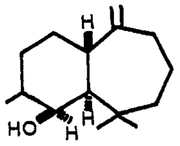
55



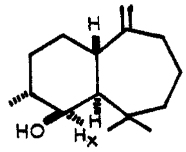
56



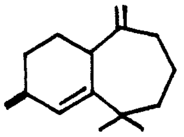
57



E



F



G

The absence of **36**, **55**, and **56** from the dehydration of diol B, in view of the preference for *trans*-coplanar elimination under the reaction conditions used, indicates that only the proton at the ring fusion has the appropriate configuration. Dehydration therefore takes place so as to give the double bond exocyclic to the seven-membered ring, and provides confirmation of the stereochemistry assigned to diol B. The products obtained from the other diols may also be rationalized.

Diol B, on vigorous acetylation, gave a mixture of the diacetate and the monoacetates **58** and **59**. The diol, on silicic acid (130°), gave alcohol F; similarly diol A gave alcohol E. Acetylation of alcohol F gave monoacetate **58**.

Vapor phase pyrolysis of **58** gave, by six-center cyclic *cis* elimination, *trans*-α-himachalene (**55**), again in agreement with the original stereochemistry.

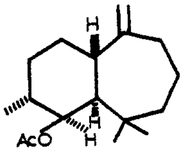
---

(53) J. R. Anderson and B. G. Baker, *Nature*, **187**, 937 (1960).

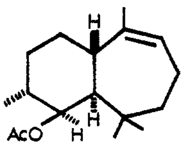
(54) It is possible that the proximity of the geminal dimethyl group to the carbonyl oxygen restricts the movement of the latter which would be necessary for the attainment of a planar mesomeric anion. Such would not be the case for **49**. A difference in rate of greater than a factor of 100 is called for.

(55) A. T. Balaban, P. T. Frangopol, and E. Keplinger, *Spectrochim. Acta*, **19**, 367 (1963); W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).

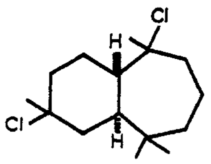
(56) C. Djerassi, E. J. Warawa, J. M. Berdahl, and E. J. Eisenbraun, *J. Amer. Chem. Soc.*, **83**, 3334 (1961).



58



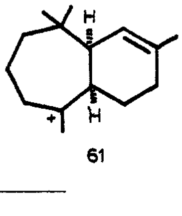
59



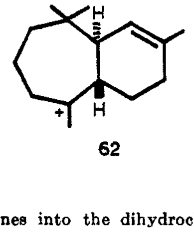
60

The structures of *trans*-α- and *trans*-γ-himachalenes were demonstrated, aside from their nmr spectra, by their conversion into crystalline himachalene dihydrochloride **60**, being the racemate of the dihydrochloride obtained from the natural himachalenes.[57] This conversion constitutes a synthesis of racemic himachalene hydrochloride, **50**. Further, himachalene dihydrochloride, with pyridine, gave a mixture of *trans*-α-, β-, and *trans*-γ-himachalenes. By this circuitous route *trans*-α- and *trans*-γ-himachalenes may be converted into β-himachalene, albeit inefficiently since the proportion of β-himachalene is low in the mixture of hydrocarbons obtained. It was recognized at the outset that the final dehydrations would give, mainly, hydrocarbons with an exocyclic methylene group. However since this would be a thermodynamically unstable system it was considered that migration of such double bonds into the ring could be induced under acid conditions. Evidently the concept could not be tested until the synthesis was completed; the nearest model available was the natural *cis*-fused α-himachalene. Treatment of this substance with formic acid–ether indeed effected a conversion into β-himachalene rapidly and in high yield. β-Himachalene itself then underwent a much slower transformation to a complex mixture which was not investigated. *trans*-α- and *trans*-γ-himachalenes underwent slow conversion into a mixture, the maximum amount of β-himachalene present at any time being *ca.* 5%.

The difference in behavior between the *cis*- and *trans*-α-hydrocarbons is probably to be attributed to the greater number of nonbonded interactions in *cis* cation **62**, than in *trans* cation **61**. The interaction in **62** may be greatly relieved by loss of a proton from the ring junction. Cation **61**, on the other hand, may be more inclined to portion itself among the various available pathways. Furthermore, if the process is comparatively slow then the further protonation of any β-himachalene produced (with the probable formation of conjugated dienes) will be an effective competitive process. However, the acid-catalyzed rearrangement of *trans*-α- and *trans*-γ-himachalenes provides another inefficient process for the generation of β-himachalene. It will be noted that cation **61** must be involved in the conversion of the natural himachalenes into dihydrochloride **60** and that here, also, the conversion into the more stable *trans* system occurs.



61



62

Experimental Section[58]

Irradiation of Dimedone in Cyclohexene.—A solution of dimedone (15.0 g) in cyclohexene (1.25 l.) and ether (4 l.) was irradiated through a Pyrex filter for 28 hr. The product was evaporated and the resultant oil, dissolved in ether, was washed with 5% aqueous sodium hydroxide and water, and the organic phase dried. The residue on evaporation (29.8 g) was distilled in a short-path still and chromatographed on alumina. The first substance eluted (with benzene) was dione **2**. Crystallized from light petroleum it had mp 92–94°, $\nu_{max}^{CCl_4}$ 5.86 μ, and was identical with the cleavage product described in the next section.

Further elution (benzene–ether) gave diol **3** in about 15% yield. Crystallized from light petroleum this had mp 79–81°; ν_{max} 3550 cm^{-1}; nmr τ 9.03 (s, 3 H), 8.86 (s, 3 H), 8.86 (s, 1 H), 7.01 (s, 1 H), 6.88 (s, 1 H). The latter two signals disappeared on exchange with D_2O.

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78; mol wt, 224. Found: C, 74.56; H, 10.46; mol wt, 224 (mass spectrum).

