vent. The dielectric constants and densities of solutions of various mole fractions were measured at 25° and are listed in Table II. Calculations of the molar polarization were carried out by the method described earlier.[24] The molar refractivities were obtained by addition of the atomic refractivities[25] and the dipole moments were calculated by use of the Debye equation.

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[24] L. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942); see also N. L. Allinger, *ibid.*, **79**, 3443 (1957).

[25] J. A. Leermakers and A. Weissberger in H. Gilman's "Organic Chemistry," Vol. II, 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 1751.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

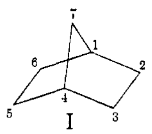
The Synthesis of 2,7-Disubstituted Norbornanes

BY C. H. DEPUY AND P. R. STORY[1]

RECEIVED MAY 15, 1959

A general method for the preparation of 7-keto-norbornanes substituted in the 2-position is reported. The reaction sequence involves the addition of α-acetoxyacrylonitrile to dimethylfulvene, hydrolysis to the ketone, reduction of the carbonyl group and the endocyclic double bond, and ozonolysis. The stereochemistry of lithium aluminum hydride and lithium tri-*t*-butoxyalumino hydride reduction in this and similar systems was investigated and some observations are made about the effect of substituents on the selectivity of catalytic hydrogenation. The keto-acetate IIb is extremely sensitive to base, and hydrolysis is accompanied by ring opening.

The norbornane system I has been one of the most fruitful of all arrangements of atoms for the study of reaction mechanisms. Derivatives of this system exhibit some of the best examples of anchimeric assistance, transannular interactions and steric inhibition to solvolysis to be found in the chemical literature. Indeed, most of the common principles of organic reaction mechanisms could be well illustrated by the reactions of variously substituted norbornanes. Only three structurally isomeric monosubstituted norbornanes can exist.



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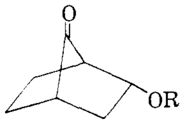
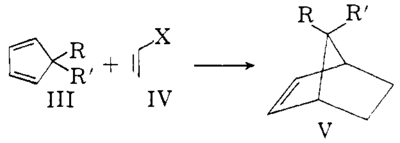


II

A number of excellent methods[2,3] are available for the synthesis of the stereoisomeric 2-substituted compounds and for the so-called bridgehead or 1-substituted norbornanes. Very few 7-substituted compounds have been prepared, however, and the reported methods did not seem very attractive for the studies in which we were interested. We were, consequently, led to the development of a new, general synthesis of 7-ketonorbornanes which allowed, at the same time, the introduction of substituents of known stereochemistry at the 2-position (II). It was anticipated that the precisely known geometry[4] of this bicyclic system would allow a careful study of transannular interactions in nucleophilic reactions to be made, and it was planned also to investigate the properties and reactivity of carbonyl groups in this unique position. The results of some of these studies will be published soon, but it was thought that the synthesis of these molecules was of sufficient interest, and enough potential utility, to warrant separate publication.

At first sight, substituents could easily be introduced at the seven position by a Diels–Alder reaction of a suitably substituted cyclopentadiene (eq. 1). In practice, however, compounds of type III are not at all available. The most favorable compound, cyclopentadienone (III, R,R′ = O), is unknown, and monosubstituted cyclopentadienes (*e.g.*, III, R = H, R = OAc) tautomerize readily due to the acidic proton on the cyclopentadiene ring.[5] 7-Substituted norbornanes have been prepared by rearrangement reactions of bicycloheptadiene and derivatives[6,7] and from acetoxycyclopentadiene and ethylene.[8]



(1)

We determined to attempt the synthesis of II by making use of the Diels–Alder reaction of equation 1 with one of the few types of readily available substituted cyclopentadienes, the fulvenes (III, R,R′ = CR_2). These compounds were known to be reactive in the Diels–Alder reaction,[9] and the product, which would contain a double bond at the 7-position, could be further elaborated through this center of unsaturation. Alder and Ruhmann,[10] and Kohler and Kable[11] had treated a double bond of this type with ozone, and more recently Wilder and Winston[12] had isolated a 7-ketone by this method. There remained the problem of a suitable choice for the dienophile IV. Fortunately, an excellent dienophile for our purpose, α-acetoxyacrylonitrile (VII), has recently been introduced by Bartlett and Tate.[13] This dienophile has the advantage of re-

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[1] Union Carbide Fellow, 1958–1959.

