Synthesis and Mass Spectra of Some αβ-Unsaturated γ-Lactones and γ-Lactams

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Migration of an alkyl or phenyl group from the γ-position of a number of γ-disubstituted αβ-unsaturated γ-lactones and one γ-lactam upon electron impact has been proved by high resolution and ^{18}O-labelling studies and by the observation of metastable ions. Improved methods for the synthesis of such compounds uncontaminated by their dihydro-derivatives are described.

SOME examples of migration of alkyl and aryl groups induced by electron impact have been reported previously, for example by Djerassi and his co-workers,[1] who noted the migration of a methyl group in the molecular ion of 4,4,5-trimethylcyclohex-2-enone. Examination of the lactone (Ia) reveals (Table 1) the loss from the molecular ion of CHO in a single step (confirmed by high resolution mass measurement and the appropriate metastable transition; see Table 2). The dideuterio-analogue (I; $R^1 = R^2 = {}^2H$, $R^3 = {}^1H$, $R^4 = Me$) shows a loss of 30 mass units from the molecular ion (M^+). These results indicate a hydrogen migration and are in agreement with the results of Friedman and Long [2] for lactones such as (I; $R^1 = H$ or Me, $R^2 = R^3 = R^4 = H$). Labelling experiments [2] proved that in the latter compounds the ring oxygen atom was expelled, thus also implying a hydrogen shift. A series of αβ-disubstituted but-2-enolides were examined by Reinhoudt and van de Graaf.[3] The loss of CHO from the molecular ion was confirmed and the sequential losses of H and CO discovered but it was not proved which atoms were lost as CO.

TABLE 1

m/e Values and relative intensities (%) of abundant ions †

2-Methylbut-2-enolide (Ia)

m/e	99	98	70	69	68	53	52	51	50
%	4·6	82·9	5·6	89·1	7·1	9·6	3·1	6·1	8·2
m/e	49	44	43	42	41	40			
%	2·5	9·2	2·3	7·6	100	21·6			

4,4-Dimethylbut-2-enolide (Ib)

m/e	112	98	97	70	69	67	59	58	55
%	18·1	4·7	100	3·5	89·9	2·8	14·6	14·2	3·4
m/e	54	53	51	50	44	43	42	41	40
%	17·8	6·1	2·9	2·9	2·2	77·9	3·7	13·4	3·2

2,4,4-Trimethylbut-2-enolide (Ic)

m/e	126	112	111	84	83	68	67	55	53
%	13·3	3·9	46·7	2·0	30·0	8·7	8·0	15·3	2·7
m/e	51	44	43	42	41	40			
%	2·3	2·3	100	2·2	7·3	8·7			

4-Methyl-4-phenylbut-2-enolide (Id)

m/e	175	174	160	159	132	131	129	128	115
%	2·4	20·5	6·3	55·4	10·2	100	2·4	2·9	5·3
m/e	105	104	103	102	99	97	78	77	76
%	16·5	2·4	18·8	2·2	2·3	2·4	2·8	21·1	2·3
m/e	69	63	57	55	54	52	51	50	49
%	3·2	2·9	2·8	2·6	2·4	2·4	12·2	5·0	2·9
m/e	47	44	43	41					
%	6·1	2·4	9·2	4·2					

4-Bromomethyl-4-phenylbut-2-enolide (Ie)

m/e	254	252	160	159	131	128	105	103	102
%	3·0	3·1	10·9	100	10·9	4·6	15·3	6·1	2·9
m/e	86	84	77	63	54	51	50	47	44
%	6·6	9·8	13·1	2·1	2·1	7·4	3·6	2·6	2·4

TABLE 1 (*Continued*)

4,4-Diphenylbut-2-enolide (If)

m/e	237	236	208	207	192	191	190	189	165
%	9·6	54·4	2·6	2·4	6·4	8·6	2·3	6·6	6·8
m/e	160	159	154	152	132	131	115	106	105
%	2·8	24·1	4·7	2·3	10·9	100	4·9	5·4	65·8
m/e	104	103	89	82	77	76	63	51	47
%	2·3	17·5	2·4	2·6	27·7	2·8	3·0	7·3	2·7

