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The Chemistry of Dicyclopentadiene. II. Addition-Rearrangement with Acids

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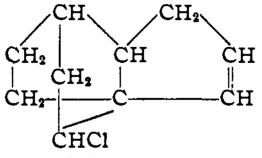
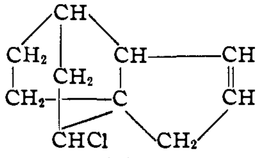
When dry hydrogen chloride is bubbled into dry dicyclopentadiene at 60–70° practically no addition of the hydrogen chloride to the double bonds of the hydrocarbon occurs. However, if a small amount of water is present, addition of the hydrogen chloride takes place readily to form a monohydrochloride. This reaction product still contains one double bond even though an excess of hydrogen chloride be used.

The chlorine atom in the dicyclopentadiene monohydrochloride is extremely resistant to hydrolysis and replacement reactions. For example it withstands boiling for twenty hours with 10% alcoholic potassium hydroxide solution, and remains unaffected upon boiling with zinc in glacial acetic acid. On the other hand, it readily forms a Grignard reagent upon warming with magnesium turnings in ether, behaving in these respects exactly like a neopentyl chloride.[1]

Furthermore, dicyclopentadiene monohydrochloride is identical with the product obtained by the action of phosphorus trichloride on hydroxy-dihydro-*nor*-dicyclopentadiene, the hydration-rearrangement product of dicyclopentadiene,[2] obtainable by the action of dilute sulfuric acid on the hydrocarbon.

In conformity with this fact and with its behavior as a substituted neopentyl chloride, dicyclopentadiene monohydrochloride is, therefore, chlorodihydro-*nor*-dicyclopentadiene, represented by one of the structures (A) or (B).

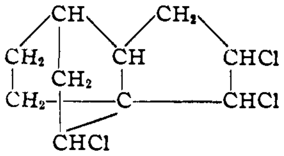

(A)


(B)

It is more readily obtained in the laboratory in 85–88% yield by simply stirring dicyclopentadiene with aqueous concentrated hydrochloric acid (35% HCl) on a steam-bath at 65–70° for several hours.

In a similar manner dicyclopentadiene readily reacts with aqueous hydrobromic or hydriodic acid to yield the corresponding bromo-dihydro-*nor*-dicyclopentadiene or iodo-dihydro-*nor*-dicyclopentadiene, respectively. It does not, however, react with aqueous hydrofluoric acid under the same conditions.

The residual double bond in these rearranged dicyclopentadiene hydrohalides, although quite inert toward the addition of a second molecule of hydrogen halide, does however add halogen. Chlorine, for example, readily combines with chloro-dihydro-*nor*-dicyclopentadiene to give trichloro-tetrahydro-*nor*-dicyclopentadiene (C) or (D).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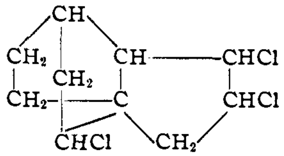
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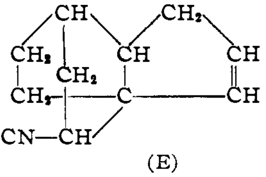
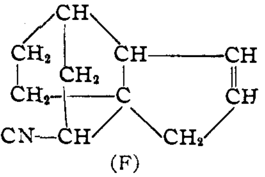
The molecular rearrangement induced by hydrogen ions on dicyclopentadiene is not limited to inorganic acids. Strong organic acids also add to dicyclopentadiene with a simultaneous molecular rearrangement of the ring system. Chloroacetic acid for example combines directly with dicyclopentadiene on heating to give the chloroacetate of hydroxy-dihydro-*nor*-dicyclopentadiene in about 40% yield. The addition-rearrangement is accelerated and the yield is considerably increased however by the presence of small quantities of inorganic acidic catalysts such as sulfuric acid, boron trifluoride or boron trifluoride complexes with water or ethers. By means of these catalysts it is possible to add even very weak organic acids, for example the higher fatty acids to dicyclopentadiene, to form the corresponding esters of hydroxydihydro-*nor*-dicyclopentadiene by rearrangement of the bridged cyclohexene ring.

This reaction was applied to a variety of organic acids and dicyclopentadiene to give the esters shown in Table I.

Upon saponification with alcoholic potassium hydroxide these esters yield hydroxy-dihydro-*nor*-dicyclopentadiene identical with that obtained by hydration of dicyclopentadiene with dilute sulfuric acid.

The addition of aqueous thiocyanic acid to dicyclopentadiene yields a hydro-isothiocyanate $C_{10}H_{15}$—NCS which, by analogy with the hydrochloride, possesses formula (E) or (F).


(E)


(F)

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(1) Whitmore and Fleming, THIS JOURNAL, **55**, 4162 (1933).