[2] J. D. Roberts, C. C. Lee and W. H. Saunders, THIS JOURNAL, **76**, 4501 (1954).

[3] Elsevier's "Encyclopedia of Organic Chemistry," Vol. 12A, Elsevier Publishing Co., Inc., New York, N. Y., 1948, p. 628.

[4] H. Krieger, *Suomen Kem.*, **31B**, 348 (1958).

[5] M. Rosenblum, THIS JOURNAL, **79**, 3179 (1957).

[6] S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

[7] S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

[8] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

[9] J. H. Day, *Chem. Revs.*, **53**, 167 (1953).

[10] K. Alder and R. Ruhmann, *Ann.*, **566**, 1 (1950).

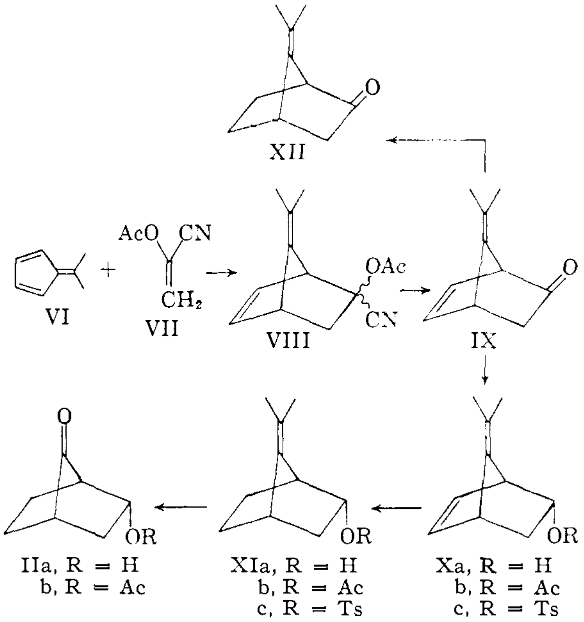
[11] E. P. Kohler and J. Kable, THIS JOURNAL, **57**, 917 (1935).

[12] P. Wilder and A. Winston, *ibid.*, **78**, 868 (1956).

[13] P. D. Bartlett and B. E. Tate, *ibid.*, **78**, 2473 (1956).

taining the activating influence of the cyano group, but the product, upon hydrolysis, is converted to a ketone. By this method a heterosubstituent may be smoothly introduced at position 2. Our synthesis of 2-acetoxy-7-keto-norbornane is outlined in Chart I.

Chart I



In the actual experiment, an excess of dimethylfulvene and the acetoxynitrile reacted smoothly when heated at 55–60° for two weeks in the absence of air. Distillation of the excess fulvene left a mixture of stereoisomeric adducts (VIII), one of which was a crystalline solid. The crude adducts, on treatment with methanolic sodium methoxide, rapidly hydrolyzed to the dienone IX. The overall yield for these two steps is 60% based on nitrile. The ultraviolet absorption spectrum of this dienone showed evidence of transannular interaction between the carbonyl group and the double bonds. The relevant data, which are summarized in Table I, show that the introduction of the double bond at the 7-position results in an increase in the λ_{max} and also in the extinction coefficient[14] over that for norcamphor or dehydronorcomphor.[13,15]

Table I

Ultraviolet Spectra of Some Bicyclic Ketones

Compound	λ_{max}, mμ	ϵ	Ref.
Norcamphor	287	29	13
Dehydronorcamphor	300	292	13
	295	315	15
Dienone IX	308	423	

