

Reactions of Substituted 3,3-Diphenyl- and 3,3-Dimethyl-1-oxaspiro-[3,5]nona-5,8-diene-2,7-diones with Nucleophiles

By KENJI OGINO, KATSUHISA YOSHIDA, and SEIZI KOZUKA

(Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Osaka 558, Japan)

Summary The reactions of substituted 3,3-diphenyl-1-oxaspiro[3,5]nona-5,8-diene-2,7-diones with nucleophiles proceed *via* *p*-quinone methides as intermediates followed by 1,6-addition of the nucleophile to give diphenyl- (*p*-hydroxyphenyl)methyl derivatives in good yields.

STAUDINGER,¹ and Martin and his co-workers,² reported that *p*-benzoquinone reacts with ketens to give the spiro- β -lactones (I), and that (Ia) and (If) undergo acid-catalysed rearrangement, thermal and photochemical, with the loss of carbon dioxide. Compounds (I) undergo ring-opening reactions by attack of a nucleophile either on the cyclohexadienone group or on the β -lactone ring.

We report that reactions of (Ia—e) with nucleophiles proceed by attack on the carbonyl carbon of the β -lactone ring, rather than on the cyclohexadienone group, giving decarboxylated *p*-quinone diphenylmethides as intermediates followed by 1,6-addition of the nucleophile to give the final product.

To a solution of (Ia) (1 mmol) in acetonitrile was added potassium cyanide (3 mmol). After stirring the reaction mixture for 15 h at room temperature, usual workup and t.l.c. separation yielded a colourless crystalline product

(80.4%) which was identified as α,α -diphenyl-*p*-hydroxybenzeneacetonitrile (IIa). Similar results were obtained from the reactions of (Ia—e) with potassium cyanide, methylmagnesium iodide, and methyl-lithium. The spectral data and elemental analyses are consistent with the proposed structures. The results are shown in the Table.

Evolution of CO₂ in the reaction of (Ia) with potassium cyanide was established by passing a stream of nitrogen into the reaction mixture and then into a saturated solution of barium hydroxide when a precipitate of barium carbonate was obtained.

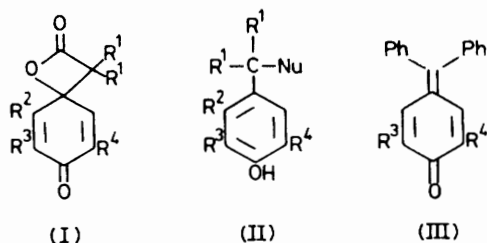
These reactions are quite different from the rearrangement³ of cyclohexadienones and also different from the reaction² of (Ia) with phenylhydrazine in ethanol giving diphenyl-*p*-(phenylazo)phenylacetic acid.

When potassium cyanide was added to acetonitrile solutions of (Ic) and (Id), orange precipitates, which were identified as the transient quinone methides (IIIc) and (IIIId),¹ were immediately formed in 78 and 69% yields, respectively. On stirring, the orange precipitates disappeared and (IIc) and (IId) were obtained. Halide (Br⁻ or I⁻) ion-catalysed decarboxylation of (Ia) gives *p*-quinone diphenylmethide (IIIa).¹

TABLE. Reactions of (Ia—e) with nucleophiles.

Compound	Reagent	Solvent	Product	Yield/%	M.p./°C
(Ia)	KCN	MeCN	(IIa)	80.4	148—153
(Ia)	MeMgI	Et ₂ O	(IIa')	64.9	121—123 ^a
(Ia)	MeLi	Et ₂ O	(IIa')	27.0	120—122 ^a
(Ib)	KCN	MeCN	(IIb)	72.5	159—160
(Ic)	KCN	MeCN	(IIc)	68.6	168—170
(Id)	KCN	MeCN	(IId)	60.1	156—158
(Ie)	KCN	MeCN	(IIe)	37.5	240—242

^a Lit. m.p. 120 °C (A. Baeyer and V. Villiger, *Ber.*, 1903, **36**, 2793).



(I)

(II)

(III)

a; Nu = CN

a'; Nu = Me

b-e; Nu = CN

- a; R¹ = Ph, R² = R³ = R⁴ = H
 b; R¹ = Ph, R² = R³ = H, R⁴ = Me
 c; R¹ = Ph, R² = H, R³ = R⁴ = Me
 d; R¹ = Ph, R² = H, R³ = R⁴ = Cl
 e; R¹ = Ph, R², R³ = [CH=CH]₂, R⁴ = H
 f; R¹ = Me, R² = R³ = R⁴ = H

The reaction of (If) with methyl-lithium does not give (II); it gives, instead, α -(4-hydroxy-3-methylphenyl)- α -methylpropionic acid (18%), m.p. 144—145 °C; δ [CDCl₃-(CD₃)₂SO] 1.52 (6H, s, CMe₂), 2.20 (3H, s, ArMe), 6.76 (1H, d, *J* 8 Hz, ArH-5), 7.07 (1H, dd, *J* 8 and 2 Hz, ArH-6), 7.13 (1H, d, *J* 2 Hz, ArH-2), and 8.30 (2H, br, s, CO₂H and OH), showing that the attack of the nucleophile in this case takes place on the cyclohexadienone group. Similar 1,3-addition of the Grignard reagent to the enone system has previously been reported.⁴

On the basis of these observations, the reactions of (Ia—e) can be explained in terms of the formation of the *p*-quinone diphenylmethides (III) as intermediates followed by 1,6-addition of the nucleophile.

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¹ H. Staudinger, *Annalen*, 1907, **356**, 51; H. Staudinger and S. Bereza, *ibid.*, 1911, **380**, 243.

² J. L. Chitwood, P. G. Gott, J. J. Krutak, Sr., and J. C. Martin, *J. Org. Chem.*, 1977, **36**, 2216.

³ B. Miller, 'Mechanisms of Molecular Rearrangements,' Pt 1, ed. B. S. Thygarajan, Interscience, New York, 1968, p. 247.

⁴ I. G. C. Coutts and M. Hamblin, *J.C.S. Chem. Comm.*, 1976, 58.