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OXYMERCURATION OF *ENDO*- AND *EXO*-DICYCLOPENTADIENES

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Abstract—Both *endo*- and *exo*-dicyclopentadienes are found to undergo oxymercuration in water and methanol, without rearrangement of the skeleton, to give *exo-cis* addition at the 5- and 6-positions. The structures have been proved by the stereospecific reduction of the mercurials with sodium amalgam, followed by hydrogenation to the corresponding saturated alcohols and ethers, which have been synthesized independently. NMR studies of the mercurials and a deuterated ether resulting from the sodium amalgam–deuterium oxide reduction of the methoxy mercuration product of *endo*-dicyclopentadiene have fixed the geometry of the mercury. Several interesting compounds in this series, which were previously unknown, have been prepared and characterized.

INTRODUCTION

Hofmann and Seiller[1] found that *endo*-dicyclopentadiene (I) adds on mercuric chloride in methanol to give it a 1:1 adduct of the diolefin and the elements of $Hg(OCH_3)Cl$. Giua and Polla[2] prepared an analogous compound, using water instead of methanol. In the latter stages of the present investigation, a paper appeared by Traylor and Baker,[3,4] in which some evidence was given that the adduct of Giua and Polla is III. The most commonly accepted mechanism for these reactions has been that proposed by Winstein *et al.*,[5] involving preliminary coordination of the olefin to the mercury atom, followed by formation of a mercurinium ion, which could be opened by the solvent, through intramolecular attack by a hydroxyl group,[6,7] or neighboring carbon.[8]

The reaction of *endo*-dicyclopentadiene with platinum$^{(II)}$ salts affords a compound,[9] which has recently been shown by X-ray crystallography to be XIX.[10] On standing for several weeks in methanol,[10] or on the addition of a small amount of sodium acetate to the refluxing methanolic suspension,[11] the compound underwent solvent attack to give a product which has been formulated as the sigma bonded platinum complex XX. This series of reactions resembles the mechanism of Winstein *et al.*

