847. cyclo*Octatetraene Derivatives. Part III.** cyclo*Octylphenols.*

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*cis-cyclo*Octene gave a 6 : 1-mixture of *o*- and *p-cyclo*octylphenol on condensation with an excess of phenol in the presence of an acidic catalyst.

It is known that phenol combines readily with unsaturated hydrocarbons in the presence of a catalyst to give a mixture of *ortho*- and *para*-substituted phenols, the latter being the principal product (Hickinbottom, "Reactions of Organic Compounds," Longmans Green, 1948, p. 32). The reaction of *cis-cyclo*octene (from *cyclo*octatetraene) with phenol in the presence of boron trifluoride has been examined. When equimolar quantities of phenol and hydrocarbon were used, the yield of mono*cyclo*octylphenols was only 12%, the major product (60%) being a di*cyclo*octylphenol. By increasing the phenol : *cyclo*olefin ratio to 3 : 1, a 75% yield of the mono-derivatives was obtained. The mixture of isomers was easily separated with cold dilute sodium hydroxide. *p-cyclo*Octylphenol, m. p. 116°, was precipitated immediately as the sparingly soluble sodium salt, whereas the *ortho*-isomer (a liquid at room temperature) was not affected and could be removed by centrifugation or by washing with an organic solvent. The *ortho*-isomer was soluble in hot 15% sodium hydroxide solution.

The ratio of *ortho*- to *para*-isomer was approximately 6 : 1, which was unexpectedly high. An instance of a high *ortho*/*para* ratio (4 : 1) has been recorded (Lefebvre and Levas, *Compt. rend.*, 1945, **221**, 301) for the *cyclo*hexylphenols obtained in the preparation of phenoxy*cyclo*hexane.

The solid isomer was shown to have the *para*-configuration, by oxidation of its methyl ether to *p*-anisic acid. This result also agrees with the general rule that *para*-isomers have higher melting points than the corresponding *ortho*-compounds.

The preparation of several derivatives of the *cyclo*octylphenols is described. After fruitless attempts to prepare 2 : 4-dinitro-6-*cyclo*octylphenol by methods similar to those employed for the preparation of the *cyclo*hexyl analogue (Pest Control Ltd., B.P. 620,026; Dow Chem. Co., U.S.P. 2,384,365), the required compound was satisfactorily prepared by nitrating *o-cyclo*octylphenol in chloroform at 0°.

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Experimental

The Reaction of cis-cyclo*Octene with Phenol.*—*cyclo*Octene (110 g. 1 mole) was added during 70 min. to a stirred mixture of phenol (284 g., 3 moles) and boron trifluoride–acetic acid complex (7·5 g.) at 60—65°. After a further 3 hr. at this temperature, the excess of phenol was removed with boiling water (4 × 250 ml.). The insoluble dark red oil was then treated with sodium hydroxide (44 g. in 500 ml. of water) which caused the separation of *sodium* p-cyclo*octylphenoxide* (glistening white plates from hot dilute sodium hydroxide) (Found: C, 61·4; H, 8·7; Na, 8·3. $C_{14}H_{19}ONa,2\frac{1}{2}H_2O$ requires C, 62·0; H, 8·9; Na, 8·5%). The crude sodium salt was isolated by centrifugation and washed thoroughly with ether. The solid was acidified with dilute hydrochloric acid and extracted with ether. The solvent layer washed and dried. p-cyclo*Octylphenol* formed needles [from light petroleum (b. p. 100—120°)], m. p. 116°, b. p. 134—136°/7 mm. (24·5 g. after one crystallisation) (Found: C, 82·3; H, 10·0. $C_{14}H_{20}O$ requires C, 82·3; H, 9·9%). The phenol was not volatile in steam, gave no colour with ferric chloride, and formed a very sparingly soluble sodium salt.

