temperature for 1 hr. and under reflux for 2 hr. with 1 g. of freshly prepared W-2 Raney nickel.[27] The cooled mixture was filtered and the ethanol was removed affording 25 mg. (93.7%) of white solid with an infrared spectrum which was indistinguishable from that of racemic lactone **17**. After two recrystallizations from hexane, 11 mg. of material with m.p. 119–121° was obtained.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.64; H, 9.97. Found: C, 75.7; H, 9.9.

The close similarity of the n.m.r. spectrum of this material with that of the racemic lactone **17** further substantiated the structure assigned to **17**.[28]

Acknowledgment.—We thank the Public Health Service for support of this work through a Research Grant (AI-04965, National Institute of Allergy and Infectious Diseases) and a Fellowship (5-Fl-GM-19,839 to N. Cohen).

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[27] R. Mozingo, *Org. Syn.*, **21**, 15 (1941).

[28] A Varian A-60 spectrometer was used.

Bicyclic Ketones. II. The 2-Acetylbicyclo[2.2.1]hept-5-ene and 2-Acetylbicyclo[2.2.1]heptane Systems[1,2]

J. GRAY DINWIDDIE, JR., AND SAMUEL P. MCMANUS[3]

Department of Chemistry and Geology, Clemson University, Clemson, South Carolina

Received July 13, 1964

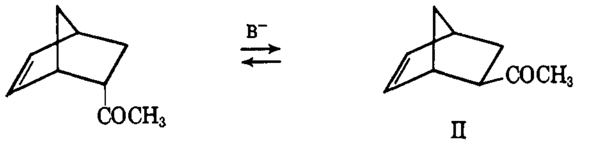
The base-catalyzed equilibration of mixtures of *endo-* and *exo*-2-acetylbicyclo[2.2.1]hept-5-ene and of mixtures of their saturated derivatives was studied as a means of preparing the pure ketone isomers. The equilibrium constants, $K_{exo-endo}$, were determined to be 2.25 and 3.25, respectively. Each isomer has been separated and characterized by derivatives.

Although the Diels–Alder adduct of cyclopentadiene and methyl vinyl ketone has been known for some time,[4-6] no reports were found concerning the stereochemistry of the product. Laszlo and Schleyer[7] have recently separated *endo*-2-acetylbicyclo[2.2.1]hept-5-ene (I) from the Diels–Alder adduct mixture by preparative vapor phase chromatography (v.p.c.). Isomer I was one of a number of *endo*-2-bicyclo[2.2.1]-hept-5-en-2-yl derivatives used in a study of their n.m.r. spectra. For our purposes, however, larger quantities of I and *exo*-2-acetylbicyclo[2.2.1]hept-5-ene (II) were needed in connection with another problem.[8] It was thought to be of interest to investigate the *endo–exo* equilibrium of the Diels–Alder mixture of I and II and to attempt to use this as means of getting both isomers from the *endo*-rich[9] mixture.

Results and Discussion

The Diels–Alder reaction between methyl vinyl ketone and cyclopentadiene proceeded exothermally in diethyl ether to give a near quantitative yield of the adduct mixture of I and II. Analysis of the adduct by v.p.c. showed the mixture to be composed of 62% I and 38% II. It was determined during purification of the mixture by distillation, that some separation of the isomers was occurring although no change in boiling point was observed. The *exo* isomer II was predominant in the early fractions.

A procedure similar to that of Cope, Ciganek, and LeBel[10] was used for equilibration to enrich the mixture in isomer II, and possibly to make distillation a feasible method for obtaining pure II. Mixtures of I and II of varying compositions were equilibrated with sodium methoxide in refluxing absolute methanol. The resulting mixtures were analyzed by v.p.c. The results of the epimerizations and the calculated equilibrium constants, $K_{exo-endo}$, are shown in Table I. The standard free energy ($\Delta G°$), at 338.6°K. for the process I $\rightleftharpoons$ II, using the equilibrium constant obtained, is calculated to be −550 cal./mole.