A solution of the diol (197 mg) and sodium metaperiodate (2.0 g) in aqueous methanol (2:1, 30 ml) was left for 16 hr. The product was isolated with ether and the crystals were recrystallized from light petroleum: mp 96–97.5°; λ_{max}^{EtOH} 305 mμ (log ε = 1.64); ν_{max} 1707 cm^{-1}; nmr τ 8.95 (s, 3 H), 8.92 (s, 3 H).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.23; H, 9.79.

The dione (42 mg) was heated in a mixture of 1 g of zinc, 5 ml of acetic acid, and 1 ml of water on a water bath overnight. After dilution the product was isolated with ether and crystallized from light petroleum to give diol **3** identical with the irradiation product.

Irradiation of the dione (30 mg) dissolved in cyclohexene (70 ml) and ether (150 ml) through a Pyrex filter (80 W arc) for 12 hr gave, after removal of the solvent, an oil (141 mg). Separation by thin layer chromatography (tlc) (benzene–ether) gave a crystalline fraction (13 mg) which was recrystallized from light petroleum to give diol **3**, mp 79–79°.

Oxidation of Dione 2.—A mixture of 304 mg of dione and 1.73 g of potassium permanganate in aqueous acetone (1:1, 20 ml) was heated to 40° for 15 hr. The product was filtered, the cake of manganese dioxode washed with hot water, and the product isolated from the combined washings with ether. The neutral material remaining after extraction with aqueous sodium bicarbonate crystallized (170 mg) and was identified as the starting dione.

The acidic material, isolated with ether from the acidified aqueous phase, (171 mg) was crystallized from ethyl acetate to give acid **4**: mp 154–156°; $\nu_{max}^{CHCl_3}$ 1710 cm^{-1}.

Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20; neut equiv, 135. Found: C, 62.41; H, 8.41; neut equiv, 143 (titration).

The acid was converted into the dimethyl ester with diazomethane (ν_{max}) 1730, 1715 sh cm^{-1}; nmr τ 8.98 (s, 3 H), 8.95 (s, 3 H), 6.42 (s, 6 H). The solution of this (98 mg) in 5 ml of concentrated nitric acid was heated on the water bath for 80 min. The mixture was evaporated under reduced pressure and 1 ml of formic acid added. Repeated evaporation gave an oil which was extracted into ether and the acidic material separated from this with aqueous sodium bicarbonate. On isolation and evaporation of the solvent the acids were obtained as a semicrystalline paste. Crystallization from ethyl acetate gave *trans*-cyclohexane-1,2-dicarboxylic acid (21 mg), mp 227–230°, undepressed on admixture with an authentic specimen.

The acidic mother liquors were esterified (diazomethane) and separated by gas–liquid partition chromatography (glpc) on a 20% Carbowax 20M column (6 ft × 0.25 in.) at 200°. In addition to the cyclohexane dicarboxylic ester there were two other major components. One was identified as the dimethyl ester of α,α-dimethylsuccinic acid by comparison of infrared spectra, and by hydrolysis of the ester (7.1 mg) to the acid which had mp 141–142.5° (from ethyl acetate) undepressed on admixture with an authentic specimen. The other component was identified as dimethyl-β,β-dimethyl glutarate by retention time only.

---

[57] Conversion of the natural himachalenes into the dihydrochloride involved epimerization at the ring junction.

[58] Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were determined on Beckman IR-5, -7, or -10 spectrometers, and nmr spectra on a Varian A-60 spectrometer. Irradiations were performed with a 450-W Hanovia medium-pressure mercury arc in a water-cooled immersion well under nitrogen unless otherwise specified.

Irradiation of Dimedone Enol Acetate in Cyclohexene.—The enol acetate of dimedone (1.0 g) in cyclohexene (200 ml) was irradiated through a Pyrex filter with an 80-W arc for 24 hr. A 3.16-g yield of product was obtained which was chromatographed on silica gel (40 g). Further separation by tlc on silicic acid (benzene–ether) gave adduct **5**: (208 mg), mp 103–105° (from methanol); $\nu_{\max}$ 1742, 1706, 1240 cm^{-1}; nmr τ 9.10, 8.96, 8.08 (each s, 3 H).

Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.68; H, 8.96.

Attempted hydrolysis of the adduct (207 mg) with 0.5% potassium hydroxide in 50% aqueous dioxane gave unsaturated ketone **7** as product (158 mg): mp 55–57°; $\lambda_{\max}^{\mathrm{EtOH}}$ 249 mμ (ϵ 9950); nmr τ 8.91 (s, 6 H), 7.98 (broad s, 4 H).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.14; H, 9.63.

Hydrolysis with N-methanolic or N-ethanolic potassium hydroxide under reflux for 16 hr gave dione **2** identified by its mixture melting point and infrared spectrum. When methanol was used as a solvent an additional compound was formed. This was isolated by preparative tlc (eluent–ethyl acetate ether 1:1). It had mp 117–118° (from methanol); $\nu_{\max}$ 1705, 1094 cm^{-1}.

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24; OMe, 13.1. Found: C, 75.93; H, 10.15; OMe, 15.20.

Irradiation of Cyclohexane-1,3-dione with Methyl Acrylate.—The dione (1.0 g) dissolved in methyl acrylate (100 g) and cyclohexane (150 ml) was irradiated through a Pyrex filter for 5 hr. The semicrystalline residue remaining after removal of solvent was crystallized from methanol and the mother liquors were separated by preparative tlc (benzene–ether). The crystals and main chromatographic fraction (1.07 g) gave, from methanol, the diketo ester (**8**): mp 104–105°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1736, 1716 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.93; H, 7.26.

The second, minor, chromatographic fraction also crystallized from methanol to give ester **9**: mp 89–91°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1745, 1715 (fresh solution) or 1744, 1713, 1649, 1610 cm^{-1} (on standing).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 61.27; H, 7.14.

