Reactions of Substituted 1-Oxaspiro- and 1-Azaspiro-[3.5]nona-5,8-diene-2,7-diones with Nucleophiles

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The reactions of substituted 3,3-diphenyl-1-oxaspiro[3.5]nona-5,8-diene-2,7-diones with nucleophiles such as potassium cyanide, methylmagnesium iodide, and methyl-lithium produce (*p*-hydroxyphenyl)diphenylmethyl derivatives in good yield. The reactions can be explained in terms of formation of a *p*-quinone diphenylmethide as intermediate followed by 1,6-addition of the nucleophiles. The reactions of 3,3-dimethyl-1-oxaspiro[3.5]nona-5,8-diene-2,7-diones, substituted 1-azaspiro[3.5]nona-5,8-diene-2,7-diones, and other spiro-β-lactams with methyl- and *p*-tolyl-lithium were also examined.

CYCLOHEXADIENONES exhibit an unusually large variety of rearrangements [1] and are useful starting or intermediate compounds for synthesis in organic and natural product chemistry.[2]

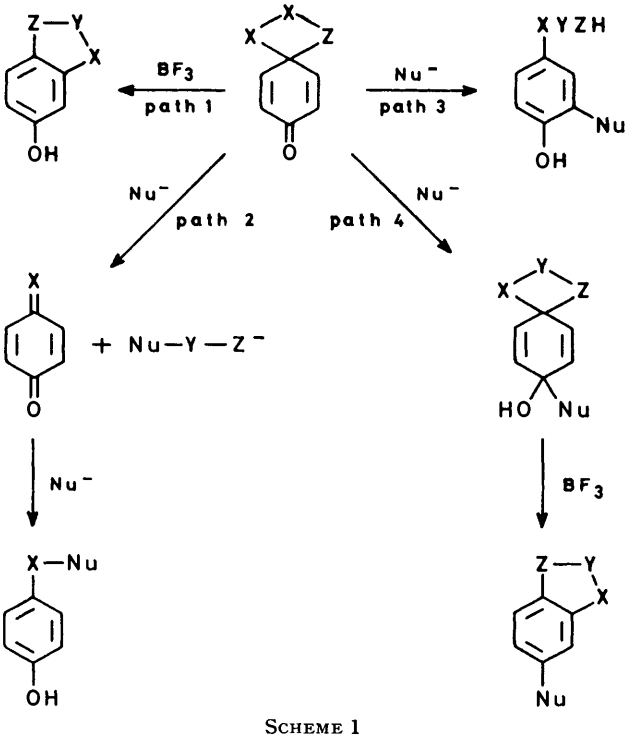
Staudinger [3] reported that *p*-benzoquinone reacts with diphenylketen to give the spiro-β-lactone (1). Martin and his co-workers [4] found that *p*-benzoquinone reacts with dimethylketen in an analogous manner to give the 3,3-dimethyl derivative (2), and (1) and (2) undergo acid-catalysed rearrangement and thermal and photochemical liberation of carbon dioxide. Compounds (1) and (2) have two components, *i.e.* β-propiolactone and cyclohexadienone moieties, in their structures.

Thermal and acid- and base-catalysed rearrangements [1,5] of cyclohexadienone derivatives are well known. Reactions of *p*-quinol acetate with nucleophiles are known to result in allylic displacement of the acetoxy group giving *ortho*-substituted phenols [6] and also to yield *meta*-substituted phenols by an addition–elimination process.[7] Another possible process was suggested involving initial 1,2-addition of Grignard reagents to the dienone carbonyl group followed by vinylogous pinacol rearrangement.[8] *O*-Alkylation of the carbonyl group was also observed in the reaction of 6-acetoxy-2,6-dimethylcyclohexa-2,4-dienone with benzylmagnesium chloride *via* a radical mechanism.[9] These results suggest that all positions of cyclohexadienones except for the tertiary carbon atoms accept the addition of nucleophiles.

It is also known that β-propiolactones can react with nucleophilic reagents in either or both of two ways; cleavage may occur at the carbonyl–oxygen bond and at the alkyl–oxygen bond to give ring-opened products.[10] β-Lactams could react with nucleophiles by cleavage at the carbonyl–nitrogen bond.[11]

We are interested in the reactions of four-membered heterocyclic spiro compounds with a cyclohexadienone group in view of the possibility of different reactivity towards nucleophilic reagents.[12] One general type of these reactions is described in Scheme 1.

