1-Methyl-6-(methylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirine (16).—A solution of 5 g (0.014 mole) of the dibromo ketone **10** in 300 ml of anhydrous ether was saturated with methylamine. The closed flask was allowed to stand at room temperature for 24 hr. Isolation of the product and recrystallization from petroleum ether (bp 60–70°) gave colorless, light-sensitive crystals: mp 99–100°; yield 70%; $\gamma^{\mathrm{CCl_4}}_{\mathrm{C=N}}$ 1667 cm^{-1}; $\lambda_{\max}$ 247 mμ (ϵ 14,600); nmr τ 7.94 (three-ring CH$_3$), 6.81 (three-ring H), 6.58 (=NCH$_3$), 2.20–2.87 (nine aromatic H's).

Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 81.93; H, 6.49; N, 11.09.

The azirine **16** was also prepared in 77% yield from the reaction of the monobromo ketone **11** with methylamine in ether solution on standing for 4 days at room temperature.

2-Hydroxy-3-phenylindenone (17).—A magenta solution of 1 g (0.0034 mole) of **12** dissolved in 10 ml of cold, concentrated sulfuric acid was poured with vigorous stirring into 800 ml of water (70°). On cooling, 0.65 g (85.3%) of a red-brown solid, mp 140–144°, was obtained. A mixture melting point with an authentic sample of **17**[15] was undepressed and infrared spectra were superimposable; infrared (CCl$_4$) bands were at 3500 (OH) and 1724 cm^{-1} (C=O); ultraviolet showed $\lambda_{\max}$ (MeOH) 252 mμ (ϵ 31,000) and 480 mμ (ϵ 1360).

In a similar manner, **17** was produced in 88.4% yield from **14**, in 72.4% from **15**, and in 81.3% from **16**.

Registry No.—**3**, 13118-12-2; **4**, 13118-13-3; **5**, 13118-14-4; **6**, 13135-39-2; **12**, 1713-38-8; **13**, 13118-15-5; **15**, 1981-53-9; **16**, 13118-16-6; **17**, 1713-37-7.

Acknowledgment.—This work was supported in part by Grant CA-02931 from the National Cancer Institute of the U. S. Public Health Service.

The Stereochemistry of Some Diphenylbicyclo[3.3.1] Ketones

HENRY M. HELLMAN, ROBERT A. JERUSSI,

Department of Chemistry, New York University, New York, New York 10453

AND JOHN LANCASTER

Central Research Division, American Cyanamid Company, Stamford, Connecticut

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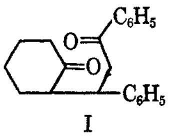
Spectral and chemical methods have been used to determine the configurations of the two epimers of 2,4-diphenylbicyclo[3.3.1]non-2-en-9-one and of the three possible stereoisomers of 2,4-diphenylbicyclo[3.3.1]nonan-9-one. Three compounds corresponding to these formulas have been reported previously, but they were not characterized stereochemically. Details of the isolation of these five compounds are described.

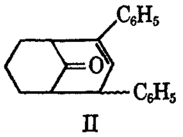
In 1933, Allen and Sallans[1] prepared 2-(α-phenyl-β-benzoylethyl)cyclohexanone (I) by the Michael addition of cyclohexanone to benzalacetophenone, and treated it with concentrated sulfuric acid in ethanol to give 55% of 2,4-diphenylbicyclo[3.3.1]non-2-en-9-one (II), mp 143°. Cyclization at a lower temperature gave about 1% of an isomeric ketone, mp 151°.

Structure II has also been prepared in 70–88% yields by heating I with acetic acid–hydrochloric acid,[2] or more simply with acetic acid–*p*-toluenesulfonic acid.[3] None of these investigations involved stereochemical identifications, but Cope, Fawcett, and Munn[2] showed from spectral data that II has the double bond in the 2 position rather than at 1 (bridgehead) as formulated by Allen and Sallans.

