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PHOTOINDUCED OXYGENATION OF DEHYDROROTENONES (1)

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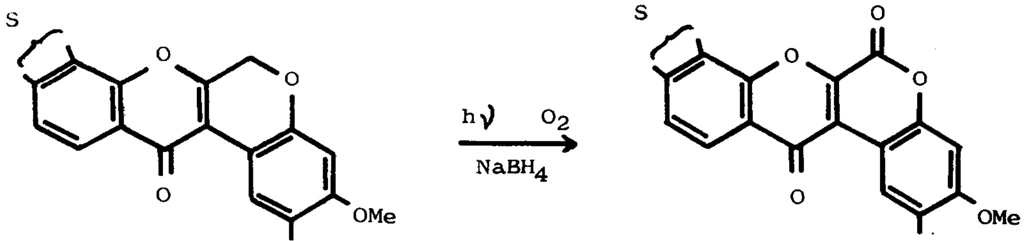
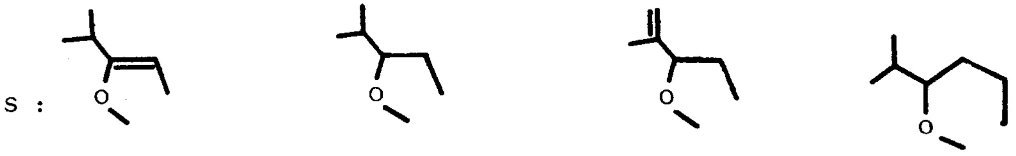
We report here the observation that the mild irradiation of the solution of dehydrorotenone (Ic) and its homologue in the presence of sodium borohydride at 25° readily affords rotenonone (IIc) and its homologue in moderate yields.



I

II



a b c d

Thus, in a typical experiment, dehydrorotenone (Ic) (2) (50 mg) in dioxane-ethanol mixture (30 ml) containing sodium borohydride (13 mg) was irradiated by a 150 W high pressure mercury arc lamp as the light source for 24 hours. The only major product was identified as rotenonone (IIc) (2a,3). In sharp contrast with this, we find that irradiation in the absence of sodium borohydride produced no isolable IIc. Best yield was obtained in the oxygenation of Ia in the presence of $NaBH_4$. Under comparable conditions, rotenone or isorotenone was recovered unchanged. These results together with those on the homologous compounds are tabulated below.

TABLE I

Irradiated compounds	Yield (%) of 6H-rotoxen-6,12-diones or 6a,12a-dihydro-6H-rotoxen-6,12-diones formed (4)		
		a	b
Ia (2C,5)	IIa* (2C,5) :	40	trace
Ib (2C)	IIb (2C) :	9	trace
Ic	IIc :	10	trace
Id (6)	IId** (6) :	16	trace
Rotenone (Ic:6a,12a-dihydro-)	IIc,6a,12a-dihydro- :	0	0
Isorotenone (Ia:6a,12a-dihydro-)	IIa,6a,12a-dihydro- :	0	0

a) In the presence of $NaBH_4$ b) In the absence of $NaBH_4$
* Irradiation for 44 hours
** Irradiation for 94 hours (benzene:dioxane 2:1)

In the autoxidation at a methylene group flanked either by an oxygen atom or an aromatic ring, the product is mostly secondary hydroperoxides (7) and a very few examples of the formation of ketones in sizable amounts have been recorded (8). The termination reaction of peroxy radicals with an α-hydrogen would seem complicated although evidence has been proposed for a certain case (9).

Although the role of borohydride in the present case is not clear, borohydride would reduce the concentration of free radical initiators and would prohibit some of the undesirable side reactions. It is certain that even in the presence of $NaBH_4$ the primary products of the present oxygenation would be secondary hydroperoxides at 6 position of 6H-rotoxen rings.

One of the probable roles of borohydride would be to destroy these hydroperoxides immediately after their formation to convert them into the hemiacetal

(10). The formation of ketones from this intermediate would be straightforward and the analogous sequence established by Bäckstrom (7) and Schenck (11) or disproportionation process may follow. During these processes dehydrorotenones themselves might have partly played the role of a sensitizer.

The reaction may have significance in transforming some of heterocyclic rings under relatively mild conditions.

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References and Footnotes

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