Lewis-acid catalysed reactions can be regarded as cyclohexadienone–phenol molecular migrations (path 1). Assuming that the carbon–X double bonds formed by elimination of Y–Z could be stabilised by conjugation with the cyclohexadienone system and the Nu–Y–Z$^-$ eliminated is stable under these reaction conditions, the reaction would proceed through path 2. In the absence of these effects, attack by nucleophiles on the cyclohexadienone is favoured and results in allylic displacement (path 3) or 1,2-addition to the dienone-carbonyl group (path 4).



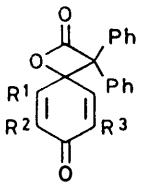
SCHEME 1

We report the reactions of substituted 1-oxaspiro-[3.5]nona-5,8-diene-2,7-diones (1) and (2), 1-azaspiro-[3.5]nona-5,8-diene-2,7-diones (3), and the β-lactams of ketens and fluoren-9-one imine (4).

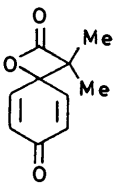
Reactions of Substituted 3,3-*Diphenyl*-1-*oxaspiro*[3.5]-*nona*-5,8-*diene*-2,7-*diones* (1) *with Nucleophiles*.—The substituted spiro compounds (1a—e) were synthesised in a similar manner to that of Staudinger and his co-workers.[3] These compounds were expected to have enhanced reactivity toward nucleophiles because of the ring strain in the β-propiolactone moiety.

To a solution of (1a) in acetonitrile was added an excess

of potassium cyanide. After stirring for 15 h at room temperature, the usual work-up, and t.l.c. separation yielded a crystalline product in 80% yield. This was identified as (*p*-hydroxyphenyl)diphenylacetonitrile (5a).

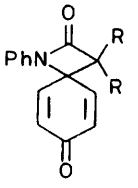


(1)



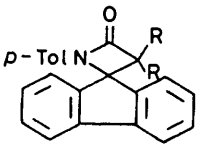
(2)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^2 = H, R^3 = Me$
c; $R^1 = H, R^2 = R^3 = Me$
d; $R^1 = H, R^2 = R^3 = Cl$
e; $R^1, R^2 = [CH{:}CH]_2, R^3 = H$



(3)

a; R = Me
b; R = Ph

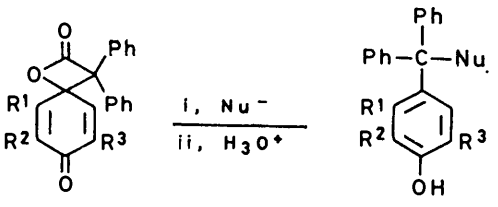


(4)

a; R = Me
b; R,R = $[CH_2]_5$
c; R = Ph

Similar treatment of (1a) with methylmagnesium iodide or methyl-lithium in ether afforded α-(*p*-hydroxyphenyl)-αα-diphenylethane (5a') in 65 and 27% yield, respectively. Spectral data and elemental analyses of the products are consistent with the proposed structures. Similar results were obtained from the reactions of (1b—e) with potassium cyanide. The results are shown in Table 1.

From these results, the nucleophiles did not attack the



(1) (5)

a; $R^1 = R^2 = R^3 = H$, Nu = CN
a; $R^1 = R^2 = R^3 = H$, Nu = Me
b; $R^1 = R^2 = H, R^3 = Me$, Nu = CN
c; $R^1 = H, R^2 = R^3 = Me$, Nu = CN
d; $R^1 = H, R^2 = R^3 = Cl$, Nu = CN
e; $R^1, R^2 = [CH{:}CH]_2, R^3 = H$, Nu = CN

SCHEME 2

TABLE 1

Reactions of 3,3-diphenylspiro-β-lactones (1a—e) with nucleophiles

Substrate	Reagent	Solvent	Product	Yield (%)
(1a)	KCN	Acetonitrile	(5a)	81
(1a)	MeMgI	Ether	(5a')	65
(1a)	MeLi	Ether	(5a')	27
(1b)	KCN	Acetonitrile	(5b)	73
(1c)	KCN	Acetonitrile	(5c)	69
(1d)	KCN	Acetonitrile	(5d)	60
(1e)	KCN	Acetonitrile	(5e)	38