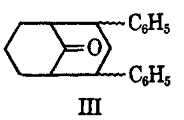
Hydrogenation of II gave 2,4-diphenylbicyclo[3.3.1]-nonan-9-one (III), mp 143–143.8°, not further identified.[2]



I



II

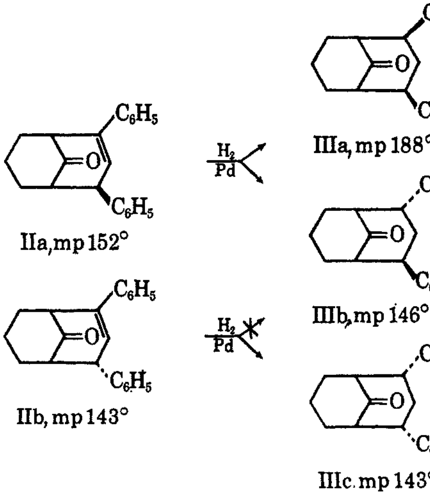


III

Results and Discussion

We have been able to prepare II in the yields reported,[2] but usually cyclization of I in acetic acid–hydrochloric acid gave a product having a wide melting range. This was identified as a mixture of the isomeric ketones originally described by Allen and Sallans[1] by isolation of both ketones, mp 152 and 143°, from one cyclization reaction. That these are the epimeric ketones IIa and IIb (Scheme I) is suggested by their mode of formation, by the fact that the 143° isomer could be isomerized to the 152° isomer with base, and by their nmr spectra. The infrared spectra of the two isomers were different and they gave different 2,4-dinitrophenylhydrazone and oxime derivatives. Each absorbed 1 mole of hydrogen, and the 143° compound reduced potassium permanganate in 95% ethanol[2] while the 152° one did not.

SCHEME I



Direct evidence concerning the stereochemistry at the C-4 position was obtained by inspection of the proton magnetic resonance spectra of the two unsaturated isomers shown in Figures 1 and 2. The spectrum of the 152° isomer (Figure 1) has singlets at τ 7.35 and

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[1] C. F. H. Allen and H. R. Sallans, *Can. J. Res.*, **9**, 574 (1933).

[2] A. C. Cope, F. S. Fawcett, and G. Munn, *J. Am. Chem. Soc.*, **72**, 3399 (1950).

[3] S. Julia and D. Varech, *Bull Soc. Chim. France*, 1127 (1959).

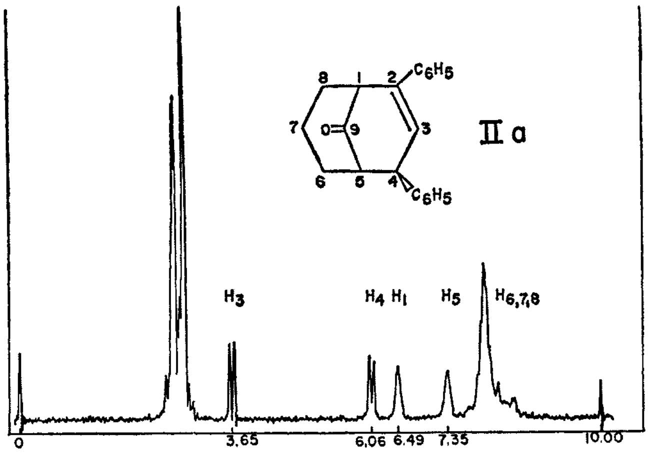

Figure 1.—Proton magnetic resonance spectrum of unsaturated isomer IIa.

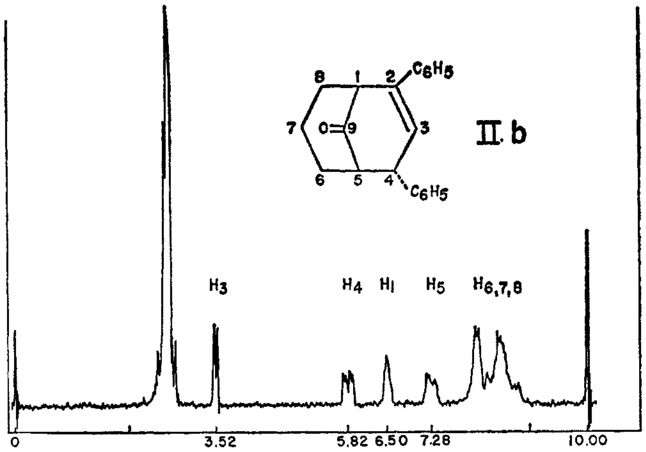

Figure 2.—Proton magnetic resonance spectrum of unsaturated isomer IIb.

