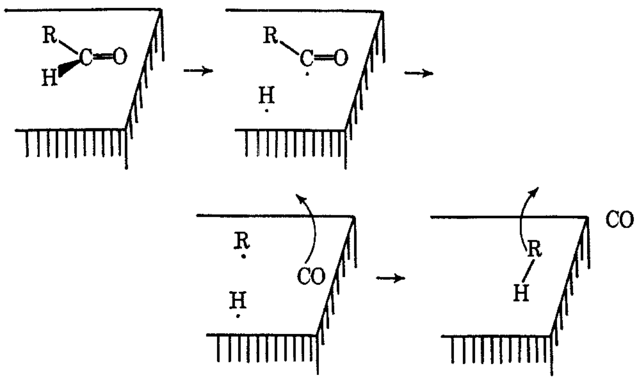
10 and a small amount of β-phenylisovaleric acid together with an undefined carbonyl compound(s).

Since it is known[11] that conversion of neophyl chloride to its Grignard reagent can produce small amounts (1–6%) of **11**, **13**, and **14** and because the starting aldehyde **10** was prepared from this Grignard reagent, **10** was carefully purified *via* its bisulfite adduct. Its spectra showed ~99% purity with a trace of neophyl chloride only. As a further precaution, **12** itself was treated with the catalyst under reaction conditions and found to be unaffected. So it is probable that these contaminants are true decarbonylation products.

Similar results were obtained when a 1 *M* solution of **10** in biphenyl was decarbonylated with palladium on charcoal. Here the reaction was slower, 220° being required for brisk carbon monoxide evolution. But again essentially only **12** was formed.

It seems clear that the process, if radical, proceeds in a fashion where the neophyl radical does not in the main become free enough to rearrange, perhaps as shown [R = $C_6H_5C(CH_3)_2CH_2$-]



where the radicals formed would be chemisorbed to the metal surface and not free to any great extent. Our results, however, do not warrant undue speculation about the detailed mechanism.

In any case, the present results add to the structural reliability of this kind of decarbonylation in degradative or synthetic studies. One can now also understand why this process is effective with compounds that fail to undergo clean peroxide-promoted decarbonylation, such as aromatic[12] and unsaturated[13] aldehydes. The radical (peroxide) path would require formation of highly reative free aromatic radicals from the former and allow acyl radical addition to the double bond of the latter. Neither trouble exists in the palladium-catalyzed process.

Experimental Section

Melting points were taken on a calibrated Fisher-Johns block but are otherwise uncorrected, as are the boiling points. For comparison purposes, hydrocarbons **11** and **12** were obtained commercially and shown to be >99% pure by glpc and spectral analysis. Spectral and glpc data for the other hydrocarbons (**13** and **14**) were available from earlier work in this laboratory on the peroxide-promoted decarbonylation of **10**.[14]

β-Phenylisovaleraldehyde (10) was prepared from neophyl chloride according to the procedure given by Rüchardt.[10] Neophylmagnesium chloride was treated with ethyl orthoformate and processed *via* the bisulfite adduct to afford **10** as a colorless, grassy-smelling oil in 22% yield: bp 76–79° (0.2 mm) in a short path unit; $n^{20}D$ 1.5148 (lit.[10] bp 79° (0.6 mm), $n^{20}D$ 1.5142); λ^{neat} 3.7, 5.83 μ (–CHO); $\delta_{\text{TMS}}^{\text{neat}}$ 9.46 t (–CHO, *J* = 3 cps), 7.10–7.45 m (ArH), 2.51 d (CH_2), 1.31 s (C–CH_3). Spectral data showed no impurities other than a trace of neophyl chloride.

The 2,4-dinitrophenylhydrazone was readily prepared and had mp 115–116°, from ethanol (lit.[10] mp 116–117°).