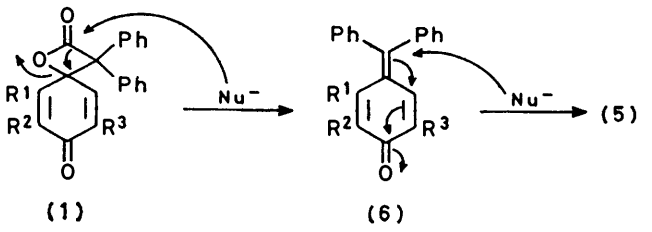
cyclohexadienone moiety but apparently the tertiary α-carbon with liberation of carbon dioxide. Evolution of carbon dioxide in the reaction of (1a) with potassium cyanide was established by passing a stream of nitrogen into the reaction mixture and then into a saturated solution of barium hydroxide when a precipitate of barium carbonate was obtained. These results are quite different from those for the reactions of cyclohexadienones which react at the allylic position with nucleophilics [6,8] and also different from the reaction of (1a) with phenylhydrazine in ethanol which gives diphenyl-[*p*-(phenylazo)-phenyl]acetic acid by initial attack on the dienone-carbonyl group.[4] The reactions of αα-diphenyl-β-propiolactone with nucleophiles, on the other hand, are known to occur at the carbonyl or at the β-carbon with cleavage of either or both carbonyl–oxygen and alkyl–oxygen bonds.[10,13] In the spiro compounds (1a—e), the α-carbon of the β-lactone ring could not be the reaction centre because it is blocked by the cyclohexadienone moiety.

A step-wise mechanism (Scheme 1) involving initial formation of *p*-quinone diphenylmethide with the aid of base followed by 1,6-addition of the nucleophile to give the phenolic system should be possible for the reactions. A possible *p*-quinone methide intermediate was proposed by Koutek and his co-workers [14] for the reaction of 4-hydroxybenzyl phenyl sulphones with nucleophiles.

The transient *p*-quinone diphenylmethide derivatives (6c and d) whose structures are consistent with the physical data were isolated as follows. When potassium cyanide was added to an acetonitrile solution of (1c and d), orange precipitates of (6c and d) were immediately formed in 78 and 69% yield, respectively. On stirring, the orange precipitates disappeared and the normal products (5c and d) were obtained in good yield. *p*-Quinone methides (6) were not found in the reactions of (1a, b, and e), probably due to the reactivities in acetonitrile. We also found that halide (Br^- or I^-) ion-catalysed decarboxylation of (1a) gives *p*-quinone diphenylmethide (6a).

From these observations, a concerted mechanism for nucleophilic attack on the 3-position with decarboxylation can be excluded, and the reactions of (1) with nucleophiles can most reasonably be explained by a mechanism which proceeds through a *p*-quinone diphenylmethide (6) as intermediate followed by 1,6-addition of a nucleophile (Scheme 3).

This reaction in which nucleophiles attack the carbonyl carbon to cause decarboxylation is the first case reported



a; $R^1 = R^2 = R^3 = H$
c; $R^1 = H, R^2 = R^3 = Me$
d; $R^1 = H, R^2 = R^3 = Cl$

SCHEME 3

for β-lactones. This is favoured in view of the energy gain for release of ring strain in the β-lactone moiety and also for formation of the stable *p*-quinone diphenylmethide derivatives and $NuCO_2^-$ groups. The following 1,6-addition [15] of nucleophiles to the *p*-quinone methides affords aromatic phenols. The spiro compounds (1) thus follow path 2 in Scheme 1.

Reaction of 3,3-*Dimethyl*-1-*oxaspiro*[3.5]*nona*-5,8-*diene*-2,7-*dione* (2) *with Methyl-lithium*.—We extended our study to the reaction of the 3,3-dimethylspiro-β-lactone (2) with nucleophiles. The reaction of (2) with potassium cyanide was complex and we could not isolate identifiable compounds. The reaction of (2) with methyl-lithium does not give the analogue of (5); it gives, instead, α-(4-hydroxy-3-methylphenyl)-α-methylpropionic acid (7) (18%). In this case, the nucleophile attacked the cyclohexadienone moiety as in the reactions of cyclohexadienones.[6] The position of the new methyl group was determined by n.m.r. analysis (see Experimental section).

Reaction may occur as follows: methyl anion attacks the position allylic to the leaving carboxy group, or the dienone-carbonyl group followed by vinylogous pinacol rearrangement. For spirocyclohexadienones, Coutts and Hamblin [16] reported similar 1,3-addition of a Grignard reagent to the enone. The two mechanisms cannot be distinguished on the basis of the products. However, in the case of the reaction of the spiro-β-lactams (3) with methyl-lithium, the carbinol formed with the dienone-carbonyl function could be isolated. Therefore, the mechanism in Scheme 4 is acceptable.

The different reactivities of the 3,3-diphenyl-(1) and 3,3-dimethyl-spiro compounds (2) can be explained by the relative stabilities of the *p*-quinone methides. Nucleophilic attack on (2) should proceed through path 3 but not path 2, as shown in Scheme 1.