The enolization could be followed in 95% ethanol using ultraviolet absorption using the maximum at 262 mμ. At 33° the following optical densities were observed for a 1-cm path or, where values were too high, corrected for a 1-mm path (min, OD): 5, 0.06; 10, 0.19; 20, 0.31; 60, 0.75; 120, 1.3; 180, 1.9; 240, 2.4; final value (24 hr) 6.5.

Irradiation of Cyclopentane-1,3-dione Enol Acetate in Cyclopentene.—The dione was converted into the enol acetate by suspension in ether and passing in ketene. After solution of the dione was complete the product was distilled. The acetate was obtained as an oil: $\nu_{\max}^{\mathrm{CCl_4}}$ 1792, 1708, 1605 cm^{-1}; nmr τ 7.74 (s, 3 H), 4.02 (t, 1 H, $J \sim 1.5$ Hz).

Anal. Calcd for $C_7H_8O_3$: C, 59.99; H, 5.73. Found: C, 59.43; H, 5.53.

The enol acetate (1 g) was dissolved in cyclopentene (100 ml) and cyclohexane (150 ml) and the mixture irradiated through a Pyrex filter for 3 hr. A 460-mg sample of the oil (total 4.6 g) was separated by tlc (eluent ether–benzene, 1:1). The adduct was obtained as an oil; $\nu_{\max}$ 1738, 1249 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.18; H, 7.68.

Glpc separation (silicone column) showed that this material consisted of two close, difficultly resolvable peaks, presumably stereoisomers.

Hydrolysis of the adduct with 4% potassium hydroxide in aqueous dioxane at 60° for 3 hr gave dione **10**, $\nu_{\max}^{\mathrm{CCl_4}}$ 1710 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.63; H, 8.59.

Reduction of the dione (lithium aluminum hydride) followed by dehydrogenation of the crude diol with palladized charcoal at 280–320° (45 min) gave naphthalene.

Irradiation of Cyclopentane-1,3-dione Enol Acetate with Dichloroethylene.—The enol acetate (500 mg) dissolved in *cis*-1,2-dichloroethylene (50 ml) and cyclohexane (200 ml) was irradiated through Pyrex for 2 hr. The product (670 mg) was separated by glpc on a silicone DC 200 column at 200°. The first adduct eluted had mp 90–91° (from ether).

Anal. Calcd for $C_9H_{10}O_3Cl_2$: C, 45.59; H, 4.25. Found: C, 45.08; H, 4.19.

The second isomer had mp 67–68° (from ether) and the third mp 77–78°.

Anal. Found: C, 45.03; H, 4.23.

γ**-Tropolone.**—The adduct, mp 90–91° (130 mg), was dissolved in 1 *N* methanolic potassium hydroxide solution and let stand for 1 min. The mixture was then diluted with water and washed with ether. The aqueous layer was adjusted to pH 4 with hydrochloric acid, and washed twice with ether (40 ml). The aqueous phase was then extracted in a continuous extractor with ether for 18 hr. Removal of the ether from the extract gave a semicrystalline mass (42 mg) which was dissolved in 2 ml of methanol (charcoal, 50 mg) and again evaporated to give 25 mg of crystals, mp 196–206° dec. Recrystallization gave 21 mg of material, mp 208–212°. Pure γ-tropolone was obtained by sublimation [170° (0.1 mm)]: $\lambda_{\max}$ 227, 333 (log ϵ 4.17, 4.04); $\lambda_{\max}^{0.1\ \mathrm{NaOH}}$ 228, 362 mμ (log ϵ 4.18, 4.19). Identity was confirmed by comparison with an authentic specimen, mp 210–212°.[59]

Stipitatonic Acid. Cycloaddition of Cyclopentanedione Enol Acetate to Dimethyl Chloromaleate.—A solution of 1.05 g of dimethyl chloromaleate in 5 ml of dioxane was freed from dissolved oxygen with a current of nitrogen for 1 hr. The enol acetate (0.59 g) was added and the solution irradiated for 40 hr in a 13-mm Pyrex tube in a Rayonet reactor using 350-mμ (max) lamps. The solvent was removed and the residue (1.54 g) was distilled (short path) [bath temperature 150–200° (0.15 mm)] to give a viscous oil (0.73 g). Some unchanged enol acetate was recovered, and the yield of distilled adduct was 80–85% in several runs based on enol acetate consumed. The crude distilled material was used for subsequent steps. A portion of the distilled adduct was purified by tlc (ether–light petroleum 7:3) and the main band ($R_f \sim 0.5$) collected. Crystallization from ethyl acetate–cyclohexane gave dehydrochlorinated adduct **30**: mp 81.5–82.5°; $\nu_{\max}^{\mathrm{CCl_4}}$ 1745, 1650 cm^{-1}; $\lambda_{\max}$ 204 (ϵ 8200) 255 (3000); nmr τ 6.1, 6.2, 7.9 (each s, 3 H), 6.45 (s, 1 H).

Anal. Calcd for $C_{13}H_{14}O_7$: C, 55.33; H, 5.00. Found: C, 55.24; H, 4.93.

Bromination, Hydrolysis, and Oxidation of Adduct 29.—The distilled adduct (635 mg) in acetic acid (50 ml) was stirred with 700 mg (1.1 equiv) of pyridinium bromide perbromide for 45 min at which time all the perbromide had gone into solution and reacted. The reaction mixture was poured into 400 ml of water and extracted with chloroform. The extract, after washing with saturated sodium bicarbonate, gave 760 mg of crude bromo adduct.

Attempted purification of the bromo adduct again led to chloride ion elimination. Tlc separation (eluent ether–light petroleum 7:3) gave material which now had absorption at 252 mμ ($\epsilon \sim 3300$).

The crude bromo compound (760 mg) in 10 ml of dioxane and 8.5 ml of water was stirred with 1.30 g of moist silver oxide for 4 hr in the dark at room temperature. After filtration the filtrate was extracted with chloroform (eight times). The product (410 mg) was purified by tlc (eluent ethyl acetate–benzene 7:3) to give a mixture of keto stereoisomers (R_f 0.40). The yield, based on adduct consumed, was 39%. The mixture of epimers showed $\nu_{\max}^{\mathrm{CHCl_3}}$ at 1740 and 1650 cm^{-1}.