From literature reports[16,17] we had anticipated that catalytic hydrogenation of the dienone IX would lead exclusively to reduction of the endocyclic double bond. Actually, however, the hydrogenation curve showed only a slight break after the uptake of one mole of hydrogen. When the reaction was stopped after one molar equivalent had reacted, and the products analyzed by gas chromatography, it was found that hydrogenation had proceeded nearly equally at both centers of unsaturation. On the other hand, lithium aluminum hydride reduction of the ketone gave a 90% yield of a crystalline alcohol, and when the acetate or *p*-toluenesulfonate of this alcohol was reduced, hydrogen uptake stopped completely after a single mole-equivalent of hydrogen had been taken up, and excellent yields of the desired dihydro compound were obtained. At first we took this to be evidence that the hydride reduction had produced the *exo*-alcohol, and that the large substituents served to block the 7-double bond from the catalyst surface. We soon showed, however, that the derivatives were actually *endo* (*vide infra*), and therefore their action in directing the catalytic hydrogenation must be more subtle. We now believe that the substituents serve as points of adsorption on the catalyst surface, and consequently control the manner in which the diene is attached to this surface.[18] Thus if the C=O or S=O group were the point of attachment, hydrogen would be absorbed from the under side of the molecule and only the endocyclic double bond would be reduced. On the other hand, the carbonyl in the dienone IX could be adsorbed from either side, and either the exocyclic or endocyclic double bond might be reduced. It is probably significant also that the reduction is highly selective only if the amount of catalyst is kept very low. For reductions of as much as 10 g. of diene we used only 30 mg. of 5% palladium-on-charcoal in 80–90 ml. of solvent. Larger amounts of catalyst led to a more random reduction. Probably the active sites were completely covered by adsorbed substituent. The hydrogenation results are summarized in Table II.

Table II

Selectivity in the Hydrogenation of Some Bicyclic Dienes

Compound	Amount of hydrogenation Δ^5	Δ^7
Dienone IX	70	30
Dienol Xa	60	40
Dienol acetate Xb	95	5
Dienol tosylate Xc	>95	..

The final step in the sequence, ozonolysis, was the only one in which excellent yields could not be obtained. The reaction was complicated by rearrangements, and higher boiling, polyoxygen compounds were formed as by-products. Nevertheless, by carrying out the ozonolysis at −35° in methylene chloride, yields as high as 45% of the keto-acetate IIb could be obtained. This keto-acetate was a liquid, and exhibited the characteristic[12,19,20] 5.62 μ band of a 7-ketone. Its structure was proved by treating it with ethanedithiol and BF$_3$ etherate. The resultant thioketal XIII was reduced with Raney nickel to an acetate which, on hydrolysis, gave

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(14) H. L. McMurray, *J. Chem. Phys.*, **9**, 231 (1941).

(15) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

(16) R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine and R. R. Whetstone, This Journal, **64**, 1985 (1942).

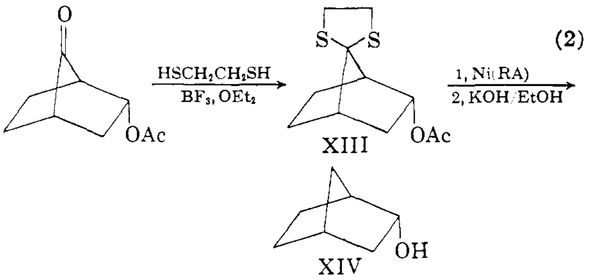
(17) R. B. Woodward and H. Baer, *ibid.*, **66**, 645 (1944).

(18) H. I. Hadler, *Experientia*, **11**, 175 (1955).

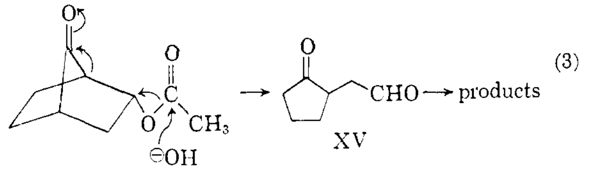
(19) C. F. H. Allen and J. A. Van Allen, *J. Org. Chem.*, **20**, 323 (1955).

(20) C. F. H. Allen, T. Davis, D. W. Stewart and J. A. Van Allen, *ibid.*, **20**, 306 (1955).

endo-norborneol (XIV) in 68% over-all yield. Thus the 2-acetoxyl group was shown to be *endo*.



