

STUDY ON THE SYNTHESSES OF TROPONOIDS

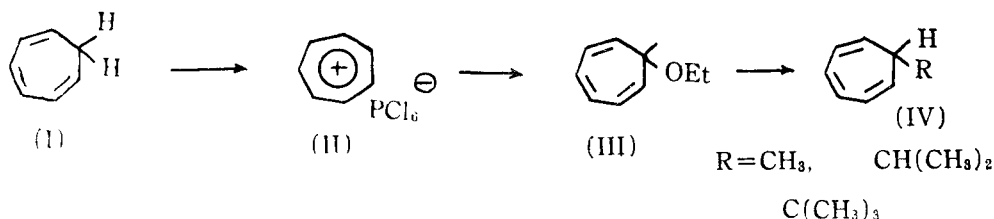
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(張 錦 得)

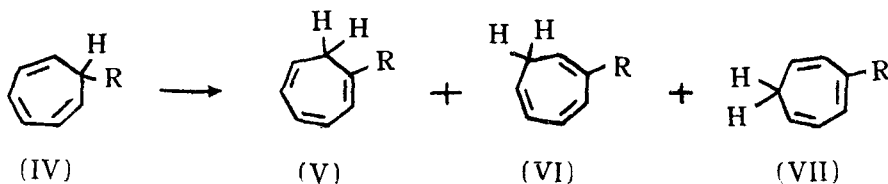
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Since W. von E. Doering et al⁽¹⁾ revealed some of the chemical properties of tropylium ion in 1954, extensive attention has been paid on its application for the synthesis of troponoid derivatives. Due to the strong electrophilicity many important reactions had been derived. However, the alkylated tropylium ion⁽²⁾ which is able to lead to the synthesis of various alkylated troponoids has not been well-studied yet. Further, the starting material, tropyliene is obtainable in industrial scale recently. To discuss on the thermal behaviours in order to find the possibility to derive alkylated troponoids and observe the abnormal chemical behaviours of highly sterically hindered t-butyltropolones are especially interesting.

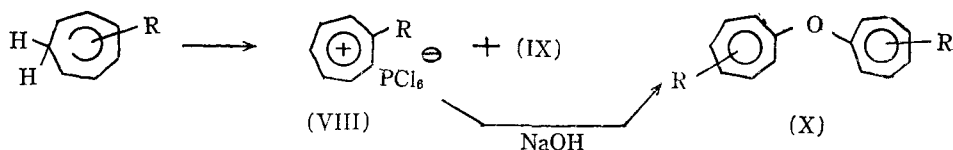
Tropyliene (I) was reacted in anhydrous carbon tetrachloride with phosphorus pentachloride, the tropylium ion (II) was obtained in quantitatively. The latter compound, anhydrous precipitate was then treated with ethyl alcohol to yield tropyliene ethyl ether (III). Alkyl Grignard's reagents reacted readily to give alkylated tropylienes (IV). Alkyltropylienes (IV) (Figure 1) were heated at 170-180°C under the



atmosphere of nitrogen gas for 2-4 hrs. Isomerized compound (VII) was first produced (Figure 2) and compound (V) second, gradually compound (VI) appeared, and the most favorable compound (VII) for the formation of further tropylium ion decreased (Figure 3) as the heating time prolonged. The presences of moisture during this isomerization led to polymerization. The reaction mixture gradually became tar like black substance.

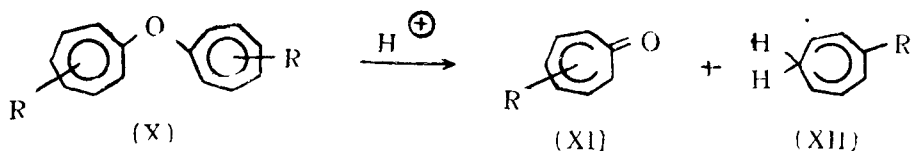


The isomerized alkylated tropyliene was further treated with phosphorus pentachloride to give compound (VIII) and unreacted substance (IX) was recovered. The recovered substance was constituted with compounds (IV) and (V) (Figure 4). It is reasonable that the hindered hydrogen is not easily removed by phosphorus pentachloride at room temperature.

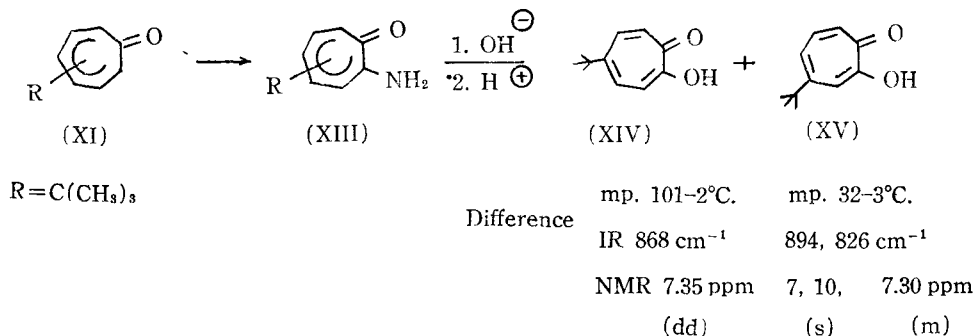


No-alkyl-substituted tropylium compound (VIII) normally afforded ether derivative (IX). It was out of the author's expectation that when the alkyl group possessed of allylic active hydrogen, it polymerized to solid tar. Merely *t*-butyl derivative gave ether derivative with satisfactory.