The ketol (204 mg) in acetic acid (5 ml) was treated with 128 mg of bismuth oxide and stirred at 85° for 3 hr. The solvent was removed under reduced pressure at room temperature and a chloroform–ether suspension of the residue was filtered through a short path of silica gel. Crude dione (145 mg) was obtained: $\nu_{\max}^{\mathrm{CHCl_3}}$ 1730 (broad) 1650; nmr τ 6.2 (two just resolved three-proton singlets), 7.9 (s, 3 H). Further purification of the dione was not possible because of its lability to heat and chromatographic media.

Preparation of Stipitatonic Acid.—The crude dione (189 mg) in 3 ml of methanol and 3 ml of 2 *N* hydrochloric acid was left for 24 hr at room temperature. These conditions were selected after a study of ultraviolet changes with time and acidity. The solvents were removed at room temperature and a methanolic solution of the residue was treated with charcoal. The resultant oil was extracted continuously with ether to give 120 mg of oil and crystals (see below).

The crude residue (after removal of solvents) from the acid hydrolysis of 66 mg of dione was dissolved in 1 ml of 2 *N* aqueous sodium hydroxide and left for 2.5 hr. The reddish brown hydrolysis mixture was acidified to pH 1 with hydrochloric acid and water removed at room temperature under reduced pressure. The residue was continuously extracted with ether to yield 41 mg of crude crystals. A small volume of acetone was added and

---

(59) We wish to thank Professor T. Mukai for a specimen of γ-tropolone.

the mother liquors were separated from the yellowish brown crystals (6 mg). The mother liquors were evaporated and the product was sublimed [110–190° (0.007 mm)] to yield an additional 4.5 mg. The sublimate was combined with the first crop and crystallized (twice) from ethyl acetate to give 7 mg (15% from crude dione) of stipitatonic acid, mp 224–229° (capillary).

The natural material[60] was crystallized (ethyl acetate) and had mp 225–230° (capillary). The mixture melting point was 225–228°. The synthetic material was identical with the natural product in all respects, R_f 0.4 (cellulose tlc; eluent *n*-BuOH, HOAc, H_2O 4:1:1), with a yellow-green fluorescence: $\nu_{\max}^{\mathrm{CHCl_3}}$ 1825, 1745 cm^{-1}; $\lambda_{\max}^{\mathrm{H_2O}}$ 260, 307, 348, 432 mμ (log ϵ 4.39, 3.90, 3.70, 4.08), immediately on dissolution; after 30 min, $\lambda_{\max}$ 252, 332, 367 mμ (log ϵ 4.59, 3.93, 4.05); isobestic points at 285, 320, 392 mμ; $\lambda_{\max}^{0.6\,N\ \mathrm{NaOH}}$ 277, 342, 378 mμ; $\lambda_{\max}^{\mathrm{dioxane}}$ 258, 352, 380, 403 mμ.

Oil and crystals (120 mg) were sublimed at 145° (0.008 mm) to yield 21 mg of oily crystals, R_f 0.9 (cellulose tlc; eluent *n*-BuOH–H_2O 8:1:1): $\nu_{\max}^{\mathrm{CHCl_3}}$ 1735, 1670, 1645, 1610 cm^{-1}; $\lambda_{\max}^{\mathrm{MeOH}}$ 255, 342, 372 mμ (ϵ 17,500, 4700, 4900); $\lambda_{\max}^{\mathrm{NaOH}}$ 282, 342, 397 mμ (ϵ 28,000, 5100, 6000). The material crystallized well from a very small volume of acetone but insufficient was available to reach constant melting point. The highest melting point recorded was near 150°.

Irradiation of Dimethyl Acetylene Dicarboxylate and Cyclopentanedione Enol Acetate.—A 960-mg sample of the dimethyl ester in 5 ml of dioxane was flushed with nitrogen for 50 min. A 613-mg sample of the enol acetate was added. The solution was irradiated for 74 hr in a Pyrex tube using the 350 mμ (max) source in a Rayonet reactor. After removal of the solvent the residue was distilled. The first fraction [260 mg, 160° (0.3 mm)] contained unreacted starting materials. The second fraction [210 mg, 160–215° (0.3 mm)] contained at least five compounds.

On addition of ether 12 mg of crystalline material was obtained. Infrared and nmr spectra suggested that this was a dimer of the enol acetate and it was not examined further. The remaining liquors on addition of light petroleum gave 60 mg of oily crystals. This was purified by tlc (R_f 0.5, ether–light petroleum 7:3) and crystallized from ether to give an adduct: mp 122–123°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1745 cm^{-1}; nmr τ 6.2 (s, 3 H), 6.25 (s, 3 H), 6.6 (s, 1 H), 7.9 (s, 3 H).

Anal. Calcd for $C_{13}H_{16}O_7$: C, 54.93; H, 5.67. Found: C, 55.09; H, 5.82.

***β*-Himachalene. Cyclohex-1-en-3-one Ethylene Ketal (38).**—Dehydrochlorination of 2-chlorocyclohexan-1-one ethylene ketal, according to the method used by Wanzlick[61] for this substance, gave a mixture of the ketals of the *α*,*β*- and *β*,*γ*-unsaturated ketones in the ratio 7:1. The mixture was resolved by glpc on a 6 ft × 0.25 in., 10% $AgNO_3$ column at 190°. The structures were assigned on the basis of nmr data.