Although the chemistry of these compounds will be discussed more thoroughly in forthcoming publications, one reaction is worthy of note. The keto-acetate IIb is remarkably sensitive to base, and hydrolyzes completely in a few minutes at room temperature with dilute alcoholic base. The product is not the expected ketol IIa, but instead is an uncharacterizable mixture which displays no infrared absorption below 5.75 μ in the carbonyl region. Apparently the hydrolysis had been accompanied by a reverse aldol condensation, as in equation 3. The keto-aldehyde XV could not be isolated from the basic reaction mixture, but if the hydrolysis were carried out in acid solution, an oil was obtained which had an infrared spectrum consistent with that expected for XV, and which was readily oxidized to a keto acid. The extremely rapid hydrolysis of the keto-acetate indicates that the ring opening must be simultaneous with hydrolysis and provide a driving force for it. This retroaldol must be especially favorable because of the release of steric strain with which it is accompanied, and also, we feel, because the carbon–carbon bond which is being broken (C_1–C_2) is very favorably oriented in space with respect to the π-orbitals of the 7-ketone. Consequently, overlap between the developing anion and the carbonyl group can take place in the very early stages of the reaction.



The highly stereospecific lithium aluminum hydride reduction of the dienone IX was useful in eliminating the problem of separating diastereomers, but it also made the isolation of the *exo*-alcohols more difficult. We were therefore led to study more carefully, with the invaluable aid of gas chromatography, the stereospecificity of hydride reductions in some bicyclo[2,2,1] systems. Literature reports[21] are conflicting about the products to be expected from such reductions, and we were especially interested in examining the stereospecificity of lithium tri-*t*-butoxy-alumino hydride,[21e] for little work with this useful reagent has been reported. We also studied the relative stability of the alcohols being formed in these reductions by equilibrating them with aluminum isopropoxide. At the same time the reduction and equilibration of norcamphor and dehydronorcamphor were investigated. The results of these experiments are reported in Table III, as well as those of Hirsjarvi[21b] for the reduction of norcamphor with lithium aluminum hydride.

TABLE III

PERCENTAGE *endo* ISOMER FORMED IN THE REDUCTION AND EQUILIBRATION OF SOME BICYCLIC KETONES

Compound	$LiAlH_4$	$LiAlH(t\text{-}OBu)_3$	Equil.[a]
Dienone IX	89	93	56
Monoenone XII	94	98	52
Dehydronorcamphor	91	77	65
Norcamphor	92[b]	>92[c]	~50[c]

[a] With aluminum isopropoxide and acetone. [b] From ref. 21b. [c] Incomplete resolution makes these values approximate.

The equilibration studies show that there is little difference in the thermodynamic stabilities of the *exo*- and *endo*-alcohols. On the other hand, attack on these bicyclic systems is appreciably less sterically hindered from the *exo* side.[22] It appears that the reduction is that expected from what Dauben[21a] has called "steric approach control." The most important result at the moment, however, is that the stereospecificity of the reduction is increased by use of the tri-*t*-butoxy hydride, and that the actual yields of isolable *endo*-alcohol can be increased by the use of this reagent. The result with dehydronorcamphor demonstrates that this greater specificity is not always to be expected.

The equilibration experiments showed that this was the most reasonable route to the epimeric *exo*-alcohols. These alcohols are apparently oils, and while we have been able to obtain samples of them with as little as 20% of the *endo* isomer as a contaminant, they have so far eluded complete purification. We intend to pursue this separation further.

Acknowledgment.—We wish to express our gratitude to Eastman Chemical Products, Inc., Kingsport, Tenn., for a generous gift of α-acetoxyacrylonitrile, without which this work would have been impossible.