Reactions of Substituted 1-*Azaspiro*[3.5]*nona*-5,8-*diene*-2,7-*diones* (3) *with Nucleophiles*.—We extended our interest in the reactions of spiro-β-lactones (1) and (2) with nucleophiles to that of spiro-β-lactam systems (3). It is known that the reactions of β-propiolactams with nucleophiles proceed through cleavage at the carbonyl–nitrogen bond to give the ring-opened products.[11]

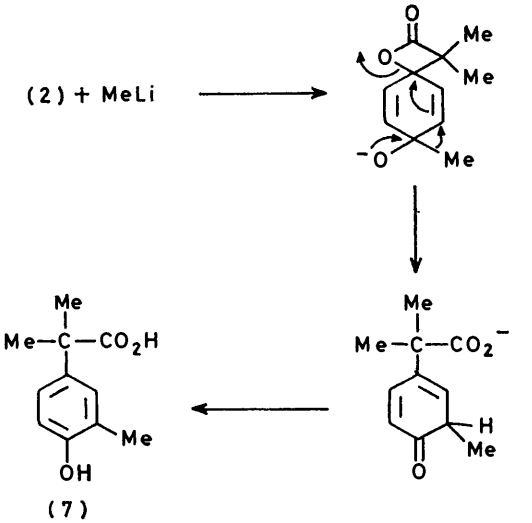
On treatment of 4-phenyliminocyclohexa-2,5-dienone with dimethyl- and diphenyl-keten, the spiro-β-lactams (3a and b), which are the aza-analogous of the oxaspiro compounds (1) and (2), were obtained. Compounds (3) are sensitive toward Lewis acids as the 5-hydroxy-*N*-phenylindolin-2-ones (8a and b), *i.e.*, the acid-catalysed rearrangement products derived from the spiro-β-lactams (3), were obtained by silica gel column chromatography of reaction mixtures. The same products were also obtained from (3) in treatment with a catalytic amount of boron trifluoride–ether. Therefore, direct crystallisation is preferred for the isolation of the spiro-β-lactams (3a and b).

On treatment of (3a) with potassium cyanide in acetonitrile, the starting material was recovered. The reaction of compound (3a) with methyl-lithium in ether resulted in the formation of the spiro cyclohexa-2,5-dienol (9a) (65%) by 1,2-addition on the dienone-carbonyl group. The structure of compound (9a) was assigned by spectroscopic data and the Lewis acid catalysed rearrangement. Treatment of (9a) with a catalytic amount of boron trifluoride–ether in benzene afforded the 5-methyl-*N*-phenylindolin-2-one derivative (10a) in quantitative yield.

Compound (9a) is the only 1,2-addition product of methyl-lithium on the dienone-carbonyl function. This type of 1,2-adduct formation was recently found by Bracct and Rieken [17] for the reactions of 1-imino-2,6-di-t-butylcyclohexa-2,5-dienone with Grignard and alkyllithium reagents. However, in a similar reaction for the oxaspiro analogue (2), the 1,2-adduct underwent a further reaction giving the ring-opened product (7). This difference may be explained in terms of the leaving abilities of carboxylate and amide anion caused by anionic pinacol migration of the methyl group.

A similar reaction of (3a) with *p*-tolyl-lithium was observed to give the carbinol derivative (9b) which also afforded the rearranged product (10b) upon catalysis by boron trifluoride. A similar result was also obtained from the reaction of (3b) with methyl-lithium (Table 2).

Acid-catalysed rearrangements of cyclohexadienones



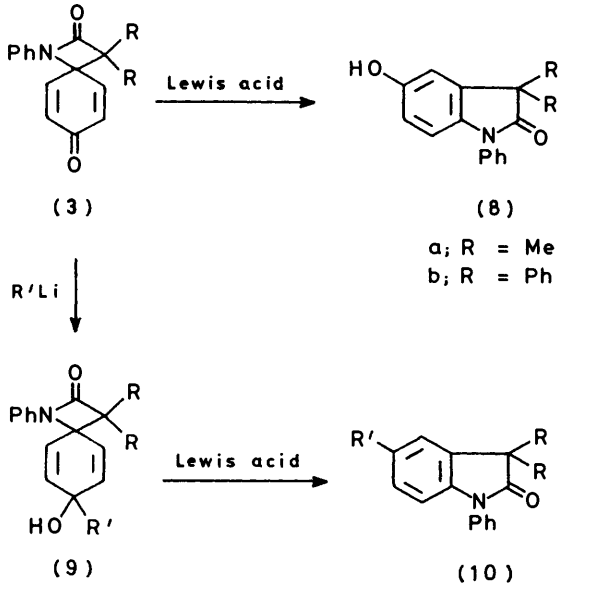
SCHEME 4

TABLE 2

Reactions of spiro-β-lactams (3) with methyl-lithium and Lewis acid-catalysed rearrangements of (3) and (9)