The method was modified as follows. Potassium hydroxide pellets (59 g) were dissolved in diethylene glycol (336 ml) at 180–190° and to the mixture, after cooling to 50°, was added 2-chlorocyclohexanone ethylene ketal (84 g) over 5 min. The mixture was then heated to 160–165° (maximum temperature) for 3.5 hr, cooled, and distilled. The distillate obtained below 115° (3 mm) was extracted with ether and the extract fractionally distilled. The desired ketal (25 g) was collected at 55° (6.5 mm) and unchanged starting material (17 g) at 65–70° (6.5 mm).

Acetylation of 2-Methylcyclopentane-1,3-dione.—Ketene was passed through a dry ethereal suspension (200 ml) of the diketone (3.14 g) at 0–5° until the solution became clear (6 hr). The ether was evaporated under reduced pressure and the residue distilled.

Enol acetate **37** (4.02 g) had bp 84–87° (2 mm); $\nu_{\max}^{\mathrm{CCl_4}}$ 1780, 1715, 1673, 118 cm^{-1}; nmr τ 8.48 (t, 3 H), 7.74 (s, 3 H), 7.1–7.4 (4 H).

Anal. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54. Found: C, 62.26; H, 6.54.

Irradiation of Enol Acetate 37 and Ketal 38.—A solution of ketal **38** (100 g) in cyclohexane (140 ml) was flushed with nitrogen for 1 hr. Acetate **37** (2.0 g) was added and the mixture irradiated through a Pyrex filter. The reaction was followed by infrared spectroscopy on the irradiation mixture (1600–1800 cm^{-1}) until the enol acetate peaks were no longer visible. The solvent was removed by distillation, the excess ketal recovered [93 g, bp 84° (15 mm)] and the residue (4.0 g) distilled in a short-path still [bp *ca.* 230° (0.4 mm)]. The yield of crude adduct was 3.3 g (90% based on enol acetate) Crystallization from ether gave the pure adduct, mp 124–125°, $\nu_{\max}^{\mathrm{CCl_4}}$ 1740 cm^{-1}.

Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.66; H, 7.39.

Sodium Borohydride Reduction of Adduct 40.—The adduct (3.7 g, not crystallized) in methanol (60 ml) was added over 5 min to a solution of sodium borohydride (1.35 g) in water (8 ml) and methanol (40 ml) at 0–5° with stirring. The mixture was kept in an ice bath for 25 min, diluted with water (500 ml), and extracted with ether (ten times). Evaporation of the extract after drying gave the alcohol, mp 178–179° (from aqueous methanol), $\nu_{\max}$ 1736 cm^{-1}.

Anal. Calcd for $C_{16}H_{24}O_5 \cdot 0.5MeOH$: C, 63.44; H, 8.39. Found: C, 63.75; H, 8.35.

To the dry reduction product (3.3 g) in dry methylene chloride (160 ml) was added dry triethylamine (54 ml) in dry methylene chloride (100 ml) with stirring and cooling in an ice bath. A solution of methanesulfonyl chloride (9 ml) in methylene chloride was then added over 5 min and stirring was continued 10 min at room temperature. The dark red solution was washed with water (ten times). From the organic phase there was obtained 5.8 g of a red oil. A pure specimen of the methanesulfonate was prepared by crystallization from ethyl acetate–light petroleum: mp 145–145.5°; $\nu_{\max}$ 1735 cm^{-1}; nmr τ 8.7 (s, 3 H), 8.0 (s, 3 H) 7.0 (s, 3 H), 5.0 (t, 1 H).

Anal. Calcd for $C_{17}H_{26}O_7S$: C, 54.54; H, 7.00. Found: C, 54.58; H, 6.83.

Fragmentation of the Methanesulfonate (45).—A solution of the unpurified sulfonate (5.5 g) in dioxane (175 ml) was treated with a solution of sodium hydroxide (1.77 g) in water (95 ml) and the mixture kept at 65–70° for 1 hr. After isolation with ether the product was chromatographed on neutral alumina (Woelm, activity I). Ketone **46** (1.0 g, 30% from the enol acetate), eluted with benzene and crystallized from light petroleum, had mp 124.0–124.5°; $\nu_{\max}^{\mathrm{CCl_4}}$ 1717 cm^{-1}; nmr τ 8.2 (s, 3 H), 4.3 (t, 1 H), 6.1 (m, 4 H).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.28; H, 8.27.

Reaction of 46 with Methylmagnesium Iodide.—To a refluxing solution of methylmagnesium iodide (from 1.0 g of magnesium, 4 ml of methyl iodide) in 35 ml of ether a solution of ketone **46** (0.97 g) in ether (70 ml) was added over 5 min. A further 20 ml of ether was added and the heating continued for 1.5 hr. After decomposition with water the product was isolated (0.97 g) and recrystallized from light petroleum. It had mp 71–72°; nmr τ 9.0 (s, 3 H), 8.1 (d, 3 H), 6.1 (m, 4 H), 4.3 (t, 1 H).

Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.08; H, 9.11.

Preparation of Ketol 49.—A zinc–copper couple (4.0 g) prepared by the method of LeGoff[62] was moistened with ether (2.5 ml) and methylene iodide (0.31 ml), and ketal **47** (4.2 g) in ether (18 ml) was added, followed by more methylene iodide (1.68 ml). The mixture was heated under reflux with vigorous stirring for 20 hr. More zinc–copper couple (2.0 g) and methylene iodide (1.5 ml) were added and the heating and stirring were continued for 22 hr. The mixture was then poured into 3% hydrochloric acid (100 ml) and the product was isolated with ether. The residue (5.62 g) was dissolved in 1.5% methanolic hydrochloric acid (50 ml) and allowed to stand at room temperature for 50 min. The solution was then evaporated to 20 ml, poured into water, and the product isolated with ether. On removal of the solvent the cyclopropane was obtained as sticky crystals. Recrystallization from ether gave the pure product as white needles, mp 122–123° dec (550 mg). The mother liquors were chromatographed on silicic acid (eluent ethyl acetate–benzene 1:4) to give a further 0.9 g (39% yield from **47**): $\nu_{\max}$ 3620, 3065 (cyclopropyl $-CH_2-$), 1700 cm^{-1}; nmr τ 8.70 (s, 3 H), 9.04 (s, 3 H), 9.35 (m, 3 H).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.32; H, 9.61.