Decarbonylation Studies.—In a representative run, aldehyde **10** (1 g), was placed into a small flask together with 0.15 g of palladium on charcoal (10%). Upon heating, gas was evolved slowly at *ca.* 140° (bath) and briskly at *ca.* 190°, essentially stopping after 30 min. Collection of the gas over water indicated over 95% decarbonylation. The volatile product was distilled as formed from the reaction vessel to give an 80% yield and was shown to be nearly pure *t*-butylbenzene (**12**) by comparison with an authentic sample: bp 170–171° (atm); λ^{neat} 7.2, 7.34 (*t*-butyl), 13.13, 14.3, and a trace absorption at 13.6 μ (*i*-butylbenzene, **11**, <2%); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 7.3–7.8 m (ArH), 1.30 s (CH_3); trace resonances appeared at 4.77 s, 2.5–2.3 m, 0.87 d (*J* = 6 cps) due to **11**, **13**, and (perhaps) **14**. Integration indicated in some samples as much as 6% of these last products, but in other cases only traces. Gas chromatographic analysis [SE-30, 170°, He carrier gas] showed *t*-butylbenzene, on occasion with a very small after-peak superimposed on some tailing from **12**.

A similar decomposition was performed on a solution of **10** 1 *M* in molten biphenyl, using 1 g of the aldehyde. The distillate from the reaction contained some biphenyl, but again it was essentially pure **12**.

The small amount of residue from these reactions was extracted with ether and filtered free from catalyst. Upon removal of the ether a semisolid material remained. Both infrared and nmr spectral analysis indicated the presence of starting **10** and β-phenylisovaleric acid by comparison with knowns, though neither of these was a major constituent. The base-washed material did not give a strong hydroxamic acid test for esters, but a 5.87-μ absorption did characterize the material as a carbonyl substance(s). Although investigated further, this part of the residue was not structurally defined.

Control Study on 12.[14]—There was no change in the nmr spectrum of pure *t*-butylbenzene (1 g) after it was heated under reflux with the catalyst (0.1 g) for 80 min.

Registry No.—**10**, 6325-41-3; **12**, 98-06-6.

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[11] C. Rüchardt and H. Trautwein, *Chem. Ber.*, **95**, 1197 (1962).

[12] F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughn, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

[13] M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949); J. W. Wilt and A. A. Levin, *ibid.*, **27**, 2319 (1962).

[14] We thank Mr. J. F. Kraemer for this data.

Stereochemistry of Thermal Reactions. III. Stereochemistry of the Thermal Rearrangement of Allylic Acetoacetates[1,2]

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Thermal additions and rearrangements which proceed by a cyclic electron reorganization process generally demand a transition state of stringent geometric requirements. A readily apparent consequence of this requirement is a high degree of stereospecificity, both in the geometry of the double bonds involved and in the transfer of asymmetry from an asymmetric center being destroyed to one being simultaneously created. In the Claisen rearrangement (I → II), this specificity has been observed both in formation of predominantly *trans*

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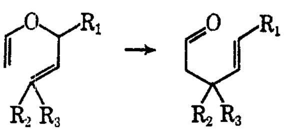
[1] This study was supported by a research grant, GP-3811, from the National Science Foundation, to whom we express our thanks.

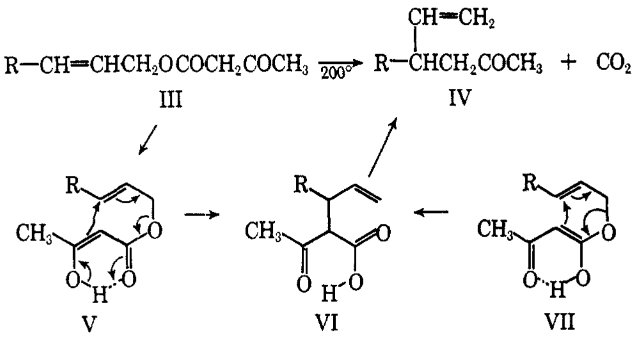
[2] For paper II in this series, see R. K. Hill and A. G. Edwards, *Tetrahedron Letters*, 3239 (1964).

double bonds[3] in II and in the retention of optical activity in the products from optically active ethers (I).[4]



I II

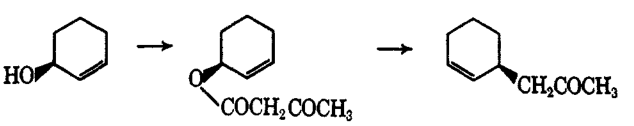
A reaction which appears to have much in common with the Claisen rearrangement is the thermal rearrangement–decarboxylation of acetoacetate esters (III) of allylic alcohols, discovered by Carroll[5] in 1940. Carroll carried out the reaction by heating allylic alcohols with ethyl acetoacetate in the presence of base, and suggested a mechanism[6] analogous to Michael addition. The true nature of the reaction was recognized by Kimel and Cope,[7] who isolated and rearranged pure allylic acetoacetates. They called attention to the similarity to the Claisen rearrangement and proposed the cyclic mechanism shown in V, involving electron reorganization in a chelated enol form. It may be noted that if the intermediate were instead the (less likely) enol VII of the ester carbonyl, the parallel with the Claisen rearrangement would be even closer. An indication that enol VII might be a feasible intermediate is the observation[8] that allylic cyanoacetates, in which only an enol corresponding to VII is possible, undergo the same thermal rearrangement.



