magnesium sulfate. Evaporation of the ether left the crude yellow colored ester which was distilled at reduced pressure: b.p. 81° (2.5 mm.), $n^{25}D$ 1.4791, wt. 6.4 g., positive test with ceric nitrate reagent.

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.48; H, 8.29. Found: C, 63.10; H, 8.85.

The Attempted Reaction of 2-*exo*Hydroxynorbornane-2-*endo*methylcarboxylate with Raney Nickel.—Using the method of Bonner, *et al.*,[6] 4.9 g. (0.03 mole) of the hydroxy ester, 21 g. of Raney nickel catalyst and 100 cc. of ethanol were placed in a Parr low pressure apparatus and subjected to 20 lb. of hydrogen pressure at a temperature of 60° for 24 hours.

The catalyst was removed by filtration and the filter cake washed with 200 cc. of ethanol. Distillation of the ethanol left a yellow oil which distilled at 76–77° under 1.5 mm. pressure; $n^{25}D$ 1.4789; $n^{25}D$ for known ester, 1.4791; wt. of recovered starting material, 4.0 g.

The Attempted Reaction of Isocamphenilanic Acid with Alkaline Potassium Permanganate.—A solution of 16.8 g. (0.099 mole) of isocamphenilanic acid[16] and 83 g. of potassium hydroxide in 235 cc. of water was mixed with 30 g. of potassium permanganate. This mixture was warmed to 50° and then allowed to stir for 8 hr. while the temperature gradually returned to room temperature (25°). The excess permanganate was decomposed with sulfur dioxide and the solution strongly acidified with 6 *N* sulfuric acid, then extracted several times with diethyl ether. After the ether extracts were dried over magnesium sulfate, the solvent was removed leaving a white crystalline solid. Following several recrystallizations from methanol–water, the compound melted at 117–118°. This acid gave a negative ceric nitrate test and on admixture with a sample of isocamphenilanic acid gave no m.p. depression or change in infrared spectrum; wt. of recovered acid, 14.5 g.

The Measurement[17] of the Conductivity of the Boric Acid Complex with the Hydroxyacid III.

(1) 0.06410 *M* 2-*exo*hydroxynorbornane-2-*endo*carboxylic acid in 0.5 *M* boric acid solution

$$R = \frac{400}{3500} \times 481 = 54.9;\ L = \frac{C}{R} = \frac{4.25}{549} = 0.0774$$

(2) 0.06410 *M* 2-*exo*hydroxynorbornane-2-*endo*carboxylic acid in water

$$R = \frac{1000}{2500} \times 1134 = 453.6;\ L = \frac{C}{R} = \frac{4.25}{453.6} = 0.00936$$

(3) 0.5 *M* boric acid solution

$$R = \frac{9000}{1000} \times 1361 = 12{,}249.0;\ L = \frac{C}{R} = \frac{4.25}{12{,}249.0} = 0.000346$$

extent of complex formation = (*L* for hydroxy acid in 0.5 boric acid) − (*L* for hydroxy acid in water + *L* for 0.5 *M* boric acid)

extent of complex formation = 0.0774 − (0.00936 + 0.000346) = 0.0677

The Relative Rates of Oxidation of I and II.—The analytical procedure involved keeping 5.0-g. samples (0.032 mole) of acid in a solution containing 24.8 g. of KOH, 11.1 g. of $NaMnO_4 \cdot H_2O$ and 70 ml. of water at 24° in a thermostat. Aliquots of 10 ml. were removed at 15-min. intervals, quenched by bubbling in SO_2 until all the MnO_2 had dissolved, acidified and extracted three times with 50-cc. portions of ether. After evaporating the extracts, 50 ml. of standard (0.1007 *N*) $Na_2Cr_2O_7 \cdot H_2O$ in 1 *M* H_2SO_4 was added and the resulting solution refluxed for 45 min. The reaction was cooled with the addition of 50 ml. of water and back titrated with 0.1003 *N* $Na_2S_2O_3$ solution. A small correction was applied to each titer for the amount of oxidation experienced by the unhydroxylated acids I and II, respectively, with the acid chromate standard reagent after 45 min. of reflux. From several determinations the average ratio k_{endo}/k_{exo} = 3.75, with an estimated accuracy of about 20%.

NEWARK, DEL.

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[16] Prepared according to the procedure given by W. R. Vaughn and R. Perry, Jr., THIS JOURNAL, **74**, 5355 (1952).

[17] The nomenclature and procedure used here is that employed by Boeseken.[4]

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, AND THE SHELL DEVELOPMENT CO.]

Bridged Polycyclic Compounds. X. The Synthesis of *endo* and *exo*-1,2-Dihydrodicyclopentadienes and Related Compounds[1]

BY STANLEY J. CRISTOL,[1a] WOLFGANG K. SEIFERT[1a] AND S. BARNEY SOLOWAY[1b]

RECEIVED SEPTEMBER 8, 1959

Syntheses of the *endo* (I) and *exo* (II) isomers of 1,2-dihydrodicyclopentadiene have been investigated. The Diels–Alder synthesis from cyclopentadiene and cyclopentene leads to mixtures of both isomers, as well as both dicyclopentadienes. The effect of the severity of reaction conditions upon the composition of the reaction mixture is described, as is the preparation of pure *endo* isomer I. Syntheses of the *endo* and *exo* isomers have been carried out by pyrolysis of the benzoate esters of the *exo*-alcohols X and VIII related to I and II. Analyses were carried out by qualitative infrared measurements on the hydrocarbons and quantitative infrared measurements on their phenyl azide addition products.

As we are interested in a study of addition reactions to the *endo* (I) and *exo* (II) isomers of 1,2-dihydrodicyclopentadiene, it seemed worthwhile to develop a convenient synthesis of each isomer in as high a state of purity as possible.

