[Contribution from the Chemistry Laboratory, University of Missouri]

SOME $\Delta^{4,10}$-OCTAHYDRONAPHTHALENE-1,2-DICARBOXYLIC ACID ANHYDRIDES

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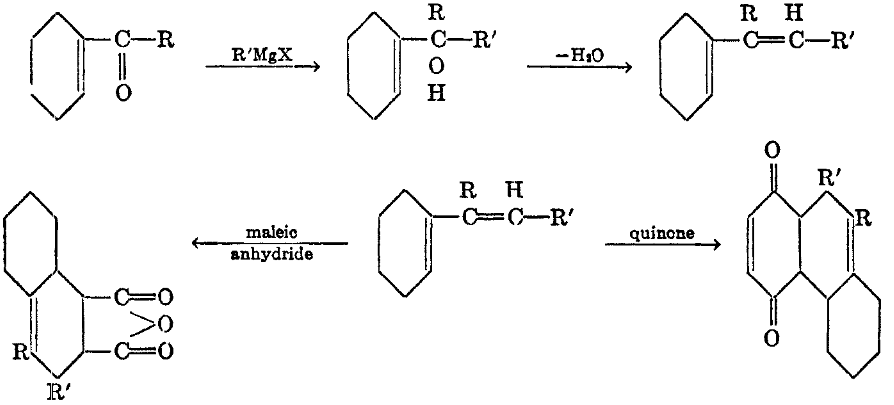
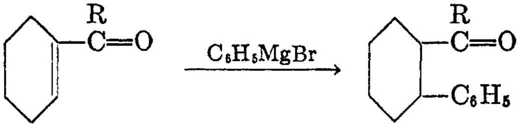
The purpose of this investigation was to prepare a series of $\Delta^{4,10}$-octahydronaphthalene-1,2-dicarboxylic anhydrides and some decahydrophenanthraquinones by the following series of reactions



The cyclohexenyl ketones were obtained in good yields from cyclohexene and acid chlorides in the presence of either aluminum chloride or stannic chloride (1, 2, 3).

The tertiary carbinols from the reaction of the cyclohexenyl ketones with the Grignard reagents dehydrated so readily that it was difficult if not impossible to obtain them free from diolefin. The reaction of 1-cyclohexenyl isopropyl ketone and isopropylmagnesium bromide yielded mainly 1-cyclohexenylisopropyl carbinol by reduction of the ketone.

Phenylmagnesium bromide reacted with 1-cyclohexenyl methyl ketone and the ethyl ketone to form the tertiary carbinol and some 2-phenylhexahydroacetophenone and 2-phenylhexahydropropiophenone respectively by 1,4-addition to the conjugated system of the ketone.



The 2-phenylhexahydroacetophenone has recently been reported as a by-product from the aluminum chloride catalyzed reaction of 1-cyclohexenyl methyl ketone with benzene (4).

The dienes were obtained from the tertiary carbinols by distillation with iodine or potassium acid sulfate in an atmosphere of nitrogen. They reacted readily with maleic anhydride to form the expected adducts in good yields, but solids were obtained from only two of the dienes and *p*-benzoquinone. Cook and Lawrence (5) have reported a Diels-Alder reaction of 1-vinyl-1-cyclohexene with maleic anhydride and benzoquinone. Meggy and Robinson (6) obtained 9-methyl-$\Delta^{4,10}$-octahydronaphthalene-1,2-dicarboxylic anhydride from 1-methyl-2-vinylcyclohexene-1 and maleic anhydride.

EXPERIMENTAL

The cyclohexenyl ketones were prepared by the slow addition of 1.2 moles of aluminum chloride to 1 mole of acid chloride and 1 mole of cyclohexene in 500 cc. of carbon disulfide (3). After the complex was decomposed, washed, and dried, the reaction product was distilled under reduced pressure to separate the intermediate 2-chloro ketone from high-boiling by-products.