6.49 and two AX-type doublets centered at 6.06 and 3.65. The integrated peak areas indicate that each of these corresponds to one proton. From these chemical-shift values, the peaks can be assigned to the bridgehead C-5, the bridgehead C-1, the benzylic C-4, and the vinylic C-3 protons, respectively.[4] No coupling is observed between the C-4 and C-5 protons ($J_{4,5}$ = 0) and $J_{3,4}$ = 4.0 cps. The spectrum of the 143° isomer (Figure 2) has a doublet centered at τ 7.28, a singlet at 6.50, a doubled doublet centered at 5.82, and a doublet at 3.52, each group corresponding to one proton by integration. These are the C-5, C-1, C-4, and C-3 protons, respectively, analogous to the assignment for the 152° isomer, with $J_{3,4}$ = 2.8 cps and $J_{4,5}$ = 6.4 cps. The bridgehead C-5 proton is coupled to its neighbor at C-4, whereas in the 152° isomer it is not.

This difference becomes explainable by inspecting Dreiding models of IIa and IIb. For IIa the models indicate that the dihedral angle between the protons on C-4 and C-5 is 82 ± 2° if the cyclohexanone ring is in the boat conformation, and 88 ± 2° if it is in the chair conformation. In IIb these angles are 39 ± 2° and 32 ± 2°, respectively. The models also suggest that the cyclohexenone ring is fairly rigid. Karplus' treatment of the correlation of coupling constants with dihedral angle indicates a coupling of about 0 in the 80–90° range.[5] Therefore, the 152° isomer has the configuration about C-4 shown in IIa and the 143° isomer has that shown in IIb.

The same assignment can be made from the hydrogenation data obtained on IIa and IIb in glacial acetic acid with 10% palladium on charcoal, assuming that hydrogenation is a *cis* process.[6] Compound IIa gives a mixture of two saturated ketones, mp 146° and 188°, separable by column chromatography, and IIb gives the saturated ketone originally described by Cope, mp 143°.[2] The Dreiding model of IIa suggests that there is no preference to the approach of the double bond to a catalytic surface from either side of the molecule. In fact, neither side appears to be able to flatten out on a catalyst. However, the situation for IIb is quite different. Approach to the catalyst surface from the carbonyl side is unrestricted while the other side is greatly hindered by the phenyl group at C-4 and, depending on the conformer, the hydrogen at C-7 or at C-6 and C-8. With these facts and the conformational analysis, structure IIa corresponds to the olefin that gave two products and IIb to the one that gave only one on hydrogenation. The ease of approach to one side of the double bond in IIb is also indicated by the fact that IIa did not decolorize permanganate in six times the time required for IIb to do so.

As shown in Scheme I, hydrogenation of each epimeric olefin can yield two products, with the phenyl groups *cis* or *trans*. The *trans* compound is the same for each, but the *cis* compounds are different. IIb forms only one product (IIIc), mp 143°, which is different from either of the two produced from IIa. Hence, IIIc must be a *cis* compound and the configuration shown is consistent with the conformational analysis.

In order to determine which of the two saturated ketones produced from IIa has configuration IIIa or IIIb, each was submitted to Baeyer–Villiger oxidation with peroxyacetic acid. Reaction of the ketone with mp 188° produced a high yield of a single lactone, mp 177.2–178°, but IIIb (*ca.* 94% pure) produced two major products, mp 158.5–161° and 182–183.3°. Oxidation of IIIc with selenic acid–hydrogen peroxide in an effort to obtain ring contraction produced only a single lactone, mp 150.5–151.9°, in good yield. These results are in agreement with the configurations shown in Scheme I and clearly indicate that IIIa and IIIc are *cis* compounds.

From the configurations of the ketones and the known stereochemical course of the Baeyer–Villiger reaction,[7] structures can be assigned to the lactones obtained. The lactone from IIIa must have the structure shown in IVa and that from IIIc, configuration IVd. The two lactones from IIIb have the configurations IVb and IVc but it is not known which material corresponds to which structure.

