The mixture of alcohols, 2.03 g. of *p*-benzoquinone, 8.1 g. of aluminum *t*-butoxide, and 95 ml. of dry benzene were heated at reflux for 21 hr., cooled, allowed to stand overnight, and filtered from insoluble material, the filter cake was washed with ether, and the combined filtrate and washings were washed successively with ice-cold 10% sulfuric acid, 10% potassium hydroxide, and water. After having been dried over magnesium sulfate, the solution was evaporated under a Vigreux column and the residue sublimed to give 0.50 g. of 2-norbornanone. This material was completely free of norborneols (<0.1%) under conditions (2 m. × 0.5 cm., 20% Ucon LB-550-X on Chromosorb P, at 127° and 10 p.s.i. helium) where the ketone and alcohols were well separated (retention times of 12.9 and 18.9 min., respectively). This material was examined in duplicate solutions in the laboratory of Professor Kurt Mislow with an automatic recording Rudolph spectropolarimeter. The following data were recorded at 23°:

Solution 1, 1.435% in isooctane, showed observed rotations of +0.024° at 320 mμ and of +0.016° at 325 mμ in a 0.1-dm. tube. The specific rotations are thus $[\alpha]_{320}$ +17.6° and $[\alpha]_{325}$ +12.2°. From the respective values for the maximum rotations at these wave lengths[12] (1234 and 983°), the optical purity is calculated to be 1.3%.

Solution 2, 1.695% in isooctane, showed $[\alpha]_{320}$ +18.6° and $[\alpha]_{325}$ +13.0°, whence the optical purity is calculated to be 1.4%.

Control.—As a control experiment on the accuracy of the method at these low rotations and on the possibility of fractionation during oxidation and isolation, the following experiment was performed. A mixture of 0.522 g. of *endo*-norbornyl acid phthalate, $[\alpha]_D$ +2.554° (51.0% optically pure[13]) and 8.588 g. of racemic *exo*-norbornyl acid phthalate was converted to alcohols by steam distillation from 30% sodium hydroxide solution. The crude alcohols were oxidized to ketone by the Oppenauer procedure described above, and the resulting product (which was homogeneous by v.p.c.) was examined in the spectropolarimeter. It showed $[\alpha]_{320}$ +34.3°, $[\alpha]_{325}$ +30.0°, 2.9% optically pure. The optical purity anticipated from the gravimetric composition of the acid phthalate mixture was 2.92%.

B. *exo*-Norbornylamine (Ix).—The conditions were those used[8] in the deamination of *endo*-amine. To a solution of 11.5 g. of (+)-*exo*-norbornylamine, 69.5% optically pure (see above), in 77 ml. of glacial acetic acid was added 11.5 g. of sodium nitrite over a 2-hr. period. After standing overnight, the mixture was treated with 3 g. more of sodium nitrite and stirred an additional 2 hr. Then 30 ml. of water was added, and the mixture was stirred for an hour, cooled, and poured into 320 ml. of cold 20% sodium hydroxide solution while the temperature was kept below 25°. The mixture was extracted with pentane, the extract was washed with water, cold 10% hydrochloric acid, and water, dried over magnesium sulfate, evaporated with a Vigreux column, and the residue was distilled to give three fractions: (1) 0.92 g., b.p. 31–80° (23 mm.); (2) 0.88 g., b.p. 80–84° (23 mm.); (3) 5.36 g., b.p. 84–87° (23 mm.). Fraction 3 was chromatographed on Merck acid-washed alumina. The acetate fraction was cleanly eluted with 20% ether in pentane; the alcohol fraction was eluted with pure ether. The acetate fraction was distilled bulb-to-bulb. It was free of alcohol or nitrate contaminant and contained less than 1% of adhering solvent. Early chromatographic fractions of acetate had $[\alpha]_D$ +1.56° (*c* 20 in HOAc) and later ones had essentially the same rotation, $[\alpha]_D$ +1.61° (*c* 20 in HOAc). Lithium aluminum hydride reduction and analysis of the resulting alcohol mixture with the Ucon capillary column showed the acetate fraction to consist of 97.9% *exo* and 2.1% *endo* material. The alcohol fraction contained approximately 99% *exo* and 1% *endo* material. In a separate run, the composition of the reaction mixture before chromatography was determined by v.p.c. with the TCEP capillary column. This is the source of the figures for % acetate, % alcohol, and % nitrate given in Table I. Three runs under the same conditions followed by examination of the chromatographed acetate fraction gave the following results. Run 1: Amine from (−)-acid of 48% optical purity gave acetate of $[\alpha]_D$ −0.795° (*c* 21 in HOAc). The acetate had the composition 97% *exo*, 3% *endo*. Run 2: Amine from (+)-acid of 69.5% optical purity gave acetate of $[\alpha]_D$ +1.58° (HOAc) containing 98% *exo*, 2% *endo*. Run 3: Amine of the same origin as in run 2 gave acetate of $[\alpha]_D$ +1.46° (HOAc) containing 98% *exo*, 2% *endo*. Control experiments showed that chromatography by the above procedure caused neither fractionation of *endo*- and *exo*-acetates nor racemization of *exo*-acetate.

Acknowledgment.—We are much indebted to Professor Kurt Mislow of New York University for the measurement of the rotations in the ultraviolet.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY, STANFORD, CALIF.]

Optical Rotatory Dispersion Studies. XCV.[1] Effect of Ring Size in Some Bicyclic Ketones[2]

BY CARL DJERASSI AND J. E. GURST

RECEIVED NOVEMBER 13, 1963

A series of bicyclic ketones of known absolute configuration was synthesized, in which the carbonyl-containing ring was five- and six-membered, while the adjacent ring possessed six, seven, or eight carbon atoms. Optical rotatory dispersion measurements demonstrated that the sign of the Cotton effect is not affected by the size of the adjacent ring in saturated bicyclic ketones, but that such a generalization was not warranted in α,β-unsaturated ones. The implications of these results for absolute configurational assignments by means of optical rotatory dispersion are emphasized.

Introduction

The guaianolides and other perhydroazulenes represent an important class of naturally occurring sesquiterpenes,[3] which are being investigated actively in a number of laboratories. Absolute configurational assignments of such sesquiterpenes by chemical correlations have proved to be quite laborious,[4] and frequently recourse has been taken to optical rotatory dispersion measurements.[5,6]

In order to apply the standard rotatory dispersion method[7] to the determination of absolute configuration of such sesquiterpenic ketones, reference compounds of known configuration are required. Since the sesquiterpenes under consideration are based on the bicyclo[5.3.0]decane system (I) with the carbonyl group in the five-membered ring, no direct models were avail-

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(1) Paper XCIV: A. Moscowitz, K. M. Wellman, and C. Djerassi, *Proc. Natl. Acad. Sci. U. S.*, **50**, 799 (1963).

(2) Supported by grants No. GM-06840 and CA-07195 from the National Institutes of Health of the U. S. Public Health Service.

(3) For leading references see (a) T. Nozoe and S. Itô in (L. Zechmeister, Ed.) "Progress in the Chemistry of Organic Natural Products," Vol. 19, Springer, Vienna, 1961, pp. 32–119; (b) W. Herz, W. A. Rohde, K. Rabindran, P. Jayaraman, and N. Viswanathan, *J. Am. Chem. Soc.*, **84**, 3857 (1962).