Methylation of Cyclopropyl Ketone (49).—To a refluxing solution of potassium (270 mg) in dry *t*-butyl alcohol (9 ml) under nitrogen was added a solution of the ketone (600 mg) in dry benzene (1.0 ml). A solution of methyl iodide (0.45 ml) in dry benzene (1.0 ml) was added to the refluxing mixture over 1 hr. After

---

[60] We are very grateful to Dr. R. Bentley for a sample of stipitatonic acid.

[61] H-W. Wanzlick, G. Gollmer, and H. Milz, *Chem. Ber.* **88**, 73 (1955).

[62] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

decomposition of the reaction mixture with water the product (650 mg) was isolated with ether. It was separated by tlc (eluent light petroleum–ether 1:1). The monomethylated material (205 mg, 50% based on consumed ketone) was crystallized from ether: mp 124–125°; $\nu_{max}^{CCl_4}$ 1700 cm^{-1}.

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 75.99; H, 10.27.

Hydrogenolysis of Cyclopropane 51.—The catalyst was prepared according to the method of Nishimura[52] and consisted of a fused mixture of rhodium and platinum oxides in a ratio of 8:3. The catalyst (50 mg) was saturated with hydrogen at atmospheric pressure and room temperature in glacial acetic acid (5 ml) containing anhydrous sodium acetate (50 mg). The cyclopropane (40 mg) was then added and hydrogenation continued until the uptake ceased (*ca.* 15 hr). The solution was then separated from the catalyst and evaporated to dryness. The solid was dissolved in water (5 ml) and extracted with chloroform. The product (**52**, 35 mg) was obtained as sticky crystals. Crystallization from ether–light petroleum gave material with mp 97–99°, ν_{max} 1710 and 1690 cm^{-1}. This material was a mixture of isomers at the secondary methyl group (**53**, **54**).

Reduction of Ketol 52. **A.**—A solution of the ketol (81 mg) in dry ether (6 ml) was stirred with excess lithium aluminum hydride (50 mg) for 30 min. The mixture was decomposed with aqueous sodium potassium tartrate, and the product (70 mg) isolated with ether. Separation by tlc (eluent ether–light petroleum 1:1) gave (R_f 0.7) diol A (44 mg, 54%) and (R_f 0.5) diol B (21 mg, 26%).

B.—To a refluxing suspension of sodium (1.3 g) in toluene (25 ml) was added the ketol (650 mg) in isopropyl alcohol (8.0 ml) and the mixture refluxed for 2 hr, by which time all the sodium had reacted. After dilution with water the product was isolated with ether. The crude product (650 mg) was separated by tlc (eluent ether–light petroleum 65:35) to give diol B (R_f 0.56, 257 mg, 40%), diol C (R_f 0.28, 120 mg, 18%) and diol D (R_f 0.21, 167 mg, 26%).

Diol A was a glass. *Anal.* Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 75.22; H, 11.92.

Diol B had mp 85–86° (from light petroleum, bp 35–40°). *Anal.* Found: C, 75.10; H, 11.72.

Diol C had mp 116.5–117.5° (from light petroleum, bp 35–40°). *Anal.* Found: C, 74.67; H, 11.62.

Diol D had mp 173–174° dec (from ether). *Anal.* Found: C, 74.84; H, 11.75.

Dehydration. **A.**—Diol A (25 mg) in chloroform solution was adsorbed onto silicic acid on a plate and the plate heated at 130° for 20 min. The plate was then developed with ethyl acetate–benzene 1:19. The major fraction, alcohol E, showed a band at 890 cm^{-1} in the infrared spectrum and the nmr showed peaks at τ 5.33 (s, 2 H), 6.14 (bs, 1 H), 9.00 (s), and 9.05 (d, total 9 H for C-CH_3). Diol B (30 mg) treated in a similar manner also gave a product, alcohol F, (20 mg), showing exomethylene characteristics. Both substances retained the secondary alcoholic function.

B.—Alcohol E (20 mg) was treated with a solution (3 ml) of phosphorus oxychloride (1 mequiv) and pyridine (10 mequiv) in benzene, and the mixture heated at 50° for 15 hr (no starting material remained). After dilution with water the product was isolated with benzene. Glpc (5 ft × 0.25 in., 20% Carbowax 20M, 140°) showed the presence of four constituents in the ratio of 65:7:25:3. The largest fraction was identified by infrared spectrum and nmr spectrum as the hydrocarbon G: ν_{max} 3075, 3040, 1630, 890; nmr τ 4.60 (broad s, 1 H), 5.32 (s, 2 H), 8.91 (s, 3 H), 8.98 (s, 3 H), 9.05 (d, $J \sim 7$ Hz, 3 H). The second largest fraction was identified as *trans*-α-himachalene by comparison of infrared and nmr spectra with those of a specimen prepared from authentic himachalene hydrochloride (see below).

C.—Alcohol F (20 mg) was treated with a solution (2 ml) of phosphorus oxychloride in pyridine–benzene as described under B. Glpc (5 ft × 0.25 in. 3% silicone 810, 142°) resolved a mixture of four components in the approximate ratio 60:30:4:6 in order of elution. The main product was very similar in retention time and ir spectrum to hydrocarbon **9**, but the three other substances appeared not to correspond with the others noted in B. None of the substances from these dehydrations had retention times corresponding with either natural himachalene.

D.—Diol C (12 mg) was treated with phosphorus oxychloride in pyridine–benzene (3 ml) at 50° under nitrogen overnight. Glpc (9 ft × 0.25 in. 20% 20M Carbowax, 150°) showed six peaks corresponding to *trans*-α-himachalene (30%), β-himachalene (8%), and *trans*-γ-himachalene (41%), the remainder making up about 20%.