I

II

TABLE I

RESULTS OF THE EQUILIBRATION OF I AND II

Starting compn.		Hr. of reflux	Final compn.		
% *endo*	% *exo*		% *endo*	% *exo*	$K_{exo-endo}$
92	8	240	33.1	66.9	2.02
90	10	44	30.2	69.8	2.31
50	50	44	31.3	68.7	2.18
20	80	44	28.7	71.3	2.54
5	95	36	31.7	68.3	2.15
		Av.	31.0	69.0	2.25
		Std. dev.	1.65	1.65	0.20

It would appear that, due to the structural similarities between the bicyclo[2.2.1]hept-5-en-2-yl ketones (I and II) and the methyl esters (III and IV) of the corresponding carboxylic acids, the relative position of equilibrium would be very similar. This is not the

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[1] Paper I: J. G. Dinwiddie and S. P. McManus, *J. Org. Chem.*, **28**, 2416 (1963).

[2] Presented in part at the 37th Annual Meeting of the South Carolina Academy of Science, Aiken, S. C., April 25, 1964.

[3] Abstracted from the thesis presented by S. P. M. in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May 1964.

[4] A. F. Plate and T. A. Meerovich, *Bull. acad. sci. URSS, Classe sci. chim.*, 219 (1947); *Chem. Abstr.*, **42**, 5440 (1948).

[5] A. A. Petrov and N. P. Sopov, *J. Gen. Chem. USSR* (Eng. Transl.), **24**, 301 (1954).

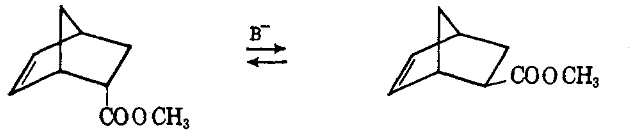
[6] C. J. Knuth, A. Bavley, and W. A. Lazier, *J. Org. Chem.*, **19**, 845 (1954).

[7] P. Laszlo and P. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2709 (1963).

[8] J. G. Dinwiddie, Jr., and S. P. McManus, paper in preparation.

[9] The *endo* isomer is predicted by "Alder's Rules": see K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

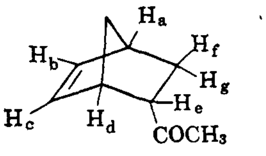
[10] A. C. Cope, E. Ciganek, and N. A. LeBel, *J. Am. Chem. Soc.*, **81**, 2799 (1959).



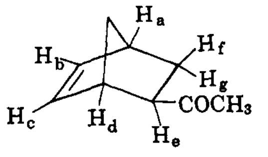
III IV

case. The K-value for the process III $\rightleftharpoons$ IV was found to be 0.961 at 73.6°.[10] Actually the equilibrium value of the esters appears to be anomalous.[11] Examination of molecular models reveals a possible interference of free rotation of the methoxyl group by the *syn* C-7 hydrogen in IV, whereas no serious interactions of this type are apparent in the *exo* ketone II. Both I and III have possible steric interactions between the ethylene bridge and the methyl group.[12]

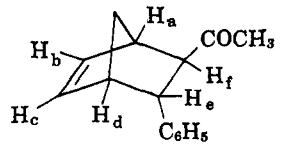
The n.m.r. spectrum of I was compared with the values recorded by Laszlo and Schleyer.[7] Except for a downfield shift of 5 c.p.s., our values were identical with those reported. Comparing the spectra of I and II proved interesting. The vinyl protons, H_b and H_c, of I appeared as two symmetrical quartets (J_{ab}, J_{cd} = 2.8, 3.1 c.p.s., respectively) centered at 349 and 366 c.p.s. The vinyl protons for II, however, appeared as a triplet (J = 1.9 c.p.s.) centered at 367 c.p.s. This substituent effect was investigated further using similar compounds. The n.m.r. spectrum of *exo*-2-acetyl-*endo*-3-phenylbicyclo[2.2.1]hept-5-ene (V)[8] showed two quartets (J_{ab}, J_{cd} = 3.0, 3.1 c.p.s., respectively) for the vinyl protons centered at 360 and 380 c.p.s. 4-Acetylcyclohexene,[13] which exists largely in the quasi-equatorial form VI, showed a triplet (J = 1.5 c.p.s.) for its vinyl protons at 340 c.p.s.



