Studies of Terpene Chemistry. II. Model Studies of the Synthesis of the C–D Ring System of Gibberellic Acid[1]

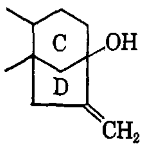
LLOYD J. DOLBY AND ROBERT H. IWAMOTO[2]

Department of Chemistry, University of Oregon, Eugene, Oregon

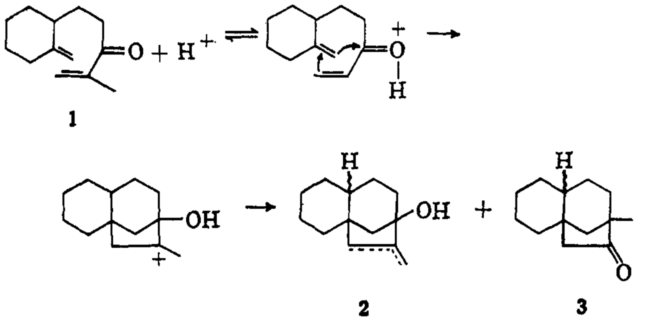
Received February 2, 1965

The acid-catalyzed cyclizations of the dienone 1 and the allylic alcohol 8 were examined as models for the synthesis of the C–D ring system of gibberellic acid and related compounds. Neither compound gave rise to the desired tricyclic materials in appreciable yield. The dienone gave 6-isopropyltetralin in modest yields and the allylic alcohol cyclized to 2-methyl-2-vinyl-Δ^9-octalin. The preparation of the allylic alcohol and the dienone are described along with an unusual olefin-forming decarboxylation.

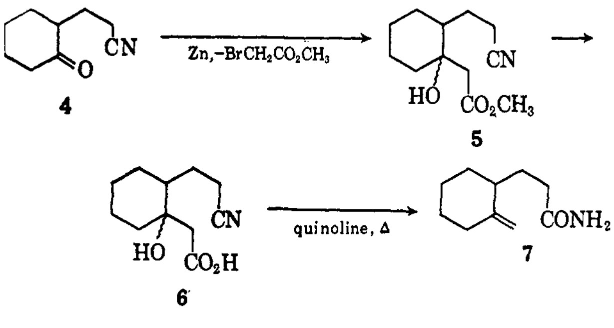
One of the most difficult aspects of the synthesis of gibberellic acid and structurally related compounds such as steviol is the construction of the C–D ring system. The synthesis of the bicyclo[3.2.1]octane system is made much more difficult by presence of a bridgehead hydroxyl group.



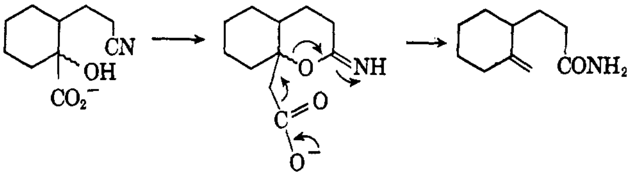
We hoped to construct the bicyclo[3.2.1]octane ring system bearing a bridgehead hydroxyl group and an *exo*-methylene group in a single step by the acid-catalyzed cyclization of a suitably constructed dienone. We chose the dienone 1 as a readily available compound to test the feasibility of this synthetic approach.



The synthesis of the dienone 1 was completed in reasonable yield by the reaction of isopropenylmagnesium bromide with the N-methylanilide of 3-(2-methylenecyclohexyl)propionic acid. The required 3-(2-methylenecyclohexyl)propionic acid was prepared by two routes. The action of methylenetriphenylphosphorane on methyl 3-(2-ketocyclohexyl)propionate afforded the required methyl 3-(2-methylenecyclohexyl)propionate in fair yields. An alternate approach is outlined below. The Reformatsky reaction proceeded normally to yield the expected β-hydroxy ester 5. Mild saponification of the β-hydroxy ester afforded the corresponding acid without appreciable hydrolysis of the nitrile. The infrared spectrum of the saponification product showed no absorption characteristic of amides but showed normal nitrile absorption. The action of hot quinoline containing a trace of copper powder has been shown to convert a variety of β-hydroxy acids to olefins with the loss of the elements of carbonic acid. The double bond is formed between the carbons initially bearing the hydroxyl and carboxyl groups.[3] However, the β-hydroxy acid 6 yielded the amide, 3-(2-methylenecyclohexyl)propionamide, rather than the expected nitrile upon exposure to hot quinoline containing some copper powder. The 3-(2-methylenecyclohexyl)propionamide obtained in this manner was identical with the amide prepared by the action of aqueous ammonia on methyl 3-(2-methylenecyclohexyl)propionate obtained by the Wittig synthesis. Copper powder did not seem to influence the course or rate of the reaction and it was deleted from subsequent runs.