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[2] M. Giua and G. Polla, *Chim. e industr.* **35**, 888 (1953).
[3] T. G. Traylor and A. W. Baker, *Tetrahedron Letters* No. 19, 14 (1959).
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[6] J. Sand and F. Singer, *Ber. Dtsch. Chem. Ges.* **35**, 3170 (1902).
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[8] S. Winstein and M. Shatavsky, *Chem. & Ind.* 56 (1956).
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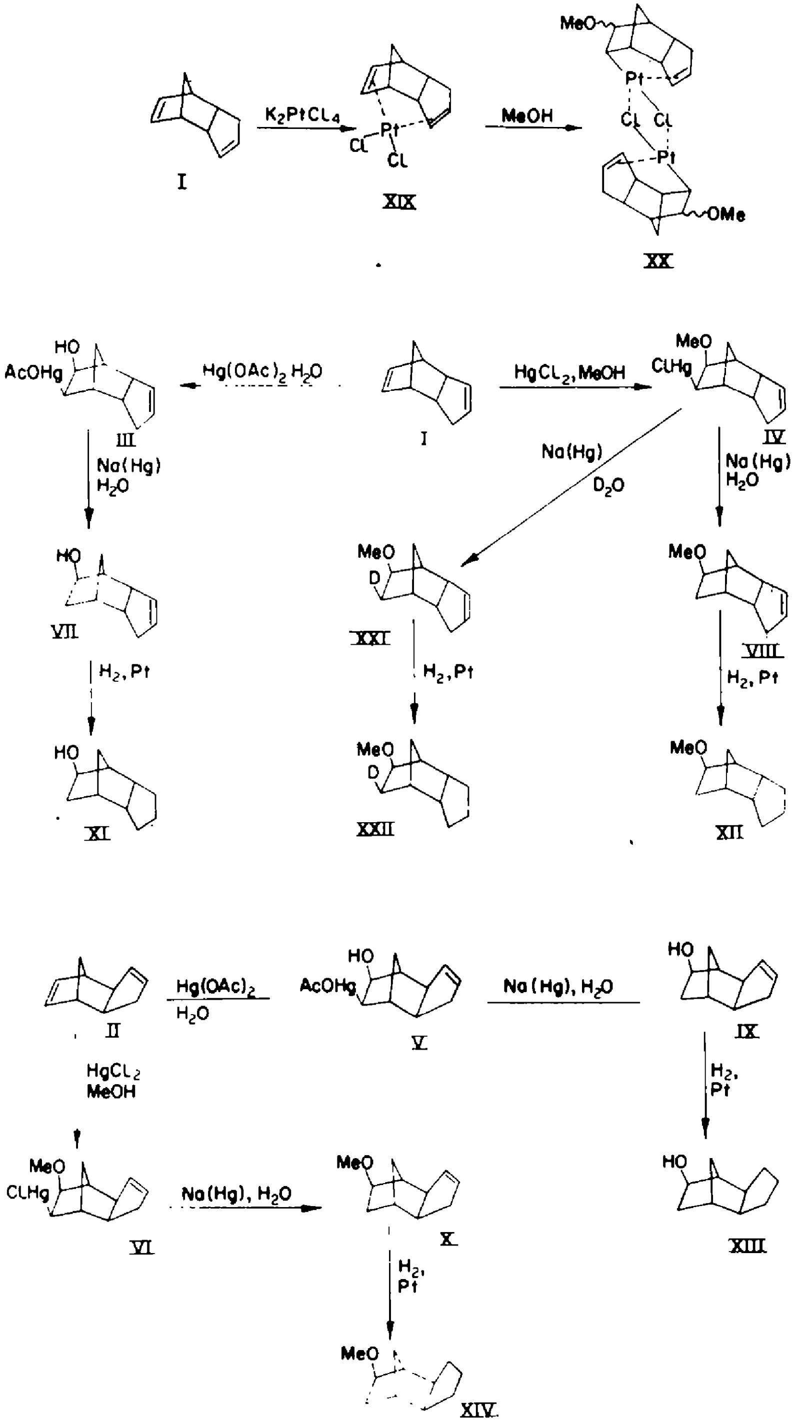
I
K_2PtCl_4
XIX
MeOH
XX
MeO
OMe
Pt
Cl
Hg(OAc)$_2$ H$_2$O
HgCl$_2$, MeOH
HO
AcOHg
ClHg
III
IV
Na(Hg)
H$_2$O
D$_2$O
D
VII
XXI
VIII
H$_2$, Pt
XI
XXII
XII
II
V
IX
Na(Hg), H$_2$O
HgCl$_2$
MeOH
VI
X
XIII
XIV

Fig. 1

and perhaps the product from the oxymercuration of *endo*-dicyclopentadiene in that the geometry, by analogy to both this platinum reaction and to the oxymercuration of cyclohexene, could have an *endo*-mercury attachment. A number of compounds containing the norbornene moiety have been shown to oxymercurate *exo-cis*,[3,4,12] although norbornadiene was known earlier to form a nortricyclenic mercurial.[8] It was considered interesting to establish whether any preliminary coordination of the *endo*-dicyclopentadiene about the mercury atom would produce compounds related in geometry to XIX and XX. The NMR and IR data of Traylor[4] show that the hydroxyl and chloromercuri groups of their mercurial corresponding to III are *cis*, and the NMR evidence indicates that they are vicinal. In view of these considerations, there might still be some question about the course of the reaction with the dicyclopentadienes in that the configurations of the adding groups are in question as to whether the *cis* addition has occurred *exo* or *endo*.

