Intramolecular Cyclisation of Phenolic α-Diazoketones. Novel Synthesis of the Spiro[4.5]decane Carbon Framework

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Summary Copper(I) halide-catalysed decomposition of phenolic α-diazoketones gave spiro[4.5]deca-6,9-diene-2,8-dione in high yield.

Intramolecular reactions between diazoalkanes and benzene rings in the presence of metal salt give cycloheptatriene derivatives *via* intramolecular carbene addition.[1] Recently, Ledon and his co-workers[2] reported that acidic hydrolysis of the cycloheptatriene derivative obtained by the copper-catalysed decomposition of *p*-methoxybenzyl methyl diazomalonate, gave the 2-oxaspiro[4.5]decane derivative. We examined the intramolecular cyclisation of phenolic α-diazoketones in the presence of copper(I) halides and report a novel synthesis of spiro[4.5]decane carbon framework.

A solution of the phenolic α-diazoketone (Ia) in benzene [or tetrahydrofuran (THF)] in the presence of copper(I) chloride [or copper(I) iodide] was heated to reflux for 4·5—5·5 h. After removing the insoluble material, preparative t.l.c. of the crude product gave spiro[4.5]deca-6,9-diene-2,8-dione (IIa)[3] in high yield (Table). Similarly, catalytic decomposition of (Ib),† m.p. 109—110 °C (decomp.), prepared from the corresponding acid chloride and diazoethane, gave 1-methylspiro[4.5]deca-6,9-diene-2,8-dione (IIb), m.p. 93—94 °C, in high yield (Table).‡

Table

Diazo-ketone	Copper halide	Solvent (concentration/M)	Reaction time/h	Spiro[4.5]-decane (yield/%)
(Ia)	CuCl	THF (0·30)	4·5	(IIa) (61)
"	"	THF (0·16)	4·5	" (79)
"	"	C_6H_6 (0·16)	5·5	" (80)
"	CuI	C_6H_6 (0·16)	5·5	" (55)
(Ib)	CuCl	THF (0·16)	2	(IIb) (60)
		C_6H_6 (0·16)	2	" (90)

When (Ia) in benzene in the presence of copper(I) chloride was heated to reflux for only 20 min (the starting material completely disappeared), preparative t.l.c. of the crude pro-

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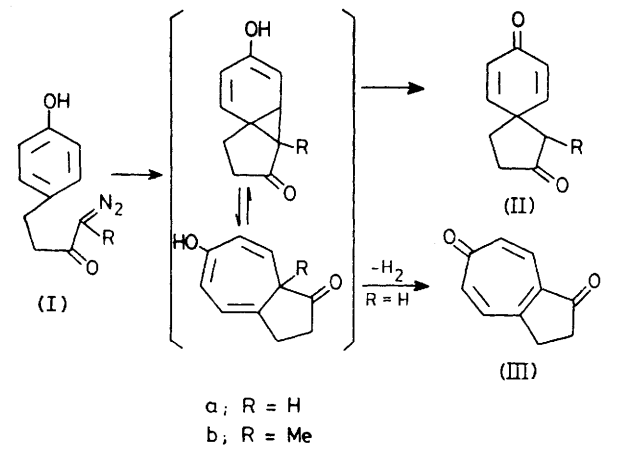
† Satisfactory analytical and spectral data were obtained for new compounds.

‡ In our hands, application of Mander's method gave (IIb) in 5—10% yield.



duct gave (IIa) (34%), 2,3-dihydroazulene-1,6-dione (III) (8%), and several unidentified products. Compound (III) is crystalline, pale brown in colour, m.p. 125—126 °C, and is very unstable. The structure of (III) was determined by the following spectral data: ν(CHCl$_3$) 1718, 1637, 1617, and 1583 (typical of tropone[4]) cm^{-1}; δ (CDCl$_3$) 7·43 [1H, d, *J* 12 Hz,[5] C(8)-H], 7·1—7·2 [2H, m, C(5)-H and C(4)-H], 6·99 [1H, br d, *J* 12 Hz, C(7)-H], and 3·2—2·8 and 2·8—2·5 [each 2H, m, C(2)-H and C(3)-H]; λ (EtOH) 233 (log ϵ 4·35), 240 sh, 309 sh, and 316 (log ϵ 3·89) nm;[5,6] *m/e* 160 (M^+), 132 (M—CO), and 104 (M—2CO).

The above results indicate that the catalytic decomposition of phenolic α-diazoketones proceeds *via* norcaradiene derivatives to give the spiro-dienone.

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