EXPERIMENTAL[1]

2,6-Dimethyl-1,4-cyclohexanediol (I). Ten grams of *m*-xyloquinone was reduced in ethanol over Raney nickel at 500 lbs. p.s.i. at 180°. The yield of product boiling at 85–90° at 0.3 mm. was 1.42 g. (13.5%). A redistilled sample was analyzed.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.70; H, 11.28.

3,5-Dimethyl-4-hydroxycyclohexanone (II). A solution of 0.9 g. (0.009 mole) of chromic oxide in 11 ml. of water was added dropwise to 2 g. (0.014 mole) of 2,6-dimethyl-1,4-cyclohexanediol in 95 ml. of glacial acetic acid. After the solution had stood for 2 hr. at room temperature and had been warmed for 15 min. on the steam bath, solvents were removed *in vacuo*. The residue was dissolved in water and extracted with chloroform. The chloroform extracts were washed with water and concentrated *in vacuo*. The residue was distilled at a bath temperature of 86° at 0.5 mm., n_D^{25} 1.4690. The ultraviolet spectrum showed absorption at 285 mμ, ϵ 25, the infrared spectrum at 2.80, 2.94, and 5.88 μ. The *2,4-dinitrophenylhydrazone* melted at 143–145° (from ethanol).

Anal. Calcd. for $C_{14}H_{18}N_4O_5$: C, 52.17; H, 5.63; N, 17.39. Found: C, 51.95; H, 5.69; N, 17.25.

The *p-toluenesulfonate* melted at 125–127° (from methanol).

Anal. Calcd. for $C_{15}H_{20}O_4S$: C, 60.78; H, 6.80; S, 10.82; mol. wt., 296.4. Found: C, 60.86; H, 7.04; S, 10.65; mol. wt. (ebull.), 266.8.

4-Acetoxy-3,5-dimethylcyclohexanone (III). A solution of 5.0 g. (0.035 mole) of 3,5-dimethyl-4-hydroxycyclohexanone and 35.8 g. (0.35 mole) of acetic anhydride in 120 ml. of dry pyridine was heated on the steam bath for 2 hr. The cooled solution was added to water which was then saturated with sodium bicarbonate. After evaporation of the solvent *in vacuo*, the residue was dissolved in water and extracted with ether. The ether extracts were dried and evaporated in *vacuo*. Distillation gave 3.33 g. (51%), b.p. 120° at 12 mm. The ultraviolet spectrum showed only end absorption; the infrared spectrum had bands at 5.78 and 5.83 μ.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.76; $CH_3CO(1)$, 23.37. Found: C, 65.01; H, 8.80; CH_3CO, 15.57.

4-Acetoxy-1,3,5-trimethylcyclohexanol (IV). A solution of methylmagnesium iodide (from 0.82 g. of magnesium and 3 ml. of methyl iodide in 10 ml. of dry ether) and 3.2 g. (0.017 mole) of 4-acetoxy-3,5-dimethylcyclohexanone was refluxed, acidified with hydrochloric acid, and extracted with ether. The extracts were dried and concentrated *in vacuo*. Distillation gave 1.3 g. (38%) of diol monoacetate, b.p. 80° at 0.3 mm., n_D^{25} 1.4608. The infrared spectrum showed absorption at 2.82, 2.90, and 5.84 μ.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.96; H, 10.02; $CH_3C(4)$, 30.02; $CH_3CO(1)$, 21.49; mol. wt., 200.3. Found: C, 66.16; H, 10.59; CH_3C, 21.65; CH_3CO, 10.48; mol. wt. (ebull.), 184.3.

2,4,6-Trimethyl-3-cyclohexenyl acetate (V). A solution of 8.3 g. (0.041 mole) of 4-acetoxy-1,3,5-trimethylcyclohexanol and 0.55 g. of iodine in 70 ml. of dry toluene was refluxed for 4 hr. removing water continuously as formed. The toluene solution was washed with 5% sodium hydrosulfite solution and water and evaporated *in vacuo*. Distillation gave 3.48 g. (46%) of product, b.p. 82–93° at 11 mm., n_D^{25} 1.4638. This material gave the usual olefin tests, and the infrared spectrum no longer showed hydroxyl absorption but did show carbonyl absorption. A fractionated sample was analyzed.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.47; H, 9.96; $CH_3CO(1)$, 23.61; $CH_3C(4)$, 33.00; mol. wt., 182. Found: C, 72.12; H, 10.24; CH_3CO, 18.68; CH_3C, 25.19; mol. wt. (ebull.), 184.2.