The alkaline filtrate from the centrifuge was shaken with the ether washings from the sodium salt, the ether layer was washed with water, dried and fractionated. The major portion (130 g.; b. p. 118—120°/0·4 mm.; n_D^{15} 1·5557) consisted of o-cyclo*octylphenol* (Found: C, 82·2; H, 10·0. $C_{14}H_{20}O$ requires C, 82·3; H, 9·9%). An extremely viscous, pale yellow liquid (11 g.) obtained at 198°/0·4 mm. was probably 2 : 4-*di*cyclo*octylphenol* (although the possibility that it is *cyclo*octyl *o*- or *p*-*cyclo*octylphenyl ether has not been ruled out) (Found: C, 83·9; H, 10·9. $C_{22}H_{34}O$ requires C, 84·0; H, 10·9%); it was not soluble in hot 50% alkali.

o-*cyclo*Octylphenol could be obtained crystalline (m. p. 20° approx.) by cooling its solution in light petroleum to −40°. The phenol was not volatile in steam; it was unaffected by sodium hydroxide solution (15%) at room temperature although it dissolved in the boiling liquid, which then deposited the crystalline sodium salt on cooling.

When equimolar quantities of *cyclo*octene and phenol were used in the condensation the principal product (70%) was 2 : 4-di*cyclo*octylphenol.

Derivatives.—The following derivatives of the two phenols were prepared by standard methods: *Methyl* o-cyclo*octylphenyl ether,* b. p. 95°/0·2 mm., f. p. $<-20°$, n_D^{22} 1·5379 (Found: C,82·6; H, 10·3. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%); *methyl* p-cyclo*octylphenyl ether*, b. p. 110°/0·3 mm., f. p. 8—9°, n_D^{21} 1·5357 (Found: C, 82·2; H, 10·4%) [treatment of the *p*-ether (2 g.) with potassium permanganate (5 g.) in boiling dilute sulphuric acid during 3 hr. gave unchanged ether (1·1 g.) and *p*-anisic acid (0·15 g.), m. p. and mixed m. p. 184°]; p-cyclo*octylphenyl benzoate*, needles, m. p. 120°, from ethanol (Found: C, 81·5; H, 8·0. $C_{21}H_{24}O_2$ requires C,81·8; H, 7·8%); o-cyclo*octylphenyl acetate*, b. p. 112°/0·2 mm., n_D^{19} 1·5251 (Found: C, 77·9; H, 9·2. $C_{16}H_{22}O_2$ requires C, 78·0; H, 9·0%); o-cyclo*octylphenoxyacetic acid*, plates [from light petroleum (b. p. 60—80°)], m. p. 106—107° (Found: C, 73·7; H, 8·4%; equiv., 260. $C_{16}H_{22}O_3$ requires C, 73·3; H, 8·4%; equiv., 262); and p-cyclo*octylphenoxyacetic acid*, needles [from light petroleum (b. p. 100—120°)], m. p. 119·5° (Found: C, 73·2; H, 8·5%; equiv., 261).

The two p-*nitrobenzyl ethers* could not be obtained by the normal method, but were readily prepared as follows. Dimethylaniline (1·2 g.) and *p*-nitrobenzyl chloride (1·7 g.) were stirred for 2 min. at 90° with a mixture of *o*-*cyclo*octylphenol (3 g.) and aqueous sodium hydroxide (20%; 2 ml.). The dimethylaniline was removed in steam, the residue dissolved in ether, and the solution washed and dried. The oil remaining after removal of the solvent crystallised on being triturated with methanol. The *o*-ether formed laths, m. p. 73—74°, from methanol (Found: N, 3·8%. $C_{21}H_{25}NO_3$ requires N, 4·1%). The *p*-ether crystallised in laths, m. p. 76·5°, from ethanol (Found: N, 4·0%).

2 : 4-*Dinitro*-6-cyclo*octylphenol.* Nitric acid (60 g.; *d* 1·42) was added during 80 min. to a solution of 2-*cyclo*octylphenol (20 g.) in chloroform (400 ml.) at −5°, which, after being set aside overnight at room temperature, was washed well with water and dried, and the chloroform distilled off. The residual oil was chromatographed on activated alumina, benzene or chloroform being used as solvents. 2 : 4-*Dinitro*-6-cyclo*octylphenol* was then obtained in pale yellow flat needles (from methanol), m. p. 57—58° (Found: C, 57·1; H, 6·2; N, 9·5. $C_{14}H_{18}O_5N_2$ requires C, 57·1; H, 6·1; N, 9·5%).

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