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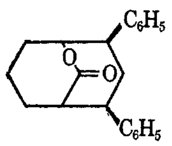
(4) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1959, Chapter 4. H. Conroy "Advances in Organic Chemistry, Methods and Results," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p 287.

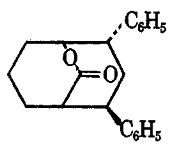
(5) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(6) There is ample evidence that catalytic hydrogenation is predominantly a *cis* process; see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw Hill Book Co., Inc., New York, N. Y., 1962, pp 282, 350.

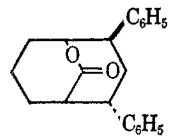
(7) C. H. Hassall, *Org. Reactions*, **9**, 73 (1957).



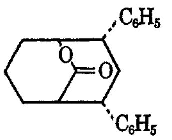
IVa



IVb



IVc



IVd

Work is in progress to prove definitively the steric relationship of IIIa to IIIc and to gather information about the conformations of all three saturated ketones.

Experimental Section[8]

2,4-Diphenylbicyclo[3.3.1]non-2-en-9-one (IIb).—2-(α-Phenyl-β-benzoylethyl)cyclohexanone (I) was prepared from cyclohexanone and chalcone in 77% yield according to the method of Allen and Sallans.[1] Compound IIb was prepared from I in 81% crude yield by the method of Cope, Fawcett, and Munn.[2] Recrystallization from 95% ethyl alcohol gave white crystals, mp 143.1–143.9° (lit. mp 143.2–143.9° [2] and 143° [1]). The nmr spectrum is shown in Figure 2. *Anal.* Calcd for $C_{21}H_{20}O$: mol wt, 288. Found: mol wt, 269 (isopiestic).

The 2,4-dinitrophenylhydrazone of IIb was prepared by the procedure of Shriner and Fuson.[9] A pure sample was obtained by recrystallization from 95% ethyl alcohol–chloroform, mp 216.2–216.9° dec (lit.[2] mp 215.8–216.8° dec).

The oxime of IIb was prepared from 200 mg of ketone to give 218 mg of crude product. Several recrystallizations from benzene–hexane gave a white product, mp 155.4–157.2° (lit. mp 156° [1] and 155–158° [2]).

2,4-Diphenylbicyclo[3.3.1]non-2-en-9-one (IIa).—Compound I (15.0 g, 0.049 mole) was heated under reflux for 41.5 hr with glacial acetic acid (500 ml) and concentrated HCl (100 ml). Water was added until the solution became turbid and the solution was allowed to cool partially. The white crystals that deposited were separated by filtration and the filtrate was cooled further to room temperature, where a second crop of crystals separated. Recrystallization of the crystals obtained first from 95% ethyl alcohol gave IIb, mp 143.1–144.9° (9.1 g). The second crop was recrystallized once from the same solvent to give IIa, mp 151.8–154.1° (1.5 g). The analytical sample had mp 152.2–153.8°, λ_{max}^{KBr} 5.77 μ, $\lambda_{max}^{C_6H_{12}}$ 249 mμ (ε 12,600) (lit.[1] mp 151°). The nmr spectrum is shown in Figure 1. *Anal.* Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99; mol wt, 288. Found: C, 87.55; H, 7.12; mol wt, 286 (isopiestic).

The 2,4-dinitrophenylhydrazone of IIa was prepared as that of IIb, mp 208.1–209.4°. *Anal.* Calcd for $C_{27}H_{24}N_4O_4$: C, 69.22; H, 5.16; N, 11.96. Found: C, 69.24; H, 5.20; N, 12.00.

The oxime of IIa was prepared from 300 mg of ketone to give 387 mg of crude oxime, mp 157.4–158.7°. The analytical sample was obtained by recrystallization from aqueous ethyl alcohol, mp 156.2–157.2°. The infrared spectrum of this oxime was different from that from IIb and a mixture melting point was 118.5–148°. *Anal.* Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.22; H, 6.53; N, 4.79.

Compound IIb (100 mg) in 3.5 ml of 95% acetone decolorized 1 drop of 2% aqueous permanganate solution in 1 min. A similar solution of IIa did not decolorize in 6 min.