E.—Diol D (8 mg) was dehydrated as under D. Glpc showed the presence of *trans*-α-himachalene (25%), β-himachalene (8%), and *trans*-γ-himachalene (29%).

F.—Diol B (10 mg) under the same conditions gave a mixture of dienes containing negligible amounts of *trans*-α-, -β-, or *trans*-γ-himachalenes.

G.—A mixture of diol C and diol D (2:3) (144 mg) was treated with a solution (25 ml) of phosphorus oxychloride (9 equiv) and pyridine (90 equiv) in benzene under nitrogen at 50° for 12 hr. A 95-mg sample of the diene mixture was obtained. On separation by glpc (20 ft × $^3/_8$ in. 20M Carbowax, 20%, 170°) there was obtained (i) *trans*-α-himachalene [ν_{max} 3070, 3015, 1638, 1450, 1390, 1366, 1150, 890 cm^{-1}; nmr τ 4.72 (m, 1 H) 5.27 and 5.33 (m, 1 H each), 9.03 (s, 3 H), 9.30 (s, 3 H); *Anal.* Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.10; H, 11.62]; (ii) β-himachalene, identical in retention time, infrared spectrum, and nmr spectrum with the natural material; and (iii) *trans*-γ-himachalene [ν_{max} 3015, 1440, 1389, 1379, 1367, 1160, 1152, 878, 825 cm^{-1}; nmr τ 4.50, 4.70 (broad, 2 H), 8.31 (m, 6 H) 9.02 (s, 3 H), 9.21 (s, 3 H)].

H.—Alcohol F (6.0 mg) and sodium acetate (9 mg), refluxed in acetic anhydride (1 ml) for 4 hr, gave monoacetate **58**. The same monoacetate was obtained together with **59** from diol B (479 mg) when heated under reflux in acetic anhydride (25 ml) containing sodium acetate. The crude product was partially purified by tlc: ν_{max} 3070, 1735, 1635, 1245, 1020, 890 cm^{-1} (462 mg). Monoacetate **58** so obtained was passed through a quartz tube (30 cm) at 540–570° (1–2 mm N_2) several times until decomposition was almost complete (infrared). Glpc (20 ft × $^3/_8$ in. 20% Carbowax, 170°) showed that the mixture (285 mg) contained about 70% *trans*-α- and 20% *trans*-γ-himachalenes with very minor amounts of other dienes.

I.—Diol A (12 mg) on dehydration with phosphorus oxychloride as with the other diols gave 2% *trans*-α, 2% β-, and 2.5% *trans*-γ-himachalene and 90% of other unidentified materials.

Himachalene Dihydrochloride. **A.**—A mixture of authentic α- and β-himachalenes (2.21 g) containing about 20% unknown impurity (retention time 0.95 relative to β-himachalene, 12 ft × 0.25 in. 20% 20M Carbowax, 170°)[63] was filtered through a short column of active alumina, dissolved in ether (100 ml), and saturated with dry hydrogen chloride at 0° over 1.25 hr. The solution was kept sealed at 0° overnight, then evaporated to dryness below 10°. The solid residue was crystallized from light petroleum to give the dihydrochloride: mp 115–118° (fast heating); $\nu_{max}^{CCl_4}$ 1449, 1385, 1110, 570 cm^{-1}; nmr τ 9.15 (s, 3 H), 9.03 (s, 3 H), 8.40 (s, 6 H).

Anal. Calcd for $C_{15}H_{26}Cl_2$: C, 64.97; H, 9.45; Cl, 25.58. Found: C, 64.87; H, 9.32; Cl, 25.61.

The dihydrochloride was stable for at least 24 hr at room temperature under N_2 in crystalline form, or in carbon tetrachloride solution. It could not be recovered from solution in methanol or nitromethane.

B.—*trans*-γ-Himachalene (19 mg) in 1 ml of ether was saturated with hydrogen chloride and allowed to stand 40 hr at 0°. Evaporation and crystallization from light petroleum gave the dihydrochloride (17 mg), mp 108–112° (fast heating). The melting point of this racemic dihydrochloride was depressed on admixture with the dihydrochloride described under A. The solution (CCl_4) infrared spectra of these two compounds were superposable.

C.—*trans*-α-Himachalene (containing some *trans*-γ isomer) (285 mg) was converted into the racemic dihydrochloride. From light petroleum it had mp 107–110° (fast heating) and had nmr and infrared spectra identical with those of the authentic dihydrochloride.

Anal. Calcd for $C_{15}H_{26}Cl_2$: C, 64.97; H, 9.45; Cl, 25.58. Found: C, 64.99; H, 9.20; Cl, 25.56.

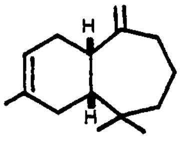
Himachalene Monohydrochloride.—Filtration of "natural" himachalene dihydrochloride through a 4 × 1 cm column of alumina in carbon tetrachloride gave the monohydrochloride.

Dehydrochlorination of (−)-Himachalene Dihydrochloride.—The dihydrochloride (96 mg) in pyridine was heated under reflux for 6.5 hr under nitrogen. The cooled supernatant liquor contained three substances which were separated by glpc as previously described. They were *trans*-α-himachalene (20% of

---

[63] We are most grateful to Dr. S. Dev for a generous sample of the mixed himachalenes.

total diene product), identical in retention time and infrared spectrum with the synthetic material; β-himachalene (8%) with retention time and infrared spectrum identical with the natural material's; and a third hydrocarbon, ν_{max} 3070, 3025, 1635, 1448, 1390, 1380, 1366, 890 cm^{-1}, which is probably i (70%).



i

Acid-Catalyzed Rearrangement of α-Himachalene.—(−)-α-Himachalene (17 mg) was dissolved in 30% formic acid–ether (*ca.* 50 μl) in a capillary tube. The tube was sealed and kept at 60° for 50 hr. Glpc then showed that one substance represented 85% of the material and this was identified by retention time and by isolation and infrared spectrum as β-himachalene.