$$\underset{\text{III}}{R\text{—}CH\text{=}CHCH_2OCOCH_2COCH_3} \xrightarrow[200°]{} \underset{\text{IV}}{R\text{—}\overset{\displaystyle CH\text{=}CH_2}{\overset{|}{C}}HCH_2COCH_3} + CO_2$$

V VI VII

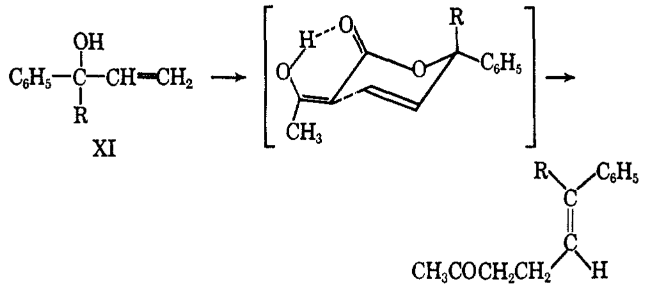
The ordering implicit in the cyclic transition state represented by V or VII suggests that this reaction should exhibit the stereospecificity characteristic of the Claisen rearrangement. We have tested this possibility by carrying out the rearrangement of cyclohexen-2-yl acetoacetate[9] with optically active material. Optically active 2-cyclohexen-1-ol (VIII), available by the method of Denney, *et al.*,[10] was converted to its acetoacetate IX with diketene. Heating IX as described by Burgstahler and Nordin[9] afforded optically active 2-cyclohexen-1-ylacetone (X). Beginning with levorotatory VIII both the ketone X and its crystalline semicarbazone were dextrorotatory.



VIII IX X

The finding that X is optically active is consistent with Kimel and Cope's description of the reaction as a concerted rearrangement. The absolute configurations of (*S*)-(−)-VIII and (*S*)-(+)-X, shown as assigned on the basis of Mills' rule,[11] are also in agreement with a cyclic rearrangement in which the new carbon–carbon bond formed must be *cis* to the C–O bond being broken.

Both the investigations of Carroll[5] and of Kimel and Cope[7] showed that the product of pyrolysis of the acetoacetate of phenylvinylcarbinol (XI, R = H) was the *trans*-cinnamyl derivative (XII, R = H). Work in our laboratory[12] has shown that the ketone (XII, R = CH_3) formed[13] from the related alcohol (XI, R = CH_3) under Carroll's conditions is also predominantly the *trans* isomer. This preference for the olefin with larger groups *trans* is also characteristic of the Claisen rearrangement,[3] where it is taken as evidence for a chair-like conformation for the six-membered transition state with the larger substituent equatorial.[14]



XI XII

The stereochemical parallel between the acetoacetate and Claisen rearrangements thus extends to both optical and geometric specificity, and the pyrolysis of allylic acetoacetates may be added to the growing list of stereospecific thermal reactions.

Experimental Section

2-Cyclohexen-1-yl Acetoacetate (IX).—2-Cyclohexen-1-ol[10] (15 g), $[\alpha]^{25}D$ −11.76° (*c* 4.45, chloroform), was warmed and stirred with 0.18 g of sodium until the metal had reacted completely. Diketene (10 g) was added slowly to the stirred mixture with cooling in an ice–salt bath. The mixture was kept overnight at −10° and for an additional 24 hr at 5°, then diluted with 50 ml of ether and washed with aqueous sodium bicarbonate. After drying the ether solution, distillation gave 13 g of the acetoacetate IX, bp 71–77° (0.3 mm) and $[\alpha]^{25}D$ −7.12° (neat, 5-cm tube) (lit.[9] bp 77–79° (0.05 mm). Vpc analysis showed the presence of a small amount of unreacted cyclohexenol.

The **semicarbazone** melted at 130°, $[\alpha]^{25}D$ −3.05° (chloroform).