Substrate	Reagent	Solvent	Product	Yield (%)
(3a)	BF_3–ether	Dichloromethane	(8a)	66
(3b)	BF_3–ether	Dichloromethane	(8b)	98
(3a)	MeLi	Ether	(9a)	65
(3b)	MeLi	Ether	(9b)	48
(9a)	BF_3–ether	Benzene	(10a)	61
(9b)	BF_3–ether	Benzene	(10b)	96

and cyclohexadienols are frequently encountered in the cyclohexadienone–phenol rearrangement [5] and are sometimes used for synthesis.[18] Therefore, Lewis acid-catalysed rearrangement of compounds such as (3) and (9), should be a useful method for the synthesis of 5-substituted *N*-arylindolin-2-ones.



SCHEME 5

Reactions of Other Spiro-β-lactams (4) *with Methyl-lithium.*—The spiro-β-lactams (4a—c), [2 + 2] cycloadducts of fluoren-9-one *p*-tolylimine, and dimethylcyclohexenyl- or diphenyl-keten, were prepared by a procedure similar to that of Singer and Davis.[19]

When compound (4a) was treated with methyl-lithium in ether, 9-methyl-9-*p*-tolylaminofluorene (12a) was obtained in good yield. Similar results were found in the reaction of (4a) with *p*-tolyl-lithium and that of (4b) with methyl-lithium (Table 3). The reaction of (4c) with an excess of methyl-lithium was also examined; however, the starting material was recovered quantitatively.

It is difficult to rationalise the product formation directly by concerted nucleophilic attack on the tertiary carbon with simultaneous elimination of keten groups. A two-step mechanism can explain the product formation as in the reactions of the spiro-β-lactones (1) with nucleophiles as shown in Scheme 1, but both steps are quite different. In the first step the nucleophile attacks the carbonyl carbon of β-lactams not to afford the fluoren-9-one methides (14) and the anion of *N*-tolylamide (15) but to give fluoren-9-one *p*-tolylimine (11) and the enolate anion of the corresponding ketone (13). The second step is nucleophilic addition to the nitrogen–carbon double bond of the imine formed to produce the product (12).

TABLE 3

Reactions of spiro-β-lactams (4a—c) with methyl- and *p*-tolyl-lithium

Substrate	Reagent	Solvent	Products	Yields (%)
(4a)	MeLi	Ether	(12a)	98
(4a)	*p*-Tol-Li	Ether	(12b) + (13b)	51 + 58
(4b)	MeLi	Ether	(12a)	53
(4c)	MeLi	Ether	No reaction	
(4c)	*p*-Tol-Li	THF	No reaction	

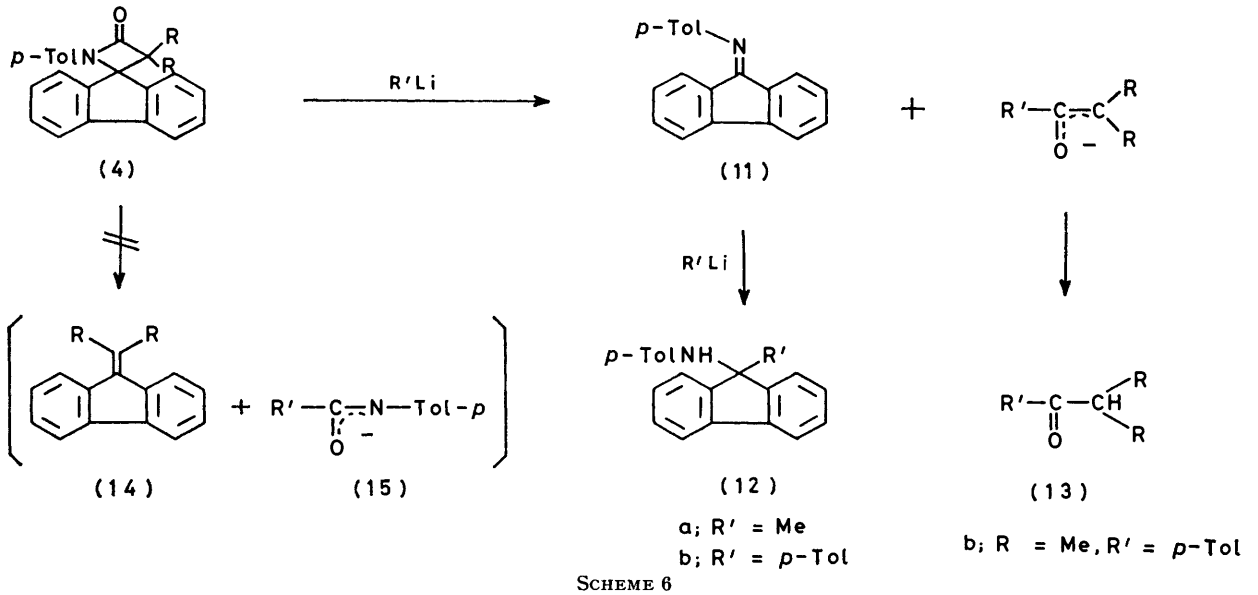
Fluoren-9-one *p*-tolylimine (11), the proposed intermediate for this reaction, was treated with methyl-lithium to produce compound (12a) which is also derived from the reaction of (4a) with methyl-lithium.