TABLE I

THE 2,4-DINITROPHENYLHYDRAZONES OF THE CYCLOHEXENYL KETONES

R	M.P. °C.	FORMULA	CARBON, %		HYDROGEN, %	
			Calc'd	Found	Calc'd	Found
CH_3	202–203	$C_{14}H_{16}N_4O_4$	55.20	55.20	5.30	5.43
C_2H_5	206–207	$C_{15}H_{18}N_4O_4$	56.6	56.42	5.70	5.69
n-C_3H_7	160–161	$C_{16}H_{20}N_4O_4$	57.88	57.62	6.07	6.29
i-C_3H_7	121–122	$C_{16}H_{20}N_4O_4$	57.88	57.86	6.07	6.33
n-C_4H_9	147–148	$C_{17}H_{22}N_4O_4$	58.95	59.06	6.40	6.27
i-C_4H_9	156–157	$C_{17}H_{22}N_4O_4$	58.95	59.11	6.40	6.38
n-C_5H_{11}	118–119	$C_{18}H_{24}N_4O_4$	61.1	60.8	6.72	6.53

The crude 2-chloro ketones were dehydrohalogenated by distillation under reduced pressure with sodium or potassium carbonate (3). The 1-cyclohexenyl ketones so obtained were redistilled from carbonate, but this product always gave a positive Beilstein test for halogen and darkened on standing, with the formation of variable amounts of high-boiling condensation products. The cyclohexenyl ketones were further purified by heating with dimethylaniline at 180° for two hours (2, 7), to yield finally a product which was halogen-free. Ketones which had been standing for some time were redistilled just before they were used in the Grignard reaction. All the ketones studied are described in the literature with the exception of the 1-cyclohexenyl *n*-butyl and *n*-amyl ketones.

1-Cyclohexenyl n-butyl ketone; yield 59%, b.p. 133–137° (27 mm.).

Anal. Calc'd for $C_{11}H_{18}O$: C, 78.21; H, 11.60.
Found: C, 78.60; H, 11.32.

1-Cyclohexenyl n-amyl ketone; yield, 44%, b.p. 121–123° (18 mm.).

Anal. Calc'd for $C_{12}H_{20}O$: C, 79.91; H, 11.21.
Found: C, 79.95; H, 11.31.

The 2,4-dinitrophenylhydrazones of the ketones were more conveniently prepared than the semicarbazones. They are listed in Table I.

The tertiary carbinols were formed by the reaction of 0.5 mole of the cyclohexenyl ketone with 0.6 mole of a Grignard reagent containing the same alkyl radical as that in the ketone. The products were worked up in the usual manner and were distilled at as low a pressure as possible to avoid dehydration of the tertiary carbinol to the diolefin, but only two of the carbinols were obtained pure enough for analysis. All the carbinols were pale yellow, even when freshly distilled.

A sample of diethylcyclohexenyl carbinol which had stood in a cork stoppered bottle for several months became viscous and developed a dark red color. The boiling point rose from 60–61° (1 mm.) to 120–155° (5 mm.) and 20% of the material was a tarry residue.

Diethyl-1-cyclohexenyl carbinol; b.p. 60–61° (1 mm.).

Anal. Calc'd for $C_{11}H_{20}O$: C, 78.51; H, 11.92.
Found: C, 78.54; H, 12.02.

Di-n-propyl-1-cyclohexenyl carbinol; b.p. 86–88° (2 mm.).

Anal. Calc'd for $C_{13}H_{24}O$: C, 79.53; H, 12.32.
Found: C, 79.02; H, 12.18.

Isopropyl-1-cyclohexenyl carbinol. The product from the reaction of 1-cyclohexenyl isopropyl ketone and 0.6 mole of isopropylmagnesium bromide distilled at 74–120° (4 mm.). Careful fractionation of this material yielded 36 g. of isopropyl-1-cyclohexenyl carbinol, b.p. 115–118° (18 mm.); n_D^{20} 1.4645.

Anal. Calc'd for $C_{10}H_{18}O$: C, 77.85; H, 11.77.
Found: C, 77.93; H, 12.07.

Reaction of 1-cyclohexenyl methyl ketone with phenylmagnesium bromide. The ketone (0.52 mole) in 100 cc. of dry ether was added to the Grignard reagent from 0.78 mole of bromobenzene in 200 cc. of ether. The reaction product was separated first into three ractions: (I) 14 g. b.p. 64–80° (4 mm.); (II) 43 g. b.p. 80–85° (4 mm.); (III) 17 g. residue. Careful fractionation of (I) and (II) and molecular distillation of the residue yielded an impure tertiary carbinol and a white solid distilling above 105° (5 mm.). Crystallization of the solid from alcohol yielded 8 g. of 2-phenylhexahydroacetophenone m.p. 79–80° (4).