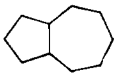
(4) *Inter alia*, E. J. Eisenbraun, T. George, B. Riniker, and C. Djerassi, *ibid.*, **82**, 3648 (1960); L. Dolejš, A. Mironov, and F. Šorm, *Collection Czech. Chem. Commun.*, **26**, 1015 (1961); H. Minato, *Tetrahedron*, **18**, 365 (1962), and earlier references cited therein.

(5) C. Djerassi, J. Osiecki, and W. Herz, *J. Org. Chem.*, **22**, 1361 (1957).

(6) For recent examples see W. Herz, A. Romo de Vivar, J. Romo, and N. Viswanathan, *J. Am. Chem. Soc.*, **85**, 19 (1963); J. B. Hendrickson, *Tetrahedron*, **19**, 1387 (1963).

(7) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, Chapter 10.

able. Instead, recourse was taken[5] to steroidal hydrindanones and it was pointed out that such substances (*e.g.*, II and III) could be employed only if the change in size of the nonoxygenated ring did not produce unexpected conformational changes which would affect the sign of the Cotton effect.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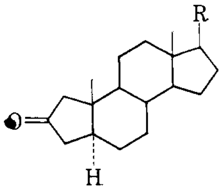

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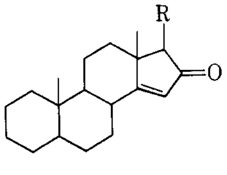

III

Until now, no evidence has been put forward to substantiate or refute the use of hydrindanones as stereochemical models for cyclopentanones of the perhydroazulene series (I). Since this problem is of some importance in the sesquiterpene field as well as of intrinsic interest, a study was undertaken of the effect of the size of the nonoxygenated ring upon the rotatory dispersion of some bicyclic ketones in which the carbonyl function formed part of a cyclopentanone or cyclohexanone.

Synthetic Studies.—Since we had to deal with substances of known absolute configuration, we selected as starting material *trans*-Δ^6-10-methyl-2-octalone (V),[8] which can be prepared readily from the camphorsulfonate IV.[9] The latter had already been related to the steroids and thus represents a convenient absolute configurational standard. Ring enlargement with diazomethane was performed under the same conditions employed earlier[10] in the cholestan-3-one series. The mixture of homologous (seven- and eight-membered) ketones was subjected directly to the Wolff–Kishner reduction[11] and the two olefins VIb and VIc separated by preparative gas-phase chromatography. The purity of the two hydrocarbons was then verified by mass spectrometry.

Using reactions from the steroid series, which have already been employed earlier[8,12,13] among certain octalins, the two olefins VIb and VIc could be transformed into a number of ketones, where the effect of ring size in the nonoxygenated ring upon the optical rotatory dispersion behavior could be evaluated. Thus, peracid oxidation of the olefin VI led to the α-oxide VII,[14] which upon lithium aluminum hydride reduction and oxidation of the axial alcohol VIII provided the seven- (IXb) and eight- (IXc) membered analogs of *trans*-10-methyl-2-decalone (IXa). In order to prepare the corresponding homologs XIIb and XIIc of *trans*-9-methyl-2-decalone (XIIa), the elements of hypobromous acid were added[15] to the olefin VI and the resulting *trans*-bromohydrin was oxidized to the 3-bromo-2-ketone XI and then debrominated with zinc dust in acetic acid solution.

The ketones IXa–c and XIIa–c form part of a six-membered ring. Of particular relevance to the sesquiterpenes mentioned in the Introduction to this paper are the cyclopentanones XIVa–c. These were obtained most effectively by oxidation of the olefin VI with the periodate–permanganate reagent in aqueous *t*-butyl alcohol,[16] followed by pyrolysis[17] of the dibasic acid XIII in the presence of barium hydroxide.

Next, attention was directed to the synthesis of some α,β-unsaturated ketones, in which the size of the nonoxygenated ring was varied. The reason was that earlier work[17–19] had shown that the Cotton effect of α,β-unsaturated bicyclic and polycyclic ketones may be quite sensitive to alterations in the adjacent, nonoxygenated ring, and the presently synthesized ketones represent very interesting model compounds for investigating this point more closely.

For the preparation of the cyclopentenones XVIIa and XVIIb, recourse was taken to a procedure employed recently in the steroid field.[20] Prolonged heating of the cyclopentanone XIV with isopropenyl acetate in the presence of *p*-toluenesulfonic acid afforded the enol acetate XV, which was brominated to give the α-bromo ketone XVI and then dehydrobrominated with lithium chloride in dimethylformamide[21] to yield the desired α,β-unsaturated ketones XVIIa and XVIIb. The rearrangement (XVI → XVII) accompanying such dehydrobromination had already been documented earlier[20] in the steroid field.

For the synthesis of the isomeric cyclohexenone types XIX and XX, advantage was taken of the earlier observation[22] that collidine dehydrobromination of 2α-bromo-3-keto steroids of the 5α-series (see XVIII) affords a separable mixture of the two isomeric Δ^1- and Δ^4-3-ketones.[22a] This sequence has already been performed[22b] in the decalone series (IXa → XVIIIa → XIXa + XXa) and was now employed to prepare the corresponding seven-membered analogs XIXb and XXb.

Catalytic hydrogenation[22b,23] of $\Delta^{1(9)}$-10-methyl-2-octalone (XXa) gives a 4:1 mixture of the *cis*- (XXIa) and *trans*- (IXa) 10-methyl-2-decalone, from which the former can be separated readily by low-temperature crystallization. Hydrogenation under identical conditions of the higher homolog XXb led to a 2:1 *cis–trans* mixture, from which the *cis* isomer XXIb could not be isolated in a completely pure state.

Optical Rotatory Dispersion Results.—The optical rotatory dispersion properties of the *trans*-fused bicyclic ketones IXa–c, XIIa–c, and XIVa–c are collected in Table I. The most important information derived from these data is that the sign of the Cotton effect of a given ketone in this series is not affected by the size of

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[8] C. Djerassi, D. Marshall, and T. Nakano, *J. Am. Chem. Soc.*, **80**, 4853 (1958).

[9] A. J. Speziale, J. A. Stephens, and Q. E. Thompson, *ibid.*, **76**, 5011 (1954). We are deeply indebted to Dr. W. S. Knowles (Monsanto Chemical Co.) for a generous gift of the starting ester IV.

[10] N. A. Nelson and R. N. Schut, *J. Am. Chem. Soc.*, **81**, 6486 (1959).

[11] Huang-Minlon, *ibid.*, **68**, 2487 (1946).

[12] L. H. Zalkow, F. X. Markley, and C. Djerassi, *ibid.*, **82**, 6354 (1960).

[13] D. Herbst and C. Djerassi, *ibid.*, **82**, 4337 (1960).

[14] For pertinent examples in the steroid field see J. G. Phillips and V. D. Parker in "Steroid Reactions," C. Djerassi, Ed., Holden-Day, San Francisco, Calif., 1963, Chapter 14.

[15] For leading references see T. Nakano, M. Hasegawa, and C. Djerassi, *Chem. Pharm. Bull.* (Tokyo), **11**, 465 (1963).

[16] See R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955), and the following two papers; J. T. Edward, D. Holder, W. H. Lunn, and I. Puskos, *ibid.*, **39**, 599 (1961).

[17] C. Djerassi, R. Riniker, and B. Riniker, *J. Am. Chem. Soc.*, **78**, 6362 (1956).