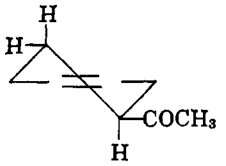
I



II



V



VI

Since Laszlo and Schleyer[7] reported obtaining an eight-line multiplet for all of the *endo*-2-bicyclo[2.2.1]-hept-5-enyl derivatives which they studied, it appears that the eight-line multiplet in this type compound is due to either steric or electronic effects (or a combination of the two) between the *endo* substituent and H_c which makes H_b and H_c unequal. In compounds where the substituent is *exo*, the group is far enough removed from the olefinic center to allow the olefinic protons to be equal. The triplet observed for II and VI is identical in appearance with that of bicyclo[2.2.1]-hept-2-ene and bicyclo[2.2.1]heptadiene,[14] both of which have adjacent olefinic protons which are identical.

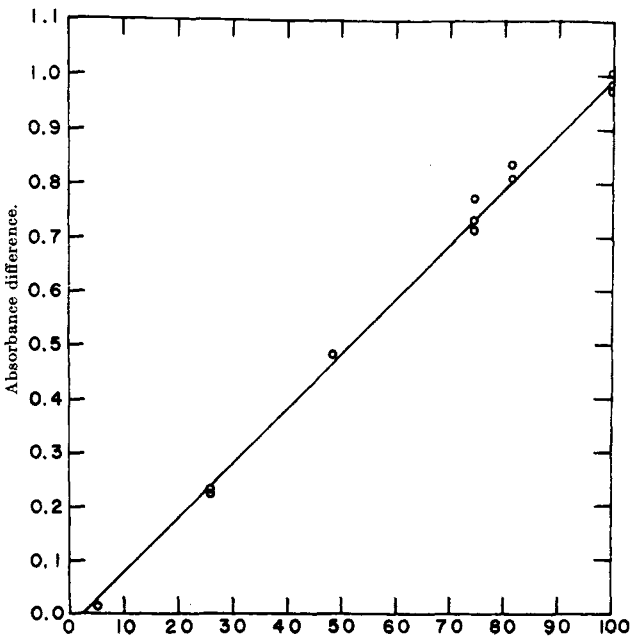
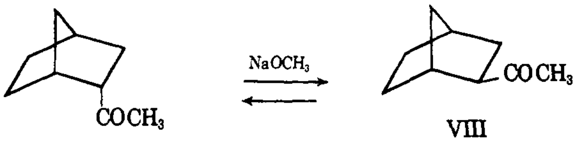


Figure 1.—Quantitative determination of the per cent of VIII in mixtures of VII and VIII using infrared spectroscopy.

Mixtures of I and II readily reduced to *endo*- and *exo*-2-acetylbicyclo[2.2.1]heptane (VII and VIII, respectively). Separation of these isomers could not be effected by vapor phase chromatography[15] with columns which readily separated I and II. It was found that by applying the empirical ratio method,[16] quantitative infrared could be used to analyze mixtures of VII and VIII. The results are plotted in Figure 1.

Equilibration of a mixture of VII and VIII with sodium methoxide in methanol and analysis of the equilibrium mixture by the infrared procedure gave a value of $K_{exo-endo}$ = 3.25, which corresponds to 76.5% VIII. The free-energy change is calculated to be −790 cal./mole at 338.6°K. The increase in the equilibrium constant is to be expected since interference in the *endo* derivative VII is enhanced with addition of another hydrogen to C-6 which now places one of the hydrogens in a quasi-axial position. This allows a more effective interaction between the *endo* 6-H and the acetyl group than was possible with the



VII VIII

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[11] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 303-304.