In spite of the structural differences between (1) and (4) this reaction should be analogous to processes through path 2 in Scheme 1. We do not have an explanation for the different reactivities for nucleophilic attacks on the carbonyl carbon in these spiro-β-lactams [between (4a and b) and (4c)], but steric interactions may be important.

EXPERIMENTAL

Materials.—Substituted 3,3-diphenyl- (1) and 3,3-dimethyl-1-oxaspiro[3.5]nona-5,8-diene-2,7-dione (2) were prepared by literature methods.[3,4] *N*-Phenyl-1-azaspiro-[3.5]nona-5,8-diene-2,7-diones (3a and b) were prepared by [2 + 2] cycloaddition of 4-phenyliminocyclohexa-2,5-dienone [20] to dimethyl- and diphenyl-keten in dichloromethane and recrystallised from dichloromethane–light petroleum. Their physical properties are shown in Table 4. The spiro-β-lactams (4) of fluoren-9-one imine were synthesised by a method similar to that reported by Singer and Davis.[19]

Reactions of 3,3-Diphenylspiro-β-lactones (1) *with Potassium Cyanide.*—A typical procedure for the reactions of (1) with potassium cyanide is as follows. To a solution of (1a) (302 mg, 1 mmol) in acetonitrile (30 ml) was added potassium cyanide (130 mg, 3 mmol). After stirring for 15 h at room temperature, the mixture was poured into water (100 ml). After neutralising with dilute hydrogen chloride, the mixture was extracted with chloroform, and the extract was washed with water, dried ($MgSO_4$), and concentrated to give an oily residue. T.l.c. on silica gel (GF_{254} type 60, Merck)–chloroform showed three products having R_F 0.75, 0.40, and 0.15. On extraction with chloroform–acetone (9 : 1), the main spot, R_F 0.15, gave a yellowish solid which was recrystallised from chloroform–n-hexane and shown to be (*p*-hydroxyphenyl)diphenylacetonitrile (5a) (228 mg, 81%). The structures of the other products were not determined. Similar reactions of (1b—e) with potassium cyanide were carried out similarly and the results and



SCHEME 6

physical properties of the products are shown in Tables 1 and 5.

Reactions of (1a) *with Methyl-lithium and Methylmagnesium Iodide.*—Ether solutions of methyl-lithium or methylmagnesium iodide was prepared as usual. An ether solution of (1a) (500 mg) was added dropwise to an ether solution of methylmagnesium iodide (3 mol equiv.) at room temperature with continuous stirring. After several hours, the mixture turned yellow. The usual work-up and t.l.c. separation yielded a crystalline product (295 mg, 65%), identified as α-(*p*-hydroxyphenyl)-αα-diphenylethane (5a′) (lit.,[21] 120—122 °C). A similar procedure was employed for the reaction of (1a) with methyl-lithium. The results are shown in Table 1.

Reaction of 3,3-*Dimethylspiro*-β-*lactone* (2) *with Methyl-lithium.*—The reaction of (2) with methyl-lithium was examined in a manner similar to that for (1a). The product was α-(4-hydroxy-3-methylphenyl)-α-methylpropionic acid (7), m.p. 144—145 °C, $\nu_{max.}$ 3 360 (OH), 3 000—2 500 and 1 705 (CO_2H), 1 270, 1 150, and 820 cm^{-1}; δ[$CDCl_3$—$(CD_3)_2$-SO] 1.52 (6 H, s, CMe_2), 2.20 (3 H, s, ArMe), 6.76 (1 H, d, *J* 8 Hz, ArH-5), 7.07 (1 H, dd, *J* 8 and 2 Hz, ArH-6), 7.13 (1 H, d, *J* 2 Hz, ArH-2), and *ca.* 8.3br (2 H, s, CO_2H and OH).