[18] C. Djerassi, R. Riniker, and B. Riniker, *ibid.*, **78**, 6377 (1956).

[19] C. Djerassi, R. Records, E. Bunnenberg, K. Mislow, and A. Moscowitz, *ibid.*, **84**, 870 (1962); see also W. B. Whalley, *Chem. Ind.* (London), 1024 (1962).

[20] W. G. Dauben, G. A. Boswell, and W. H. Templeton, *J. Am. Chem. Soc.*, **83**, 5006 (1961); see also W. F. Johns, *J. Org. Chem.*, **28**, 1616 (1963).

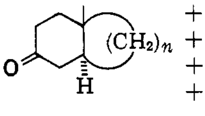
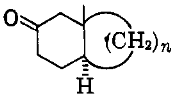
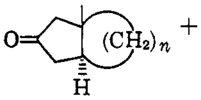
[21] R. P. Holysz, *J. Am. Chem. Soc.*, **75**, 4432 (1953).

[22] (a) C. Djerassi and C. R. Scholz, *ibid.*, **69**, 2404 (1947); (b) C. Djerassi and D. Marshall, *ibid.*, **80**, 3986 (1958).

[23] F. Sondheimer and D. Rosenthal, *ibid.*, **80**, 3995 (1958).

TABLE I

OPTICAL ROTATORY DISPERSION CONSTANTS OF SATURATED BICYCLIC KETONES

Compound	Cotton effect extrema (methanol)				Amplitude	Amplitude reduction
	[Φ]	λ, mμ	[Φ]	λ, mμ	a^a	(MeOH + HCl)
(n = 3)[8] 	+2087	310	−2168	265	+42.5	+10.4 (75%)
IXa (n = 4)	+2328	308	−2826	264	+51.5	+11.3 (78%)
IXb (n = 5)	+2145	307	−1969	260	+41.1	+7.2 (82%)
IXc (n = 6)	+1183	309	−2137	265	+33.2	+4.1 (88%)
XIIa (n = 4) 	+3526	308	−3591	265	+71.2	+57.1 (20%)
XIIb (n = 5)	+2906	307	−3002	264	+59.1	+54.4 (8%)
XIIc (n = 6)	+1889	306	−2868	263	+47.6	+36.7 (13%)
XIVa (n = 4) 	+11,326	312	−10,230	275	+216	...
XIVb (n = 5)	+7810	312	−7810	270	+156	...
XIVc (n = 6)	+7954	313	−8178	272	+161	...

[a] For definition of molecular amplitude see C. Djerassi and W. Klyne, *J. Chem. Soc.*, 4929 (1962).

the adjacent, nonoxygenated ring, at least over the range (five- to eight-membered) covered by us. This generalization applies to cyclohexanones (IX and XII) as well as cyclopentanones (XIV).. Furthermore, ketal formation—as studied by the amplitude reduction of the Cotton effect upon addition of hydrochloric acid to a methanol solution of the ketone[24]—is similarly unaffected by the size of the adjacent ring. Where no serious new 1,3-diaxial interaction is set up (IX), ketal production to the extent of *ca.* 80% is observed, in contrast to the greatly reduced ketal formation (see XIIa–c) when a diaxial interaction with the angular methyl group is generated.

Some quantitative variations are noticeable in Table I. Considering first *trans*-10-methyl-2-decalone (IXa) and *trans*-9-methyl-2-decalone (XIIa), it can be observed that the amplitude of the Cotton effect is lowered when the adjacent ring becomes seven- (IXb, XIIb) or eight- (IXc, XIIc) membered. Presumably, this is a reflection of the much greater conformational mobility of such medium-sized rings, where many different flexible forms may be present, one or more of which may project into a negative octant. The same decrease in amplitude can also be noted when the cyclohexane ring in *trans*-8-methyl-2-hydrindanone (XIVa) is replaced by a cycloheptane (XIVb) or cyclooctane (XIVc) ring. One explanation for this observation may be the one cited above for the corresponding six-membered ketones IX and XII. A second possibility is that fusion of a cyclopentanone with a seven- or eight-membered ring does not produce as much twisting in the cyclopentanone ring as occurs in a hydrindanone (XIVa). Klyne[25] has pointed out that this twist and hence the unsymmetrical nature of the cyclopentanone ring is responsible for the greatly increased amplitudes observed among such hydrindanones (XIVa) as compared to the corresponding decalones (IXa, XIIa).

In any event, the results summarized in Table I permit the important generalizations that, for purposes of absolute configurational assignments, the optical rotatory dispersion approach[5,17] may be employed between substances in which the size of the ring not bearing the carbonyl group is different. *This generalization applies only if additional "nonchromophoric" substituents in the second ring do not alter drastically the conformation of the ketone-containing ring or if these additional substituents do not affect fundamentally the over-all balance of the various octant[26] contributors.*

The conformational flexibility of *cis* fused bicyclic ketones[27] raises complications. Insufficient examples are available to test the effect of ring size—as was done among the *trans* fused ketones—but the single pair of *cis*-10-methyl-2-decalone (XXIa)[22b] and its next higher homolog XXIb suggests that qualitatively the rotatory dispersion picture (see Fig. 1) is not altered greatly

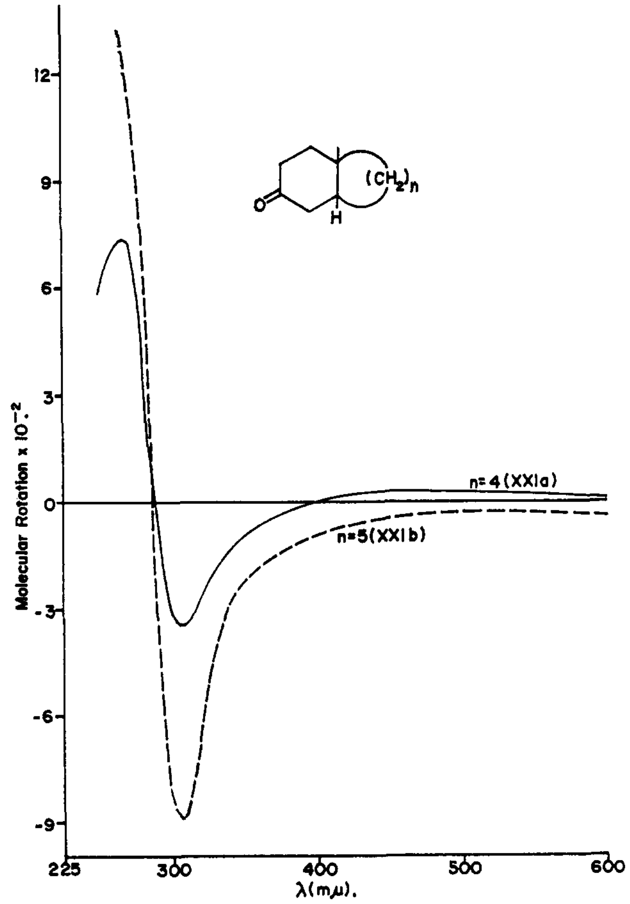


Fig. 1.—Optical rotatory dispersion curves (methanol solution) of *cis*-10-methyl-2-decalone (XXIa) and *cis*-1β-methylbicyclo[5.4.0]-9-undecenone (XXIb).

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[24] C. Djerassi, L. A. Mitscher, and B. J. Mitscher, *J. Am. Chem. Soc.*, **81**, 947 (1959).