2,4-Diphenylbicyclo[3.3.1]nonan-9-one (IIIc).—2,4-Diphenylbicyclo[3.3.1]non-2-en-9-one (IIb) was hydrogenated *via* the procedure of Cope, Fawcett, and Munn[2] in 85% yield. The analytical sample was obtained by recrystallization from methyl alcohol, mp 142.9–143.8° (lit.[2] mp 143–143.8°). A mixture melting point of IIb and IIIc was 121.6–127.7°. *Anal.* Calcd for $C_{21}H_{22}O$: mol wt, 290. Found: mol wt, 296 (Rast).

2,4-Diphenylbicyclo[3.3.1]nonan-9-one (IIIa and IIIb).—Compound IIa (164 mg, mp 152.4–153.7°) was hydrogenated in 4.5 ml of glacial acetic acid with 10% palladium on carbon (29 mg) at atmospheric pressure. In 2 hr, 109% of 1 molar equiv of hydrogen had been taken up. The catalyst was removed by filtration and washed with small portions of acetic acid and ether. The filtrate was removed to give 147 mg of product which was chromatogrammed on 20 g of acid-washed alumina eluting with 2% $CHCl_3$–CCl_4. Several fractions of oil were removed (10 mg) and then nine fractions were collected eluting with 7% $CHCl_3$–CCl_4. Fraction 1 (9 mg), mp 181.6–185.5°, was recrystallized from methyl alcohol to give IIIa, mp 185.2–186.7°. The infrared spectrum of this material was identical with that of an analytical sample of IIIa (see below). Fractions 2, 3, and 4 (33 mg) contained solids with wide melting ranges between 143.7 and 181.1°. Fractions 5, 6, 7, and 8 (93 mg) had sharp melting points all of which were between 140 and 146.5°. Fraction 9 (5 mg) was discarded; total recovery was 150 mg. Fractions 5, 6, 7, and 8 were combined and recrystallized from methyl alcohol to give IIIb: mp 145.4–146.2°, λ_{max}^{KBr} 5.88 μ. A mixture melting point with compound IIIc was 114.4–131.4°. *Anal.* Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64; mol wt, 290. Found: C, 87.11; H, 7.61; mol wt, 286 (Rast).

In another experiment, 73 mg of IIIa was obtained by chromatography, mp 187.6–188.8°. The analytical sample was obtained by recrystallization from methyl alcohol: mp 187.6–188.2°, λ_{max}^{KBr} 5.82 and 5.86 μ. *Anal.* Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64; mol wt, 290. Found: C, 86.71; H, 7.50; mol wt, 294 (Rast).

Another sample of IIa was hydrogenated in glacial acetic acid in a Parr apparatus at 1.5 atm. The crude product, mp 131.5–136.5°, was analyzed by glpc[8] (column temperature 220°, helium flow 85 ml/min) and found to contain 22% of the ketone, IIIa, mp 188° (retention time 7 min) and 78% of the ketone, IIIb, mp 146° (retention time 9 min).

Isomerization of IIb.—Compound IIb (993 mg, mp 143.7–144.6°) was heated under reflux with potassium hydroxide (5 g), water (3.5 ml), and methanol (15 ml) for 65.5 hr. A solid phase was present during the entire reaction. The mixture was acidified with concentrated hydrochloric acid and filtered, and the crystalline material was collected, washed with water, and dried. The crude product, mp 151.7–154.3°, was recrystallized twice from 95% ethyl alcohol to give IIa (370 mg, 37%), mp 151.4–153.3°. The infrared spectrum of this material was identical with the spectrum of the analytical sample of IIa.

Baeyer–Villiger Oxidation of IIIa.—Compound IIIa (16.2 mg, mp 188.8–190.2°) was oxidized in the same manner as IIIb to give 17.4 mg of white product, mp 168–171.5°. Thin layer chromatography indicated that this was only one product and had the same R_f value as the third, minor component, from the oxidation of IIIb. Several recrystallizations from methyl alcohol gave IVa: mp 177.2–178°, λ_{max}^{KBr} 5.84 and 8.62 μ. *Anal.* Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.36; H, 7.31.

