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PHOTOCHEMICAL SYNTHESIS OF 2-CHLORO-3-(2-THIENYL)-1,4-NAPHTHOQUINONES AS A PROMISING PRECURSOR OF NATURALLY OCCURRING QUINONES

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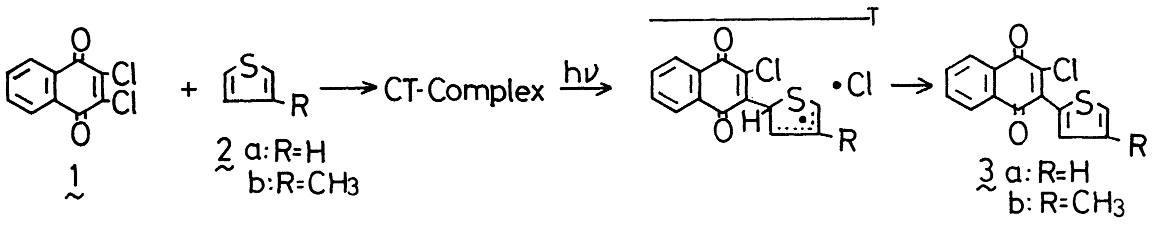
The photochemical reaction of 2,3-dichloro-1,4-naphthoquinone **1** with thiophene derivatives **2** gave 2-chloro-3-(2-thienyl)-1,4-naphthoquinone **3**. The products **3** were transformed further to alkyl substituted 1,4-naphthoquinone derivatives.

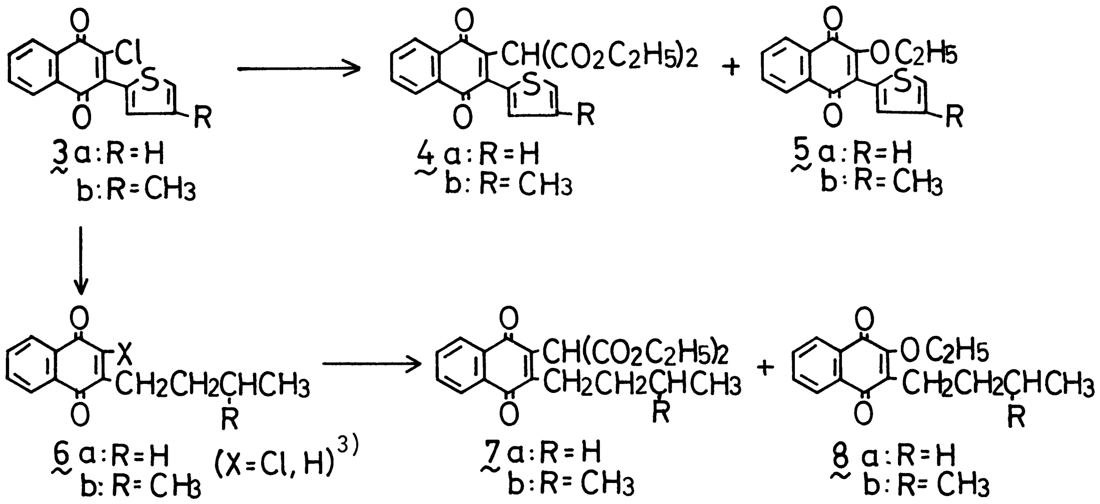
It is well known that alkyl substituted quinones such as coenzyme Q and vitamin K have an important biological activity in the nature. Here we wish to report a new synthetic route to the alkyl substituted quinones, applying the photochemical reaction of 2,3-dichloro-1,4-naphthoquinone **1** with thiophene derivatives **2**.

Irradiation of a benzene solution of 2,3-dichloro-1,4-naphthoquinone **1** (1.25×10^{-3}M) and an excess amount of **2a** (4.5×10^{-2}M) by a high pressure Hg arc lamp gave in a 57% yield of the photo-substituted product, 2-chloro-3-(2-thienyl)-1,4-naphthoquinone **3a** as red prisms from ethanol, mp 95°C. The structure of **3a** was compatible with the spectral data; Mass:m/e=276, 274(M^+), 239(M^+-Cl), 211(M^+-Cl-CO), IR(KBr):1670 cm^{-1}, NMR($CDCl_3$):δ;7.18(1H,t,J=4Hz), 7.70(1H,d,J=4Hz), 7.92(1H,d, J=4Hz), 7.56-7.80(2H,m), 8.05-8.20(2H,m), UV max($CHCl_3$):441nm(ε:4.4×10^3), 320(5.0×10^4), 275(2.3×10^4).

When the photochemical reaction was investigated by means of ^{1}H-CIDNP technique, polarized signals due to 2-thienyl ring protons of **3a** were observed during the course of the reaction. The fact suggests stongly that the photo-substituted product **3a** is produced *via* a radical pair intermediate(Scheme 1).[1)]



(Scheme 1)



a) $NaCH(CO_2C_2H_5)_2$, ethanol, r.t., 0.5h b) Raney-Ni(W-7), ethanol, reflux, 10h c) [O]

(Scheme 2)

The chlorine atom of 3a was substituted by alkyl group by treating 3a with carbanion.[2] For example, the reaction with sodium diethyl malonate in ethanol gave 4a(72%) and 5a(20%) (Scheme 2).

In addition, desulfurization of 3a by Raney-Ni(W-7) gave 2-butyl-1,4-naphthoquionone derivatives 6a (X=Cl or H)(80%).[3] Moreover, treatment of 6a (X=Cl or H) with sodium diethyl malonate in ethanol gave 7a(35%) together with 8a(12%)(Scheme 2).

When 3-methylthiophene 2b was submitted to photochemical reaction with 1 2-chloro-3-(2-4-methylthienyl)-1,4-naphthoquinone 3b(53%) was yielded. Similarly 3b was transformed into 7b(15%) together with 8b(5%). These results disclose that the present photochemical reaction can provide a route to naturally occurring isoprenoid quinones.

*) The structures of the compounds described here were all consistent with their spectral data.

References and Notes

1) When 2 was added to a benzene solution of 1, a new peak(shoulder) appeared at about 465 nm, ascribable to the CT-complex between 1 and 2. Irradiation of the band led to the exclusive formation of 3.

2) The substitution of chlorine atom of 2,3-dichloro-1,4-naphthoquinone by carbanion was reported. *Cf.* Fr.Michel, Ber., 33 , 2402 (1900).

3) The relative ratio, X=Cl/X=H, was infulenced by the reaction conditions. However, both derivatives gave 7 and 8 by treatment with sodium diethyl malonate in ethanol.

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