[25] W. Klyne, *Tetrahedron*, **13**, 29 (1961); P. M. Bourn and W. Klyne, *J. Chem. Soc.*, 2044 (1960).

[26] See W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

[27] C. Djerassi, J. Burakevich, J. W. Chamberlin, D. Elad, T. Toda, and G. Stork, *ibid.*, **86**, 465 (1964), and references cited therein.

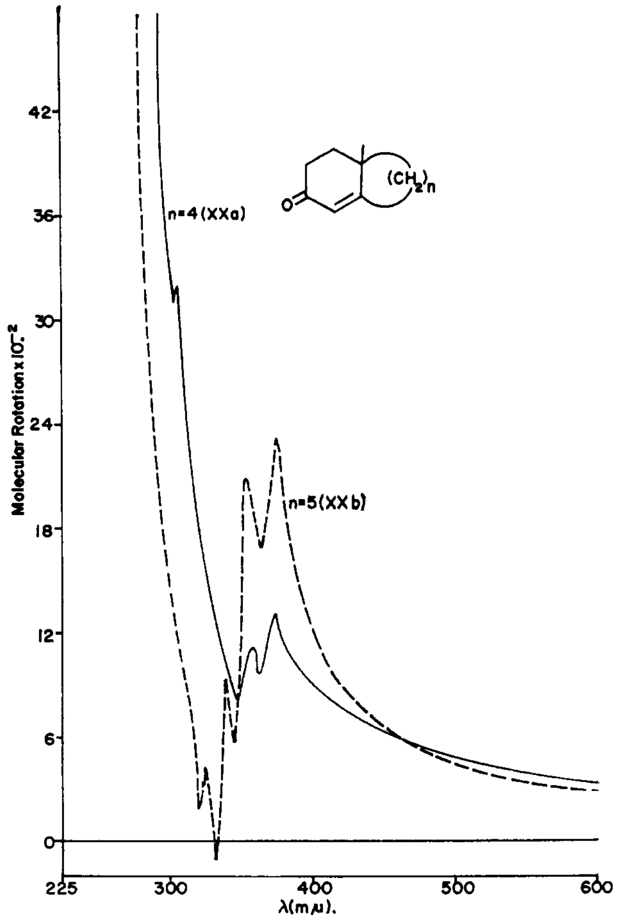
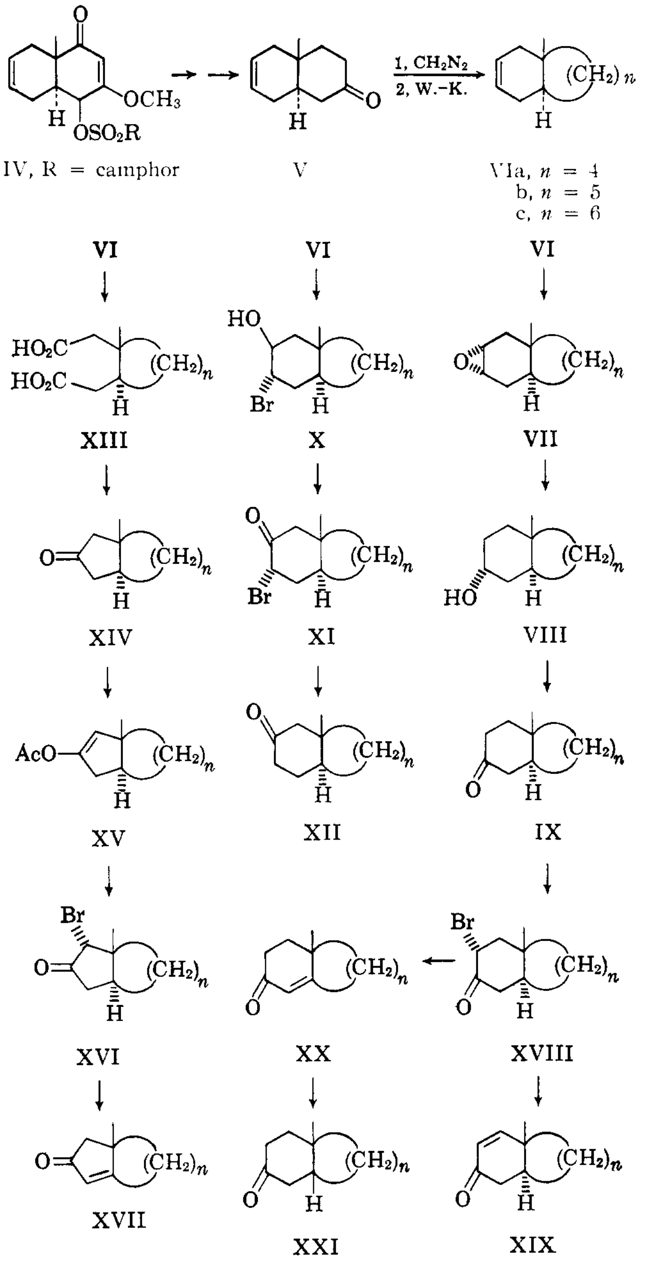


Fig. 2.—Optical rotatory dispersion curves (dioxane solution) of $\Delta^{1(9)}$-10-methyl-2-octalone (XXa) and Δ^{7}-1β-methylbicyclo-[5.4.0]-9-undecenone (XXb).

when the six-membered nonoxygenated ring is replaced by a seven-membered ring.

Rather different results are encountered among the α,β-unsaturated ketones. $\Delta^{1(9)}$-10-Methyl-2-octalone (XXa),[22b] the bicyclic analog of a Δ^4-3-keto steroid, exhibits a multiple Cotton effect (Fig. 2) which still retains its characteristic features upon enlarging the adjacent ring to a seven-membered one (XXb). On the other hand, the homologous pair XIXa (the bicyclic analog of a Δ^1-3-keto steroid) and XIXb exhibit mirror image curves (Fig. 3) even though they belong to the same absolute configurational series. A similar situation is observed among the homologous cyclopentenones XVIIa and XVIIb, where an increase from a six- to a seven-membered ring results in an inversion of the Cotton effect (Fig. 4). As noted earlier,[19] the chirality of the inherently dissymetric α,β-unsaturated keto chromophore plays a crucial role in determining the sign of its Cotton effect and evidently very subtle structural alterations may affect it.

We conclude that in contrast to the situation among the saturated bicyclic ketones, α,β-unsaturated ones should be used only with great caution for absolute configurational assignments and only in those instances[17,18] where the conformational relationship between the reference substance and the (absolute configurationally) unknown compound is unambiguous.



Experimental[28]

(+)-*trans*-Δ^6-10-Methyl-2-octalone (V).—A solution of (+)-*trans*-$\Delta^{3,6}$-10-methyl-2-hexalone[9] (1.0 g.) in 30 cc. of absolute ethanol was shaken in an atmosphere of hydrogen at room temperature and atmospheric pressure in the presence of 200 mg. of 2% palladium-on-calcium carbonate catalyst and 50 cc. of a 2% ethanolic sodium hydroxide solution. Hydrogen uptake corresponding to one equivalent ceased after 2–3 hr., whereupon the catalyst was filtered, the filtrate neutralized with dilute hydrochloric acid, and the product extracted with ether. Distillation at 70° (0.5 mm.) provided in 70% yield the octalone V which solidified at room temperature and whose infrared spectrum was identical with that of a specimen[8] prepared by lithium–ammonia reduction. The purity of the product was substantiated further by the n.m.r. spectrum (unresolved doublet due to olefinic protons at 5.6 p.p.m.), by the absence of ultraviolet absorption in the 230 mμ region, and by the mass spectrometrically determined molecular ion peak at *m/e* 164.