RESULTS

The *exo*-dicyclopentadiene used in these studies was made by the method of Bartlett and Goldstein.[13] Methoxymercuration of *endo*- and *exo*-dicyclopentadienes was carried out by the method of Hofmann and Seiler,[1] and hydroxumercuration by the method of Giua and Polla.[2] In both cases it was observed that *exo*-dicyclopentadiene reacts faster than the *endo* isomer. The methoxymercuration of *exo*-dicyclopentadiene was complete in about half the time required for the *endo*-hydrocarbon; and the hydroxymercuration of the *exo* compound was noticeably exothermic, whereas that of *endo*-dicyclopentadiene was not. The mercurials were reduced to unsaturated alcohols and ethers by sodium amalgam,[14] (Fig. 1) in which it was observed that, in the case of the mercuri ethers, there was roughly 50% regenerated diolefin in the reduced product. The derivatives VII and VIII of *endo*-dicyclopentadiene are interesting, because addition of ionic reagents to the parent hydrocarbon usually results in rearrangement, giving derivatives of *exo*-dicyclopentadiene.[15–18] The location of the double bonds in the mercurials III, IV, V and VI, and in their reduced products VII, VIII, IX and X, is uncertain relative to the hydroxyl or methoxyl group in the norcamphane moiety. Therefore they were hydrogenated to the completely saturated compounds XI, XII, XIII and XIV, which could be independently synthesized. Alternate compounds XV, XVI, XVII and XVIII (Fig. 2) were also prepared.[15,16,19,20] The unknown ethers XVI and XVIII were prepared by Williamson ether syntheses from the known alcohols. Cristol has found that acid catalyzed addition of methanol to *endo*-dicyclopentadiene produces about 15% of *exo-cis* unrearranged product XII, as well as the major product XIV.[21,22] Therefore,

[12] U. K. Yuriev, N. S. Zefirov and L. P. Prikazchikova, *Zh. Obshch. Khim.* **32**, 2744B (1962).

[13] P. D. Bartlett and I. S. Goldstein, *J. Amer. Chem. Soc.* **69**, 2553 (1947).

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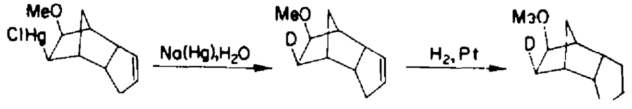
[21] S. J. Cristol, L. K. Gaston and D. W. Johnson, *Tetrahedron Letters* No. 4, 185 (1963).

[22] S. J. Cristol, W. K. Seifert, D. W. Johnson and J. B. Jurale, *J. Amer. Chem. Soc.* **84**, 3918 (1962).

XIV was prepared by Cristol's method from pure XIII. Although Cristol's experiments indicated that only a small amount of XI could be present as an impurity in XIII, only carefully purified XIII was used in preparations of other derivatives of tetrahydro-*exo*-dicyclopentadiene.

The IR spectra of XI, XII, XIII and XIV are significantly different from those of XVII, XVIII, XV and XVI respectively. Likewise, the NMR spectra are not superimposable for the two sets of compounds. The melting points of intimate mixtures of the alcohols XI and XIII from the mercurials III and V and of unambiguously synthesized XI and XIII were not depressed. NMR spectra of the mercurials IV and VI show that the proton attached to the carbon bearing the methoxyl group at 6·55τ, is split by about 7 c/s. In the case of these mercuri ethers, it was difficult to estimate the exact degree of splitting, due to the appearance of the three methoxyl protons in this region, which obscured part of the pattern. Nevertheless, the splitting was definitely not of the order of 2–3 c/s, as would be expected in the case of *trans* oxymercurated species. In the mercury alcohol V, the corresponding proton vicinal to the hydroxyl function is centered at 6·09τ, and is split by about 6·0 c/s. The assignment of the peak representing these protons was made by repeating the work of Traylor[4] and Cristol[21] in synthesizing deuterated compounds from reduction of the mercurial IV with sodium amalgam in deuterium oxide. The NMR spectrum of the deutero ether XXII shows the proton *gem* to the methoxyl group, split by 6·8 c/s, and again by 1·2 c/s. Comparison of this spectrum with that of undeuterated XII determined the proton assignment, and confirmed Traylor's observation[4] that sodium amalgam reduction of mercurials is stereospecific in these systems, with the deuterium appearing *exo*, just as the mercuri function it replaced.