[12] Recent work has shown that the bulky atoms prefer conformations away from the ethylene bridge; however, all possible interactions must be considered in order to reach a logical conclusion: see L. P. Kuhn, P. R. Schleyer, W. F. Baitinger and L. E. Berson, *J. Am. Chem. Soc.*, **86**, 650 (1964).

[13] Prepared by the method of A. A. Petrov [*J. Gen. Chem. USSR* (Eng. Transl.), **11**, 309 (1941)]; b.p. 55° (5 mm.), $n^{20}{}_D$ 1.4692.

[14] Serial numbers 240 and 243 of the American Petroleum Institute Project No. 44, Chemical Thermodynamic Properties Center, Department of Chemistry, A. and M. College of Texas, College Station, Texas.

[15] R. S. Bly (private communication) also has had trouble separating *endo*- and *exo*-bicyclo[2.2.1]heptane derivatives by v.p.c. Certain nitrile derivatives have been used successfully as substrates, however, in some cases: *cf.* ref. 10, and J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **86**, 1749 (1964), and references cited therein.

[16] (a) Wright, *Ind. Eng. Chem., Anal. Ed.*, **13**, 1 (1941); (b) W. H. Brown, R. E. Ansel, C. A. Lucchesi, and J. D. McGinness, *Offic. Dig., Federation Soc. Paint Technol.*, **33**, 54 (1961).

C-6 hydrogen on the trigonal carbon of I or with the π-electrons of the double bond.

Samples of VII and VIII, pure enough for most purposes, could be prepared by reduction of the purest samples of I and II obtained by distillation. Derivatives were prepared and the physical constants of ketones VII and VIII were compared with those previously reported.[17-19]

Experimental[20]

Reaction of Methyl Vinyl Ketone with Cyclopentadiene.—A cooled solution of 125 g. (1.78 moles) of methyl vinyl ketone in 150 ml. of ethyl ether was mixed with 132 g. (2.0 moles) of freshly distilled cyclopentadiene in 150 ml. of ether and was allowed to warm to room temperature. The heat of the reaction vigorously refluxed the solvent. After standing overnight, the solvent was removed to give a mixture of *endo*- and *exo*-2-acetylbicyclo[2.2.1]-hept-5-ene (I and II). Distillation gave the colorless mixture: b.p. 72–73° (12 mm.), $n^{20}\text{D}$ 1.4880; lit.[4] b.p. 48–48.5° (2 mm.), $n^{20}\text{D}$ 1.4841; and lit.[5] b.p. 84–86° (18 mm.), $n^{20}\text{D}$ 1.4856.

The mixtures obtained from three separate reactions were analyzed by gas chromatography (v.p.c.). Analyses were carried out at 175° at a flow rate of 90 ml./min. on a 0.25-in.-o.d. 2-m. column packed with Ucon oil LB-550-X on 60–100-mesh diatomaceous earth, Perkin-Elmer column R_x. The method was found from analysis of known mixtures to be accurate to ±3%. Retention time of the *exo* isomer was 10.8 min. compared to 13.0 min. for the *endo* isomer.

Sample no.	Av. % *exo*	Av. % *endo*
1	40.6	59.4
2	39.0	61.0
3	34.4	65.6
Av.	38.0	62.0

Isomerization of the Mixture of I and II with Sodium Methoxide in Absolute Methanol.—Several equilibrations were run by treating mixtures of I and II of varying compositions with an equal weight of sodium methoxide in a 20-fold excess of refluxing absolute methanol (65.4°). After a certain amount of time, samples were diluted with water, extracted with ether, and dried over anhydrous magnesium sulfate. The ether solutions were analyzed by v.p.c. procedures. Runs were analyzed more than once to obtain mean values, which are reported in Table I.

Separation of I and II by Distillation.—Mixtures of I and II of varying compositions were distilled using a Precision Distillation GE-197 spinning-band column (about 75 theoretical plates) operating at 1800 r.p.m. It was found that there was no noticeable difference in boiling point between I and II since at the same temperature and pressure both isomers were obtained, although the *exo* predominated in the early fractions. For maximum separation, a distillation pressure of 50 mm. (b.p. 100–101°) was found to be best, since above this pressure considerable decomposition and polymerization occurred.