Ring Expansion of (+)-*trans*-Δ^6-10-Methyl-2-octalone (V).—N-Methylnitrosourea (20 g.) was added over a 30-min. period to an

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[28] Melting points were determined on the Kofler block. We are indebted to Dr. L. J. Durham for the n.m.r. studies (Varian A-60 spectrometer, using tetramethylsilane as internal standard and reporting all values in δ-units), to Mrs. R. Records for the optical rotatory dispersion measurements (Japan Spectroscopic Co., Ltd., recording spectropolarimeter), to Dr. H. Budzikiewicz, J. M. Wilson, and M. Ohashi for the mass spectra (CEC mass spectrometer No. 21-103C using an all-glass inlet system heated to 200°), and to Messrs. E. Meier and J. Consul for the microanalyses. All specific rotations at the D line were measured in chloroform solution.

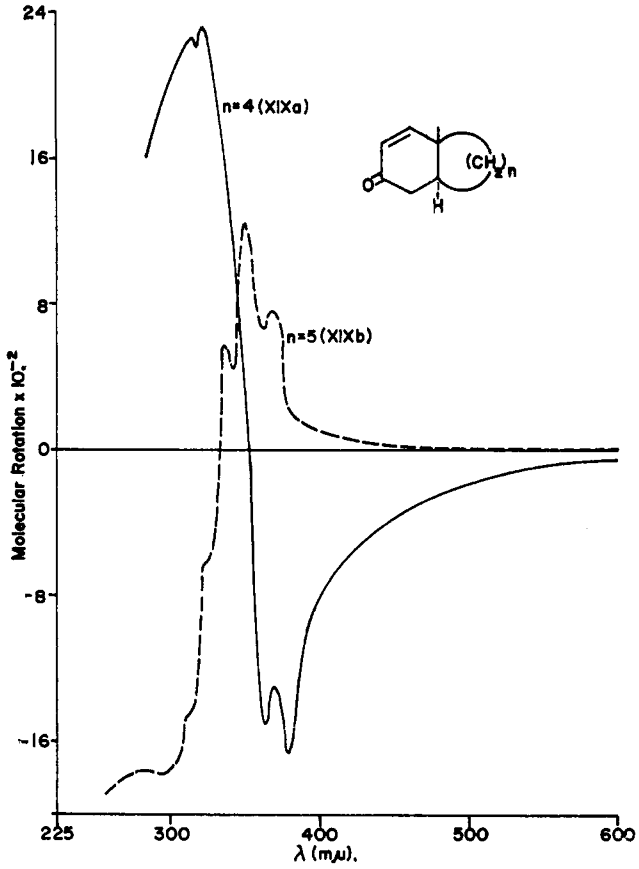

Fig. 3.—Optical rotatory dispersion curves (dioxane solution) of Δ^3-*trans*-10-methyl-2-octalone (XIXa) and Δ^{10}-*trans*-1β-methylbicyclo[5.4.0]-9-undecenone (XIXb).

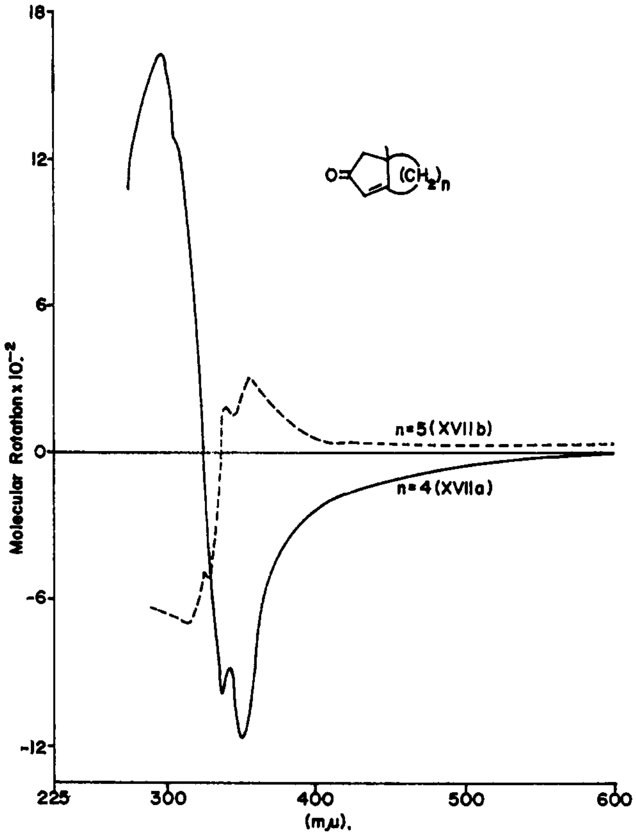

Fig. 4.—Optical rotatory dispersion curves (dioxane solution) of $\Delta^{3(9)}$-8-methylhydrinden-2-one (XVIIa) and Δ^7-1β-methylbicyclo[5.3.0]-9-decenone (XVIIb).

ice-cooled solution of 5.74 g. of the octalone V in 850 cc. of ether, 500 cc. of methanol, and 28 g. of potassium hydroxide. After stirring at 0° for 5 hr., the mixture was neutralized with 300 cc. of 10% hydrochloric acid, filtered, and concentrated, and the product (5.0 g.) was extracted with ether. Analytical gas-phase chromatography demonstrated the presence of several ketones, which in general were not separated but subjected directly to Wolff–Kishner reduction.[11]

The crude product (19.0 g.) from several runs was dissolved in 20 cc. of absolute ethanol and 100 cc. of diethylene glycol. Hydrazine hydrate (95%, 40 cc.) was added and the mixture was heated under reflux in an atmosphere of nitrogen for 1 hr. Upon cooling, 5 g. of potassium hydroxide was added and refluxing was continued for 5 hr., after which time the boiling point was raised to 200° by the distillation of excess hydrazine, ethanol, and water. After maintaining the solution at this temperature overnight, it was acidified with sulfuric acid and extracted with ether; the organic solution was added to an ether extract of the original distillate in which some of the product had been carried over. The resulting oil (14 g.) exhibited no infrared carbonyl band and consisted predominantly of the desired olefins VIb and VIc. Separation was effected by preparative gas-phase chromatography using Ucon polar columns in a Beckman Megachrome instrument operating with 10 p.s.i. of helium at 180°.

The first fraction consisted of 6 g. of (+)-*trans*-1β-**methylbicyclo[5.4.0]-9-undecene** (VIb) with $[\alpha]_D$ +49° (*c* 1.06).

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27; mol. wt., 164. Found: C, 88.08; H, 12.40; mol. wt. (mass spec.), 164.

The more polar fraction was (+)-*trans*-1β-**methylbicyclo[6.4.0]-10-dodecene** (VIc) (3 g.), which exhibited $[\alpha]_D$ +9° (*c* 1.62).

Anal. Calcd. for $C_{13}H_{22}$: C, 87.56; H, 12.44; mol. wt., 178. Found: C, 87.60; H, 12.48; mol. wt. (mass spec.), 178.