Baeyer–Villiger Oxidation of IIIb.—Compound IIIb (59.7 mg, mp 145.1–146.3°) was oxidized with 40% peroxyacetic acid at ambient temperature using the procedure of Meinwald and Frauenglass.[10] After 5 days, the mixture was slowly poured into 30 ml of 20% sodium carbonate solution and extracted with ether containing a small amount of chloroform and ethyl acetate. The extract was washed with water and saturated salt solution and was dried over magnesium sulfate. The dried extract was filtered to remove drying agent and the filtrate was removed at the aspirator to give 59.3 mg of white product, mp 146–161.5°. Thin layer chromatography of 56 mg of product on silica gel in 85:15 benzene–ethyl acetate indicated the absence of starting ketone and the presence of three products, one minor, all more polar than starting material. The most polar band yielded 28 mg after elution from the silica gel with acetone. The analytical sample, mp 158.5–161°, was obtained by recrystallization from methyl alcohol: λ_{max}^{KBr} 5.82, 8.43, and 8.56 μ (IVb or IVc). *Anal.*

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[8] All melting points are corrected. Elemental analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., John Dionarine, American Cyanamid, and Weiler and Strauss, Oxford, England. Nmr spectra were obtained with a Varian DP-60 spectrometer operating at 56.4 Mc, using 10% solutions in $CDCl_3$ containing tetramethylsilane as an internal reference. Infrared spectra were taken in a Baird-Atomic Inc. Model 4-55 spectrophotometer and a Perkin-Elmer Infracord. Ultraviolet spectra were taken in Cary Model 14 and a Beckman DK 2 spectrophotometers. Gas chromatographic analyses were carried out in an F & M Model 500 using a 4 ft × 0.25 in. column packed with 3% XE 60 on ABS.

[9] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1965.

[10] J. Meinwald and E. Frauenglass, *J. Am. Chem. Soc.*, **82**, 5239 (1960).

Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.27; H, 7.34.

Elution of the band of intermediate polarity gave 20.6 mg. A second chromatography removed a small amount of the most polar material and gave 17.5 mg of white product, mp 177–179.5°. The analytical sample was obtained by recrystallization from methyl alcohol: mp 182–183.3°; λ_{max}^{KBr} 5.84, 8.41, and 8.56 μ (IVb or IVc). *Anal.* Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.04; H, 7.15.

Elution of the least polar (minor) zone gave 4.1 mg of a yellow solid. Both the R_f value and an infrared spectrum indicated that this material was identical with the lactone, mp 177.2–178°, obtained from oxidation of IIIa.

Glpc analysis[8] of the sample of ketone IIIb used in the Baeyer–Villiger oxidation (column temperature 220°, helium flow 85 ml/min) indicated the presence of 5.7% of the mp 188° ketone (retention time 7 min).

Baeyer–Villiger Oxidation of IIIc.—A solution of IIIc (720 mg, mp 142.1–142.9°), tetrahydrofuran (5 ml), 30% aqueous hydrogen peroxide (0.6 ml), and 40% aqueous selenic acid (0.04 ml) was heated at reflux for 25 hr. The solvent was removed at the aspirator and the residue was taken up in ether. The ether solution was extracted with 15% aqueous sodium carbonate solution, washed with water, and dried over magnesium sulfate. The ether was filtered and the filtrate was removed at the aspirator to give 672 mg of a pink solid (mp 144.6–149.1°, λ_{max}^{KBr} 8.51 μ) which appeared to be homogeneous. The compound was recrystallized from methyl alcohol to constant melting point (150.5–151.9°) and gave a satisfactory analysis for 2,4-diphenyl-5-hydroxycyclooctanecarboxylic acid lactone (IVd). *Anal.* Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.18, 82.01; H, 7.55, 7.53.

See Table I for ultraviolet data for saturated ketones.

Table I

Ultraviolet Absorption Data for the Saturated Ketones

	ε			
$\lambda_{max}^{C_6H_{12}}$, mμ	IIIa	IIIb	IIIc	Lit.[a] for IIIc
252–253	415	414	442	477
258–259	565	535	579	545
265	400	393	433	433

[a] See ref 2.