IV XXI XXII

DISCUSSION

The fact that the mercurial III can be reduced to the known, saturated alcohol XI proves that the hydroxyl group of this oxymercuration reaction adds *exo*, and that the reaction proceeds without rearrangement of the carbon skeleton. If the system had undergone the rearrangement so often observed in these systems the reduction reactions of the mercurial would have given rise to XIII. A similar argument may be advanced for the structure of IV, since the methoxyl group is clearly *exo*, and a derivative of the unrearranged compound XII was obtained.

Derivatives of *endo*-dicyclopentadiene are frequently observed to rearrange to derivatives of the *exo* isomer,[15,16] but the rearrangement from the *exo* to the *endo* series is not generally encountered.[13] Nevertheless, some instances of rearrangement from *exo* to *endo* fusion of the trimethylene ring have been observed.[23,24] From the hydroxymercuration product V and the methoxymercuration product VI come the known alcohol XIII and ether XIV, rather than the products from a rearranged nucleus, XI and XII.

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[23] L. Kaplan, H. Kwart and P. von R. Schleyer, *J. Amer. Chem. Soc.* **82**, 2341 (1960).

[24] S. J. Cristol, W. K. Seifert and S. B. Soloway, *J. Amer. Chem. Soc.* **82**, 2351 (1960).

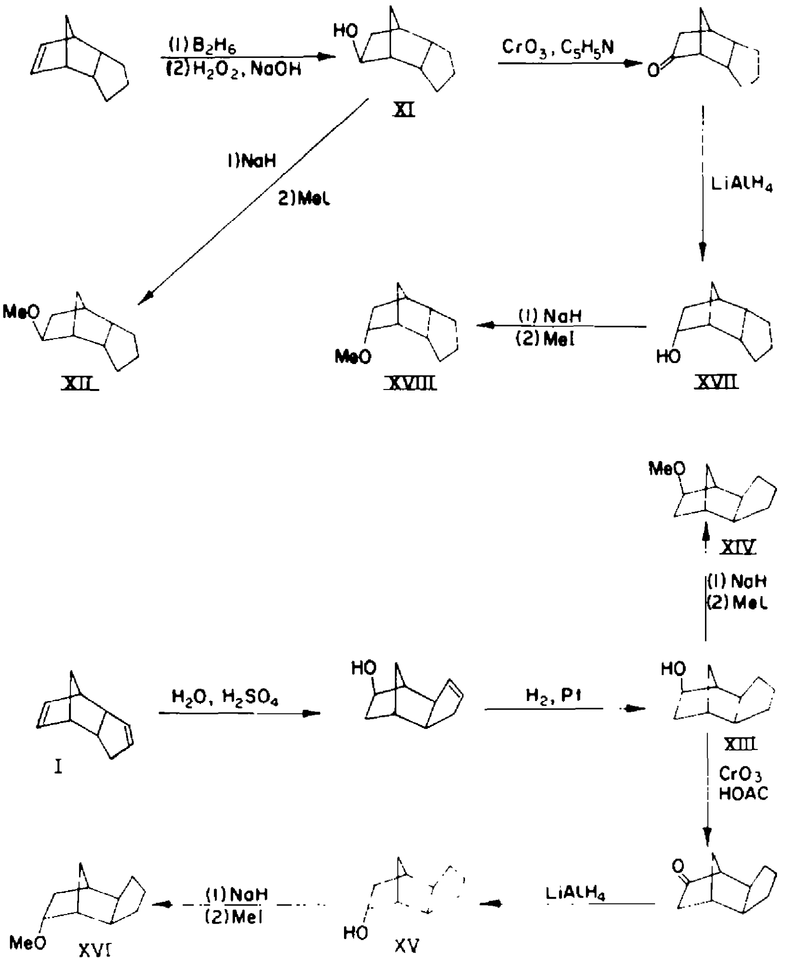

FIG. 2

The fact that the splitting of the peak for the proton *gem* to the hydroxyl and methoxyl groups in the mercurials is of the order of 6–7 c/s rather than 2–3 c/s indicates that the mercuri groups are *cis* to the methoxyl and hydroxyl groups, and therefore also *exo*. Considerable amounts of olefins may be regenerated from the mercurials by reduction with sodium amalgam, but the products from these reductions were purified to 97–100% purity, before submission for NMR or IR analysis. The deutero ether XXI was not found suitable for NMR studies of this type, since the three methoxyl protons interfere too much with the pattern of the *endo*-5 proton; the same was true of VIII. Therefore, the spectra of XII and XXII were used for this purpose.