***trans*-1β-Methylbicyclo[5.4.0]-9-undecanone (IXb).**—A solution of 1.0 g. of the olefin VIb was kept at room temperature for 24 hr. with 1.2 g. of *p*-nitroperbenzoic acid[29] in 100 cc. of dry ether in the presence of some anhydrous magnesium sulfate. The crude epoxide was isolated in the usual manner and after chromatography on 200 g. of silica gel and elution with 2% ether in hexane led in 74% yield to the **α-oxide VIIb**, which was shown to be homogeneous by thin-layer and gas-phase chromatography; $[\alpha]_D$ ±0°.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.60; H, 10.87.

Lithium aluminum hydride reduction of 640 mg. of the oxide VIIb was effected in the usual manner in ether solution at room temperature. Thin-layer chromatography of the product demonstrated the presence of a major (more mobile) and a minor (less mobile) spot. Separation of the two alcohols was achieved on 50 g. of silica gel with 2% ether in benzene, which provided first the predominant axial **3α-alcohol VIIIb** (475 mg.), which could be crystallized from pentane at −80° to afford crystals with m.p. 56–58°, $[\alpha]_D$ +26° (*c* 1.02).

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.67; H, 12.04.

The more polar minor component (46 mg.) with $[\alpha]_D$ +22° (*c* 0.92) could not be crystallized, but its constitution as the equatorial 3β-epimer of VIIIb was demonstrated by oxidation to the identical ketone IXb.

The axial 3α-alcohol VIIIb was oxidized in 98% yield by the conventional Jones procedure[30] to give the desired **ketone IXb**, which was distilled at 60° (0.08 mm.). The infrared spectrum (film) exhibited a band at 5.85 μ, while the optical rotatory dispersion properties are summarized in Table I.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18; mol. wt., 180. Found: C, 80.19; H, 11.34; mol. wt. (mass spec.), 180.

The semicarbazone of IXb was recrystallized from ethanol whereupon it showed m.p. 195–195.5°.

Anal. Calcd. for $C_{13}H_{23}N_3O$: C, 65.78; H, 9.77; N, 17.72. Found: C, 66.10; H, 10.00; N, 17.66.

The 2,4-dinitrophenylhydrazone crystallized from ethanol as yellow needles, m.p. 141–142°, $\lambda_{\max}^{CHCl_3}$ 368 mμ, log ε 4.29.

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.71; H, 6.72; N, 15.36.

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[29] M. Vilkas, *Bull. soc. chim. France*, 1401 (1959).

[30] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); see also C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

trans-**1β-Methylbicyclo[6.4.0]-10-dodecanone (IXc)**.—The olefin VIc was epoxidized exactly as described above with *p*-nitroperbenzoic acid to the **α-oxide VIIc** ($[\alpha]_D$ −6°), which was then reduced with lithium aluminum hydride and oxidized by the Jones procedure[30] to give the **ketone IXc**, m.p. 46–48°; for rotatory dispersion constants, see Table I.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41; mol. wt., 194. Found: C, 79.90; H, 11.43; mol. wt. (mass spec.), 194.

Recrystallization of the **semicarbazone** from ethanol led to colorless crystals, m.p. 186–188°.

Anal. Calcd. for $C_{14}H_{25}N_3O$: C, 66.89; H, 10.03; N, 16.72. Found: C, 66.70; H, 10.26; N, 16.46.

(+)-*trans*-**9-Methyl-2-decalone (XIIa)**.—To a mixture of 325 mg. of *trans*-9-methyl-2-octalin (VIa)[31] in 10 cc. of dioxane, 1 cc. of water, and 19 cc. of *t*-butyl alcohol was added at room temperature 500 mg. of N-bromosuccinimide in 5 cc. of dioxane as well as 1 cc. of perchloric acid (60%) in 5 cc. of water. After standing for 4 hr., water was added and the product isolated by extraction with ether. Gradient elution chromatography using petroleum ether and benzene on a silica gel (100 g.) column provided 335 mg. of the **bromohydrin Xa**, which was oxidized directly at room temperature in 10 cc. of acetone with 8 *N* chromium trioxide reagent.[30] The crude **bromo ketone XIa** solidified (m.p. 75–78°, $\lambda_{max}^{CHCl_3}$ 5.85 μ) and was debrominated without further purification by dissolving in 15 cc. of glacial acetic acid and stirring at room temperature for 4 hr. with 1 g. of zinc dust. Distillation at 100° (0.1 mm.) gave 275 mg. of the desired decalone XIIa,[32] whose optical rotatory dispersion properties are collected in Table I.

The infrared spectrum (film) exhibits a split carbonyl band centered at 5.88 μ, which may be due to Fermi resonance.[33] This splitting was also observed in cyclohexane solution, while in chloroform only an unsymmetrical peak was encountered. No such band separation was observed in the $\alpha,\alpha,\alpha',\alpha'$-$d_4$-derivative.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92; mol. wt., 166. Found: C, 79.03; H, 10.79; mol. wt. (mass spec.), 166.

The 2,4-dinitrophenylhydrazone of the decalone XIIa crystallized as orange platelets from ethanol; m.p. 176.5–178°, $\lambda_{max}^{CHCl_3}$ 368 mμ (log ε 4.35).

Anal. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.40; N, 16.18. Found: C, 58.85; H, 6.45; N, 16.25.

(+)-*trans*-**1β-Methylbicyclo[5.4.0]-10-undecanone (XIIb)**.—Employing the identical conditions but starting with 430 mg. of the homologous olefin VIb, there was obtained after distillation at 100° (0.1 mm.) 270 mg. of the **ketone XIIb**, λ_{max}^{film} 5.87 μ, whose rotatory dispersion data are collected in Table I.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18; mol. wt., 180. Found: C, 79.62; H, 11.44; mol. wt. (mass spec.), 180.

The 2,4-dinitrophenylhydrazone formed yellow needles after recrystallization from ethanol; m.p. 105.5–107.5°, $\lambda_{max}^{CHCl_3}$ 368 mμ (log ε 4.40).

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.07; H, 6.72; N, 15.83.

(+)-*trans*-**1β-Methylbicyclo[6.4.0]-11-dodecanone (XIIc)**.—In a similar manner, 350 mg. of the olefin VIc was transformed in 45% over-all yield into the **ketone XIIc**, λ_{max}^{film} 5.88 μ; for rotatory dispersion constants, see Table I.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41; mol. wt., 194. Found: C, 80.05; H, 11.17; mol. wt. (mass spec.), 194.

The orange **2,4-dinitrophenylhydrazone** exhibited m.p. 143–143.5°, $\lambda_{max}^{CHCl_3}$ 368 mμ (log ε 4.34).

Anal. Calcd. for $C_{19}H_{26}N_4O_4$: C, 60.94; H, 7.00; N, 14.96. Found: C, 60.79; H, 7.13; N, 14.75.

(+)-*trans*-**1-Methylcycloheptane-1,2-diacetic Acid (XIIIb)**.—To a stirred mixture of 485 mg. of the olefin VIb, 30 cc. of *t*-butyl alcohol, 8 cc. of water, and 300 mg. of potassium carbonate was added dropwise at room temperature over a period of 30 min. a solution of 4 g. of sodium metaperiodate in 50 cc. of water. Simultaneously, sufficient 1% aqueous potassium permanganate solution (total of *ca.* 5 cc.) was added to maintain a pink color. Potassium carbonate was added at periodic intervals to keep the pH at 8. After an additional 2 hr. of stirring, the mixture was concentrated under reduced pressure, sodium bisulfite was added to discharge the color, and after acidification the product was extracted with ether. Crystallization from ether–hexane provided 300 mg. of the **dibasic acid XIIIb**, m.p. 133–133.5°, $[\alpha]_D$ +17° (*c* 1.16).