Experimental

Melting and boiling points are uncorrected. Analyses were performed by Midwest Microlab, Indianapolis, Ind. Gas chromatographic analyses were performed using an apparatus constructed from a Gow-Mac thermal conductivity cell. The columns were 10′ to 12.5′ × 1/4″ copper tubes. Ketones and esters were analyzed using a packing which was 27% by weight a mixture of 2/3 Apiezon-M and 1/3 Dow-Corning Silicon 702 on firebrick. The alcohols were analyzed using a packing 23% by weight Ucon 50-HB-2000[23] on Celite. Catalytic hydrogenations were carried out in an especially designed apparatus which was suitable for the atmospheric pressure reduction of relatively large amounts of material.[24]

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[21] (a) W. G. Dauben, G. J. Fonken and D. S. Noyce, THIS JOURNAL, **78**, 2579 (1956); (b) P. Hirsjarvi, *Ann. Acad. Sci. Fennicae* AII, **81** (1957); (c) O. H. Wheeler and J. L. Mateos, *Can. J. Chem.*, **36**, 1431 (1958); (d) S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956); (e) H. C. Brown and R. F. McFarlin, THIS JOURNAL, **80**, 5372 (1958); (f) W. Hückel and M. Hanack, *Ann.*, **616**, 18 (1958).

[22] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

[23] Available from Union Carbide Chem. Co. Described as a water-soluble monoalkyl ether of a mixed polyoxyethylene-oxypropylene.

[24] P. R. Story and C. H. DePuy, *J. Chem. Ed.*, in press.

Dimethylfulvene was prepared from acetone and cyclopentadiene according to the procedure of Crane, *et al.*[25]

α-Acetoxyacrylonitrile was generously supplied in part by Eastman Chemical Products, Inc., Kingsport, Tenn., and in part was prepared from the reaction of ketene and HCN according to the method of Johnston and Newton.[26] In our hands the best yields (80%) were obtained with potassium acetate as a catalyst.

2-Acetoxy-2-cyano-7-isopropylidene-bicyclo[2,2,1]-5-heptene (VIII).—Dimethylfulvene (100 g., 0.94 mole) and α-acetoxyacrylonitrile (50 g., 0.45 mole) were heated at 55–60° for 15 days in a stoppered flask which had been flushed with nitrogen. Most of the excess fulvene was removed at 35° under vacuum, and the resultant mushy solid washed with 200 ml. of pentane. Filtration gave 60 g. (61% yield) of the solid isomer. The cyanoacetate was generally hydrolyzed without further purification. An analytical sample recrystallized three times from pentane melted at 122.5–123.5°. It had infrared peaks ($CHCl_3$) at 4.44 and 5.75 μ.

Anal. Calcd. for $C_{13}H_{15}O_2N$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.92; H, 6.79; N, 6.50.

7-Isopropylidene-bicyclo[2,2,1]-5-heptene-2-one (IX).—The solid cyanoacetate (60 g., 0.28 mole) was dissolved in 530 ml. of 1 *N* sodium methoxide in methanol and allowed to stand at room temperature for three hours. At the end of that time 1700 ml. of a mixture of ice and water was added and the ketone extracted with methylene chloride. After washing with water and drying over sodium sulfate, the solvent was removed and the product distilled to yield 24 g. (60% yield) of yellow ketone, b.p. 46° (0.3 mm.). The pentane washings of the solid cyanoacetate (*vide supra*) were hydrolyzed, after removal of the solvent, in a similar way. From 76 g. of this heavy oil an additional 16 g. of ketone IX was formed. The combined yield of dienone IX, based on α-acetoxyacrylonitrile, was 60%. The ketone had an infrared absorption maximum at 5.77μ. It could not be completely freed from traces of dimethylfulvene, but it formed a semi-carbazone, m.p. 209–210° dec., in nearly quantitative yield.

Anal. Calcd. for $C_{11}H_{15}ON_3$: C, 64.36; H, 7.37; N, 20.47. Found: C, 64.32; H, 7.19; N, 20.40.

***endo*-7-Isopropylidene-bicyclo[2,2,1]-5-heptene-2-ol (Xa).**—The dienone IX (10 g., 0.067 mole) was reduced with lithium aluminum hydride (10 g., 0.067 mole) in the usual way. The excess hydride was destroyed with a slurry of wet sodium sulfate, the ether filtered, the solid washed with an additional portion of ether, and the combined extracts dried. The solvent was carefully removed (the alcohol product is very volatile) and the dienol recrystallized from pentane. It formed beautiful, long, thin needles, m.p. 74–75°. The yield of crystalline product was 8 g. (80%).