1-(4-Methoxyphenyl)-5,5-diphenyl-Δ^3-pyrrolin-2-one (III)

m/e	343	342	341	340	313	312	265	264	237
%	10·4	24·2	100	4·4	8·2	22·0	3·8	17·0	8·8
m/e	236	220	211	210	194	193	192	191	190
%	48·9	2·7	4·9	29·6	5·5	11·0	31·8	24·7	3·3
m/e	189	165	131	129	123	122	115	92	77
%	7·1	5·2	11·0	2·2	8·2	2·7	4·7	2·4	7·1

4,4-Dimethylbutyrolactone (IVa)

m/e	114	100	99	81	71	70	59	58	56
%	1·4	5·4	100	2·3	20·9	67·4	23·3	3·3	30·2
m/e	55	43	42	41					
%	67·4	69·8	20·9	3·3					

4-Methyl-4-phenylbutyrolactone (IVb)

m/e	176	161	148	121	120	106	105	104	103
%	1·4	7·0	11·9	4·9	17·5	8·4	100	7·0	5·6
m/e	95	94	91	79	78	77	66	65	63
%	2·8	41·0	2·8	7·0	5·6	38·5	6·3	7·0	3·5
m/e	55	52	51	50	47	45	43		
%	2·8	2·1	14·0	5·6	2·1	2·1	23·1		

4,4-Diphenylbutyrolactone (IVc)

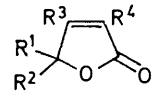
m/e	239	238	194	193	192	191	189	184	183
%	10·5	63·0	4·2	5·3	4·2	3·2	2·1	14·7	100
m/e	182	181	180	179	178	166	165	163	162
%	2·1	2·1	4·2	5·3	6·3	2·1	9·5	2·1	4·2
m/e	161	160	154	153	152	139	133	117	116
%	38·9	2·1	3·2	2·1	3·2	2·1	3·2	3·2	4·2
m/e	115	106	105	103	91	89	87	85	83
%	12·6	5·3	66·7	4·2	10·5	3·2	2·1	16·8	25·2
m/e	78	77	76	75	65	63	57	56	55
%	4·2	33·7	5·3	2·1	2·1	3·2	3·2	7·4	3·2
m/e	51	50	48	47	43	41			
%	11·6	3·2	2·1	4·2	2·1	4·2			

† Ions of *m/e* <40 or % <2 are omitted (except for molecular ions).

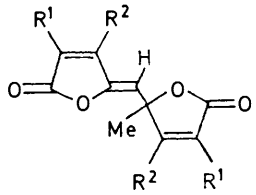
The molecular ion of the lactone (Ic) (Table 1) loses C_2H_3O; a metastable ion (Table 2) indicates a one-step process suggestive of a methyl migration analogous to that proposed by Djerassi *et al.*[1] A series of similar

[1] R. L. N. Harris, F. Komitsky and C. Djerassi, *J. Amer. Chem. Soc.*, 1967, **89**, 4765, 4775.
[2] L. F. Friedman and F. A. Long, *J. Amer. Chem. Soc.*, 1953, **75**, 2832.
[3] D. N. Reinhoudt and B. van de Graaf, *Rec. Trav. chim.*, 1970, **89**, 417.

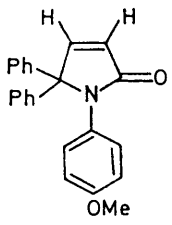
lactones has been prepared by the methods described below; their mass spectra are given in Table 1. Compounds (Ib) and (Id) both show $M - 43$ peaks with transitions in either the first (by refocusing) or the second field-free region of the spectrometer indicative of one-step losses of C_2H_3O from the molecular ions. The metastable data (Table 2) indicate also sequential losses



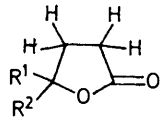
(I) a; $R^1 = R^2 = R^3 = H$, $R^4 = Me$
b; $R^1 = R^2 = Me$, $R^3 = R^4 = H$
c; $R^1 = R^2 = R^4 = Me$, $R^3 = H$
d; $R^1 = Me$, $R^2 = Ph$, $R^3 = R^4 = H$
e; $R^1 = CH_2Br$, $R^2 = Ph$, $R^3 = R^4 = H$
f; $R^1 = R^2 = Ph$, $R^3 = R^4 = H$