It has been calculated,[25] that the proton *gem* to the methoxyl or hydroxyl groups of the mercurials should be split by 8·2 c/s by a proton *cis* to it, and by 2·1 c/s by a proton *trans* to it, discounting differences in electronegativity between methoxyl and hydroxyl groups.[25b,26,27] In practice, Anet has obtained values of 7·7 and 8·9 c/s for

[25a] M. Karplus, *J. Chem. Phys.* **30**, 11 (1959); [b] M. Karplus, *J. Amer. Chem. Soc.* **85**, 2870 (1963).
[26] K. L. Williamson, *J. Amer. Chem. Soc.* **85**, 516 (1963).
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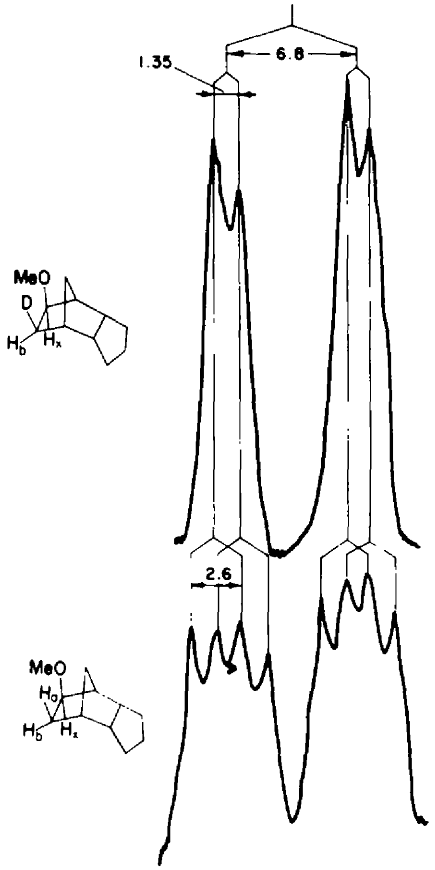

Fig. 3

the *cis* protons of norcamphane-2,3-diols,[28] whereas Anderson and Henry,[29] applying the method specifically to the oxymercuration product of norbornene obtained a value of 6·8 c/s, which is in good agreement with the values found in the present work. A similar argument may be advanced that the deuterium of XXI is *cis* to the methoxyl group and therefore *exo* also, since the proton *gem* to the methoxyl group is split by 6·0 c/s. In the NMR spectrum of ether XXI, a further splitting of 1·3–1·4 c/s was also noted (Fig. 3). The amount of interaction seemed a little low for coupling between the *endo*-5 and the *anti*-8 protons, corresponding to what was observed by Meinwald in the chlorocamphors.[30] The spectrum of XII shows that the coupling between the *endo*-5 and *endo*-6 proton is 2·5–2·6 c/s.

Intermediate complexes of the type XIX do not seem to affect the stereochemistry of oxymercuration reactions of dicyclopentadiene and *exo*-*cis* addition in the 5- and 6-positions occurs. Nevertheless, it is not now possible to denote precisely the location of the unsaturated linkage with respect to the methoxyl or hydroxyl group in these compounds.

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EXPERIMENTAL[21]

Octahydro-exo-4,7-*methanoinden*-exo-5-*ol* (XIII). This compound was prepared by the method of Bruson and Riener[15] and recrystallized from nitromethane to give pure product, m.p. 53–54° (lit. m.p. 53–54°[15]).

Octahydro-exo-5-*methoxy*-exo-4,7-*methanoindene* (XIV). This compound was prepared from pure XIII. A 44% yield of product, b.p. 84–6°/8 mm, $n_D^{19\cdot5}$ 1·4869 (lit. b.p. 43–44°/0·2 mm, n_D^{22} 1·4857[20]), was obtained.