TABLE II

THE DIENES

	B.P., °C./MM	n_D, t	FORMULA	CARBON, %		HYDROGEN, %	
				Calc'd	Found	Calc'd	Found
2-(1-Cyclohexenyl)-2-propene	66–68/20	26° 1.4978	C_9H_{14}	88.45	88.13	11.55	11.36
3-(1-Cyclohexenyl)-2-butene	55–56/4	28° 1.4863	$C_{11}H_{18}$	87.86	87.95	12.07	12.27
3-(1-Cyclohexenyl)-2-heptene	70–71/3	27° 1.4892	$C_{13}H_{22}$	87.56	87.70	12.44	12.34
2, 6 - Dimethyl - 4 - (1 - cyclohexenyl)-3-heptene	76–77/1	26° 1.4708	$C_{15}H_{26}$	87.28	86.95	12.74	12.94

Anal. Calc'd for $C_{14}H_{18}O$: C, 83.13; H, 8.97.
Found: C, 82.99; H, 9.13.

The 2,4-dinitrophenylhydrazone of this ketone melted at 140–141°, the recorded melting point (4).

1-Cyclohexenyl ethyl ketone reacted similarly to yield impure tertiary carbinol and 6–8% of 2-phenylhexahydropropiophenone, a viscous oil which would not solidify, and which could not be purified. The oil reacted with 2,4-dinitrophenylhydrazine to form a 2,4-dinitrophenylhydrazone of 2-phenylhexahydropropiophenone which crystallized from alcohol in pale orange plates, m.p. 132–133°.

Anal. Calc'd for $C_{21}H_{24}N_4O_4$: C, 63.60; H, 6.10.
Found: C, 63.75; H, 6.26.

Analyses of the tertiary carbinol fractions indicated the presence of diolefin.

The dienes. The dienes were obtained from the tertiary carbinols either by heating them with potassium bisulfate or with iodine in an atmosphere of nitrogen just prior to distillation under diminished pressure. They were dried briefly and used directly in the Diels-Alder reactions. The samples for analyses and physical constants listed in Table II were dried over sodium and were carefully fractionated in an atmosphere of nitrogen. They were analyzed immediately after distillation.

The Diels-Alder reactions. The dienes were added to maleic anhydride dissolved in xylene (5). After warming on a water-bath, the solution was allowed to stand for several days. The solvent was removed under diminished pressure, leaving a sticky solid which was purified by digestion with water and finally by crystallization from petroleum ether. The acid anhydrides were obtained as fine colorless needles. Yields ranged from 21% to 41%.

The condensations of the dienes with *p*-benzoquinone were carried out in methyl alcohol solution. The reactants were mixed, allowed to stand overnight, then refluxed two hours. The solvent was removed on a water-bath, leaving a red oil which solidified on standing in the ice-chest. The solid was crystallized from methyl alcohol to yield yellow needles. Pure diketones were obtained from only two of the dienes.

These condensation products are listed in Table III.

TABLE III

THE $\Delta^{4,10}$-OCTAHYDRONAPHTHALENE-1,2-DICARBOXYLIC ANHYDRIDES

R	R′	M.P., °C.	FORMULA	CARBON, %		HYDROGEN, %	
				Calc'd	Found	Calc'd	Found
CH_3	H	76.2	$C_{13}H_{16}O_3$	70.88	70.68	7.32	7.82
C_2H_5	CH_3	92.8	$C_{15}H_{20}O_3$	72.53	72.22	8.12	8.49
n-C_3H_7	C_2H_5	105.8	$C_{17}H_{24}O_3$	73.88	73.58	8.75	8.75
i-C_4H_9	i-C_3H_7	145	$C_{19}H_{28}O_3$	74.95	74.76	9.27	9.23
THE 5,8-DIKETO-$\Delta^{6,7}$, $\Delta^{10,10a}$-DECAHYDROPHENANTHRENES							
CH_3	H	102	$C_{15}H_{18}O_2$	78.23	78.01	7.88	7.88
n-C_3H_7	C_2H_5	84	$C_{19}H_{26}O_2$	79.68	79.59	9.15	9 23

SUMMARY

A convenient method has been developed for the preparation of substituted 1-vinyl-1-cyclohexenes. These dienes react readily with maleic anhydride to form $\Delta^{4,10}$-octahydronaphthalene-1,2-dicarboxylic anhydrides.

2-Phenylhexahydroacetophenone and 2-phenylhexahydropropiophenone were isolated from the reaction of 1-cyclohexenyl methyl and ethyl ketones respectively with phenylmagnesium bromide.

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