Bruson and Riener[2] have reported that the Diels–Alder reaction of cyclopentadiene with cyclopentene gives 1,2-dihydrodicyclopentadiene, and it seemed reasonable from the Alder rule[3] that the product might be largely the *endo* isomer I, perhaps contaminated with the *exo* isomer II, as well as with the corresponding dicyclopentadienes III and IV resulting from dimerization of cyclopentadiene. We decided to scrutinize the composition of this mixture and to investigate the effect of reaction conditions upon the *endo*/*exo* ratio, looking toward synthesis of the pure *endo* isomer or of a mixture rich in that isomer. While our work was in progress, Wilder, Culbertson and Youngblood[4] showed that the Bruson–Riener product was in fact largely the *endo* isomer I, although no quantitative analysis was given. The proof of structure of I was carried out by Wilder and his co-workers.[4]

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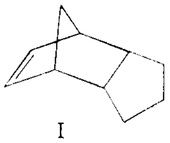
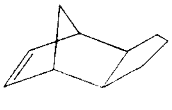
[1] Previous paper in series: S. J. Cristol and R. T. LaLonde, THIS JOURNAL, **81**, 5417 (1959); (a) University of Colorado; (b) Shell Development Co.

[2] H. A. Bruson and T. W. Riener, THIS JOURNAL, **67**, 723 (1945).

[3] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[4] P. Wilder, Jr., C. F. Culbertson and G. T. Youngblood, THIS JOURNAL, **81**, 655 (1959).


I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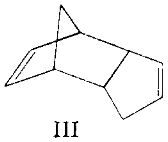
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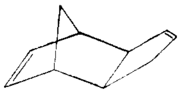
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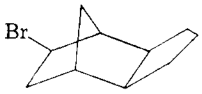
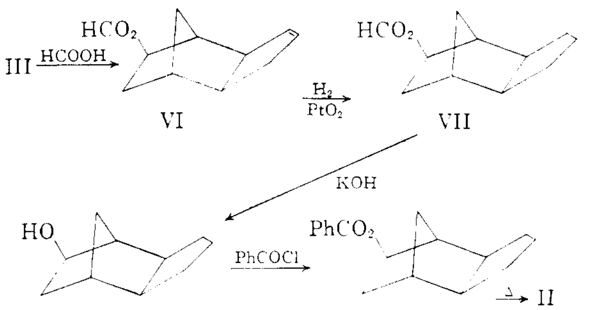

V



The *exo* isomer II has been reported[5] as being formed by elimination of hydrogen bromide from compound V, which in turn was prepared by hydrogenation of the corresponding 1,2-dehydro compound. Compound II was also prepared by dehydroiodination of the corresponding iodo compound.[6] The 1,2-dehydro compound related to V was prepared by the addition of hydrogen bromide to *endo*-dicyclopentadiene (III) and was assumed to have *exo* configurations for both the bromine atom and the ring junctions. It was assumed that in such addition reactions, Wagner–Meerwein isomerization of the ring system yielded the *exo* ring junction exclusively.[7-12]

Thus, the pioneering work of Bruson and Wilder and others suggested paths for our synthesis. Unfortunately, both isomers I and II were reported to be liquids, and infrared spectra had not been reported. Each could be converted to a phenyldihydrotriazole derivative with phenyl azide, but again no criterion for purity had been applied. When we repeated the procedure of Youngblood and Wilder,[5] the sample of *exo* isomer II which we obtained showed peaks in the infrared spectrum which are absent in the sample of pure *exo* isomer prepared later and which are present in products containing *endo* isomer I.[13]

Quantitative analysis (based upon an infrared analysis of the phenyldihydrotriazoles) suggests that about 20% of the product was *endo* (I). This result may not be precisely applicable to the Youngblood–Wilder product, as our yield of the elimination product was much lower than theirs.

A sample of relatively pure *exo* isomer II (containing about 1% of *endo* contaminant) was prepared by pyrolysis of the corresponding benzoate (IX), following the reaction scheme III → IX.

The addition of formic acid to III was conducted as described by Bergmann and Japhe.[9] Hydrogenation of VI to VII was carried out over Adams catalyst rather than Raney nickel,[9] but the properties of VI and VII were similar to those of the previous preparation. Saponification of VII gave crystalline VIII. When acetic acid was added[14] to III and the product transformed to VIII, the alcohol did not crystallize and had to be purified *via* the acid phthalate to give crystalline alcohol.[13] In each case, however, VIII was found to be contaminated with very small amounts of X. The composition of these mixtures will be described in a later publication. Treatment of the recrystallized alcohol with benzoyl chloride in pyridine gave the benzoate IX. Pyrolysis of IX gave *exo*-1,2-dihydrodicyclopentadiene (II) which, by analysis of its phenyldihydrotriazole, contained not more than 1% of the *endo* isomer. This material did not have four peaks in the infrared region which appear to be specific for the *endo* isomer, and had three bands that distinguish it from the *endo* isomer (see Experimental section).

When cyclopentadiene was treated with cyclopentene to give I under the conditions described by Bruson and Riener[2] (5 hours at 200°, 1:1.2 mole ratio diene:olefin), the product contained significant quantities of III and IV, as well as some *exo* isomer. It soon became clear that cyclopentadiene dimerized substantially faster than it reacted with cyclopentene, even when cyclopentene was in fair excess; for example, a mixture of 3 parts of cyclopentadiene and 10 of cyclopentene heated

TABLE I

THE REACTION OF DICYCLOPENTADIENE (1 PART) WITH CYCLOPENTENE (3 PARTS)

Expt.	Heating Temp., °C.	Heating Time, hr.	Total yield of C_{10}-fract.,[a] %	Composition of product,[e] % I	II	III	IV
1	154	15	. .	. .	. .	****	. .
2[b]	185	0.6	. .	. .	. .	****	. .
3	168	15	40	*	. .	***	. .
4	182	24	35	**	. .	**	**
5	200	5	32	***	*	**	*
6	200	11	34	81	9	*	*
7	293	3.5	33	71	20	*	
8	240	87	26	56	47	. .	. .
9	300	5	29	46	50	*	
10	300	40	25	29	72	. .	. .
11	198	5.3	25[c]	97	3	. .	. .
12[b,c,d]	195	14	14[c]	***	*	*	
13[b,c,d]	180	60	16[c]	98	2	. . *	. .