Anal. Calcd. for $C_{10}H_{12}O$: C, 79.95; H, 9.39. Found: C, 80.06; H, 9.48.

Gas chromatographic analysis of the crude reduction product, before recrystallization, showed it to contain 88–90% *endo*-alcohol and 12–10% *exo*-alcohol. The mother liquors from the recrystallization contained roughly equal amounts of the two alcohols, but despite repeated attempts by various methods they could not be separated. The *exo* isomer is apparently an oil at room temperature.

The *endo*-dienol Xa was converted to its acetate, b.p. 66–68° (0.4 mm.), in 92% yield with pyridine and acetic anhydride. The tosylate, m.p. 65.5–66.5° (from pentane), was prepared by the method of Tipson.[27]

Anal. Calcd. for $C_{17}H_{20}O_3S$: C, 67.09; H, 6.62; S, 10.52. Found: C, 67.06; H, 6.64; S, 10.61.

The dienol Xa was also prepared on a small scale by reduction of the ketone with lithium tri-*t*-butoxyalumino hydride. *t*-Butyl alcohol (2 ml.) was slowly added to a cold solution of 400 mg. of lithium aluminum hydride in 30 ml. of tetrahydrofuran. The dienone IX (1.0 g., 0.0067 mole) in 30 ml. of THF was slowly added to the cold solution and the reaction mixture was stirred at 0° for 0.5 hour and at room temperature for an additional hour. The solution was acidified with 1 *N* HCl and extracted with ether. The ether layer was washed with $NaHCO_3$ solution, dried and the solvent carefully removed. Gas phase chromatography analysis of the product showed it to be 94% *endo*-X.

***endo*-2-Acetoxy-7-isopropylidene-bicyclo[2,2,1]-heptane (XIb) (Monoene-acetate).**—The *endo*-diene-acetate Xb (4 g., 0.021 mole) was catalytically reduced at atmospheric pressure in a mixture of 45 ml. of 95% alcohol and 45 ml. of ether. The catalyst was 32 mg. of 5% palladium-on-charcoal (U. S. Plat. Co.). The apparatus has already been described.[24] Hydrogenation stopped after the uptake of one equivalent of hydrogen. Gas phase chromatography and infrared[28] analysis of the crude product indicated that 95% of the product was that resulting from reduction of the endocyclic double bond. Distillation yielded 3.65 g. (90% yield) of the acetate, b.p. 48–50° (0.2 mm.).

***endo*-7-Isopropylidene-bicyclo[2,2,1]-2-heptanol (XIa) (Monoeneol).**—This alcohol was prepared in three different ways. The dienone IX was catalytically reduced as described for the acetate. G.p.c. analysis showed that the product was 70% that expected from hydrogenation of the endocyclic double bond. Lithium aluminum hydride reduction of the crude reduction product gave an oily product from which the *endo*-alcohol could be separated by crystallization from pentane. G.p.c. analysis of the crude reduction mixture showed that the *endo–exo* ratio in the reduction was 97:3. Pure *endo*-monoeneol had m.p. 81.5–82.5°. The same alcohol was obtained by saponification of a portion of the monoene-acetate XIb with KOH in ethanol, and also by catalytic hydrogenation of the dienol Xa. In the latter case only 61% of the product was that resulting from reduction of the endocyclic double bond. When either the dienol or dienone was catalytically reduced, hydrogen uptake did not stop after the absorption of one mole-equivalent of hydrogen.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.66; H, 10.31.

Monoene-tosylate XIc could best be prepared by catalytic hydrogenation of the diene-tosylate Xc. Hydrogen uptake stopped after the absorption of one mole of hydrogen, and removal of solvent gave a quantitative yield of practically pure tosylate. An analytical sample was prepared by recrystallization from pentane, m.p. 72.3–72.8°. The same tosylate was prepared by the reaction of tosyl chloride with the monoene alcohol XIa.