(2) Bruson and Riener, *ibid.*, **67**, 723 (1945).

TABLE I

ESTERS OF HYDROXY-DIHYDRO-*nor*-DICYCLOPENTADIENE

Ester	B. p., °C.	Mm.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Acetate[a]	119–121	10	$C_{12}H_{16}O_2$	74.95	8.39	75.15	8.30
Propionate[a]	131–133	10	$C_{13}H_{18}O_2$	75.72	8.73	75.61	8.60
Levulinate[a]	190	10	$C_{15}H_{20}O_3$	72.53	8.12	72.35	8.03
α-Hydroxyisobutyrate[a]	155–157	10	$C_{14}H_{20}O_3$	71.13	8.54	71.34	8.66
Crotonate[a]	128–130	3	$C_{14}H_{18}O_2$	77.01	8.25	77.03	8.31
Lactate[a]	150–155	8–9	$C_{13}H_{18}O_3$	70.22	8.16	69.92	8.25
2-Ethyl-hexoate[b]	150–152	2	$C_{18}H_{28}O_2$	78.20	10.21	78.29	10.25
Laurate[b]	195–200	2	$C_{22}H_{36}O_2$	79.45	10.92	79.30	10.75
Benzoate[b]	164	2	$C_{17}H_{18}O_2$	80.23	7.13	80.31	7.17
Salicylate[a]	174–176 m. p. 94	3	$C_{17}H_{18}O_3$	75.51	6.71	75.64	6.75
Furoate[b]	165–167 m. p. 73	2	$C_{15}H_{16}O_3$	73.77	6.60	73.85	6.56

[a] H_2SO_4 catalyst. [b] Boron trifluoride etherate, $BF_3 \cdot O(C_2H_5)_2$, catalyst.

The reaction takes place on warming dicyclopentadiene with aqueous ammonium thiocyanate and gradually adding hydrochloric acid to the rapidly stirred mixture. The thiocyanic acid momentarily liberated in aqueous solution reacts immediately with the dicyclopentadiene.

The dihydro-*nor*-dicyclopentadienyl-isothiocyanate thus obtained reacts with ammonia to yield a crystalline thiourea $C_{10}H_{13}NHCSNH_2$, and with acetic acid to yield the corresponding acetylamino-dihydro-*nor*-dicyclopentadiene $C_{10}H_{13}NHCOCH_3$.

With thioglycolic acid, however, dicyclopentadiene does not give an ester, but forms instead a crystalline thioether $C_{10}H_{13}SCH_2COOH$. The reaction which occurs is strongly exothermic. It is very probable that here too the ring system of dicyclopentadiene has rearranged in a manner analogous to that caused by the other acids as described above.

Experimental

Chloro-dihydro-*nor*-dicyclopentadiene (A or B).—A mixture of 132 g. of freshly distilled dicyclopentadiene and 200 g. of concentrated hydrochloric acid (35% HCl) was rapidly stirred and heated at 60–70° for five hours. The product was washed and the oil layer was separated, dried over a little sodium sulfate and distilled *in vacuo*. The product distilled at 102–104° (10–12 mm.) as a colorless oil; yield 147.5 g. or 87.5%. Upon redistillation, the sample for analysis boiled at 100–102° (11 mm.); $n^{25}\mathrm{D}$ 1.5208; $d^{25}{}_4$ 1.1121.

Anal. Calcd. for $C_{10}H_{13}Cl$: Cl, 21.03. Found: Cl, 20.89. It was identical with the product obtained by treating phosphorus trichloride with hydroxy-dihydro-*nor*-dicyclopentadiene.[3]

Bromo-dihydro-*nor*-dicyclopentadiene.—A mixture of 132 g. of dicyclopentadiene and 338 g. of 48% hydrobromic acid was stirred at 65–70° for three hours and worked up as above. The product distilled at 113–114° (11 mm.) as a colorless oil; yield 85–90%; $n^{25}\mathrm{D}$ 1.5437; $d^{25}{}_4$ 1.3489.

Anal. Calcd. for $C_{10}H_{13}Br$: Br, 37.51. Found: Br, 36.97.

Iodo-dihydro-*nor*-dicyclopentadiene.—A mixture of 132 g. of dicyclopentadiene and 270 g. of 47% hydriodic acid was stirred at 65° for five hours and worked up as above to give 95 g. of purified product boiling at 130–132° (11 mm.). It is a pale yellow oil which darkens on standing; $d^{25}{}_4$ 1.5617.

Anal. Calcd. for $C_{10}H_{13}I$: I, 48.81. Found: I, 48.64.