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.07; H, 8.91.

(+)-*trans*-**1β-Methylbicyclo[5.3.0]-9-decanone (XIVb)**.—An intimate mixture of 120 mg. of the dibasic acid XIIIb and 8 mg. of barium hydroxide was heated at 330° for 30 min. in a microdistillation flask. The contents of the flask were extracted with ether and the ethereal solution was washed with bicarbonate solution, dried, and evaporated. Chromatography on neutral alumina (activity I) and elution with ether–hexane mixtures led to 50 mg. of the desired ketone, which proved to be homogeneous according to thin-layer and gas-phase chromatography; λ_{max}^{film} 5.75 μ. The optical rotatory dispersion data are summarized in Table I.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92; mol. wt., 166. Found: C, 79.25; H, 10.91; mol. wt. (mass spec.), 166.

The 2,4-dinitrophenylhydrazone was recrystallized from aqueous methanol; m.p. 162–162.5°, $\lambda_{max}^{CHCl_3}$ 363 mμ (log ε 4.24).

Anal. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.40; N, 16.18. Found: C, 59.10; H, 6.38; N, 16.13.

(+)-*trans*-**1β-Methylbicyclo[6.3.0]-10-undecanone (XIVc)**.—Periodate–permanganate oxidation of 470 mg. of the olefin VIc in the above-described fashion furnished in 57% yield (−)-*trans*-**1-methylcyclooctane-1,2-diacetic acid (XIIIc)**, m.p. 161–163°, $[\alpha]_D$ −15° (*c* 1.06 in acetone).

Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.23; H, 9.07.

Pyrolysis of 260 mg. of the acid with 20 mg. of barium hydroxide yielded 136 mg. of the required **ketone XIVc**, λ_{max}^{film} 5.75 μ; for optical rotatory dispersion data see Table I.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18; mol. wt., 180. Found: C, 79.64; H, 11.25; mol. wt. (mass spec.), 180.

The yellow **2,4-dinitrophenylhydrazone** was recrystallized from aqueous methanol; m.p. 158.5–159.5°, $\lambda_{max}^{CHCl_3}$ 363 mμ (log ε 4.38).

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.83; H, 6.76; N, 15.60.

Δ^7-**1β-Methylbicyclo[5.3.0]-9-decenone (XVIIb)**.—A mixture of 124 mg. of the ketone XIVb, 10 cc. of isopropenyl acetate, and 150 mg. of *p*-toluenesulfonic acid hydrate was heated under reflux for 7 days and then concentrated under reduced pressure. The residue was taken up in petroleum ether and passed through 10 g. of neutral alumina (activity III) to yield 93 mg. of the **enol acetate XVb**, λ_{max}^{film} 5.65 and 6.10 μ. The material was dissolved immediately in chloroform and a carbon tetrachloride solution of 75 mg. of bromine was added dropwise. The **bromo ketone XVI** was isolated by extraction with ether and purified by passage in benzene solution through a short column of neutral alumina (activity III). The material could not be crystallized, but its structure (XVIb) was confirmed by the infrared spectrum, λ_{max}^{film} 5.70 μ, and especially the n.m.r. spectrum (carbon tetrachloride solution), which exhibited a one-proton singlet at 3.75 p.p.m. due to the proton on the same carbon atom as the bromine atom.

The bromo ketone XVIb was not analyzed, but was dehydrobrominated directly by heating under reflux for 24 hr. (nitrogen atmosphere) with 20 mg. of lithium chloride in 10 cc. of dimethylformamide. The resulting oil (35 mg.) was purified by preparative thin-layer chromatography on silica gel HF_{254} containing a small amount of added disodium salt of 3,5-dihydroxypyrene-8,10-disulfonic acid (Farbenfabriken Bayer, Leverkusen, Germany) with 10% ether in benzene as developer. The appropriate band was located by irradiation with short wave length ultraviolet light; elution with chloroform provided 20 mg. of the oily unsaturated ketone XVIIb which was distilled at 45° (0.1 mm.). The material was homogeneous by thin-layer and gas-phase chromatography and exhibited λ_{max}^{EtOH} 233 mμ (log ε 4.11) as well as n.m.r. signals (carbon tetrachloride) at 1.21 (angular methyl), 2.15 (methylene protons adjacent to carbonyl group), and 5.72 p.p.m. (olefinic proton) in a ratio of 3:2:1; R.D. (Fig. 4) in dioxane (*c* 0.14): $[\Phi]_{589}$ +35°, $[\Phi]_{357}$ +305°, $[\Phi]_{345}$ +145°,

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(31) Prepared by Wolff–Kishner reduction from V as described for the higher homologs VIb and VIc: $[\alpha]_D$ +70°. *Anal.* Calcd. for $C_{11}H_{18}$: C, 87.92; H, 12.08; mol. wt., 150. Found: C, 87.69; H, 12.30; mol. wt. (mass spec.), 150.

(32) The synthesis of the racemic ketone by a different procedure has been reported recently by W. Nagata and I. Kikkawa, *Chem. Pharm. Bull.* (Tokyo), **11**, 289 (1963).

(33) See P. Yates and L. L. Williams, *J. Am. Chem. Soc.*, **80**, 5896 (1958); C. L. Angell, P. J. Krueger, R. Lauzon, L. C. Leitch, K. Noack, R. J. D. Smith, and R. N. Jones, *Spectrochim. Acta*, **11**, 926 (1959).

$[\Phi]_{340}$ +173°, $[\Phi]_{330}$ −393°, $[\Phi]_{326}$ −345°, $[\Phi]_{315}$ −697°, $[\Phi]_{290}$ −644°.

Anal. Calcd. for $C_{11}H_{16}O$: mol. wt., 164. Found: mol. wt. (mass spec.), 164.

$\Delta^{3(9)}$-8-Methylhydrinden-2-one (XVIIa).—Starting with *trans*-8-methylhydrindan-2-one (XIVa)[34] and proceeding in the same fashion as described above for the higher homolog, there was obtained the hydrindenone XVIIa, $\lambda_{\max}^{\mathrm{EtOH}}$ 230 mμ (log ϵ 3.73); n.m.r. signals (carbon tetrachloride) at 1.18, 2.05, and 5.60 p.p.m. with a ratio of 3:2:1; R.D. (Fig. 4) in dioxane (*c* 0.175): $[\Phi]_{589}$ −15°, $[\Phi]_{350}$ −1172°, $[\Phi]_{342}$ −871°, $[\Phi]_{338}$ −991°, $[\Phi]_{295}$ +1622°, $[\Phi]_{275}$ +1082°.

(+)-*trans*-1β-Methyl-10α-bromobicyclo[5.4.0]-9-undecanone (XVIIIb).—Bromine (210 mg.) in acetic acid (5 cc.) was added dropwise to an ice-cooled solution of 230 mg. of the ketone IXb in 5 cc. of glacial acetic acid. After stirring for 30 min. at room temperature, water was added and the product (250 mg.) filtered and recrystallized from aqueous acetone; m.p. 158–162°, $\lambda_{\max}^{\mathrm{KBr}}$ 5.80 μ; R.D. in methanol (*c* 0.265): $[\Phi]_{589}$ +78°, $[\Phi]_{309}$ +1957°, $[\Phi]_{267}$ −2877°, $[\Phi]_{255}$ −2721°.