Distillation of 125 g. of a mixture of I (45%) and II (55%) gave fractions shown by v.p.c. analysis to be composed of (1) 20 g., 85% *exo;* (2) 25 g., 80% *exo;* (3) 20 g., 70%; *exo;* (4) 15 g., 50% *exo;* (5) 15 g., 10% *exo;* and (6) 5 g., 10% *exo*. Redistillation of fractions 2 and 3 gave in the first fraction 12 g. of material shown to be 95% *exo*-2-acetylbicyclo[2.2.1]hept-5-ene (II), $n^{20}\text{D}$ 1.4823.

The 2,4-dinitrophenylhydrazone of II was prepared and recrystallized from ethanol–ethyl acetate, m.p. 159–160°. After three other recrystallizations from the same solvent, the yellow crystals melted at 163–164°.

Anal. Calcd. for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.10; N, 17.71. Found: C, 56.98; H, 5.10; N, 17.66.

The oxime was prepared from 26.5 g. of the ketone, 40 ml. of absolute ethanol, 25 g. of hydroxylamine hydrochloride, and 75 ml. of dry pyridine. The 27.3-g. yield crystallized from petroleum ether (b.p. 30–60°) as fluffy white crystals, m.p. 54–55°. After three further recrystallizations, the pure material melted at 58–59°.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.44; H, 8.80; N, 9.42.

Distillation, by the same procedure as above, of 50 g. of an *endo*-rich fraction (~80% *endo* by v.p.c.) gave 10 g. of I which was analyzed by v.p.c. and shown to be 95% *endo*-2-acetylbicyclo-[2.2.1]hept-5-ene, $n^{20}\text{D}$ 1.4843.

The 2,4-dinitrophenylhydrazone of I was prepared from a small amount of an *endo*-rich distillation fraction. The melting point rose steadily to a constant reading, after ten recrystallizations from ethanol–ethyl acetate, of 129–130°.

Anal. Calcd. for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.10; N, 17.71. Found: C, 56.94; H, 5.04; N, 17.66.

The oxime of I was prepared in theoretical yield by refluxing 23 g. of the ketone with 24.5 g. of hydroxylamine hydrochloride and 100 ml. of absolute ethanol in 150 ml. of pyridine for 4 hr. Eight recrystallizations from petroleum ether (b.p. 30–60°) changed the melting point from 38–42° to the steady 74–75° value of the analytical sample.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.61; H, 8.81; N, 9.13.

***exo*-2-Acetylbicyclo[2.2.1]heptane (VIII).**—Reduction of II, as prepared above, using 10% palladium on carbon in ethanol, yielded VIII. Only one peak was obtained by v.p.c. analysis using 2-m. columns packed with either Ucon LB-550-X oil, silicone grease, or silicone 710 fluid. Distillation of the purest VIII gave a mixture of VII and VIII, rich in VIII: b.p. 91° (30 mm.), $n^{24}\text{D}$ 1.4710, lit.[18] $n^{24}\text{D}$ 1.4709, and lit.[17] $n^{25}\text{D}$ 1.4710. Comparison with Stockmann's pure sample[19] of VIII showed slight impurities due to the *endo* isomer VII.

The 2,4-dinitrophenylhydrazone (2,4-DNP) prepared in the normal way crystallized from ethanol–ethyl acetate as transparent orange-red plates, m.p. 112–113°. After filtration, the material apparently underwent a polymorphic transformation changing rapidly to opaque yellow crystals, m.p. 132–133°, m.m.p. 111–115° with the yellow crystals of the 2,4-DNP of VII.

Anal. Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.60; H, 5.70; N, 17.60. Found: C, 56.55; H, 5.70; N, 17.56.

The oxime prepared by the alcohol–pyridine procedure crystallized from petroleum ether (b.p. 30–60°) as white needles, m.p. 41–42°. The analytical sample melted at 43–44°.