Trichloro-tetrahydro-*nor*-dicyclopentadiene (C or D).—Chlorine was bubbled into a solution of 84 g. of carbon tetrachloride and 84 g. of chloro-dihydro-*nor*-dicyclopentadiene at 10–20° until the gain in weight amounted to 50 g. The solution was washed with water, then with dilute soda solution and finally with water. It was then dried over $CaCl_2$ and distilled *in vacuo*. The product distilled at 143–153° (2–3 mm.) as a faintly yellow oil; yield 98 g. The sample for analysis boiled at 175–180° (11 mm.). It was a colorless oil.

Anal. Calcd. for $C_{10}H_{13}Cl_3$: Cl, 44.42. Found: Cl, 44.26.

Esters of Hydroxy-dihydro-*nor*-dicyclopentadiene

Chloroacetate.—A mixture of 132 g. of dicyclopentadiene and 132 g. of chloroacetic acid was stirred and heated for twelve hours at 95°. The product was distilled *in vacuo*. The ester distilled at 125–130° (1 mm.) as a colorless oil; yield 90 g. or 40%. The sample for analysis boiled at 154–156° (10 mm.); $n^{25}\mathrm{D}$ 1.5111; $d^{25}{}_4$ 1.1916.

Anal. Calcd. for $C_{12}H_{15}O_2Cl$: C, 63.59; H, 6.60; Cl, 15.67. Found: C, 63.58; H, 6.70; Cl, 15.30.

The yield is improved by using an acidic catalyst as follows. To a stirred mixture of 189 g. of chloroacetic acid and 5 g. of 40% sulfuric acid at 75° there was added dropwise 278 g. of dicyclopentadiene during the course of forty-five minutes. The reaction is exothermic. During the addition, the temperature was maintained at 75–85°. After all the dicyclopentadiene was added the mixture was stirred for three hours longer at 95°, then cooled, washed with water twice, then soda solution and again with water. The yield of dihydro-*nor*-dicyclopentadienyl chloroacetate boiling at 123–128° (0.5 mm.) was 335 g. or 74%.

Acetate.—A mixture of 250 g. of glacial acetic acid, 4 g. of 98% sulfuric acid, 6 g. of water and 100 g. of dicyclopentadiene was stirred at 60–70° for five hours. The mixture was cooled, poured into a liter of water and the oil layer was separated, washed with water and dilute soda solution, dried over sodium sulfate and distilled *in vacuo*. The ester distilled at 95–100° (1 mm.) as a colorless liquid having a characteristic melon-like odor; yield 121 g. or 83%. The sample for analysis boiled at 119–121° (10 mm.) and possessed $n^{25}\mathrm{D}$ 1.4935, $d^{25}{}_4$ 1.0714.

Anal. Calcd. for $C_{12}H_{16}O_2$: iodine no., 132; sapn. no., 292. Found: iodine no. (Wijs), 134; sapn. no., 290.

The propionate, levulinate, α-hydroxyisobutyrate, crotonate, lactate, and salicylate (see Table I) were prepared in a manner similar to the acetate. The yields were between 55 and 70%.

Laurate.—To a stirred mixture of 200 g. of lauric acid and 132 g. of dicyclopentadiene, 30 g. of boron fluoride-diethyl ether $BF_3 \cdot O(C_2H_5)_2$ was added gradually. The mixture was stirred and heated at 80–85° for five hours, then washed with water and soda solution, dried, and distilled *in vacuo*. The dihydro-*nor*-dicyclopentadienyl laurate distilled at 195–200° (2 mm.) as a colorless oil; yield 145 g. or 44%; n^{25}_D 1.4797; d^{25}_4 0.955; sapn. no., 167 (calcd. 169).

The 2-ethyl hexoate, benzoate and furoate (see Table I) were prepared in a manner similar to the laurate. The yields were between 50 and 65%.

Dihydro-*nor*-dicyclopentadienyl Isothiocyanate (E or F).—A mixture of 132 g. of dicyclopentadiene, 75 g. of water, and 76 g. of ammonium thiocyanate was rapidly stirred and heated at 90–95° under a reflux condenser. To the hot, stirred solution, 100 g. of concentrated hydrochloric acid (37% HCl) was added dropwise during the course of one hour while the reaction mixture was maintained at 90–95° and rapidly agitated. The mixture was then stirred for three hours longer at 90–95°, filtered hot by suction to remove traces of polythiocyanic acid, and the clear, filtered oil layer was separated, washed with water and distilled *in vacuo*. The product distilled at 127–132° (2 mm.) as a pale yellow oil, having a characteristic odor; yield 120 g. or 62%. The analytical sample boiled at 140–142° (6 mm.); n^{25}_D 1.5580; d^{25}_4 1.1318.

Anal. Calcd. for $C_{11}H_{13}NS$: N, 7.33; S, 16.75. Found: N, 6.96; S, 16.93.

