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RADICAL-INDUCED DIMERIZATION OF TROPOLONE

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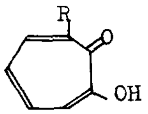
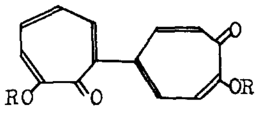
Even though many reports have been published on various ionic substitution reactions, few researches have been made on radical reactions of tropolones[1]. Dewar[2] predicted that radical reactions would occur predominantly at the 5-position of tropolone(I) from the result of calculation by molecular orbital theory, whereas Kurita and Kubo[3] at the 3- or 7-position from the value of its free valence index. As far as we know, it appears that notable reports on this subject have not been published since then. We have attempted to verify the above predictions with a reaction of I and benzoyl peroxide, the result of which will be described in this paper.

When a mixture of I and benzoyl peroxide was heated at 60-70° for 6 hours, two reaction products were obtained. The first(II), $C_{14}H_{10}O_4$, colorless needles, m.p.125-126°, ν_{max}^{KBr} : 1736, 1580, 735, 704 cm^{-1}, afforded 3-hydroxytropolone(III)[4] and benzoic acid on an alkaline hydrolysis. The second(IV), $C_{14}H_{10}O_4$, yellow needles, m.p.225°, ν_{max}^{KBr} : 3230, 1618, 1553, 1420, 1252,



I: R=H
II: R=OCOPh
III: R=OH



IV: R=H
V: R=CH_3

1215 cm^{-1}, gave a known dimethyl derivative (V) by reaction with diazomethane, indicative of its 3,5′-bitropolonyl (IV)[5].

The above-mentioned result follows that radical reactions are capable of occurring at the every 3-, 5- and 7-positions similar to electrophilic substitutions[1] and tropolonyl radical induced by benzoyl radical may participate in this reaction.

The 3- and 4-isopropyl derivatives of I afforded also respective bitropolonyl type of product, m.p.186° and 195°, the detail of which will be described elsewhere in full paper.

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