Octahydro-exo-4,7-*methanoinden*-endo-5-*ol* (XV)[19]. To a solution of 2·2 g (58 mmoles) $LiAlH_4$ in 15 ml ether was added 10·35 g (69 mmoles) octahydro-*exo*-4,7-methanoinden-5-one,[15,16] prepared from pure XIII, on 20 ml ether, at such a rate as to cause the solvent to reflux gently. Refluxion was continued with external heating for 1 hr beyond completion of the addition. The excess hydride was destroyed with ethyl acetate and the addition complex was decomposed with NaOH aq. The mixture was extracted with three 50 ml portions of ether; the combined extracts were dried (Na_2SO_4) and distilled to give 6·00 g (57%) alcohol, b.p. 73°/1·5 mm, n_D^{19} 1·5127. Vapor phase chromatography showed the product to be 99% pure. It could not be crystallized to give a product with m.p. above 25°. (Found: C, 78·78; H, 10·24. Calc. for $C_{10}H_{16}O$: C, 78·95; H, 10·53%).

Octahydro-endo-*methoxy*-exo-4,7-*methanoindene* (XVI). Cristol's method[20] was employed to synthesize XVI from alcohol XV in 52·8% yield. Vapor fractometry showed that it was 99% pure. It had b.p. 81°/9 mm, $n_D^{19\cdot5}$ 1·4860. (Found: C, 79·20; H, 10·61. Calc. for $C_{11}H_{18}O$: C, 79·52; H, 10·84%).

Octahydro-endo-4,7-*methanoindene*-exo-5-*ol* (XI). Hydroboration of 2,3,3a,4,7,7a-hexahydro-*endo*-4,7-methanoindene was employed to prepare (XI). Recrystallization from nitromethane afforded pure product, m.p. 79·5–81° (lit. m.p. 81·5–82·5° [19,20]).

Octahydro-exo-5-*methoxy*-endo-4,7-*methanoindene* (XII). This compound was made in 47% yield from the alcohol XI and had b.p. 84–86°/6 mm, $n^{19\cdot5}$ 1·4923 (lit. b.p. 40–43°/0·2mm, n_D^{22} 1·4924[20]).

Octahydro-endo-4,7-*methanoinden*-endo-5-*ol* (XVII). Chromium trioxide oxidation of the alcohol XI in pyridine to the ketone, followed by reduction with $LiAlH_4$ gave XVII. The product was recrystallized from pet. ether (b.p. 30–60°) to give pure product, m.p. 119·5–120° (lit. m.p. 120–121°[15,19,20]), in 50·0% yield, based on the crude ketone.

Octahydro-endo-5-*methoxy*-4,7-*methanoindene* (XVIII). This compound was prepared from the alcohol XVII by Williamson ether synthesis, after the method of Cristol.[20] The yield was 52·8% of product, b.p. 81°/9 mm, $n_D^{19\cdot5}$ 1·4860. Vapor fractometry indicated 99% purity. (Found: C, 79·20; H, 10·61. Calc. for $C_{11}H_{18}O$: C, 79·52; H. 10·84%).

Methoxymercuration of endo-*dicyclopentadiene* (IV). This adduct was obtained in 79% yield, m.p. 133° (lit. m.p. 133°[1]). In the procedure of Hofmann and Seiler, the yield could be augmented by boiling the liquor obtained from filtration of the first crop of crystals, adding water, and allowing the mixture to stand overnight. The additional product can also be obtained by evaporating the liquor under red. press. without external heating, whereupon the crystalline material separated.

Methoxymercuration of exo-*dicyclopentadiene* (VI).[19] This adduct was prepared in 50% yield by the method of Hofmann and Seiler[1] for the preparation of IV. The product was recrystallized from 2:1 methanol–water, in which it was noticeably less soluble than the adduct IV, to give pure product, m.p. 135–137°. An intimate mixture of the two adducts IV and VI was found to melt sharply at 117°. Although the yield of VI was less under the same conditions, it was formed faster than IV. (Found: C, 33·06; H, 3·92. Calc. for $C_{11}H_{15}OClHg$: C, 33·08; H, 3·76%).