We would propose that the amide arises from an intermediate imino lactone.



Another possible pathway would involve the formation of the expected 3-(2-methylenecyclohexyl)propionitrile and subsequent hydrolysis by a small amount of water present in the quinoline solution. While this pathway cannot be rigorously excluded, we find that *n*-valeronitrile is not hydrolyzed by wet quinoline under the conditions used for the decarboxylation of the β-hydroxy acid 6.

The acid-catalyzed cyclization of the dienone 1 was carried out under a wide variety of conditions. In all cases more than a dozen products were formed and 6-isopropyltetralin was the only compound identified (see Experimental). The infrared spectra of the crude reaction products exhibited carbonyl absorption characteristic of α,β-unsaturated ketones as well as absorption at 1720 cm.$^{-1}$. Only shoulders appeared in the region of 1740 cm.$^{-1}$ and it was not possible to isolate

---

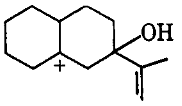
[1] Supported by a grant from the National Institutes of Health (Grant NB 03232-03).

[2] U. S. Public Health Service Predoctoral Fellow.

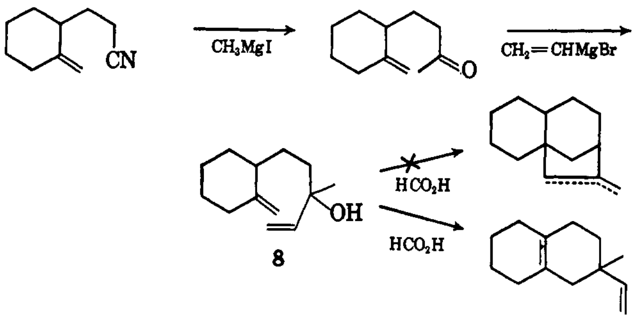
[3] M. Vilkas and N. Q. Abraham, *Bull. soc. chim. France*, 1196 (1960).

even traces of pure cyclopentanones. The crude reaction products were also subjected to vigorous acidic conditions which should effect the rearrangement of the unsaturated tricyclic alcohols **2** to the corresponding ketones **3**. The infrared spectra of the products of this vigorous acid treatment did not show any indication of cyclopentanone formation. Although there may have been minute amounts of the desired tricyclic compounds formed, the intractable mixtures which are obtained from the attempted cyclizations indicate that this approach to the C–D ring system of gibberellic acid is not practicable.

The formation of 6-isopropyltetralin from the dienone **1** indicates that the first step of the proposed cyclization takes place at least in part. Hence, it appears that the carbonium ion shown below does not cyclize to the desired tricyclic system. Examination of models of the carbonium ion reveals good reasons for the lack of cyclization. Mainly, the vinyl side chain must be in the unfavored axial conformation for cyclization and, even in the required conformation, the p-orbital of the carbonium ion is perpendicular to the π-orbital of the double bond and the overlap would appear to be very poor.

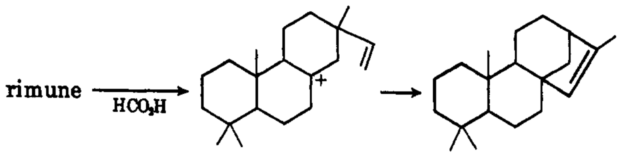


We have also attempted to cyclize the allylic alcohol **8** to the tricyclic olefins bearing the B–C–D portion of the phyllocladene skeleton. The required allylic alcohol is readily obtained by the action of vinylmagnesium bromide on 4-(2-methylenecyclohexyl)-butan-2-one which is prepared from 3-(2-methylenecyclohexyl)propionitrile and methylmagnesium iodide.