Isolations of the Transient Intermediates (6c *and* d).—When potassium cyanide (130 mg, 2 mmol) was added to acetonitrile solution of (1c) (200 mg, 0.63 mmol), an orange precipitate was immediately formed. After 10 min, the orange precipitate was filtered and recrystallised from chloroform–n-hexane to give orange needles of (6c) (135 mg, 78%), m.p. 198—201 °C (lit.,[3,22] 198 °C). A similar procedure for (1d) yielded orange needles of (6d) (69%), m.p. 218—221 °C (lit.,[3,22] 217 °C). The structure of the *p*-quinone methides (6c and d) were consistent with the physical data.

Boron Trifluoride catalysed Rearrangements of (3a *and* b).—To a solution of spiro-β-lactam (3a) (213 mg, 1 mmol) in benzene (10 ml) was added a catalytic amount of boron

TABLE 4

Syntheses of (3) and (4) and their physical properties

Compound	Yield (%)	M.p. (°C)	$\nu_{max.}$/cm^{-1}	δ ($CDCl_3$)
(3a)	24	124—126	1 750 (CO)	6.50 (2 H, d, *J* 10 Hz), 6.81 (2 H, d, *J* (10 Hz), 7. 18—7.83(10 H, m)
(3b)	84	156—157	1 750	1.38 (6 H, s), 6.50 (2 H, d, *J* 10 Hz), 7.10 (2 H, d, *J* 10 Hz), 7.24—7.32 (5 H, m)
(4a)	69	279—284	1 750	2.10 (3 H, s), 6.41—7.81 (22 H, m)
(4b)	79	155—156	1 775	1.27 (6 H, s), 2.12 (3 H, s), 6.83 (4 H, s), 7.20—7.82 (8 H, m).
(4c)	19	174—175	1 745	1.0—2.0br (10 H, s), 2.15 (3 H, s), 6.85 (4 H, s), 7.08—7.87 (8 H, m).

TABLE 5

Physical properties of the reaction products (5a—e)

				Found (%)			Required (%)		
Product	M.p. (°C)	$\nu_{max.}$/cm^{-1}	δ ($CDCl_3$)	C	H	N	C	H	N
(5a)	148—153	3 400(OH), 2 230(CN)	4.0br (1 H, s), 6.95 (4 H, AA′BB′), 7.27—7.37 (10 H, m)	83.9	5.0	4.7	84.2	5.3	4.7
(5a)	120—122	3 330	2.14 (3 H, s), 6.83 (4 H,AA′BB′), 7.07—7.27 (10 H, m)	87.1	6.3		87.6	6.6	
(5b)	156—160	3 470, 2 230	2.17 (3 H, s), 5.26 (1 H, s), 6.72 (1 H, s), 6.75br (1 H, s), 6.98br (1 H, s), 7.27 (10 H, s)	84.4	5.8	4.9	84.3	5.7	4.7
(5c)	168—170	3 430, 2 245	2.16 (6 H, s), 5.8br (1 H, s), 7.18 (2 H, s), 7.30 (10 H, s)	84.7	6.1	4.3	84.3	6.1	4.5
(5d)	156—158	3 400, 2 250	6.04br (1 H, s), 7.15 (2 H, s), 7.25—7.39 (10 H, m)	67.5	3.6	3.7	67.8	3.7	3.9
(5e)	240—242	3 400, 2 250	5.53 (2 H, ABq), 7.27br (12 H, s), 7.42 (2 H, s)	85.5	5.0	4.2	85.9	5.1	4.2

TABLE 6

Physical properties of (8)—(10)