Hydroxymercuration of endo-*dicyclopentadiene* (III). A solution of 35 g (78 mmoles) mercuric acetate in 100 ml water was shaken mechanically with 10·7 g (11·0 ml, 81 mmoles) *endo*-dicyclopentadiene for 10 hr. The aqueous solution was decanted and the adduct was scraped from the sides of the flask. After drying in air, it was recrystallized from carbon tetrachloride, in which it was, however, appreciably soluble. The yield of material, after work up of the recrystallization liquors, was 14·1 g (42·8%) product, m.p. 129–131° (lit. m.p. 130°[2]).

Alternatively, the crude adduct was taken up in boiling carbon tetrachloride, evaporated under red. press. without external heating to a pellucid jelly, from which the adduct was precipitated as a fine,

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[21] All m.ps are corrected. IR spectra were obtained both from 0·4% CCl_4 and CS_2 solutions on a Perkin-Elmer Model 421 IR Spectrophotometer. The spectra of the mercurials were obtained in $CHCl_3$.

white solid by addition of the minimum of ether. In half the preparations carried out of this material, the crude adduct was white; but otherwise it was gray with free mercury.

Hydroxymercuration of exo-*dicyclopentadiene* (V). This compound was prepared by the method given for III.[18] The reaction was faster and slightly exothermic. After 10 hr mechanical shaking, however, the product was still a light yellow, viscous resin. There was never a gray color in this product in all the preparations carried out. It was isolated by decantation of the water, extraction into boiling carbon tetrachloride, followed by evaporation of the solvent under red. press., without external heating. The yellow, viscous jelly which remained was treated with the minumum amount of ether, whereupon the fine, white, solid adduct separated. Recrystallization of this product from carbon tetrachloride gave 13·9 g (42·3%) product, m.p. 130–135°. The yield could not be augmented by workup of the recrystallization liquors. The elemental and spectral analyses had to be done within an hour of the recrystallization. (Found: C, 34·98; H, 4·17. Calc. for $C_{12}H_{16}O_2Hg$: C, 35·24; H, 3·92%).

Reduction of the methoxymercuration product of endo-*dicyclopentadiene with sodium amalgam* (VIII). A suspension of 40·0 g (0·1 mole) mercurial IV in 400 ml water was shaken vigorously with 152 g (4·6 g, 0·2 g atom Na) 3% sodium amalgam, in small portions. The mixture was extracted with 4 × 100 ml portions ether and the combined extracts, after being dried (Na_2SO_4), were evaporated (red. press.). At this point, vapor fractometry showed a mixture of 50% regenerated *endo*-dicyclopentadiene and 50% VIII, identified from comparison of their retention times with those of authentic samples. This oil was distilled to give 9·7 g pure product, shown to be 98% pure by vapor fractometry, b.p. 77–78°/7 mm, n_D^{20} 1·5007. The IR spectrum showed maxima at 3045 (C═C—H str.), 1096 (C—O str.), and 697 cm^{-1} (C═C—H wag). (Found: C, 79·87; H, 9·85. Calc. for $C_{11}H_{16}O$: C, 80·49; H, 9·67%).

Reduction of the methoxymercuration product of exo-*dicyclopentadiene with sodium amalgam* (X). The reduction of the mercurial VI was carried out in the same way as for IV. From 35·5 g (0·88 moles) mercurical, 7·4 g (50·2%) of product was obtained, b.p. 81–3°/9 mm. Vapor phase chromatography showed the product to be 99% pure; $n_D^{19.5}$ 1·4976. The IR spectrum showed maxima at 3050 (C═C—H str.), 1096 (C—O str.) and 697 cm^{-1} (C═C—H wag). (Found: C, 80·03; H, 9·86. Calc. for $C_{11}H_{16}O$: C, 80·49; H, 9·67%).