Anal. Calcd for $C_{11}H_{17}O_3N_3$: C, 55.21; H, 7.16; N, 17.56. Found: C, 55.17; H, 7.20; N, 17.23.

2-Cyclohexen-1-ylacetone (X).—The levorotatory acetoacetate was heated under reflux at 200–220° for 12 hr. Distillation of

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[3] (a) S. J. Rhoads in "Molecular Rearrangements," part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 655 ff; (b) E. N. Marvell, J. L. Stephenson, and J. Ong, *J. Am. Chem. Soc.*, **87**, 1267 (1965); (c) H. L. Goering and W. I. Kimoto, *ibid.*, **87**, 1748 (1965).

[4] E. R. Alexander and R. W. Kluiber, *ibid.*, **73**, 4304 (1951); see also ref 2 and 3c.

[5] M. F. Carroll, *J. Chem. Soc.*, 704, 1266 (1940).

[6] M. F. Carroll, *ibid.*, 507 (1941).

[7] W. Kimel and A. C. Cope, *J. Am. Chem. Soc.*, **65**, 1992 (1943).

[8] E. C. Kooyman, R. Louw, and W. A. M. de Tonkelaar, *Proc. Chem. Soc.*, 66 (1963).

[9] A. W. Burgstahler and I. C. Nordin, *J. Am. Chem. Soc.*, **83**, 198 (1961).

[10] D. B. Denney, R. Napier, and A. Cammarata, *J. Org. Chem.*, **30**, 3151 (1965).

[11] J. A. Mills, *J. Chem. Soc.*, 4976 (1952).

[12] Ph.D. Theses of R. M. Carlson, 1965, and J. W. Morgan, 1967. Vpc analysis showed the ketone to be a 9:1 *trans*:*cis* mixture. The *trans* geometry of the major isomer was shown by its uv absorption at 246 nm and synthesis from *trans*-β-methylcinnamic acid.

[13] J. Colonge and J. C. Brunie, *Bull. Soc. Chim. France*, 42 (1963).

[14] *Cf.* the similar results found in the Cope rearrangement by W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

the residue gave 1.4 g of ketone X, bp 92–102° (22 mm) and $[\alpha]^{25}{}_{\mathrm{D}}$ +1.43° (neat, 1-dm tube).

The **semicarbazone**, mp 169–170° (lit.[9] mp 170–171°), had[15] $[\alpha]^{22}{}_{\mathrm{D}}$ +1.11°, $[\alpha]^{27}{}_{450}$ +3.0°, $[\alpha]^{27}{}_{300}$ +13.2° (c 1.8, chloroform).

Anal. Calcd for $C_{10}H_{17}ON_3$: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.00; H, 8.96; N, 21.31.

Registry No.—IX semicarbazone, 15643-73-9; X, 15562-33-1; X semicarbazone, 15562-34-2.

(15) We thank Dr. P. Laur for determining the rotations at 300 and 450 mμ on a Cary spectropolarimeter.

The Absolute Configuration of 2-Cyclohexen-1-ol[1]

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During the course of a study of asymmetric induction in thermal rearrangements of derivatives of cyclic allylic alcohols,[2] it became necessary to provide an unambiguous assignment of the absolute configuration of 2-cyclohexen-1-ol (I). Additional impetus for this investigation comes from the formation of optically active 2-cyclohexen-1-ol in several reactions involving optically active catalysts. Denney, *et al.*,[3] found recently that the use of copper salts of optically active carboxylic acids to catalyze the *t*-butyl hydroperoxide oxidation of cyclohexene affords optically active I. Elucidation of the role played by the metal salt in this striking example of asymmetric induction by an optically active catalyst will depend on a knowledge of the absolute configuration and optical purity of the product. Dextrorotatory I may also be obtained by enzymatic oxidation,[4] using liver alcohol dehydrogenase and NAD with acetaldehyde as the hydrogen acceptor to oxidize selectively the levorotatory enantiomer. Here again a knowledge of the absolute configuration is necessary to correlate this result with theories of stereospecificity in enzymatic oxidations and reductions.[5]

Though Denney's synthesis was the first report of optically active 2-cyclohexen-1-ol, the absolute configuration had already been predicted by Mills.[6] Mills formulated an empirical rule based on rotations of terpene alcohols which states that cyclohexenols containing the moiety II are more levorotatory than their epimers. The same conclusion is reached in the empirical rule of Bose and Chatterjee[7] correlating configuration with rotation of cyclic compounds and in Brewster's conformational asymmetry arguments for optical rotations of cyclic olefins.[8]