[a] Based upon cyclopentadiene. [b] Monomer cyclopentadiene used rather than dicyclopentadiene. [c] Run in steel autoclave, rather than glass tube; see Experimental section for discussion of pyrolysis which followed. [d] Ratio of reactants 1:2. [e] *, trace; **, considerable amount; ***, predominant product; ****, exclusive product.

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(5) G. T. Youngblood and P. Wilder, Jr., *J. Org. Chem.*, **21**, 1436 (1956).

(6) P. v. R. Schleyer and M. M. Donaldson, THIS JOURNAL, **78**, 5702 (1956).

(7) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946).

(8) H. A. Bruson and T. W. Riener, *ibid.*, **68**, 8 (1946).

(9) F. Bergmann and H. Japhe, *ibid.*, **69**, 1826 (1947).

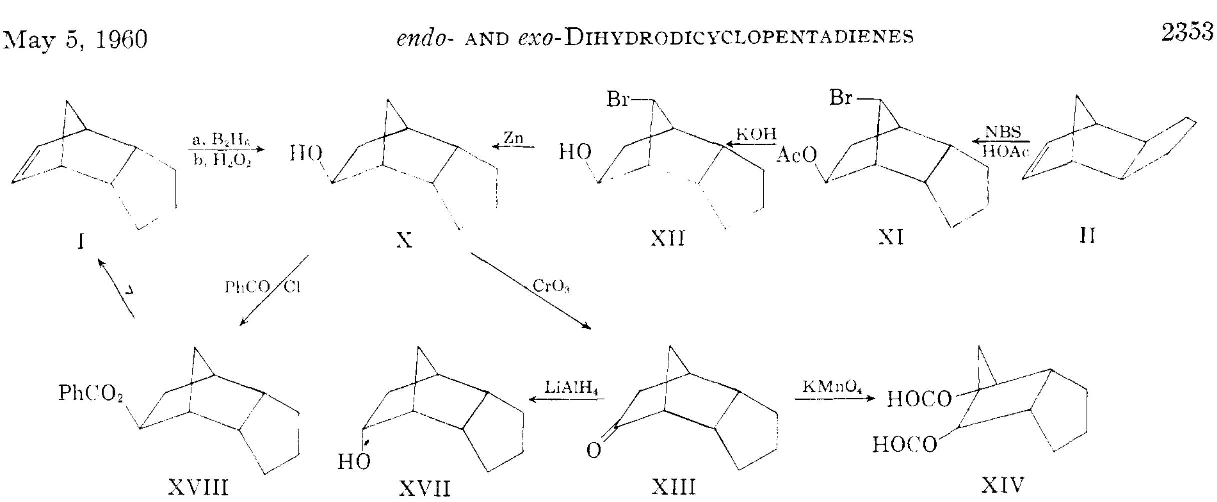
(10) P. D. Bartlett and I. S. Goldstein, *ibid.*, **69**, 2553 (1947).

(11) M. Gates and P. S. Malchick, *ibid.*, **76**, 1378 (1954).

(12) K. Alder, F. H. Flock and H. Wirtz, *Chem. Ber.*, **91**, 1609 (1958).

(13) We are investigating additions to I, II, III and IV to determine the amount of *endo* and *exo* ring system present in the addition products. Evidence thus far implies that the *endo–exo* isomerization is not complete in the addition of hydrogen bromide and acetic acid to III, for example.

(14) H. A. Bruson and T. W. Riener, THIS JOURNAL, **67**, 1178 (1945).



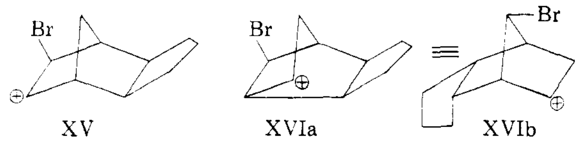
for 36 minutes at 185° gave relatively pure *endo*-dicyclopentadiene, so that one could start with dicyclopentadiene rather than cyclopentadiene. As the severity of the reaction conditions increased (see Table I), either by lengthening the time of reaction or by increasing the temperature, the amount of the dicyclopentadienes III and IV diminished, but unfortunately, as is generally the case,[15] the *exo*/*endo* ratio of the dihydrodicyclopentadienes also increased, so that the *pure endo* isomer I was not obtained, even under the best conditions, directly from the diene synthesis. However, it was found that heating a 1:2 mixture of cyclopentadiene or dicyclopentadiene (III) and cyclopentene for 60 hours at 180 ± 2° gave a C_{10}-fraction that (after 100 hours at reflux pyrolysis to remove III) was substantially free of II. This fraction, upon cooling, gave crystalline I, m.p. 0–2°. Analysis of this material indicated that it contained about 2% *exo* (II) isomer.

In the course of this work, it seemed worthwhile to consider the preparation of *endo*-olefin I by pyrolysis of a benzoate ester with the carbon skeleton of I. For this purpose the alcohol X or its epimer would be necessary. One synthesis leading to X involves the rather interesting, although impractical, reaction path II → XI → XII → X, developed in connection with other studies to be reported later.