Dihydro-*nor*-dicyclopentadienyl Thiourea.—A mixture of 19 g. of dihydro-*nor*-dicyclopentadienyl isothiocyanate and 100 g. of concentrated ammonium hydroxide was rapidly stirred and heated under a reflux condenser on a steam-bath for two hours during which time a semi-solid mass formed. One hundred grams additional ammonium hydroxide was then added and the mixture stirred for three hours longer at 90–95°. The solid mass obtained in almost quantitative yield was recrystallized from ethanol to give colorless plate-like crystals, m. p. 203–204° (uncor.).

Anal. Calcd. for $C_{11}H_{16}N_2S$: C, 63.46; H, 7.69; N, 13.46; S, 15.38. Found: C, 63.51; H, 7.56; N, 13.49; S, 15.00.

Acetylamino-dihydro-*nor*-dicyclopentadiene.—A mixture of 180 g. of glacial acetic acid and 145 g. of dihydro-*nor*-dicyclopentadienyl isothiocyanate was boiled under reflux for four hours and the product was then distilled *in vacuo*. The fraction boiling at 155–175° (4 mm.) was a viscous oil; yield 63 g. It was distilled to give a heart cut (28.5 g.) boiling at 170–175° (3 mm.) which crystallized on standing. After recrystallization from petroleum ether, m. p. 129–130° (uncor.).

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.39; H, 8.90; N, 7.33. Found: C, 75.14; H, 8.88; N, 7.22.

Dihydro-*nor*-dicyclopentadienyl Thioacetic Acid.—To 26.4 g. of dicyclopentadiene there was added 18.4 g. of thioglycolic acid. A vigorous reaction occurred during which the temperature rose rapidly to 90°. At this point cooling was applied and, after the reaction had subsided, the mixture was heated for one hour longer at 90° to complete the reaction. The product was then distilled *in vacuo* to give 30 g. of thick oil boiling at 190–200° (4 mm.).

Upon redistillation it boiled at 182° (2 mm.) and crystallized on standing; m. p. 53–54° (from petroleum ether).

Anal. Calcd. for $C_{12}H_{16}O_2S$: C, 64.29; H, 7.14; S, 14.28; acid no., 251. Found: C, 64.01; H, 6.88; S, 13.84; acid no., 252.

Acknowledgment.—The analyses of the above products were performed by Mr. Clyde W. Nash of these laboratories.

Summary

1. Dicyclopentadiene reacts with hydrochloric, hydrobromic, hydriodic and thiocyanic acids to yield unsaturated addition-rearrangement products. It also adds organic carboxylic acids to one of its double bonds to yield esters of hydroxy-dihydro-*nor*-dicyclopentadiene. These reactions are catalyzed by hydrogen ions or by acidic catalysts. Thioglycolic acid adds to dicyclopentadiene to yield an unsaturated thioether instead of an ester.

2. The addition product of dicyclopentadiene and thiocyanic acid is a hydroisothiocyanate.

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[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT OF THE MONSANTO CHEMICAL COMPANY]

Isomerization of Alkylphosphites. III. The Synthesis of *n*-Alkylphosphonic Acids

BY GENNADY M. KOSOLAPOFF

Although the preparation of some members of the *n*-alkylphosphonic acid series has been reported occasionally since the middle of the last century, the amount of accurate scientific data on the properties and on the satisfactory synthetic methods remains meager.

This series of organo-phosphorus compounds is one of the basic series in the field of phosphorus derivatives, being comparable in position to the aliphatic monocarboxylic acids in the carbon realm. Yet, at the present time only the methyl-, ethyl-, propyl-, butyl- and *n*-heptyl-phosphonic acids appear to have been prepared in a state of sufficient purity to have been reported in the chemical literature.

It was felt that the information required to fill the gap should be obtained in order to study the properties of this important series. The review of the available synthetic methods showed that the preparation through the isomerization of alkyl phosphites under the influence of alkyl halides showed the best promise of synthesis of compounds of definite structure with satisfactory yields. Thus, in the modern times, Nylen[1] prepared methyl-, ethyl- and *n*-propyl-phosphonic acids through the reaction of sodium diethylphosphite with the corresponding alkyl halides, followed by hydrolysis of the resulting diethyl *n*-alkylphosphonates. Arbuzov and Arbuzova[2] prepared *n*-butylphosphonic acid through isomerization of tri-butylphosphite by *n*-butyl iodide, followed by hydrolysis of the dibutyl *n*-butylphosphonate. Finally, Fossek[3] reported the synthesis of a higher alkylphosphonic acid, *n*-heptylphosphonic acid, through reduction of 1-hydroxyheptylphosphonic acid.

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(1) P. Nylen, "Studien über org. Phosphorverbindungen," Upsala, 1930.

(2) Arbuzov and Arbuzova, *J. Russ. Phys.-Chem. Soc.*, **62**, 1533 (1930).

(3) Fossek, *Monatsh.*, **7**, 29 (1886).