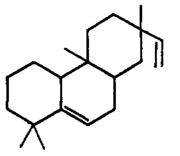


The action of formic acid on the allylic alcohol **8** gives 2-methyl-2-vinyl-Δ^9-octalin in good yield. The structure of the product follows from its proton magnetic resonance spectrum. The three-spin system of the vinyl group is apparent but no other vinyl protons are observed (see Experimental). The eight allylic protons appear as a broad peak at τ 7.9–8.3. That the allylic protons appear at such high field is not unexpected since the proton magnetic resonance spectrum of Δ^9-octalin is reported to show peaks only at τ 8.44 and 8.96.[4] More vigorous acidic conditions polymerized the 2-methyl-2-vinyl-Δ^9-octalin and we could find no evidence of tricyclic products.

It should be noted that this type of cyclization has been reported for the conversion of rimuene to isophyllocladene.[5]



However, recent studies have led two groups of investigators to propose structure **9** for rimuene.[6,7] Although it is still possible to write a pathway for the conversion of rimuene to isophyllocladene,[7] the Glasgow group was not able to effect this transformation.[6]



9

Experimental[8]

Methyl 3-(2-Methylenecyclohexyl)propionate.—Sodium hydride (5.52 g.) was heated at 75–85° under nitrogen with 125 ml. of dry dimethyl sulfoxide until the evolution of hydrogen ceased. To this cooled solution was added 82.1 g. of methyltriphenylphosphonium bromide in 250 ml. of dimethyl sulfoxide. Methyl 3-(2-ketocyclohexyl)propionate (37.8 g., 0.206 mole), prepared by the procedure of Stork and Landesman,[9] was added and the reaction mixture was stirred overnight at room temperature. The reaction was worked up in the usual manner and the crude product was fractionated to yield 21.4 g. (57%) of methyl 3-(2-methylenecyclohexyl)propionate, b.p. 90–94° (1.4 mm.), $n^{25}\text{D}$ 1.4648.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.17; H, 9.96.

The N-Methylanilide of 3-(2-Methylenecyclohexyl)propionic Acid.—Methyl 3-(2-methylenecyclohexyl)propionate (38.0 g., 0.209 mole) was dissolved in 250 ml. of 10% methanolic potassium hydroxide and stored overnight at room temperature. The free acid (34.1 g., 97%) was isolated in the usual manner and used without purification.

A solution of dry pyridine (200 ml.) and 33.5 g. of freshly distilled N-methylaniline was cooled to 0° and freshly distilled phosphorus trichloride (18.4 g.) was added dropwise. The resulting mixture was stored at 0° for 45 min. after which a solution of 34.1 g. (0.202 mole) of crude 3-(2-methylenecyclohexyl)-propionic acid in benzene (200 ml.) was added. The reaction mixture was heated on a steam bath with stirring for 3 hr. and stored at room temperature overnight; then it was poured into 1 l. of crushed ice containing 300 ml. of concentrated hydrochloric acid. The resulting mixture was extracted three times with 600-ml. portions of ether and the combined ether extracts were washed with sodium carbonate solution and water. The ether solution was dried over magnesium sulfate and concentrated under reduced pressure to yield 45.0 g. (86%) of the crude amide which could not be crystallized. The infrared spectrum (chloroform solution) showed carbonyl absorption at 1660 and a peak at 890 cm.$^{-1}$ ascribed to the *exo*-methylene group.

Dienone 1.—A solution of 16.94 g. (0.14 mole) of 2-bromopropene in 45 ml. of dry tetrahydrofuran was added to 3.40 g. (0.14 g.-atom) of magnesium in 40 ml. of tetrahydrofuran. The reaction was initiated with a few drops of 1,2-dibromoethane.

---

(4) M. Mousseron, M. Mousseron-Canet, G. Phillippe, and J. Wylde, *Compt. rend.*, **256**, 51 (1963).

(5) L. H. Briggs, B. F. Cain, and R. D. Cambie, *Tetrahedron Letters*, **No. 8**, 17 (1959).

(6) J. D. Connolly, R. McCrindle, R. D. H. Murray, and K. H. Overton, *ibid.*, **No. 29**, 1983 (1964).

(7) R. E. Corbett and S. G. Wyllie, *ibid.*, **No. 29**, 1903 (1964).