Treatment of *exo*-II with N-bromosuccinimide in glacial acetic acid led to a bromoacetate, which upon saponification and debromination with zinc gave the alcohol X. The latter has been described by Bartlett.[16]

We have confirmed the structural assignment of X by oxidation to the known ketone XIII[17] and the known dicarboxylic acid XIV.[18]

The fact that the alcohol X has the *endo* ring fusion is clear from the oxidation products and indicates that a Wagner–Meerwein rearrangement has occurred in the transformation II → X, undoubtedly in the addition of the elements of acetyl hypobromite to *exo*-dihydrodicyclopentadiene. This addition is interesting as it represents a unique example of the conversion of an *exo* ring fusion in such a bicyclic system to an *endo* ring fusion. Apparently those factors that control the addition of acetic acid to the intermediate bromocarbonium ions XV and XVI—such that measurable addition occurs solely at the cationic center in XVI rather than to that in XV—are more important than those factors which generally lead from *endo* to *exo* ring fusion.[19]



The assignment of the position and configuration of the bromine atom as on carbon 7 and *syn* to the hydroxyl is based upon analogy to addition reactions to norbornenes[20] together with the knowledge that rearrangement has occurred. That the bromine atom and hydroxyl group are not on vicinal carbon atoms is demonstrated by (a) the fact that base did not convert XI to an epoxide or ketone and (b) the fact that zinc did not convert XII to an olefin, both of which would be expected were XII a vicinal bromohydrin.

Another synthesis of alcohol X was investigated briefly, starting with I, and could probably be developed as a procedure for converting crude I to relatively pure I. The preparation involves the new synthesis of alcohols by addition of diborane to olefins, followed by oxidation.[21] This procedure gave relatively pure X from I, indicating that no rearrangements occurred in the addition or oxidation reactions, and that the addition proceeds from the *exo* side, as established by Brown and Zweifel.[21c] These authors had obtained *exo*-norborneol from norbornene. The isomeric alcohol XVII[2,16] was prepared by reduction of the ketone XIII with lithium aluminum hydride.

Alcohol X was converted readily to the benzoate XVIII with benzoyl chloride in pyridine. Pyroly-

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(15) See, among others: (a) K. Alder and R. Rühmann, *Ann.*, **566**, 1 (1950); (b) D. Craig, THIS JOURNAL, **73**, 4889 (1951); (c) S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954).

(16) P. D. Bartlett, Abstracts of the 12th National Organic Chemistry Symposium, Denver, Colo., 1951, p. 1.

(17) K. Alder, G. Stein and H. Finzenhagen, *Ann.*, **485**, 223 (1931).

(18) F. Bergel and E. Widmann, *ibid.*, **467**, 76 (1928).

(19) (a) The question of whether XV and XVI are separable isomers or resonance structures is not pertinent to this discussion; (b) L. Kaplan, H. Kwart and P. v. Schleyer, Abstracts of the Atlantic City, N. J., Meeting of the American Chemical Society, September, 1959, p. 29P, report two other examples of such a rearrangement.

(20) H. Kwart and L. Kaplan, THIS JOURNAL, **76**, 4072 (1954); S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956).

(21) (a) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 5694 (1956); (b) *J. Org. Chem.*, **22**, 1135 (1957); (c) H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 247 (1959).

sis of this ester at 275–295° gave the *endo*-olefin I. This olefin was relatively pure, with 5% or less of *exo*-II contaminant. It is possible that this small amount of contaminant represents *exo* ring structure material present in the benzoate subjected to pyrolysis, or conversely, that the pyrolysis procedure leads to a small amount of rearrangement.[22]

Analyses of the mixtures of I and II were carried out by preparing the phenyldihydrotriazoles by treatment of the hydrocarbons with phenyl azide and then by measuring the infrared intensities of the mixtures of the phenyldihydrotriazoles as solids in potassium bromide disks (see Experimental). The method gave reproducible and apparently reliable results to ±2–3%.

Acknowledgment.—The authors are indebted to the National Science Foundation for partial support of this work. Elemental analyses are by Paul Saliman.

Experimental

Octahydro-*exo*-4,7-methanoinden-*exo*-5-yl formate (VII) was prepared by hydrogenation of 113 g. of VI[9] in 100 ml. of ethyl acetate using 300 mg. of platinum oxide catalyst at room temperature and 3 atm. The product boiled at 111–114° (7–8 mm.), weighed 105 g. (92%) and had $n^{22.5}\text{D}$ 1.4913. Bergmann and Japhe,[9] who carried out the hydrogenation over Raney nickel in ethanol, report b.p. 137° (35 mm.), $n^{27}\text{D}$ 1.4870.

Octahydro-*exo*-4,7-methanoinden-*exo*-5-ol (VIII).—A solution of 315 g. (1.76 moles) of VII and 149 g. (2.60 moles) of potassium hydroxide in 500 ml. of ethanol was heated at reflux for 8 hours. The ethanol was removed *in vacuo*, and the residue was extracted with ether. The ethereal solution was dried over calcium sulfate. The ether was removed and the product distilled to give 229 g. (85%) of a viscous oil which solidified upon being cooled and scratched at −20°, m.p. 35–39°. Recrystallization from nitroethane and nitromethane gave VIII, m.p. 53–54° (reptd.[2] 53–54°). The crude product and the recrystallized product showed infrared absorptions at 14.35 μ, characteristic of the presence of a double bond. This suggests that some unsaturated alcohol, presumably arising from a small amount of unhydrogenated formate ester VI, was present.

The acetate of VIII (**octahydro-*exo*-4,7-methanoinden-5-yl acetate**) was prepared by hydrogenation of 810 g. (4.22 moles) of hexahydro-*exo*-4,7-methanoinden-5-yl acetate[14] in 1 l. of methanol over reduced platinum oxide catalyst at 4 atm. pressure. The mixture was filtered through Celite, and a solution of 200 g. of sodium hydroxide in 300 ml. of water was added to the filtrate. The mixture was heated at reflux for 15 hours. Most of the methanol was removed by distillation; the product, crude VIII, was isolated by ether extraction and distillation; b.p. 72–75° (0.5 mm.), 617 g. (96%). Attempts to crystallize the alcohol failed.