Anal. Calcd. for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.75; H, 9.84; N, 9.07.

Preparation of *endo*-2-Acetylbicyclo[2.2.1]heptane (VII).—To a suspension of 0.1 g. of 10% palladium on carbon in 25 ml. of ethanol was added 0.5 g. of I (95% by v.p.c.). The mixture was shaken for 1 hr. at 40 p.s.i. and then filtered to remove the catalyst. The solvent was removed *in vacuo* to leave 0.5 g. of the light yellow oil, $n^{25}\text{D}$ 1.4722, lit.[17] $n^{25}\text{D}$ 1.4723.

The 2,4-dinitrophenylhydrazone prepared in the usual manner crystallized as orange-red plates, m.p. 104–105°. Two more recrystallizations from ethyl acetate–ethanol gave the pure derivative, m.p. 107–108°. After standing for about 30 hr., the derivative had slowly transformed into cloudy yellow crystals, m.p. 117–118°. Recrystallization, however, gave back the initial product ruling out any isomerization.

Anal. Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.60; H, 5.70; N, 17.60. Found: C, 56.77; H, 5.57; N, 17.75.

Equilibration of *endo*- and *exo*-2-Acetylbicyclo[2.2.1]heptane.—To a solution of 7.23 g. of a mixture of VII and VIII in 50 ml. of absolute methanol was added 7.08 g. of sodium methoxide. The mixture was refluxed under nitrogen (65.4°) for 48 hr., then poured into water. Ether was used to extract the ketone mixture from the aqueous methanol solution. The ether extracts were dried and evaporated.

Because of the inability to analyze the mixtures of VII and VIII by v.p.c., the empirical ratio method of infrared analysis was used. Known mixtures of VII and VIII were prepared by either mixing pure VII with known mixtures of VII and VIII or

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(17) J. A. Berson and S. Suzuki, *J. Am. Chem. Soc.*, **81**, 4088 (1959).

(18) H. Stockmann, *J. Org. Chem.*, **29**, 245 (1964).

(19) We wish to thank Dr. M. R. Lytton, American Viscose Division, FMC Corp., for a generous sample of VIII, prepared by Stockmann, ref. 18.

(20) Analyses were performed by Alfred Bernhardt, Mülheim (Ruhr), West Germany. Infrared spectra were taken on a Perkin-Elmer Model 221 spectrophotometer as liquid films or in Irtran-2 (zinc sulfide) cells. A Perkin-Elmer Model 154D vapor fractometer was used for vapor phase chromatography work. N.m.r. spectra were obtained in carbon tetrachloride solution on a Varian A-60 instrument using tetramethylsilane as the internal reference. Melting points were taken using a Hershberg apparatus and are uncorrected.

by reducing known mixtures of I and II. The mixtures were placed in 0.1-mm. Irtran-2 cells and the infrared spectra from 11.0 to 12.4 μ were recorded. The difference between the absorbance value of the 11.9-μ maximum (due to VIII) and the value of the minimum at 11.7 μ was plotted *vs.* per cent of VIII (see Figure 1). The value obtained in the same way for the equilibration mixture gave, from the curve, 76.5% *exo*- and 23.5% *endo*-2-acetylbicyclo[2.2.1]heptane.

A New Diene-Addition Reaction of Steroids. The Synthesis of Steroidal Analogs Containing a Substituted Bicyclo[2.2.1]heptene System[1]

A. J. SOLO,[2] H. S. SACHDEV, AND S. S. H. GILANI

Department of Medicinal Chemistry, School of Pharmacy, State University of New York at Buffalo, Buffalo 14, New York

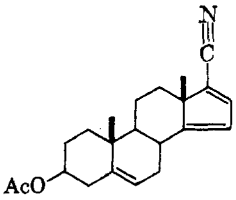
Received November 5, 1964

The D-ring diene system of 3β-acetoxy-17-cyano-5,14,16-androstatriene (I) has been found to undergo the Diels–Alder reaction. Maleic anhydride, acrolein, methyl acrylate, and 4-phenyl-1,2,4-triazoline-3,5-dione (IV) have been added to I. The scope of the reaction and the stereochemistry of the adducts are discussed.