(8) All melting points and boiling points are uncorrected; distillations were carried out with a 100-cm. modified Podbielniak tantalum-spiral column. Infrared spectra were determined with a Beckman IR-5 infrared spectrophotometer. Proton magnetic resonance spectra were measured in carbon tetrachloride solution using tetramethylsilane as internal standard with a Varian A-60 spectrometer. Microanalyses are by Micro-Tech Laboratories, Skokie, Ill., Pascher and Pascher Laboratories, Bonn, Germany, and Berkeley Analytical Laboratories, Berkeley, Calif.

(9) G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5128 (1956).

After the addition was complete the resulting solution was stirred at room temperature for 2 hr. and then a solution of the N-methylanilide of 3-(2-methylenecyclohexyl)propionic acid (18.0 g., 0.07 mole) in tetrahydrofuran (75 ml.) was added during 1 hr. The reaction mixture was stirred 18 hr. at room temperature after which it was poured over 600 ml. of crushed ice and 50 ml. of concentrated hydrochloric acid. The resulting mixture was extracted with ether and the combined ether extracts were washed with aqueous sodium carbonate and water. Distillation of the crude dienone afforded 4.92 g. (36.6%) of material, b.p. 100–110° (1.0 mm.), $n^{25}\text{D}$ 1.4911. The infrared spectrum (chloroform solution) showed peaks at 1665 and 1640 cm.$^{-1}$ typical of an α,β-unsaturated ketone and a band at 890 cm.$^{-1}$ ascribed to the *exo*-methylene group; the ultraviolet spectrum showed $\lambda_{\text{max}}^{\text{EtOH}}$ 220 mμ (ϵ 8410). The proton magnetic resonance spectrum exhibited absorption for two protons as two multiplets centered at τ 5.48 and 5.38 (*exo*-methylene protons) and a three-proton multiplet at τ 7.96 (methyl protons).

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.19; H, 10.48. Found: C, 80.76; H, 10.55.

β-Hydroxy Ester 5.—A solution of methyl bromoacetate (26.0 g., 0.17 mole), 3-(2-ketocyclohexyl)propionitrile (21.4 g., 0.14 mole), prepared by the procedure of Stork, *et al.*,[10] and 50 ml. of dry benzene was added to a stirred mixture of zinc foil (10.40 g., 0.16 g.-atom) and dry benzene (200 ml.). The reaction was warmed on the steam bath until 25 ml. of bromo ester solution had been added after which the steam bath was removed and the remainder of the bromo ester solution was added at a rate which maintained gentle reflux. The reaction mixture was heated under reflux for 1 hr. after the addition was complete; then it was cooled to 0° and hydrolyzed with 250 ml. of 10% sulfuric acid. The organic layer was separated and washed with sodium bicarbonate solution and water. The benzene was removed under reduced pressure and the residue was distilled to afford 14.8 g. (44%) of the β-hydroxy ester, b.p. 165–172° (0.4 mm.), obtained as a viscous liquid which soon solidified. The analytical sample melted at 46–58° after several crystallizations from hexane.

Anal. Calcd. for $C_{12}H_{19}NO_3$: C, 63.97; H, 8.50; N, 6.22. Found: C, 63.49; H, 8.10; N, 6.45.

3-(2-Methylenecyclohexyl)propionamide.—The β-hydroxy ester **5** (13.4 g., 0.0596 mole) was dissolved in 75 ml. of methanolic potassium hydroxide (10%) and stored overnight at room temperature. The crude hydroxy acid (10.2 g., 81%) was isolated in the usual fashion and used without deliberate purification. The infrared spectrum (chloroform solution) of the hydroxy acid showed maxima at 3500, 2200, and 1700 cm.$^{-1}$.

A solution of the crude β-hydroxy acid (7.15 g., 0.034 mole) in 13 ml. of dry quinoline was heated at 200° with stirring for 8 hr. Most of the quinoline was distilled under reduced pressure and the residue was taken up in 100 ml. of ether. The ether solution was washed with cold 6 *N* hydrochloric acid until the aqueous layer remained acidic, after which the ether solution was washed with water and dried over anhydrous sodium carbonate. Evaporation of the ether solution afforded the crude amide (1.62 g.) as a tan solid which was recrystallized from methylcyclohexane to give the pure amide (1.43 g., 25%), m.p. 92–94°. This material was identical in every respect with a sample of 3-(2-methylenecyclohexyl)propionamide, m.p. 92–93°, prepared by the action of concentrated aqueous ammonia on methyl 3-(2-methylenecyclohexyl)propionate prepared by the Wittig synthesis.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.24; N, 8.38. Found: C, 71.86; H, 10.21; N, 8.31.

