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QUINONES VIII[1]. SYNTHESIS OF 3-t-BUTYL-5,8-DIMETHYL-1,10-ANTHRAQUINONE

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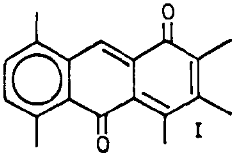
Abstract: An 1,10-anthraquinone - stabilized only by alkylgroups - is prepared (in a four step synthesis) and described for the first time.

Several calculations and theoretical considerations of quinoid systems have been published in the last time[2-4]. Prognoses of properties of yet unknown quinones[3,4], constitute a challenge to the preparative working chemist to synthesize these unknown quinoid systems.

1,10-Anthraquinone is one of these unknown quinones. It is too instable to be prepared in substance[5]. Only derivatives with chlorine[6] or amino groups[7,8] as stabilizing substituents are described. These substituents stabilize the quinoid system not only by steric effects but also by lowering the ground state energy, thereby enhancing the thermodynamic stability. But by the same means these substituents will influence the π-electron system by conjugation. Therefore we tried to synthesize 1,10-anthraquinones stabilized only by alkyl groups, which are shielding the quinone against the attack of reaction partners without influencing essentially the π-electron system. Therefore these groups are enhancing the kinetic stability.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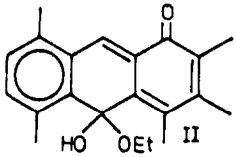
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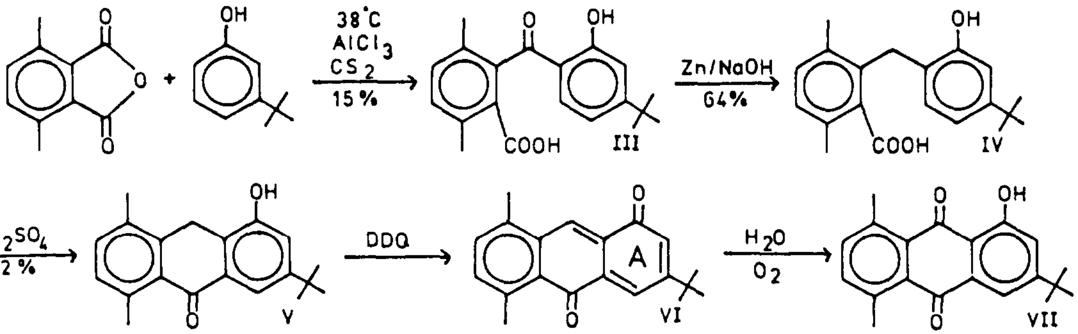

An attempt to synthesize the pentamethyl-1,10-anthraquinone(I) failed. Overcrowding - especially in position 4, 10, 5 - turned out to be so severe that only the hemiacetal II could be isolated 5).

Therefore we planned to synthesize VI. As in the case of 3,7-di-t-butyl-1,5-naphthoquinone 3) the t-butyl group should shield ring A against attack of water and prevent Diels-Alder-reaction with another quinone molecule 3), whilst - as in the case of I or II - the 8-methyl group should prevent the attack of water in 9-position.

The synthesis of VI is shown in the formula scheme. The yield of III in the Friedel-Crafts acylation of 3-t-butylphenol at 38°C was only poor. But at higher temperatures the t-butyl group was removed. Oxidation of the anthrone V with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) under exclusion of water yielded dark red 3-t-butyl-5,8-dimethyl-1,10-anthraquinone (VI) UV(CHCl$_3$): λ_{max} 491 nm. - ^{1}H-NMR(CDCl$_3$): δ = 1.13 (s, C(CH$_3$)$_3$, 2.77 (s, 8-CH$_3$), 2.86 (s, 5-CH$_3$), 7.32 and 7.39 (dd, J = 8 Hz, H-6 and H-7), 6.77 (d, J = 2 Hz, H-2), 7.26 (s, H-9), 7.65 (d, J = 2 Hz, H-4). - MS(70 eV): m/e = 292 (100 %, M$^+$), 277 (14 %, M$^+$-CH$_3$), 249 (19 %, M$^+$-CH$_3$-CO).

High resolution MS: $C_{20}H_{20}O_2$ calc. 292.1463, found 292,1464.

Surprisingly even with traces of water 1-hydroxy-3-t-butyl-5,8-dimethyl-9,10-anthraquinone [(VII), m.p. 166.5°C] is formed rapidly. III-V and VII are well characterized by elemental analyses and spectral data.

References and footnotes

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