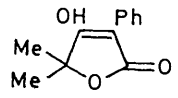
(II) a; $R^1 = Me$, $R^2 = H$
b; $R^1 = R^2 = Me$



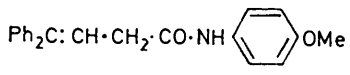
(III)



(IV) a; $R^1 = R^2 = Me$
b; $R^1 = Ph$, $R^2 = Me$
c; $R^1 = R^2 = Ph$



(V)



(VI)

of CH_3 and CO from M^+. The one- and two-step processes probably represent parallel fragmentation routes since it is doubtful if two rapidly consecutive processes occurring in the first field-free region can give rise to a metastable ion for the apparently concerted loss of both fragments.[4] The driving force for the rearrangement appears to be the formation of the stable ion (*a*), *m/e* 69, identical with that proposed by Djerassi *et al.*,[1] as shown in Scheme 1.

4,4-Diphenylbut-2-enolide (If) gives an abundant ion (*d*), *m/e* 131, corresponding to the loss of C_7H_5O from the molecular ion. The metastable ions (Table 1) again suggest parallel one- and two-step processes, rationalized in Scheme 2. The weak ions of *m/e* 192 (*g*), 191 (*h*), 189 (*j*), and 165 (*k*) are absent in the spectra of the other compounds and are evidently derived by fragmentation of the $Ph_2C{\cdot}CH{:}CH$ unit. Phenyl migration occurs in preference to methyl migration in the lactone (Id), in agreement with previous observations,[1,5,6] resulting again in the formation of the ion *m/e* 131. The much greater ion current carried by the latter ion compared with that carried by the ion *m/e* 69 reflects its greater stability,

[4] D. H. Smith, A. M. Duffield, and C. Djerassi, *Org. Mass Spectrometry*, 1973, **7**, 366.
[5] M. A. T. Kerkoff and N. M. M. Nibbering, *Org. Mass Spectrometry*, 1973, **7**, 37.

TABLE 2

Metastable transitions in the first † and second * field-free regions

(i) 2-Methylbut-2-enolide (*M* 98)

$98 \xrightarrow{*} 97$, $98 \xrightarrow{*} 69$, $69 \xrightarrow{*} 41$

(ii) 4,4-Dimethylbut-2-enolide (*M* 112)

$112 \xrightarrow{*} 97$, $112 \xrightarrow{\dagger} 69$, $112 \xrightarrow{\dagger} 59$, $112 \xrightarrow{\dagger} 58$,
$97 \xrightarrow{\dagger} 69$, $97 \xrightarrow{\dagger} 43$, $84 \xrightarrow{\dagger} 43$, $82 \xrightarrow{\dagger} 54$,
$69 \xrightarrow{\dagger} 41$

(iii) 2,4,4-Trimethylbut-2-enolide (*M* 126)

$126 \xrightarrow{*} 111$, $126 \xrightarrow{\dagger} 98$, $126 \xrightarrow{*\dagger} 83$, $111 \xrightarrow{\dagger} 83$,
$111 \xrightarrow{\dagger} 43$, $98 \xrightarrow{\dagger} 43$, $83 \xrightarrow{\dagger} 68$, $83 \xrightarrow{\dagger} 55$

(iv) 4-Methyl-4-phenylbut-2-enolide (*M* 174)

$174 \xrightarrow{*\dagger} 131$, $174 \xrightarrow{\dagger} 105$, $159 \xrightarrow{\dagger} 131$, $159 \xrightarrow{\dagger} 105$,
$133 \xrightarrow{\dagger} 105$, $131 \xrightarrow{\dagger} 103$, $130 \xrightarrow{\dagger} 115$, $120 \xrightarrow{\dagger} 105$,
$103 \xrightarrow{*} 77$

(v) 4-Bromomethyl-4-phenylbut-2-enolide (*M* 252/254)