3-(2-Methylenecyclohexyl)propionitrile.—Sodium hydride (12.4 g. of 55% sodium hydride in mineral oil, 0.28 mole) was heated in 100 ml. of dry dimethyl sulfoxide at 75–80° for 1 hr. To this cooled solution was added 100 g. of methyltriphenylphosphonium bromide in 250 ml. of dimethyl sulfoxide. The ylide solution was stirred at room temperature for 20 min. and then treated with 40 g. (0.26 mole) of 3-(2-ketocyclohexyl)propionitrile added in one portion. The resulting mixture was warmed to 55° and stirred overnight at room temperature. The reaction was processed in the usual manner and the crude product was distilled to afford 29.3 g. (74%) of the olefinic nitrile, b.p. 110–114° (8.0 mm.), $n^{25}\text{D}$ 1.4758.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.51; H, 10.03; N, 9.38. Found: C, 80.53; H, 10.14; N, 9.48.

4-(2-Methylenecyclohexyl)butan-2-one.—To the Grignard reagent prepared from magnesium turnings (3.36 g., 0.14 g.-atom) and 21.3 g. (0.14 mole) of methyl iodide in 50 ml. of ether was added a solution of 3-(2-methylenecyclohexyl)propionitrile (14.0 g., 0.094 mole) in ether (150 ml.). After the addition of the nitrile was complete, the reaction mixture was stirred for 20 min. at room temperature and then was heated under reflux for 2 hr. The reaction mixture was hydrolyzed with ammonium chloride solution and the crude ketone was isolated in the usual manner. Distillation of the products afforded 6.2 g. (40%) of the desired ketone, b.p. 101–103° (1.4 mm.), $n^{25}\text{D}$ 1.4870. The ketone did not give satisfactory analytical data. The 2,4-dinitrophenylhydrazone, m.p. 89–91°, was prepared in the usual manner and crystallized from ethanol.

Anal. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.40; N, 16.18. Found: C, 58.52; H, 6.57; N, 16.27.

4-(2-Methylenecyclohexyl)-3-methylpent-1-en-3-ol.—To the Grignard reagent prepared from 1.76 g. (0.072 g.-atom) of magnesium turnings and 72.5 g. (0.072 mole) of vinyl bromide in tetrahydrofuran (13 ml.) was added a solution of 4-(2-methylenecyclohexyl)butan-2-one (6.1 g., 0.037 mole) in tetrahydrofuran (50 ml.). The addition was carried out at 0° and, after the addition was complete, the reaction mixture was stirred for 20 min. at 0° and then stored at room temperature for 3.5 hr. The reaction mixture was hydrolyzed with ammonium chloride solution, and distillation of the crude product afforded 6.2 g. (87%) of the desired alcohol, b.p. 62–65° (0.25 mm.), $n^{25}\text{D}$ 1.4891. The n.m.r. spectrum exhibited two multiplets at τ 5.05 and 5.45 (2H) ascribed to the *exo*-methylene protons. The three-spin system of the vinyl group was analyzed with aid of a computer program that yields peak positions and intensities from chemical shifts and coupling constants.[11] The parameters which gave the best agreement with the observed 12-line spectrum are: τ 4.16 (H_A), 4.83 (H_B), 5.02 (H_C), and J_{AC} = 17.5 c.p.s., J_{AB} = 10.5 c.p.s., J_{BC} = 1.5 c.p.s.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.28; H, 11.41. Found: C, 80.37; H, 11.32.