Reduction of the hydroxymercuration product of endo-*dicyclopentadience with sodium amalgam* (VII). The reduction of the mercurial III was carried out as for IV, except that much more vigorous shaking was necessary to prevent agglomeration of the suspended material. From 41·0 g (0·1 mole) mercurial, 5·0 g (33·3%) product was obtained, b.p. 91°/4 mm, which crystallized on standing in the refrigerator. Recrystallization from nitromethane gave a white solid, m.p. 42–44°. The IR spectrum showed maxima at 3630 (OH str.), 3060 (C═C—H str.), and 698 cm^{-1} (C═C—H wag). The *p*-nitrobenzoate ester had m.p. 121·5–122·5°. (Found: C, 80·77; H, 9·33. Calc. for $C_{10}H_{14}O$: C, 80·00; H, 9·33%).

Reduction of the hydroxymercuration product of exo-*dicyclopentadiene with sodium amalgam* (IX). The mercurial V was reduced in the same manner as III. From 49·2 g (0·12 mole) V, reduced with 185 g (5·53 g, 0·24 g atom Na) 3% sodium amalgam, 2·2 g (12·5%) of product was produced, b.p. 92°/3·5 mm, $n_D^{19.5}$ 1·5262. Vapor fractometry showed that the product was 97% pure. The IR spectrum showed maxima at 3625 (OH str.), 3055 (C═C—H str.), and 697 cm^{-1} (C═C—H wag). The *p*-nitrobenzoate ester had m.p. 126·5–128·5°. (Found: C, 79·70; H, 9·61. Calc. for $C_{10}H_{14}O$: C, 80·00; H, 9·33%).

Octahydro-exo-*methoxy*-4,7-endo-*methanoindene* XII (*from* VIII). Hydrogenation of 5·65 g (33·8 mmoles) VIII in ethyl acetate with PtO_2 catalyst gave 3·60 g (64·3%) product, b.p. 85–87°/9 mm, n_D^{19} 1·4921. The IR and NMR spectra of the product were superimposable upon those of pure XII, but not upon those of XVIII.

Octahydro-exo-5-*methoxy*-exo-4,7-*methanoindene* XIV (*from* X). Hydrogentation of 4·8 g (0·03 moles) X as above for VIII gave 3·2 g (75%) of product, b.p. 81°/7 mm, $n_D^{22.5}$ 1·4855. The IR and NMR spectra of the product were superimposable upon those of authentic XIV, but not upon those of XVI.

Octahydro-endo-4,7-*methanoinden*-exo-5-*ol* XI (*from* VII). Hydrogenation of 2·28 g (15·4 mmoles) of the alcohol VII gave 1·46 g (67·5%) of product, m.p. 79–80° after recrystallization from nitromethane. The m.p. of an intimate mixture of this product and authentic XI was not depressed.

Octahydro-exo-4,7-*methanoinden*-exo-5-*ol* XIII (*from* IX). Hydrogenation of 4·80 g (32 mmoles) IX gave 1·58 g (32·5%) product, which was chilled to −78° and then allowed to come slowly to room temp, whereupon it crystallized. Recrystallization from nitromethane gave pure product, m.p. 50·5–51°. The m.p. of an intimate mixture of this product with authentic XIII was not depressed.

Reduction of mercurial IV *in deuterium oxide with sodium amalgam* (XXI). From 20·4 g (50 mmoles) of the mercurial IV in 200 ml deuterium oxide reduced with 114 g (3·45 g, 0·15 g atom Na) 3% sodium amalgam, 3·00 g (36·4%) of product, b.p. 81–83°/8 mm was obtained. Vapor fractometry showed that the product was 100% pure.

Octahydro-exo-5-*deutero*-exo-6-*methoxy*-endo-4,7-*methanoindene* (XXII). The hydrogenation of 2·50 g (15·2 mmoles) XXI in ethyl acetate gave 1·27 g (50%) product, b.p. 85–86°/6 mm.

Nuclear magnetic resonance spectra. The NMR spectra were run in carbon tetrachloride or deuterochloroform with tetramethylsilane as an internal standard. The instrument used was a Model A-60 NMR Spectrometer manufactured by Varian Associates, Inc.

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