32. On the Syntheses of *tert.*-Butyltropolones.

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It has been found from the studies on various reactions on tropolone (I)¹⁾ and its methyl, ethyl²⁾ and isopropyl homologs³⁾ that in the substitution and rearrangement of hinokitiol (II), i.e. *m*-isopropyltropolone, the steric effect of its isopropyl side-chain was quite strong and specific. The present experiments were undertaken in order to prepare the tropolone homologs with *tert.*-butyl group, which should exert a far larger steric hindrance than the isopropyl, and to observe its substitution reactions and rearrangement⁴⁾ of its azo compound to a hinopurpurin-type compound.

The course of the present syntheses followed those already reported for tropolone⁴⁾ and hinokitiol⁵⁾. *p*-*tert.*-Butylcyclohexanol (III) was oxidized to *p*-*tert.*-butylcyclohexanone (IV). (III) was fairly resistant to oxidation, being indifferent to oxidation under Killiani's conditions⁶⁾. It finally yielded the ketone in ca. 25% yield when heated for 15 hours at 60° with a mixture of chromic and sulfuric acids in glacial acetic acid. G. Darzens⁷⁾ described 4-*tert.*-butylcyclohexanone-(I) (IV) as an oil but that obtained in the present experiment was colorless scaly crystals, m.p. 52–52.5°, as recrystallized from ethanol, (Anal. Calcd. for C₁₀H₁₈O: C, 77.92; H, 11.69. Found: C, 77.80; H, 11.75.), giving a semicarbazone of colorless scaly crystals, m.p. 257°, as recrystallized from diluted ethanol. During the oxidations of (III), β -*tert.*-butyladipic acid⁸⁾, m.p. 115°, a product of further oxidation, was also obtained besides the unreacted material.

By the ring-expansion of (IV) with diazomethane, 4-isopropylcycloheptanone-(I) (A) (V), b.p. 95–100°/7 mm., was obtained in a

55% yield. n_D^{20} 1.4710. Semicarbazone crystallized from diluted ethanol in colorless scaly crystals, m.p. 195–195.5°. Anal. Calcd. for $C_{12}H_{22}ON_3$: C, 64.29; H, 9.82. Found: C, 64.11; H, 9.95.

Oxidation of (V) with selenium dioxide in ethanol yielded a pale yellow, viscous liquid (VI), b.p. 105–110°/3 mm., n_D^{20} 1.4842. This was certain to be a mixture of 5-tert.-butyl-(B) and 4-tert.-butyl-cycloheptanedione (C), but no crystalline products were obtained with semicarbazide or 2,4-dinitrophenylhydrazine.

Two moles of N-bromosuccinimide was applied to the chloroform solution of this dione mixture, then dehydrobrominated by heating for 3 hours. This yielded an oily, acid substance (VII) which gave red coloration by ferric chloride. Recrystallization of (VII) from water as its sodium salt, and neutralization with mineral acids yielded crystals which recrystallized from petroleum ether to colorless rhomboprisms (VIII), m.p. 99–100°. Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.16; H, 7.86. Found: C, 73.56; H, 7.50. The sodium salt less soluble in water only yielded some oil (IX) which did not crystallize even on cooling to -15° or by inoculation of some crystals of (VIII).

From the fact that both (VIII) and (IX) give yellowish green copper complex and dark red ferric complex salts, and from the course of their syntheses, it is beyond doubt that they are the objective tert.-butyltropolone.

Treatment of (IX) with an excess of bromine in ethanol yielded monobromo compounds (X), m.p. 90–91°, pale yellow prisms (from ethanol) and (XI), m.p. 150–151°, pale yellow needles (from ethanol) (Anal. Calcd. for $C_{11}H_{13}O_2Br$: C, 51.37; H, 5.06. Found: C, 51.13; H, 4.93.). The same bromination of (VIII) yielded dibromo compound (XII), pale yellow needles (from ethanol). Anal. Calcd. for $C_{11}H_{12}O_2Br_2$: C, 39.28; H, 3.03. Found: C, 39.95; H, 3.43.

Due to the lack of material the structural determination of these compounds has not been made yet but from various facts, it is assumed that the product (VIII) of m.p. 99–100° is the p-tert.-butyltropolone (D) while the oily product (IX) is the meta compound (E)

No detailed study has been possible owing to the lack of material but by a presumption from the case of hinokitiol, (X),

(XI) and (XII) are assumed to be of structures as in (F), (G) and (H), respectively.

According to preliminary tests with a minute amount of the sample, not only p-tert.-butyltropolone (IX), but also its meta isomer (VIII), do not undergo azo coupling with diazonium salts. In the case of the meta isomer, it seems certain that this indifference to azo coupling in spite of the vacancy of its para position, is due to the large steric hindrance of its tert.-butyl group.

This brings the interesting conclusion that the rearrangement of an azo compound to a hinopurpurin-type compound³⁾ is limited to tropolone homologs possessing isopropyl group in their meta-position.

Details of substitution reactions of these compounds will be reported after further study.

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