Acid-Catalyzed Rearrangement of *trans*-α-Himachalene. i.—The hydrocarbon, obtained from 95 mg of the dihydrochloride, was dissolved in 30% formic acid–ether (300 μl) in a capillary tube. The tube was sealed and heated at 80° for 24 hr. Separation of the contents by glpc gave β-himachalene identified by retention time and infrared spectrum.

ii.—The change in composition on heating such a mixture was followed with time: 2 hr, 70° (2% β, 4% *trans*-γ); 6 hr, 80° (65% *trans*-α-, 2% β, 25% *trans*-γ); 18 hr, 80° (40% *trans*-α, 5% β, 50% *trans*-γ + others). The *trans*-γ-himachalene was isolated by glpc.

Registry No.—**2**, 18766-90-0; **3**, 18766-91-1; **4**, 18791-06-5; **5**, 18766-92-2; **6**, 18791-07-6; **7**, 18766-93-3; **8**, 18766-94-4; **9** dione, 18766-95-5; cyclopentane-1,3-dione enol acetate 18766-96-6; cyclopentane-1,3-dione enol acetate in cyclopentene, 18766-97-7; **10**, 18766-98-8; **11** stereoisomers, 18766-99-9; **20**, 18767-00-5; **28**, 18767-01-6; **30**, 18767-02-7; **37**, 3883-57-6; **40**, 17894-21-2; **44**, 18791-08-7; **45**, 18766-73-9; **46**, 18766-74-0; **47**, 18766-75-1; **49**, 17928-70-0; **51**, 18791-09-8; **53**, 18791-10-1; **54**, 18791-11-2; diol A, 18766-77-3; diol B, 18766-78-4; diol C, 18766-79-5; diol D, 18766-80-8; alcohol E, 18766-81-9; hydrocarbon G, 18766-82-0; **55**, 17928-72-2; **56**, 18766-84-2; **60**, 18067-37-3.

The Mechanism of the Sulfuric Acid Catalyzed Rearrangement of Methyl and Carbonyl Carbon-14-Labeled 3,3-Dimethyl-2-butanone[1]

Kishan Bhatia and Arthur Fry

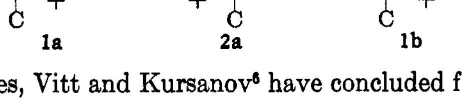
Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

Received January 29, 1968

The rates of the arrangements of 3,3-dimethyl-2-butanone-1-^{14}C to 3,3-dimethyl-2-butanone-4-^{14}C and of 3,3-dimethyl-2-butanone-2-^{14}C to 3,3-dimethyl-2-butanone-3-^{14}C have been studied as a function of sulfuric acid concentration in the range from 65 to 101.5%. Rearrangement rates for both compounds are proportional to the fraction of ketone present as conjugate acid. Methyl rearrangement takes place about ten times as fast as oxygen function rearrangement in acid concentrations below 90%. At higher acid concentrations, oxygen function rearrangement becomes relatively more important. No oxygen function rearrangement mechanism *by itself* can account for this difference; the results are interpreted in terms of carbonium ion rearrangements of the ketone conjugate acid. Since the rate of the oxygen function rearrangement does not decrease in high acid concentrations where water activity is very low, the reversible pinacol formation mechanism seems to be ruled out.

Although considerable research on the scope and mechanisms of acid-catalyzed rearrangements of aliphatic and aromatic ketones has been carried out in recent years,[2] many of the mechanistic details of the reactions remain unresolved. One of the most studied compounds is pinacolone, 3,3-dimethyl-2-butanone.

3,3-Dimethyl-2-butanone-1-^{14}C has been shown[3] to rearrange reversibly to 3,3-dimethyl-2-butanone-4-^{14}C upon treatment with sulfuric acid at 30°. A careful search was made, and none of the activity originally present in the α methyl group was found in C-2 or C-3. The simplest mechanism which can account for this rearrangement is the *concerted or stepwise* interchange, **1a** ⇄ **1b**, of a labeled ($^{\alpha}$C) and an unlabeled methyl group in the conjugate acid of the ketone (eq 1).[4,5]



$$\mathrm{C\overset{C}{\underset{C}{C}}\!-\!\overset{OH}{\underset{+}{C}}\!-\!{}^{\alpha}C \rightleftharpoons C\overset{C}{\underset{+}{C}}\!-\!\overset{OH}{\underset{C}{C}}\!-\!{}^{\alpha}C \rightleftharpoons {}^{\alpha}C\overset{C}{\underset{C}{C}}\!-\!\overset{OH}{\underset{+}{C}}\!-\!C} \qquad (1)$$

1a **2a** **1b**

Parnes, Vitt and Kursanov[6] have concluded from the results of exchange experiments between D_2SO_4 and 3,3-dimethyl-2-butanone that ion **2** is not formed at low temperatures, or is short-lived and does not have time to react with D_2SO_4. However, in exchange experiments

---

[1] Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234; taken from the Ph.D. dissertation of K.B. and presented in part at the 16th Annual Midwest Chemistry Conference, Kansas City, Mo., Nov 19, 1964.

[2] For leading references to recent work, see W. H. Corkern and A. Fry, *J. Amer. Chem. Soc.*, **89**, 5888 (1967).

[3] T. S. Rothrock and A. Fry, *ibid.*, **80**, 4349 (1958).

[4] This is a simplified interpretation of the mechanism given by T. E. Zalesskaya, *Zh. Obshch. Khim.*, **16**, 1813 (1946).

[5] Arabic numerals represent specific chemical species; different letters identify isotopic isomers of these species. The counterion, specific solvation and general medium effects are undoubtedly important in these reactions, but for simplicity are omitted for the present from these mechanistic formulations.

[6] Z. N. Parnes, S. D. Witt, and D. N. Kursanov, *Zh. Obshch. Khim.*, **28**, 410 (1958).