Anal. Calcd. for $C_{17}H_{22}O_3S$: C, 66.65; H, 7.24; S, 10.44. Found: C, 66.37; H, 7.39; S, 10.24.

***endo*-2-Acetoxy-bicyclo[2,2,1]-heptanone-7 (IIb) (Keto-acetate).**—The monoene-acetate XIb (7.2 g., 0.037 mole) was dissolved in 200 ml. of methylene chloride, cooled to −35° and treated with a stream of ozone. Absorption of ozone ceased (as indicated by a sodium iodide trap placed in series after the reaction vessel) after the uptake of one molar equivalent. The methylene chloride solution was washed with saturated sodium chloride and dried over anhydrous sodium sulfate. After careful removal of the solvent the product was distilled. The keto-acetate had a boiling point of 57° (0.5 mm.) and showed strong absorption at 5.62 and 5.75 μ. The yield was 2.8 g. (45%).

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.40; H, 7.46.

The 2,4-dinitrophenylhydrazone was formed in the usual way, m.p. 150–151°.

Anal. Calcd. for $C_{15}H_{16}O_6N_4$: C, 51.72; H, 4.63. Found: C, 51.52; H, 4.83.

The remainder of the product from the ozonolysis was an oil which distilled at 120° (0.5 mm.) and analyzed for the original monoene-acetate plus three atoms of oxygen.

Ozonolyses were also attempted in methanol, acetic acid and ethyl acetate. No improvement in yield was observed.

Reduction of the Keto-acetate to *endo*-Norborneol.—The keto actate (1.0 g., 0.006 mole) was dissolved in a mixture of 25 ml. of boron trifluoride etherate and 2.5 ml. of ethanedithiol and allowed to stand at room temperature overnight. The reaction mixture was diluted with water, extracted with ether, the ether washed, dried and finally distilled. The oily product, which no longer had an infrared band at 5.60 μ, was dissolved in 50 ml. of absolute ethanol and 18 g. of W-7 Raney nickel[29] was added. The mixture

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[25] G. Crane, C. E. Boord and A. L. Henne, This Journal, **67**, 1237 (1945).

[26] F. Johnston and L. W. Newton, U. S. Patent 2,395,930 (1946).

[27] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[28] P. von R. Schleyer, This Journal, **80**, 1700 (1958).

[29] H. R. Billica and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 176.

was heated at reflux for one hour, filtered, and potassium hydroxide, 2 g., was added. After standing for 12 hours the solution was diluted with water and the product extracted with ether. After removal of the ether there remained 0.45 g. (70% yield) of a solid, m.p. 130–142°. Two crystallizations from pentane gave 0.34 g. (51%) of pure *endo*-norborneol, m.p. and mixed melting point with an authentic sample 149–150°.[3,30] *exo*-Norborneol melts at 127–128°.[3,30]

Hydrolysis of the *endo*-Keto-acetate IIb.—The keto-acetate (100 mg., 0.0006 mole) was dissolved in 1.5 ml. of 1 *N* sodium methoxide in methanol. After 4 minutes at room temperature water was added and the mixture was extracted with ether. The product, about 90 mg., was a neutral amorphous solid which had infrared bands at 5.75 and 6.1 μ. It readily absorbed Br_2 in CCl_4. In a separate experiment 200 mg. of the keto acetate was heated at reflux for 1.5 hours with 5 ml. of 2 *N* aqueous HCl. Extraction with methylene chloride gave a good yield of a colorless oil which had infrared peaks at 5.75 (cyclopentanone) and 3.75 and 5.81 μ (aldehyde). Oxidation with $KMnO_4$ gave an oily keto acid (100 mg.); infrared peaks at 5.75 and 5.83, and a broad peak in -OH region.

Equilibration of Alcohols.—In a typical experiment the alcohol (5 g., 0.03 mole), aluminum isopropoxide (6.8 g., 0.03 mole) and acetone (0.1 ml.) were dissolved in 100 ml. of pure dry isopropyl alcohol. The mixture was heated at reflux for 72 or 120 hours, dilute acid was added and the products extracted with ether. The extracts were washed, dried and the solvent removed. The products were analyzed by g.p.c. Identical results were obtained after 72 and 120 hours of heating.