2,4,6-Trimethyl-3-cyclohexenol (VI). A solution of 2,4,6-trimethylcyclohexenylacetate (prepared from 4.0 g. of IV and not distilled) and 10 g. of sodium hydroxide in 40 ml. of 50% alcohol was refluxed for 3 hr. The reaction mixture was diluted with water and extracted with ether. The ether extracts were dried, evaporated *in vacuo* and the residue was distilled. The yield of product boiling at 85–97° at 12 mm. was 0.8 g. The infrared spectrum showed absorption at 2.80 2.94, and 6.05 μ.

Anal. Calcd. for $C_9H_{16}O$: C, 77.10; H, 11.50; mol. wt., 140.2. Found: C, 77.96; H, 11.53; mol. wt. (ebull.), 131.

2,4-Dimethyl-3-hydroxy-6-oxoheptanal (VII). The 2,4,6-trimethyl-3-cyclohexenol from 2.0 g. of V was dissolved in 100 ml. of purified ethyl acetate. Ozone was bubbled through the cooled solution for 1.5 hr. After removal of the ethyl acetate *in vacuo* the residue was stirred for 18 hr. in 10 ml. of dry ether and 1.1 g. of glacial acetic acid with 0.8 g. of zinc dust. The zinc was removed and washed with ether which was added to the filtrate. This solution was washed with 5% sodium carbonate solution. The ether solution was dried and concentrated *in vacuo*. Attempted purification of the product was unsuccessful as distillation caused decomposition. The infrared spectrum had a band at 2.90 μ indicative of hydroxyl and carbonyl absorption bands at 5.82 and 5.88 μ.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.77; H, 9.37; $CH_3C(3)$; 26.19. Found: C, 62.98; H, 9.31; CH_3C, 18.50.

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[1] Melting points are uncorrected.

An Adduct of Hexachlorocyclopentadiene with Acenaphthylene

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Hexachlorocyclopentadiene has been shown to be an extremely versatile reactant in the diene synthesis.[1] During the course of a study involving Diels-Alder reactions of hexachlorocyclopentadiene, its addition to acenaphthene was tried. In view of the fact that naphthalene acts as a dienophile in this reaction,[2] it was expected that acenaphthene also might function in this manner, either through the five-membered ring or the naphthalene part of the molecule.

The reaction was effected by prolonged heating of the reactants and gave a monoadduct together with considerable tar. The properties and analysis of the product were best explained by assuming it was an addition product of acenaphthylene, the latter having been formed by the dehydrogenating action of hexachlorocyclopentadiene (chlorination followed by dehydrochlorination).

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[1] H. E. Ungnade and E. T. McBee, *Chem. Revs.*, **58**, 249 (1958).

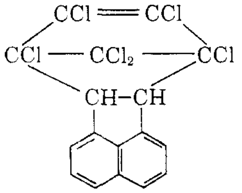
[2] A. A. Danish, M. Silverman, and Y. A. Tajima. *J. Am. Chem. Soc.*, **76**, 6144 (1954).

Accordingly, the addition of hexachlorocyclopentadiene to acenaphthylene was attempted and it was found that these interact readily in the cold to form the same adduct as is formed from acenaphthene but without tar production.

The adduct is a very stable substance, m.p. 192.5–194°, and unlike the naphthalene adducts[2] could not be cracked back to the components by pyrolysis under vacuum. Instead, it was distilled unchanged with slight decomposition at a low pressure.

The ultraviolet spectrum resembled that of a substituted acenaphthene, giving evidence that the five-membered ring only is attacked. The absorption peaks are given with ϵ values in parentheses: 225 (44,000), 268 (3710), 278 (6370), 288 (8020), 300 μ (5710). The corresponding figures for acenaphthene are: 227 (87760), 268 (3650), 279 (5780), 288 (6500), 300 μ (4150).

Structure I was thought to explain best the properties of the compound. The analytical values and the molecular weight are in agreement with this. The adduct undergoes nitration to give a mononitro derivative.