The acid phthalate of VIII was prepared by treating 470 g. (3.09 moles) of the distilled alcohol in 400 ml. of pyridine with 488 g. (3.3 moles) of phthalic anhydride for 4 hours on a steam-bath. The reaction mixture was cooled to room temperature, dissolved in 1.5 liters of ethyl acetate, and the solution was washed once with water. When the ethyl acetate solution was washed with 700 ml. of 6 *N* hydrochloric acid, a solid separated. It was collected on a filter, washed with water, and air dried overnight to give 1075 g. (theory 927 g.) of crude product, m.p. 139–147°. Crystallization of the solid from 1500 ml. of acetone gave 316 g. (32%) of pure acid phthalate of VIII as clusters of plates, m.p. 156.5–157° (Bartlett[16] reports m.p. 152°).

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.0: H, 6.71. Found: C, 71.8; H, 6.69.

Two additional crops of acid phthalate were obtained amounting to 187 g., m.p. 156–157°. The total yield was 52%.

The alcohol VIII was obtained by saponifying 372 g. (1.24 moles) of the above acid phthalate with 198 g. (3 moles) of 85% potassium hydroxide dissolved in 1 liter of water. The mixture was heated on a steam-bath with stirring for four hours and then cooled. The precipitated oil was extracted with ether. The ether solution was washed with water until the washings were neutral to litmus, and then dried over anhydrous sodium sulfate. Evaporation of the ether gave 195 g. (theory 189 g.) of crude VIII as an oil. Crystallization of a small portion from nitromethane gave a solid, m.p. 46–49.5°, which upon recrystallization from the same solvent gave pure alcohol VIII as fern-shaped crystals, m.p. 53.5–54°.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.9; H, 10.6. Found: C, 79.0; H, 10.6.

The *p*-nitrobenzoate of VIII was prepared by heating 1.0 g. (6.6 mmoles) of alcohol with 1.46 g. of *p*-nitrobenzoyl chloride in 15 ml. of pyridine on a steam-bath overnight. The mixture was poured into ice-water and triturated with sodium carbonate. A crude solid, m.p. 90–93°, was collected and crystallized from hexane to yield 1.0 g. (50%) of product as small crystalline plates, m.p. 94–94.5° (Bartlett[16] reports m.p. 92–93°).

Anal. Calcd. for $C_{17}H_{19}NO_4$: C, 67.8; H, 6.36. Found: C, 67.4; H, 6.16.

The benzoate IX of the alcohol VIII was prepared by adding 45 g. (0.30 mole) of slightly impure VIII, m.p. 49.5–50°, to a solution of 50.4 g. of benzoyl chloride in 70 ml. of pyridine. The resulting solution was heated on a steam-bath overnight. The reaction mixture was poured into water and extracted with ether; the ether extracts were washed with water and sodium carbonate solution, then dried over anhydrous sodium sulfate. Distillation of the ether left an oil which solidified. The solid was collected on a filter and washed with cold pentane; yield 66 g. (87%), m.p. 70–71°. Crystallization from pentane gave IX, m.p. 71.5–72°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.7; H, 7.86. Found: C, 79.3; H, 7.60.

1,2-*exo*-Dihydrodicyclopentadiene (II).—Sixty grams (0.23 mole) of the benzoate IX (m.p. 70–71°) was placed in a Claisen flask and heated in a silicone-oil-bath. Pyrolysis proceeded smoothly at a bath temperature of 280–360°. The olefin was contaminated with benzoic acid, which was removed by treating the pentane solution with a 10% sodium carbonate solution. The pentane solution was dried over Drierite, the solvent evaporated and the olefin distilled, b.p. 28–32° (1 mm.). The yield of hydrocarbon was 11.5 g. (37%), $n^{25}\text{D}$ 1.4961. In another run, a yield of 62% was obtained. Distillation with a fractionating column gave a center fraction, $n^{25}\text{D}$ 1.4943, which gave a phenyldihydrotriazole derivative, m.p. 141.5–142.5°, analyzing for 1% *endo* (I)–99% *exo* (II) composition. The recrystallization from ethanol gave pure triazole derivative, m.p. 142–143.5°.

Preparation of Phenyldihydrotriazole Derivatives.—The triazole derivatives[23] of I to IV were prepared by treatment of the bicycloheptene derivative with an excess of phenyl azide[24] overnight at room temperature. The crystalline dihydrotriazoles were cooled at −20° for two hours; the excess of phenyl azide was removed by suction filtration, and the crystals were then washed with a few drops of cold ethanol. The samples were dried for 5 hours at 80° and 0.01 mm. A test with a known mixture of I and II indicated that no fractionation occurred during this procedure.

5-Bromo-3a,4,5,6,7,7a-hexahydro-*exo*-4,7-methanoindene was prepared by the addition of hydrogen bromide to dicyclopentadiene.[5,14] It had b.p. 75° (1.5 mm.) and $n^{22}\text{D}$ 1.5444. The reported[14] values are b.p. 113–114° (11 mm.), $n^{25}\text{D}$ 1.5437. Hydrogenation[5] yielded **5-bromo-octahydro-*exo*-4,7-methanoindene** (V), b.p. 85° (3.5 mm.), $d^{24}{}_4$ 1.3274, $n^{22}\text{D}$ 1.5333 (reported[5] b.p. 79° (0.5 mm.), $d^{20}{}_4$ 1.308, $n^{25}\text{D}$ 1.5359). Treatment of 99 g. (0.46 mole) of V with 103 g. (1.84 moles) of potassium hydroxide in 800 ml. of 95% ethanol for 36 hours at reflux gave 5 g. (8%) of dihydrodicyclopentadiene. The crude phenyldihydrotriazole prepared from this sample melted at 107–118° and analyzed for 20% *endo* isomer (I) and 75% *exo* isomer (II). The

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(22) The latter explanation seems reasonable since we have shown (*cf.* Table I) that *endo* I rearranges to *exo* II at high temperatures.