Compound	M.p. (°C)	$\nu_{max.}$ cm^{-1}	δ ($CDCl_3$)
(8a)	243—244	3 240, 1 685	6.83 (3 H, m), 7.41 (10 H, s), 7.56 (5 H, s), 7.71 (1 H, s)
(8b)	212—214	3 380, 1 685	1.42 (6 H, s), 6.68 (2 H, d), 6.82 (1 H, m), 7.45 (5 H, s)
(9a)	*	3 380, 1 750, 1 735	1.58 (3 H, s), 5.62 (2 H, d, *J* 10 Hz), 6.20 (2 H, d, *J* 10 Hz), 7.20—7.90 (15 H, m)
(9b)	147—148	3 380, 1 755, 1 715	1.21 (6 H, s), 1.36 (3 H, s), 2.57 (1 H, s), 5.88 (2 H, d, *J* 10 Hz), 6.20 (2 H, d, *J* 10 Hz), 6.97—7.50 (5 H, m)
(10a)	223—224	1 725	2.32 (3 H, s), 6.75—7.21 (3 H, m), 7.40 (10 H, s), 7.56 (5 H, s)
(10b)	149—150	1 725	1.46 (6 H, s), 2.33 (3 H, s), 6.70 (1 H, d), 6.96 (1 H, m), 7.05 (1 H, m), 7.32—7.60 (5 H, m)

* Amorphous solid.

TABLE 7

Physical properties of (12) and (13b)

Compound	M.p. (°C)	$\nu_{max.}$ cm^{-1}	δ ($CDCl_3$)	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
(12a)	145—147	1 520	1.61 (3 H, s), 2.00 (3 H, s), 4.01 (1 H, s), 5.93 (2 H, d, *J* 8 Hz), 6.61 (2 H, d, *J* 8 Hz), 7.80 (8 H, m)	88.8	6.7	4.7	88.5	6.7	4.9
(12b)	161—162	1 515	2.06 (3 H, s), 2.24 (3 H, s), 4.30—4.70 (1 H, s), 6.15 (2 H, d, *J* 8 Hz), 6.68 (2 H, d, *J* 8 Hz), 6.93—7.73 (12 H, m)	89.4	6.6	4.0	89.7	6.4	3.9
(13b)	Oil	1 685	1.20 (6 H, d, *J* 7 Hz), 2.38 (3 H, s), 3.51 (1 H, m), 7.21 (2 H, d, *J* 8 Hz), 7.86 (2 H, d, *J* 8 Hz)						

trifluoride–ether (3 drops). After 30 min evaporation of the solvent gave a residue which was filtered through a silica gel column (10 g) using ether. 3,3-Dimethyl-5-hydroxy-*N*-phenylindolin-2-one (8a) was obtained in quantitative yield. 3,3-Diphenylindolin-2-one (8b) was also obtained from a similar reaction of (3b) by BF_3 catalysis (Table 6).

Reaction of 3,3-*Dimethylspiro*-β-*lactam* (3a) *with Methyl-lithium*.—To an ether solution of methyl-lithium (5 mmol) was added dropwise the spiro-β-lactam (3a) (600 mg, 1.7 mmol) in ether (50 ml) at room temperature. After 2 h the mixture was poured into water. The water layer was neutralised with dilute hydrogen chloride and extracted with ether. The organic layer was dried and evaporated to yield a residue which was subjected to t.l.c. (silica–chloroform). The main product was recrystallised from ether–light petroleum. The physical properties are shown in Table 6. 7-*Hydroxy*-3,3,7-*trimethyl*-1-*phenyl*-1-*azaspiro*-[3.5]*nona*-5,8-*dien*-2-*one* (9a) had *m/e* 269 (M^+, 4%), 251 (81), 136 (54), 208 (30), 119 (19), 149 (33), 135 (100), 91 (24), and 87 (25) (Found: C, 75.5; H, 7.0; N, 5.1. $C_{17}H_{19}NO_2$ requires C, 75.8; H, 7.1; N, 5.2%).

Rearrangement of (9a) *catalysed by Boron Trifluoride*.—A rearrangement similar to that of (3a) was employed for the reaction of (9a) (107 mg, 0.5 mmol) and gave crystalline 3,3,5-*trimethyl*-1-*phenylindolin*-2-*one* (10a) in good yield, (Found: C, 75.5; H, 7.0; N, 5.1. $C_{17}H_{19}NO_2$ requires C, 75.8; H, 7.1; N, 5.2%).

Reactions of (4a *and* b) *with Methyl- and* p-*Tolyl-lithium*.—The reaction of (4a) with methyl-lithium was carried out as for (2) or (3a). The results are shown in Tables 3 and 7.

Reaction of Fluoren-9-*one* p-*Tolylimine* (11) *with Methyl-lithium*.—The reaction of (11) with methyl-lithium was carried out as for (2). 9-Methyl-9-*p*-tolylaminofluorene (12a) was obtained as crystals (95%), m.p. 145—147 °C. The i.r. and n.m.r. spectra and m.p. of this compound were identical with those for the product from the reaction of the spiro-β-lactams (4a and b) with methyl-lithium.

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