$252/254 \xrightarrow{\dagger} 173$, $252/254 \xrightarrow{\dagger} 159$, $252/254 \xrightarrow{\dagger} 131$,
$173 \xrightarrow{\dagger} 131$, $159 \xrightarrow{\dagger} 131$, $159 \xrightarrow{\dagger} 105$, $131 \xrightarrow{\dagger} 103$

(vi) 4,4-Diphenylbut-2-enolide (*M* 236)

$236 \xrightarrow{\dagger} 131$, $208 \xrightarrow{\dagger} 131$, $191 \xrightarrow{\dagger} 165$, $180 \xrightarrow{\dagger} 165$,
$159 \xrightarrow{\dagger} 131$, $159 \xrightarrow{\dagger} 115$, $159 \xrightarrow{\dagger} 105$, $131 \xrightarrow{\dagger} 103$

(vii) 1-(4-Methoxyphenyl)-5,5-diphenyl-Δ^3-pyrrolin-2-one (*M* 341)

$341 \xrightarrow{\dagger} 264$, $341 \xrightarrow{*\dagger} 236$, $341 \xrightarrow{\dagger} 210$, $341 \xrightarrow{\dagger} 192$,
$341 \xrightarrow{*} 313$, $341 \xrightarrow{*} 312$, $341 \xrightarrow{\dagger} 131$, $313 \xrightarrow{\dagger} 312$,
$313 \xrightarrow{\dagger} 236$, $220 \xrightarrow{\dagger} 192$

(viii) 4,4-Dimethylbutyrolactone (*M* 114)

$114 \xrightarrow{\dagger} 99$, $114 \xrightarrow{\dagger} 70$, $114 \xrightarrow{\dagger} 59$, $99 \xrightarrow{*} 81$,
$99 \xrightarrow{*} 71$, $99 \xrightarrow{*} 43$, $99 \xrightarrow{*} 42$

(ix) 4-Methyl-4-phenylbutyrolactone (*M* 176)

$176 \xrightarrow{\dagger} 121$, $161 \xrightarrow{\dagger} 133$, $161 \xrightarrow{\dagger} 105$, $148 \xrightarrow{\dagger} 133$,
$148 \xrightarrow{\dagger} 105$, $133 \xrightarrow{\dagger} 105$, $120 \xrightarrow{\dagger} 105$

(x) 4,4-Diphenylbutyrolactone (*M* 238)

$238 \xrightarrow{*} 183$, $238 \xrightarrow{*} 161$, $161 \xrightarrow{*} 105$

presumably resulting from the increase in conjugation. It is noteworthy that the substituted vinyl group rearranges at the expense of methyl in the dilactones (IIa and b) and virtually the same mechanism has been proposed.[7] The fragmentation of the bromo-compound (Ie) can be explained similarly.

To confirm the proposed methyl and phenyl migrations the carbonyl oxygen atom in compounds (Ib) and (Ic) was partially labelled with ^{18}O by Friedman and Long's method. This involves exchange with $H_2{}^{18}O$ in the presence of $Na^{18}OH$ at room temperature, a process known to involve only the carbonyl oxygen atom.[2]