In order to provide an unambiguous chemical proof of configuration, we have correlated I with a standard of known configuration. The method chosen was to introduce a new asymmetric center in a stereospecific manner and then determine its configuration. A suitable reaction for this purpose is the Simmons–Smith reaction to form *cis*-bicyclo[4.1.0]heptan-2-ol (III). Dauben and Berezin[9] have shown that the directing influence of the hydroxyl group in the Simmons–Smith reaction results in addition exclusively *cis* to the hydroxyl in I. Consequently the determination of configuration at either of the two new asymmetric centers of III would permit an assignment of configuration to I.

Racemic I was converted into the acid phthalate and partially resolved with dehydroabietylamine. Alcohol resolved in this way had $[\alpha]_{\mathrm{D}}$ −15°, a rotation comparable with that obtained by Denney's method. Reaction with methylene iodide and zinc–copper couple afforded optically active III, which was oxidized with chromic acid to optically active bicyclo-[4,1,0]-heptan-2-one (IV). Though IV was unaffected by zinc in refluxing acetic acid, it was readily reduced by lithium in liquid ammonia to optically active 3-methylcyclohexanone (V). The lithium–ammonia reduction of cyclopropyl ketones has been shown to be highly stereospecific;[10,11] the cyclopropane bond cleaved is that which possesses maximum overlap with the π orbital system of the carbonyl group.

Beginning with (+)-I, this sequence yielded (*S*)-(−)-3-methylcyclohexanone, whose absolute configuration has been firmly established.[12] Repetition of the sequence with (−)-I led to (*R*)-(+)-V. These correlations provide a conclusive assignment of configuration to (*R*)-(+)-I and confirm the validity of Mills' rule.

From the maximum rotation ($[\alpha]^{26}{}_{\mathrm{D}}$ 12.01°, neat, 1 dm) reported[12] for 3-methylcyclohexanone and assuming that no racemization occurs during the sequence $\mathrm{I} \rightarrow \mathrm{V}$, it is possible to calculate a minimum value of 152° for the rotation of optically pure I.[13] This value allows an estimate of the optical yield in Denney's synthesis as about 7%. Despite the low optical yield, the rotation of the pure alcohol is high enough that his convenient synthesis gives material with an optical rotation adequate for most purposes.

A final point concerns the sign of the Cotton effect of the bicyclic ketone IV. It has been shown recently that the Cotton effects of most optically active cyclopropyl ketones can be correlated with absolute configuration using a reversed cyclohexanone octant rule.[14] Unfortunately, the simplest bicyclo[4.1.0]heptanone studied to date, (+)-carone (VI), does not fit this generalization. Djerassi, *et al.*,[14] have suggested that the geminal dimethyl group makes a strong contribution to the positive Cotton effect of VI and accounts for its failure to follow a reversed octant rule. The ORD

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[1] This investigation was supported by a research grant, GP-3811, from the National Science Foundation, and by a predoctoral fellowship to J. W. Morgan from the Public Health Service, to whom we express our appreciation.

[2] R. K. Hill and M. E. Synerholm, in press.

[3] D. B. Denney, R. Napier, and A. Cammarata, *J. Org. Chem.*, **30**, 3151 (1965).

[4] J. Rétey, private communication, 1966.

[5] See, *e.g.*, V. Prelog, *Pure Appl. Chem.*, **9**, 119 (1964).

[6] J. A. Mills, *J. Chem. Soc.*, 4976 (1952).

[7] A. K. Bose and B. G. Chatterjee, *J. Org. Chem.*, **23**, 1425 (1958).

[8] J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5493 (1959).

[9] W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

[10] T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965).

[11] W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).

[12] E. J. Eisenbraun and S. M. McElvain, *J. Am. Chem. Soc.*, **77**, 3383 (1955).

[13] An attempt was made to determine the optical purity of partially resolved I by the nmr method of M. Raban and K. Mislow, *Tetrahedron Letters*, 4249 (1965), but the nmr spectrum of the O-methylmandelate ester of I showed no splitting of the benzylic hydrogens.

[14] C. Djerassi, W. Klyne, T. Norin, G. Ohloff, and E. Klein, *Tetrahedron*, **21**, 163 (1965).