Anal. Calcd. for $C_{12}H_{19}BrO$: C, 55.61; H, 7.39; Br, 30.84. Found: C, 55.77; H, 7.35; Br, 30.60.

Δ^{10}- (XIXb) and Δ^{7}- (XXb) 1β-Methylbicyclo[5.4.0]-9-undecenone.—The dehydrobromination of 850 mg. of (+)-*trans*-1β-methyl-10α-bromobicyclo[5.4.0]-9-undecanone (XVIIIb) with collidine was performed exactly as described earlier[22b] for *trans*-3-bromo-10-methyl-2-decalone (XVIIIa). Chromatography of the reaction product on 100 g. of activity I neutral alumina provided 230 mg. of the Δ^{10}-(XIXb) and 57 mg. of the Δ^{7}-(XXb) isomers. The former was distilled at 100° (0.1 mm.) to give a clear oil with $\lambda_{\max}^{\mathrm{EtOH}}$ 227 mμ (log ϵ 3.99), $\lambda_{\max}^{\mathrm{film}}$ 5.98 and 6.22 μ; R.D. (Fig. 3) in dioxane (*c* 0.25): $[\Phi]_{589}$ 0°, $[\Phi]_{369}$ +758°, $[\Phi]_{362}$ +660°, $[\Phi]_{351}$ +1239°, $[\Phi]_{342}$ +437°, $[\Phi]_{338}$ +570°, $[\Phi]_{323}$ −632°, $[\Phi]_{295}$ −1792 (infl.), $[\Phi]_{257}$ −1890°.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18; mol. wt., 178. Found: C, 80.50; H, 10.09; mol. wt. (mass spec.), 178.

The red **2,4-dinitrophenylhydrazone of XIXb** was recrystallized from ethanol–chloroform; m.p. 179.5–181.5°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 382 mμ[35] (log ϵ 4.40).

Anal. Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.24; H, 6.32; N, 15.77.

Similar distillation of the Δ^{7}-bicycloundecenone XXb afforded a colorless oil, $\lambda_{\max}^{\mathrm{EtOH}}$ 240 mμ (log ϵ 4.17), $\lambda_{\max}^{\mathrm{film}}$ 6.01 and 6.22 μ; R.D. (Fig. 2) in dioxane (*c* 0.32): $[\Phi]_{589}$ +267°, $[\Phi]_{376}$ +2300°, $[\Phi]_{365}$ +1676°, $[\Phi]_{356}$ +2068°, $[\Phi]_{346}$ +570°, $[\Phi]_{341}$ +909°, $[\Phi]_{333}$ −107°, $[\Phi]_{326}$ +410°, $[\Phi]_{321}$ +196°, $[\Phi]_{310}$ +963 (infl.), $[\Phi]_{270}$ +5526°.

Anal. Calcd. for $C_{12}H_{18}O$: mol. wt., 178. Found: mol. wt. (mass spec.), 178.

The red **2,4-dinitrophenylhydrazone of XXb** was recrystallized from ethanol; m.p. 135–136° (crystal structure change at 124°), $\lambda_{\max}^{\mathrm{CHCl_3}}$ 391 mμ[35] (log ϵ 4.42).

Anal. Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.62; H, 6.05; N, 15.90.

Catalytic Hydrogenation of Δ^{7}-1β-Methylbicyclo[5.4.0]-9-undecenone (XXb).—The catalytic hydrogenation of the enone XXb (100 mg.) was performed in methanol solution with palladium–charcoal catalyst. Under identical conditions, the corresponding octalone XXa provided[22b] without difficulty the pure *cis*-decalone XXIa. In the present instance, the hydrogenation product (absence of conjugation established by ultraviolet absorption spectrum), which could not be crystallized, was homogeneous by thin-layer chromatography and standard gas-phase chromatography. However, when the latter was performed at 200° on a 150 ft. Goulay capillary column (internal diameter 0.002 in.) packed with Carbowax and a helium flow of 15 p.s.i., two components could be observed with retention times of 23 and 24.2 min., of which the latter corresponded to the *trans*-ketone IXb. Analysis of the areas under the peaks indicated the presence of 66 ± 5% *cis* (XXIb) and 34 ± 5% *trans* (IXb) ketone. The optical rotatory dispersion curve (methanol) reproduced in Fig. 1 represents a calculated curve in which the contribution of the *trans* contaminant (34%) has been subtracted.

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(34) For preparation of antipode see ref. 17.

(35) See C. Djerassi and E. Ryan, *J. Am. Chem. Soc.*, **71**, 1000 (1949).

[CONTRIBUTION FROM THE CHANDLER LABORATORIES, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

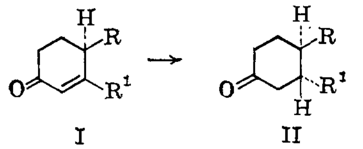
The Stereochemistry of the Lithium–Ammonia Reduction of α,β-Unsaturated Ketones[1]

BY GILBERT STORK AND S. D. DARLING

RECEIVED NOVEMBER 12, 1963

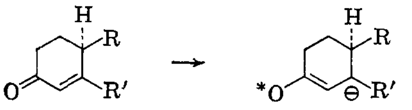
The stereoelectronic requirements which have to be met in the possible transition states for the addition of a proton to the β-carbon of an α,β-unsaturated ketone undergoing reduction with lithium and ammonia are discussed. It is shown that the saturated ketone formed by such a reduction is not simply the more stable of the two possible isomers at the β-carbon. The energies of the stereoelectronically allowed transition states, rather than those of the reduction products, determine the stereochemistry of the latter.

It has been accepted since the classical investigations of Birch that the reaction of ammonia solutions of the alkali metals with α,β-unsaturated ketones involves transfer of electrons with the formation of a carbanionic species which leads, after suitable work-up, to the saturated ketone.[2]

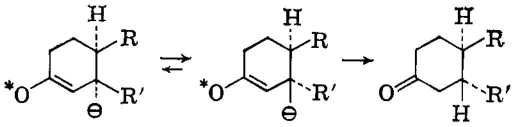


I II

It was noted early that in many cases only one of the two possible epimers of a structure such as II was formed and, as this turned out to be the more stable isomer, it was postulated that rapid equilibration of a carbanion intermediate (*cf.* IIIa → IIIb) must take place, thus leading to the thermodynamically more stable system.[3] In the case of an α,β-unsaturated ketone such as I the product normally obtained would have groups R and R′ *trans* to each other (R and R′ both equatorial).[4]



I III



IIIb IIIa II

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(1) A preliminary communication outlining some of the results in this paper has been published: G. Stork and S. D. Darling, *J. Am. Chem. Soc.*, **82**, 1512 (1960).

(2) *Cf.* A. J. Birch and H. Smith, *Quart. Rev.* (London), **12**, 17 (1958).

(3) D. H. R. Barton and C. H. Robinson, *J. Chem. Soc.*, 3045 (1954).

(4) In all the transition states we have written in this paper, a star is used on the oxygen of the enols to denote either one or two electrons. It is not known whether β-carbon protonation takes place at a radical anion or dianion stage.