AMES, IOWA

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(30) H. Toivonen, *Ann. Acad. Sci. Fennicae*, AII, **72**, 1 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Cyclopentene-3,5-dione. II. Conversion to Cyclopentadienone

BY C. H. DEPUY AND C. E. LYONS

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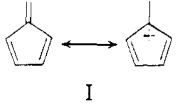
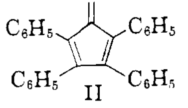
Cyclopentene-3,5-dione has been converted into its anthracene adduct and thence, by methylation and reduction, into the anthracene adduct of cyclopentadienone. On pyrolysis at 350° a reverse Diels–Alder reaction takes place and anthracene and cyclopentadienone (I) are formed. The latter immediately undergoes dimerization followed by decarbonylation to yield 8,9-dihydroindenone (X). An authentic sample of the dimer of cyclopentadienone has also been pyrolyzed and shown to give the same product. An attempted synthesis of β-methoxycyclopentadienone by an analogous method also led, apparently, to dimeric products.

In recent years a number of unsaturated, odd-numbered ring compounds have been prepared whose remarkable stability may be ascribed to the fact that their rings contain $4n + 2\pi$-electrons. Among these compounds may be mentioned cyclopheptatrienone,[1] diphenylcyclopropenone[2] and diazocyclopentadiene.[3] The first two of these owe their stability to the fact that the oxygen of the carbonyl group withdraws electrons, leading to rings with 6- and 2π-electrons, respectively. In the last case the diazo grouping donates electrons, leading again to six electrons in a single cycle. The success of the $4n + 2$ rule is made even more striking when it is recognized that no simple planar molecules which violate it have been prepared in stable form. The numerous attempts to prepare the simplest example, cyclobutadiene, are extremely well known. In many ways cyclopentadienone (I) would be an even more valuable example of such a system to have available for study, since the reactivity of the carbonyl group could readily be correlated with that of more normally situated ones, and studies of the reactivity of cyclopentadienone as a diene and/or dienophile in the Diels–Alder reaction and spectral studies of a variety of types would shed a great deal of light on the electronic interactions in this interesting molecule.



I



II

Until recently,[4] cyclopentadienone itself had never been formed. Nevertheless, a number of substituted cyclopentadienones are known and in general show some remarkable properties.[5,6] Tetraphenylcyclopentadienone (II) which has been studied more extensively perhaps than any other cyclopentadienone,[7] is a black-violet compound whose spectral properties have occasioned interest.[8] With fewer than three phenyl groups attached to the nucleus cyclopentadienones are ordinarily dimers, although sometimes the dimers dissociate to monomers in solution. Allen and Van Allan[6] have summarized the structural requirements for the existance of monomeric and dissociable dimeric cyclopentadienones. Cyclopentadienone oxime may be prepared from cyclopentadiene and ethylnitrite,[9] but exists solely in the dimeric form.

Two recent reports indicate that cyclopentadienones may be prepared, at least transiently, by pyrolysis of their Diels–Alder adducts. Pavolini[10] pyrolyzed what was claimed to be the anthracene adduct of 3-methylcyclopentadienone (III). When heated beyond its melting point of 231°, the adduct regenerated anthracene and a second compound which gave a correct analysis for 3-methylcyclopentadienone, although its boiling point (218–220°) was surprisingly high. This compound readily polymerized, but was not otherwise characterized.

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(2) R. Breslow, R. Haynie and J. Mirra, *ibid.*, **81**, 247 (1959).

(3) W. von E. Doering and C. H. DePuy, *ibid.*, **75**, 5955 (1953).

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(5) For leading references see C. F. H. Allen, *Chem. Revs.*, **37**, 209 (1945).

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(9) J. Thiele, *Ber.*, **33**, 669 (1900).

(10) T. Pavolini, F. Gambarin and L. Verza, *Ann. chim.*, **42**, 158 (1952).