(23) K. Alder and G. Stein, *Ann.*, **504**. 220 (1933).

(24) R. O. Lindsay and C. F. H. Allen in E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 710.

fact that the hydrocarbon was not pure suggests that the sample of V also contained some *endo* ring-fusion product.

Reaction of Dicyclopentadiene with Cyclopentene.—The first experiments (runs 1 to 10) were conducted in sealed glass tubes. In general the procedure was to take a mixture of 12 g. of dicyclopentadiene and 40 g. of cyclopentene in a sealed glass tube or steel autoclave and heat at an elevated temperature.

After the appropriate time, the tubes were cooled, opened and the contents distilled. The cyclopentene was removed at atmospheric pressure and the C_{10}-fraction, which contained I, II, III and/or IV, was distilled at reduced pressure. The remainder, which presumably contained C_{15}, C_{20} and higher materials, was discarded. Qualitative analyses were made by infrared on the hydrocarbons and their phenyl azide derivatives in the first five experiments; the remaining samples were converted to phenyldihydrotriazoles for analysis.

It soon became clear that, to remove impurities of III and IV, it would be necessary to pyrolyze these materials to cyclopentadiene.[2] Experiments 11 to 13 describe the results of such a procedure; after the initial heating in the autoclave and distillation at reduced pressure to isolate the C_{10}-fraction, the latter was heated at very gentle reflux for about 100 hours. Our best preparation is that of experiment 13, where 80 g. (1.2 moles) of cyclopentadiene was heated with 163 g. (2.4 moles) of cyclopentene for 60 hours at 180 ± 2°. After 100 hours of pyrolysis at reflux followed by second distillation, b.p. 29.5–33° (0.45–0.55 mm.), 26 g. (16%) of *endo* product I was obtained, $n^{27}D$ 1.4987, m.p. 0–2°. The crude phenyldihydrotriazole melted at 125–128° (pure 128–129°[23]) and the product analyzed for 2% *exo* (II) isomer.

syn-**8-Bromoöctahydro-***endo***-4,7-methanoinden-***exo***-5-yl Acetate (XI).**—A solution of 17.0 g. (0.127 mole) of II in 100 ml. of acetic acid was stirred and 24.8 g. (0.139 mole) of N-bromosuccinimide was added gradually. After 3 hours the solution gave a negative test for positive halogen. It was poured into 200 ml. of water, the precipitated oil was extracted with ether, and the ether extract was washed with sodium bicarbonate and dried over anhydrous sodium sulfate. Distillation yielded 25.3 g. (73%) of XI, b.p. 107–114° (0.5 mm.), $n^{26.5}D$ 1.5271, as a pale yellow oil.

Anal. Calcd. for $C_{12}H_{17}BrO_2$: C, 52.8; H, 6.27. Found: C, 52.2; H, 6.06.

syn-**8-Bromoöctahydro-***endo***-4,7-methanoinden-***exo***-5-ol (XII).**—The bromo ester XI, 25.3 g. (0.0926 mole), was added to 15.6 g. (0.237 mole) of 85% potassium hydroxide in 100 ml. of methanol and the resulting solution was heated at reflux for 18 hours. The product was isolated by pouring the reaction solution into water and extracting with a mixture of pentane and ether. Evaporation of most of the solvent and subsequent chilling in a refrigerator yielded 15.7 g. of XII as fine needles, m.p. 52–53°; a second crop weighed 2.7 g., m.p. 48–50°; total yield 86%. Recrystallization of a specimen from hexane gave the analytical sample, m.p. 56–56.5°.

Anal. Calcd. for $C_{10}H_{15}BrO$: C, 52.0; H, 6.54. Found: C, 51.6; H, 6.42.

Octahydro-*endo***-4,7-methanoinden-***exo***-5-ol (X).**—In a typical experiment, debromination of 6.4 g. (0.0277 mole) of bromohydrin XII was carried out by heating at reflux with 10 g. (0.15 g.-atom) of zinc dust in 50 ml. of 80% ethanol for 64 hours. The mixture was filtered, the filtrate was diluted with water, and the product was isolated by extraction with pentane. Analysis of the aqueous phase for bromide ion showed the removal of 0.026 g.-atom of bromine. Concentration and cooling of the pentane extract yielded 3.5 g. (83%) of alcohol X, m.p. 78–79°. Recrystallization from cold hexane gave 1.3 g. of the pure compound, m.p. 80.5–81.5°.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.9; H, 10.6. Found: C, 79.1; H, 11.0.

The alcohol X was also prepared by hydroboration of I followed by oxidation and hydrolysis, according to the general procedure of Brown.[21] A stream of diborane in nitrogen was prepared by adding a solution of 15.2 g. (0.4 mole) of sodium borohydride in 300 ml. of diethylene glycol methyl ether to a solution of 150 g. (1.07 moles) of boron trifluoride etherate in 150 ml. of diethylene glycol methyl ether. The dropwise addition required two hours; magnetic stirring was used, and the diborane was swept out with dry nitrogen and bubbled into a solution of 29 g. (0.22 mole) of fairly pure I (product of expt. 12, Table I) in 20 ml. of dry tetrahydrofuran at 0°. After 10 hours standing at room temperature, the solution was cooled by the addition of crushed ice; 50 ml. of 3 *M* sodium hydroxide solution was added and then 28 ml. of 30% hydrogen peroxide was added over a period of 2 hours. The solution was stirred and cooled in an ice-bath during the addition, then allowed to come to room temperature and stirred for an additional 4-hour period. The product was extracted with ether, washed with water, potassium bisulfate solution and again with water. The ethereal solution was dried over anhydrous calcium sulfate, and the ether was then distilled. Cooling a solution of the residual oil in nitromethane to −20° gave crystalline material which was pressed on a clay plate to remove oil (m.p. 58–62°). Trituration with cold pentane gave 9.3 g. (28%) of X, m.p. 60–74°. Recrysallization from nitromethane gave pure X, m.p. 81.5–82.5°.