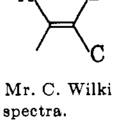
Cyclization Studies. Dienone 1. A. With Moist Acidic Alumina.—The dienone (0.203 g.) was dissolved in benzene (5 ml.) saturated with water and adsorbed onto a column of Woelm acidic alumina (5.1 g.) prepared in benzene saturated with water. The material was allowed to remain on the column for 56 hr. at room temperature protected from light, after which the material was eluted with chloroform. The chloroform was evaporated under reduced pressure to give 0.178 g. of crude product which contained at least 15 compounds as determined by vapor phase chromatography on a 5 ft. × 0.25 in. column of 20% Carbowax 20-M on firebrick at 190°. One product (retention time 6.0 min.) was identified as 6-isopropyltetralin by comparison of its retention time and the infrared spectrum of a collected sample with authentic material. The crude product was diluted to a known volume and the absolute yield of 6-isopropyltetralin was found to be 23% from its peak area on vapor phase chromatography and a plot of peak area and sample size. The infrared spectrum of the total crude product (chloroform solution) showed absorption at 1695, 1720, and a very small shoulder at 1754 cm.$^{-1}$ as well as absorptions for 6-isopropyltetralin and weak hydroxyl absorption at 3460 cm.$^{-1}$. Repeated chromatography over alumina concentrated the material absorbing at 1754 cm.$^{-1}$ in the infrared but it was not possible to isolate the pure material even by vapor phase chromatography. The absorption at 1754 cm.$^{-1}$ was not enhanced by the action of hot 0.1 *N* ethanolic hydrochloric acid for 2 hr.

In another experiment in which the dienone was allowed to remain in contact with the alumina for only 8 hr., the crude product showed four additional peaks on vapor phase chromatography (retention times 3.0, 3.6, 4.2, and 5.1 min.). The action of hot ethanolic hydrochloric acid destroyed the four compounds of short retention time with a concomitant increase in the 6-isopropyltetralin peak, and it seems likely that the compounds of short retention time are trienes isomeric with 6-isopropyltetralin.

---

[10] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 217 (1963).

[11] The protons of the vinyl group were lettered as follows.



The authors are indebted to Mr. C. Wilkins and Mr. C. Klopfenstein for their assistance in analyzing the spectra.

B. **With Mineral Acid.**—The dienone (0.200 g.) was dissolved in purified 1,2-dimethoxyethane (5 ml.) and treated with concentrated sulfuric acid (0.5 ml.). The reaction mixture was stored overnight at room temperature and then diluted with water and extracted with ether. The ether extracts were washed with sodium carbonate solution and with water and dried over magnesium sulfate. The ether was evaporated under reduced pressure to yield 0.129 g. of crude product. Vapor phase chromatography analysis showed the presence of at least seven compounds. The major product was 6-isopropyltetralin obtained in an absolute yield of 12%. Polymerization seemed to be a major side reaction under these conditions. The infrared spectrum of the crude product showed carbonyl absorption at 1695 cm.$^{-1}$. A variety of other acidic conditions were examined and in every case a complex mixture of products was obtained. The crude products were subsequently treated with hot ethanolic hydrochloric acid and examined for cyclopentanone absorption in the infrared region. In no case was there any indication of more than a trace of cyclopentanone formation.

C. **5-(2-Methylenecyclohexyl)-3-methylpent-1-en-3-ol in Formic Acid.**—The alcohol (1.62 g., 0.0083 mole) was dissolved in benzene (15 ml.) and added during 15 min. to 95–97% formic acid (25 ml.) at 0–5°. The reaction mixture was stirred overnight at room temperature and then poured into 100 ml. of water. The resulting mixture was extracted with ether and the ether extracts were washed with saturated sodium hydrogen carbonate solution and water. The dried (magnesium sulfate) ether solution was concentrated under reduced pressure to give 1.40 g. of crude product which was chromatographed over 35 g. of Woelm neutral alumina, grade I. Elution with 150 ml. of petroleum ether (b.p. 30–60°) afforded 1.2 g. of hydrocarbon material which showed two peaks (retention times 4.0 and 7.1 min.) on vapor phase chromatography on a 5 ft. × 0.25 in. column of 20% Carbowax 20-M on firebrick at 190°. The predominant (15:1) 4.0-min. peak was collected and its infrared spectrum (chloroform solution) showed no carbonyl absorption, but had olefinic absorption at 1640 and a peak at 910 cm.$^{-1}$ ascribed to a terminal vinyl group. The infrared spectrum (carbon disulfide solution) did not show absorption at 890 cm.$^{-1}$ characteristic of an *exo*-methylene group and no peaks in the 830-cm.$^{-1}$ region which could be ascribed to a trisubstituted double bond. The n.m.r. spectrum exhibited a three-proton singlet at τ 9.03 (methyl protons), a broad singlet centered at τ 8.28 (eight protons) ascribed to the allylic protons, and 12 lines in the vinyl proton region (three protons). The following parameters gave the best agreement for the vinyl group: τ 4.36 (H_A), 5.15 (H_B), 5.15 (H_C), and J_{AB} = 10.0 c.p.s., J_{AC} = 18.0 c.p.s., J_{BC} = 1.5 c.p.s. It was not possible to get satisfactory analytical data for the compound and it appeared to take up oxygen because the sum of the carbon and hydrogen values was about 96% in two attempts.