Registry No.—IIa, 13116-61-5; 2,4-dinitrophenylhydrazone of IIa, 13116-62-6; oxime of IIa, 13116-63-7; IIb, 13116-64-8; IIIa, 13116-65-9; IIIb, 13116-66-0; IIIc, 13116-67-1; IVa, 13116-68-2; IVb, 13116-69-3; IVc, 13116-70-6; IVd, 13116-71-7.

The Stereochemistry of Favorskii Rearrangement of Chloromethyl Ketones[1a]

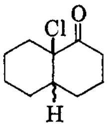
Herbert O. House and Forrest A. Richey, Jr.[1b]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

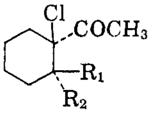
Received January 11, 1967

The *cis* and *trans* isomers of 2-methylcyclohexyl chloromethyl ketone **12** and **13** have been synthesized and allowed to react with sodium methoxide in methanol or in 1,2-dimethoxyethane. In all cases the major volatile products are the two esters **24** and **25** formed in approximately equal amounts by nonstereospecific Favorskii rearrangement. These results indicate that a planar intermediate, presumably an enolate anion, precedes further steps in the Favorskii rearrangement of these compounds.

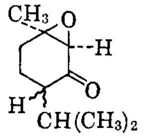
The reactions of α-chloro ketones **1** and **2** and the α,β-epoxy ketone **3** with metal alkoxides[2,3] in aprotic nonpolar solvents such as 1,2-dimethoxyethane (DME) were each found to yield the Favorskii rearrangement product expected from a stereospecific displacement of the α-halogen atom (or epoxide oxygen atom) as illustrated in structure **4** (Scheme I). When the more polar, protic solvent methanol was employed in the same reactions,[2] both solvolysis products (methoxy derivatives) and products of a nonstereospecific Favorskii rearrangement were obtained from ketones **2** and **3** and only solvolysis products were obtained from the decalones **1**. Since the rates of stereospecific rearrangement of the *trans*-chloro ketone **1a** (axial chlorine atom) and the *cis* isomer (mixture of axial and equatorial chlorine atoms) were approximately equal, the expecta-



1a, *trans*-fused rings
b, *cis*-fused rings

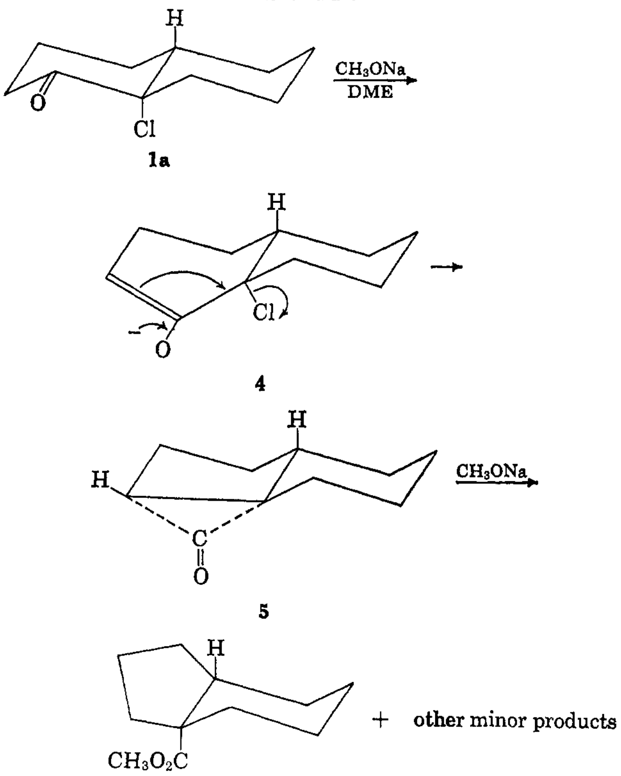


2a, $R_1 = CH_3$; $R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$



3

Scheme I



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[2] (a) H. O. House and W. F. Gilmore, *J. Am. Chem. Soc.*, **83**, 3972, 3980 (1961); (b) H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 164 (1963); (c) H. O. House and G. A. Frank, *ibid.*, **30**, 2948 (1965).

[3] G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **82**, 4307 (1960).