I

EXPERIMENTAL

Melting points are uncorrected and were taken on a Fisher-Johns block.

Addition to acenaphthylene. A mixture of 5 g. (0.033 mole) of acenaphthylene and 10 ml. (0.063 mole) of hexachlorocyclopentadiene was warmed for solution and then left to stand at room temperature. Deposition of crystals began in a few hours and, after 2 days, the paste of product was worked up. It was stirred with a mixture of equal volumes of ether and peteroleum ether (b.p. 30–60°) (35 ml.) and filtered. The material was washed three times with this solvent mixture and dried; yield 11.45 g. (best obtained), 81.8%. Without recrystallization, this melted at 190.5–193° and, when mixed with the purified material from acenaphthene, it melted 191.5–193.5°.

Addition to acenaphthene. A solution of 25.4 g. (0.165 mole) of acenaphthene in 80 ml. (0.5 mole) of hexachlorocyclopentadiene was heated by a bath of boiling pinene (155–156°) for 130 hr. During this time, the mixture darkened and slow evolution of hydrogen chloride occurred. After cooling, the contents formed a nearly solid black mass. This was warmed, mixed with a little benzene to promote fluidity, and then stirred with a mixture of equal volumes of ether and petroleum ether (b.p. 30–60°). Crystalline grains soon formed and the suspension was left overnight. The product was filtered and washed with the same solvent mixture. Concentration of the filtrates and washings afforded a little more product. Yield of crude dark material was 49.1 g., 70%.

The compound was recrystallized a number of times from benzene-hexane and from ether with use of Norit. A pure white product was finally obtained, m.p. 192.5–194°. It forms characteristic sandy grains from these solvents.

Anal. Calcd. for $C_{17}H_8Cl_6$: Cl 50.12. Mol. wt.: 425. Found Cl 50.0. Mol. wt.: (Rast) 415.

In an attempt to crack the compound, it was heated with a free flame in a small flask at a pressure of 1 mm. A very high boiling material slowly distilled leaving a black tar in the flask. The solid distillate was recrystallized from benzene–petroleum ether (b.p. 30–60°) and formed grains, m.p. 187–190°. When mixed with the purest sample of starting adduct, the melting point was 188–191°.

Nitration. A solution of 2 g. of the adduct in 100 ml. of boiling glacial acetic acid was treated with 5 ml. of sulfuric acid. Then 4 ml. of concd. nitric acid was added cautiously, in portions. The orange solution was kept at 100–115° for 20–25 min. It was then cooled to about 80° and 10 ml. of water added, with stirring and cooling. The product separated as a yellow crystalline powder which was filtered, washed, and dried; yield 2.1 g. (95%). The nitro compound was recrystallized from acetone-water and from benzene–petroleum ether (b.p. 30–60°). On heating it sintered at 195–200° with melting point at 230.5–233°.

Anal. Calcd. for $C_{17}H_7Cl_6NO_2$: N 2.98. Found: N 2.83.

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Reaction of Isopropylzinc Iodide with Terebic Acid Chloride. A Suggested New Mode of Action of the Blaise Reagent

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In the course of a study on the synthesis of a certain terpenoid compound, the authors became interested in the reaction of isopropylzinc iodide with terebic acid chloride. The reaction has been investigated by M. Matsui, *et al.*,[1] who by the reaction obtained pyrocin[2] (I), in 5% yield based on the acid chloride. They interpreted their unusual result by scheme A.

It is well known that a number of branched-chain Grignard reagents reduce carbonyl compounds to carbinols.[3] However, similar reduction by alkylzinc iodide seems never to have been described before the appearance of the above-cited work.[4] The present study was undertaken to ex-

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(1) M. Matsui, T. Ohno, S. Kitamura, and M. Toyano, *Bull. Chem. Soc. Japan*, **25**, 210 (1952).

(2) Pyrocin was first isolated from the pyrolysate of pyrethrum flowers [M. Nagase and M. Matsui, *J. Agr. Chem. Soc. Japan*, **20**, 249 (1944)]. For structural studies, see S. H. Harper *et al.*, *J. Sci. Food Agr.*, **2**, 414 (1951).

(3) For a review, see M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall Inc., New York, 1954, pp. 147–165.