A second run was carried out as just described except that the reaction mixture was hydrogenated at atmospheric pressure over 100 mg. of 5% palladium-on-carbon catalyst. The crude product was isolated as previously described and vapor phase chromatography under the conditions used previously showed two peaks in the ratio of 15:1. The analysis of the major product was satisfactory for a 2-methyl-2-ethyldecalin.

Anal. Calcd. for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.77; H, 12.88.

The Conformation and Nuclear Magnetic Resonance Spectrum of Mesityl Oxide

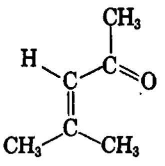
JOHN E. BALDWIN

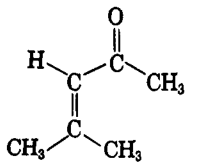
The Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61803

Received March 2, 1965

From comparisons of the n.m.r. spectra of mesityl oxide, 1,1,1-trideuterio-4-methyl-3-penten-2-one, and *cis*- and *trans*-3-penten-2-one, assignments for methyl n.m.r. absorptions in mesityl oxide are deduced. The evidence for stereospecific collision complexes between mesityl oxide and benzene is examined.

The n.m.r. spectrum of mesityl oxide (I) has been reported[1] to show a doublet at τ 8.14 (3H), a singlet at 7.95 (6H), and a broad signal at 4.03 (1H). The doublet at τ 8.14 was assigned[1] to one of the two allylic methyl groups, since the CH_3CO– protons were considered incapable of significant coupling with the olefinic proton. From the results of n.m.r. investigations[2] of *cis* and *trans* α,β-unsaturated carboxylic esters, it seems reasonable to infer that the most deshielded of the two allylic methyl groups is *cis* to the carbonyl function and that this strong deshielding may be associated with a predominant (*S*)-*cis* (Ia) rather than an (*S*)-*trans* (Ib) conformation.


Ia


Ib

An inference from n.m.r. data that the (*S*)-*cis* conformation for mesityl oxide is favored at room temperature would agree with conclusions from stereochemical investigations of the molecule based on infrared,[3,4] Raman,[5] and ultraviolet[3] spectrophotometry, and on dipole moment determinations.[6,7]

More recent investigations[8] of the n.m.r. spectrum of mesityl oxide with equipment capable of higher resolution showed absorptions for the methyl groups at τ 7.893, 8.137, and 7.907. The signals at 7.893 and 8.137 are split into doublets by couplings of 1.2 and 1.4 c.p.s., respectively. A tentative assignment of the allylic methyl group *trans* to the carbonyl function for the doublet at 7.893 was made; the smaller coupling (1.2 rather than 1.4 c.p.s.) was assumed to be indicative of a *cis* relationship between methyl and the olefinic proton.[8] The other allylic methyl, *cis* to the carbonyl function, then corresponded to the signal at 8.137, and CH_3CO– protons to the singlet at 7.907.

Further, from a study[8] of the changes in chemical shifts experienced by the methyl groups of mesityl oxide in benzene, a stereospecific complex or collision complex between mesityl oxide and benzene was deduced (II).

---

(1) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp. 84–85.

(2) L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958); *J. Chem. Soc.*, 2886 (1960).

(3) R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).

(4) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(5) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2201 (1961).

(6) J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949).

(7) G. K. Estok and J. H. Sikes, *J. Am. Chem Soc.*, **75**, 2745 (1953).

(8) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **5**, 153 (1962).