Compound (X) was disproportionated⁽⁹⁾ with concentrated hydrochloric acid to give tropones (XI) and recovered tropyliene (XII), which was composed with compounds (V), (VI) and (VII) as the NMR shown in (Figure 5).



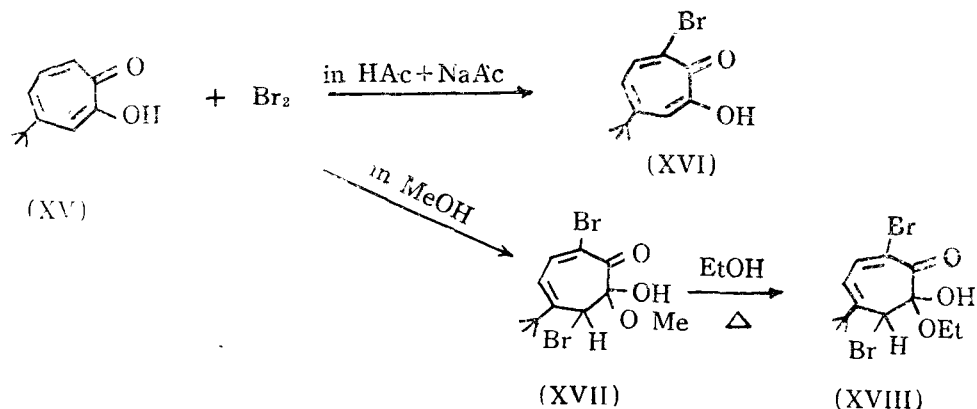
The tropone (XI) was heated with hydrazine in alcohol to give aminotropone (XIII), which was further treated with strong base, potassium hydroxide to give tropolones (XIV) and (XV)⁽⁴⁾.



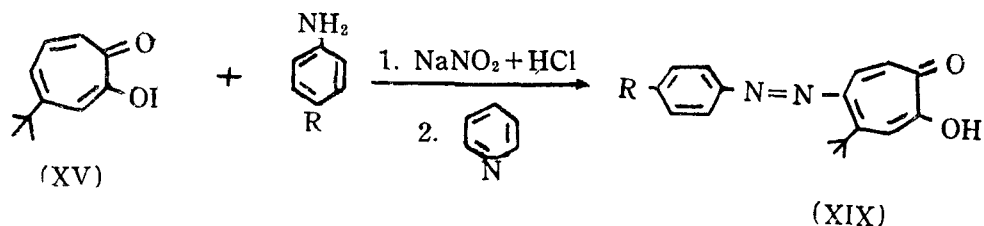
The main product, compound (XV) was isolated as Na-salt, though contaminated with (XIV) was detected from the Infra-red absorption and NMR spectras. Repeated reprecipitation of sodium salt afforded pure tropolone (XV). To isolate pure minor product (XIV) was not easily attainable. Through many studies on separation, finally found out that compound (XIV) could be extracted as free tropolone from the sodium aqueous solution by chloroform under certain pH value. This is the first time that these kind of mixture can be separated satisfactory by extraction with organic solvent

from its aqueous salt solution as free phenolic compound.

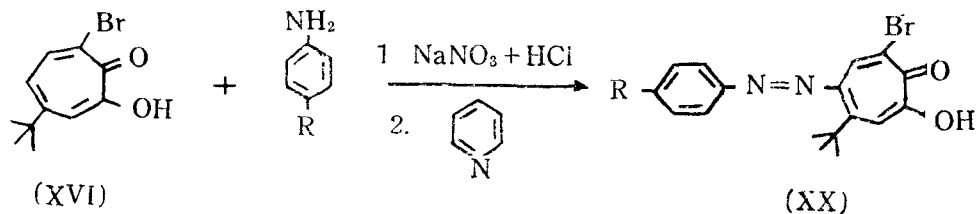
Regarding the bromination of tropolones⁽⁵⁾ has been investigated in detail. The present study showed that when the bromination was carried out in acetic acid with sodium acetate it afforded 7-bromotropolone (XVI). A new fact was found that the dibromide of solvated product (XVII) was obtained when the bromination was carried out in methanol in the presence of sodium acetate. Further, from the NMR study the methyl derivative (XVII) was changed to ethyl derivative (XVIII) by recrystallization in ethyl alcohol.



Tropolone (XV) yielded azo-coupling⁽⁶⁾ compound readily by the reaction of diazonium compound in the presence of pyridine.



7-Bromotropolone also gave azo-coupling compound (XX)



From the facts of bromination and azo-coupling product the steric factor of t-butyl group seems to be not serious in this 7-membered ring compound, probably due to the non-planar structure.

Methylation, thionylchloride chlorination and some other reactions were also studied. The separation of the reaction mixture is still under progress.

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