A number of steroids having double bonds at the 14- and 16-positions have been reported.[3] These ring-D conjugated dienes are considered to be highly reactive,[4] a conclusion which has thus far been based on the ease with which such systems undergo catalytic hydrogenation,[4,5] on analogy, and on the reported difficulty of introducing two units of unsaturation into the D-ring of steroids.[6] However, to our knowledge, the Diels–Alder reactivity of these systems has not been determined.

The product of such a diene addition would constitute a novel system in which the bridged D-ring may be viewed as a bicyclo[2.2.1]heptene-2 with a nitrile substituted at position 1, and with ring C of the steroid bridging positions 4 and 7. Moreover, the stereochemistry of the D-ring of such a system would correspond closely with that of one of the rotomers of 17α-alkyl or 17α-O-acyl steroids. Since 17α-substituted progesterone and testosterone derivatives are known to possess high biological activity,[7] the ring-D bridged analogs of these hormones might also be expected to be active.

3β-Acetoxy-17-cyano-5,14,16-androstatriene[5] (I) was chosen as starting material since, of the known 14,16-dienes, it appeared relatively to be both readily available and capable of being converted to the desired hormone analogs. Initial attempts to effect reaction of I with maleic anhydride in refluxing benzene or xylene failed. However, heating I overnight at 95–100° in an excess of molten maleic anhydride resulted in formation of adduct II in 69% yield. The reaction could most conveniently be followed by n.m.r. spectroscopy. The starting material (I) has peaks at δ 5.96 and 7.07 arising from the 15- and 16-vinyl hydrogens, respectively. These peaks are replaced in adduct II by a pair of doublets at δ 6.22 and 6.47.



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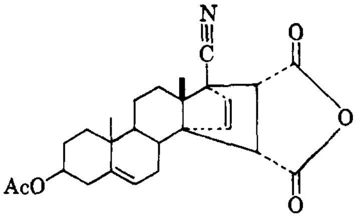
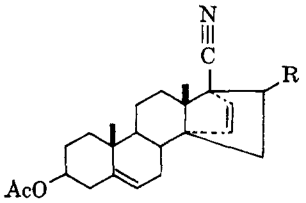


II

Heating I in acrolein at 105–107° for 64 hr. afforded adduct IIIa in 27% yield. The ring-D vinyl hydrogens of this substance appeared in the n.m.r. spectrum at δ 5.97 and 6.28.

Similarly, heating I in an excess of methyl acrylate at 115° for 7 days resulted in the formation of adduct IIIb in 69% yield. The n.m.r. spectrum of this substance has peaks at δ 5.88 and 6.20 corresponding to the ring-D vinyl hydrogens.



IIIa, R = CHO

b, $R = \underset{\underset{\displaystyle O}{\|}}{C}{-}OMe$

Substitution of electron-withdrawing substituents on a conjugated diene is known to lower the reactivity of the diene toward normal dienophiles.[8] In a recent study, 1-cyanocyclohexa-1,3-diene was reported to be so deactivated toward Diels–Alder reaction that it underwent rearrangement prior to addition.[9] The above addition reactions, therefore, demonstrate high Diels–Alder reactivity for steroidal 14,16-dienes.

The recent report of Sauer and Wiest[10] indicates that while substitution of electron-withdrawing groups on a double bond normally increases the activity of the olefin as a dienophile, the inverse effect is observed if the diene is heavily substituted with electron-with-

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[1] This work was supported, in part, by Grants AM-06900-01 and AM-06900-02 (National Institute of Arthritis and Metabolic Diseases), and 2 G-555-R 1 (Division of General Medical Sciences) from the National Institutes of Health, U. S. Public Health Service.

[2] To whom inquiries regarding this work should be addressed.

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