This alcohol (X) and its ring fusion isomer VIII both have very large cryoscopic constants, as is typical of bicyclic compounds. For example, a mixture of 4.7% of X with 95.3% of VIII melts at 41–43°, and a mixture of 8.7% of X with 91.3% of VIII (m.p. 54°) is an oil at room temperature.

The *p***-nitrobenzoate of X** was prepared by treating 500 mg. (3.3 mmoles) of alcohol with 0.73 g. (3.9 mmoles) of *p*-nitrobenzoyl chloride in 5 ml. of pyridine for 4 hours on a steam-bath. Work-up by digestion with cold sodium bicarbonate solution gave 1.1 g. of product, m.p. 127–129°, which upon recrystallization from hexane yielded 0.44 g. (44%) of diamond-shaped plates, m.p. 129.5° (Bartlett[16] gives m.p. 123–124°).

Anal. Calcd. for $C_{17}H_{19}NO_4$: C, 67.8; H, 6.36. Found: C, 68.0; H, 6.56.

The acid phthalate of X was prepared by heating 500 mg. (3.3 mmoles) of alcohol with 0.5 g. (3.4 mmoles) of phthalic anhydride in 3 ml. of pyridine on a steam-bath overnight. Work-up by ether extraction gave 0.95 g. (96%) of product, m.p. 175–177.5°. Recrystallization from acetone–hexane yielded 0.60 g. (61%) of needles, m.p. 179–179.5° (Bartlett[16] gives 159–160°).

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.0; H, 6.71. Found: C, 72.2; H, 6.78.

Octahydro-*endo***-4,7-methanoinden-***exo***-5-yl Benzoate (XVIII).**—Six and one-half grams (0.046 mole) of benzoyl chloride was added to a solution of 2.73 g. (0.018 mole) of X (m.p. 68–77°) in 5 ml. of pyridine. The solution was heated to about 130° for 45 minutes and then cooled. The mixture was poured into water and extracted with ether. The ether extracts were combined and washed with sodium carbonate solution and with water. The ethereal solution was dried over calcium sulfate; the ether was then removed by distillation. The remaining oil was crystallized from *n*-pentane in a Dry Ice-bath, giving 2.4 g. of material which liquefied at room temperature. Recrystallization from nitromethane gave 1.9 g. of product, m.p. 55–57°; the analytical sample melted at 57.0–58.0°. After the mother liquors were worked up, the total yield was 2.5 g. (54%). When the isomeric benzoate IX was mixed with this material, a substantial m.p. depression was noted.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.52; H, 7.74.

Pyrolysis of the Benzoate XVIII to 1,2-*endo***-Dihydrodicyclopentadiene (I).**—One and four-tenths grams (5.5 mmoles) of XVIII, m.p. 55–57°, was heated slowly in a silicone-oil-bath at 275–295°. The olefin and benzoic acid distilled from the reaction mixture. The reaction was complete in one hour. The condenser and receiver were washed with ether; the ethereal solution was washed with sodium carbonate solution and the ether was distilled. The olefin I distilled at 30–40° (0.2 mm.), 0.3 g. of product being obtained. This sample had an m.p. of 1–2.5°, which is the highest m.p. we have found for this material, and $n^{25}D$ 1.5012. The phenyldihydrotriazole derivative melted at 123–126° and analyzed for a maximum of 5% *exo* contaminant.

Octahydro-*endo***-4,7-methanoinden-5-one (XIII).**—A chromium trioxide–pyridine complex was formed by treating 10.8 g. (0.108 mole) of chromium trioxide with 100 ml. of pyridine.[25] To this mixture 5.6 g. (0.036 mole) of alcohol X dissolved in 50 ml. of pyridine was added slowly with stirring. The reaction mixture turned dark brown, but

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[25] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 422 (1953).

there was no heat evolution. Stirring was stopped after 4 hours and after one week the product was isolated by filtering the mixture, diluting the filtrate with water, and extracting with pentane. The pentane extract was washed free of pyridine with dilute hydrochloric acid and upon evaporation there was obtained 4.47 g. (83%) of XIII, m.p. 97–103° (lit.[17] m.p. 109–110°). The infrared spectrum showed a characteristic carbonyl peak at 5.71 μ, but no peaks for hydroxyl. **The semicarbazone of XIII** formed slowly. Treatment of 0.47 g. (3.13 mmoles) of XIII with 0.38 g. (3.4 mmoles) of semicarbazide hydrochloride and 1 ml. of pyridine in 5 ml. of methanol and 3 ml. of water did not give a product after three days. The addition of 0.4 g. of sodium acetate, 0.4 g. (3.6 mmoles) of semicarbazide hydrochloride and 1 ml. of of acetic acid and cooling in a refrigerator finally yielded 0.12 g. (18%) of semicarbazone, m.p. 225–226° (lit.[17] m.p. 229°).

Anal. Calcd. for $C_{11}H_{17}N_3O$: N, 20.3. Found: N, 20.2.

Oxidation of XIII to octahydro-*cis*-pentalene-*cis*-1,*cis*-3-dicarboxylic acid (XIV), was accomplished by treating 1.0 g. (6.7 mmoles) of the ketone XIII suspended in 50 ml. of water containing 1.0 g. of sodium hydroxide with 4.1 g. (0.026 mole) of potasssium permanganate over a period of 20 hours. The manganese dioxide was decomposed with sodium bisulfite solution and the clear solution was extracted with seven 25-ml. portions of ether. The combined ether extracts were dried and the solvent was evaporated leaving 1.12 g. (85%) of XIV as clusters of plates, m.p. 226–229°. Recrystallization from water gave 0.64 g. as fine needles, m.p. 231.5–232° (lit.[18] m.p. 232°).

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.6; H, 7.12; neut. equiv., 99. Found: C, 60.7; H, 6.80; neut. equiv., 100.

Octahydro-*endo*-4,7-methanoinden-*endo*-5-ol (XVII).—To a solution of 2.4 g. (0.063 mole) of lithium aluminum hydride in 50 ml. of dry ether, 3.17 g. (0.0211 mole) of the ketone XIII dissolved in 50 ml. of ether was added slowly. After the reaction mixture was stirred for 16 hours, the excess lithium aluminum hydride was destroyed with 25 ml. of ethyl acetate and the complex was decomposed with water. When the inorganic hydroxides had coagulated, the ether solution was decanted, dried over anhydrous sodium sulfate, and evaporated. Dissolution of the residual solid in hexane and chilling yielded 2.37 g. (74%) of XVII, m.p. 115–120°. Recrystallization of 1 g. from cold hexane gave 400 mg. of XVII as prismatic plates, m.p. 121.5–122° (lit.[2] m.p. 120–121°).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.9; H, 10.6. Found: C, 79.2; H, 10.3.

The *p*-nitrobenzoate ester, m.p. 98.5–99° (lit. m.p. 98–99°,[2] 96–97°[16]) and *acid phthalate ester*, m.p. 197–197.5° (lit.[16] m.p. 188–189°) were prepared in the usual fashion.

Anal. for acid phthalate: Calcd. for $C_{18}H_{20}O_4$: C, 72.0; H, 6.71; neut. equiv., 300. Found: C, 72.0; H, 6.50; neut. equiv., 302.

Infrared Spectra.—A Perkin-Elmer model 21 infrared spectrometer was used. All four hydrocarbons (I–IV) have a common peak at 6.35 μ.[6] The double bond in the five-membered ring, present in III and IV, is responsible for a peak at 6.18 μ.[6] The following peaks appear to be specific for each material if the others are present: I, 8.74 μ (IV interferes slightly); II, 6.23 μ, 11.27 μ; III, 8.62 μ (I interferes slightly); IV, 7.92 μ. In the absence of the dihydro isomers (I and II), an absorption maximum at 7.55 μ can be used to detect IV in III. In materials containing over 90% of I and II, with substantial amounts of II present, the presence of III and/or IV can be recognized from the 6.18 μ band, but the two isomers cannot be further distinguished. In the absence of III and IV, I has peaks at 6.08, 7.42, 8.06 and 8.74 μ and II at 6.23, 11.27 and 13.05 μ which distinguish these isomers from each other.

The phenyldihydrotriazoles of I and II have analytical wave lengths at 12.21 and 9.88 μ, respectively. Unfortunately that of IV has weak absorption at 12.21 μ and that of III at 9.88 μ. Thus the errors in quantitative analysis of I and II increase with increasing amounts of dicyclopentadiene isomers present.

The composition of the mixture of phenyl azide addition products has been determined by a quantitative infrared analytical procedure. The solid mixtures were suspended in potassium bromide disks, and the principle of the ratio method[26] combined with a technique developed for the analysis of rubber films[27] has been applied. The advantage of plotting ratios of extinction coefficients against composition is that the variables due to pellet thickness are eliminated. Applying transmittances from 20 to 85% for the *exo*-II derivative (analytical wave length: 9.88 μ) and 60–85% for the *endo*-I derivative (analytical wave length: 12.21 μ) a linear working curve was obtained covering compositions from 0 to 100% *endo* and from 0 to 75% *exo*. In order to determine higher concentrations of II, a known amount of pure I derivative has to be added to the sample to bring the *exo* component in the accurately measurable range below 75%.

The assumption that the composition of the isomers I and II is unchanged in their crude dihydrotriazole derivatives has been established by a test analysis. In the absence of considerable amounts of dicyclopentadienes III and IV which show weak absorptions at the analytical wave lengths, mixtures of I and II may be analyzed with an experimental error of ±2% for II and ±3% for I. The percentages given in Table I are the average values of several quantitative determinations.

The third selected wave length for the analytical procedure[26] has a maximum rather independent of the composition at 9.66 μ, with an intensity lying between 20 and 50% transmittance. For the latter absorption, the I^0 values were taken from the base line. To avoid stray energy the measured values were taken relative to the maximum at 6.70 μ.[26] Mixtures of the pure phenyldihydrotriazoles of I and II were prepared and appropriate ratios of corrected extinction coefficients were plotted against the composition. The data obtained are given in Table II, Q_{exo} and Q_{endo} being the ratio of extinction coefficients at 9.88 and 12.21 μ to that at 9.66 μ, respectively.

TABLE II

MELTING POINT AND INFRARED INTENSITY DATA FOR MIXTURES OF THE PHENYLDIHYDROTRIAZOLES OF *endo* AND *exo*-DIHYDRODICYCLOPENTADIENES

—Composition, %—				
endo (I)	*exo* (II)	Q_{endo}[a]	Q_{exo}[b]	M.p., °C.
100	0	0.345	0.045	128–129
83.7	16.3	.275	.173	.....
77.0	23.0	.266	.230	105–109
65.8	34.2	.227	.350	104–106.5
51.3	48.7	.183	.452	103–105
37.5	62.5	.131	.613	104–112
24.0	76.0	.169[c]	.723	118–126
6.3	93.7	.015	.839[c]	134–138
0	100	.000	[c]	142–143.5

[a] Ratio of extinction coefficient at 12.21 μ to that at 9.66 μ. [b] Ratio of extinction coefficient at 9.88 μ to that at 9.66 μ. [c] Not utilized; see text.

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(26) H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis," 3rd Edition, D. Van Nostrand Co., Inc., Princeton, N. J., 1958, p. 147.

(27) H. L. Dinsmore and D. C. Smith, *Anal. Chem.*, **20**, 11 (1948).