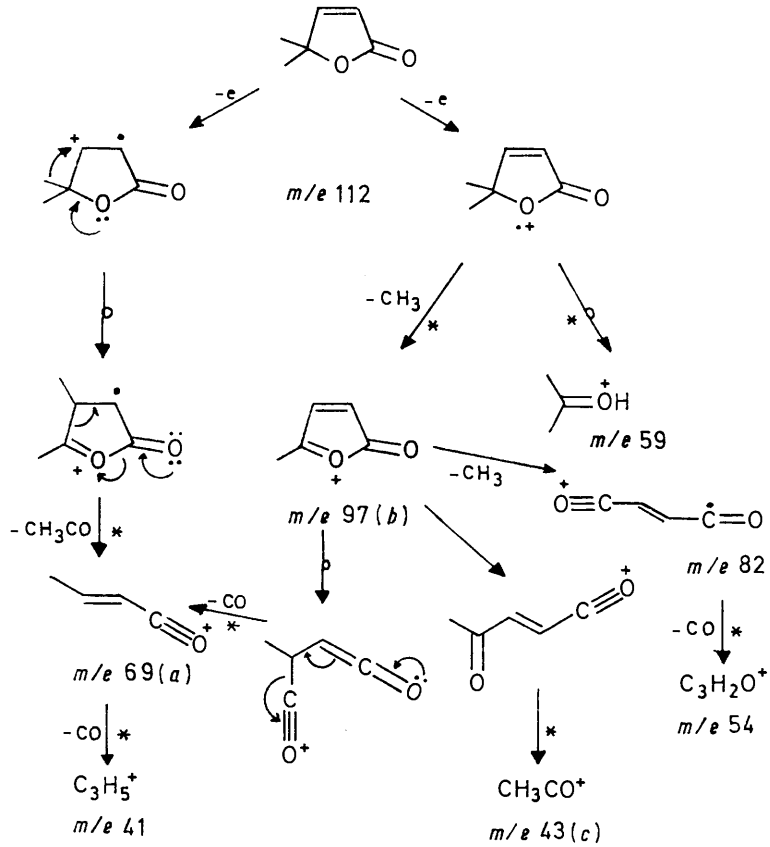
[6] H. E. Audier, J. F. Dupin, M. Fetizon, and Y. Hoppilliard, *Tetrahedron Letters*, 1966, 2077.
[7] P. Kolsaker, *Org. Mass Spectrometry*, 1973, **7**, 535.

The mass spectral results are summarized in Table 3. Within experimental error there is no loss of ^{18}O in forming the ions $(M - CH_3)^+$ and $(M - CH_3CO)^+$, and the ion CH_3CO^+ contains no more than the natural abundance of ^{18}O. Thus the ring oxygen atom must be lost as CH_3CO and migration of methyl must occur.

To study the effect of replacing the ring oxygen atom by a nitrogen atom the fragmentation (Table 1) of the lactam (III) has been examined. The one-step formation of the ions *m/e* 210 (*q*) and 131 (*d*) must involve migration of a phenyl group as indicated in Scheme 3; no metastable ions in either field-free region could be detected (Table 2) for the formation of the ions (*q*) and (*d*) from the ion *m/e* 264 $(M - Ph)^+$.

The saturated lactones (IVa—c) have also been examined. Their fragmentation (Table 1) follows the well-established pattern,[8,9] namely loss of a substituent at C-4 followed consecutively by loss of CO and C_2H_4, or of CO_2, or of C_3H_3O, as shown in Scheme 4.

There is no evidence of migration of an alkyl or an aryl group; such a process thus requires the presence of the carbon–carbon double bond.



SCHEME 1

The mass spectra of tetronic acids, which differ from the butenolides already discussed above in having a hydroxy-group at C-3, have been analysed by Haynes *et al.*[10] Compounds such as (V) give intense ions corresponding to $(M - CH_3CO)^+$, $(M - CH_3CO - CO)^+$, and CH_3CO^+, which it is now suggested are derived by migration of methyl to C-3 as in the butenolides. It was previously proposed[10] that the carbonyl oxygen atom is lost as CO following loss of a methyl group at C-4, but no labelling studies were carried out. No 4,4-diphenyl derivatives were investigated but benzoyl ions (*m/e* 105) are present in the spectra of tetronic acids with one phenyl group at C-4, which suggests a hydrogen migration in such compounds.

Synthetic Work.—A versatile method for synthesis of butenolides involving semihydrogenation of the appropriate hydroxy-acetylenic acid[11–13] was originally devised by Haynes and Jones.[11] Unfortunately the products tend to be contaminated with the fully saturated lactone, which is difficult to remove and which complicates ^{18}O-labelling studies. The preparation of butenolides by the addition of bromine to the substituted butenoic acid followed by dehydrogenation with triethylamine[14] also results in mixtures of saturated and

[8] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 205.

[9] J. H. Beynon, R. A. Saunders, and A. E. Williams, 'The Mass Spectra of Organic Molecules,' Elsevier, Amsterdam, 1968, p. 254.

[10] L. J. Haynes, A. Kirkien-Konasiewicz, A. G. Loudon, and A. Maccoll, *Org. Mass Spectrometry*, 1968, **1**, 743.

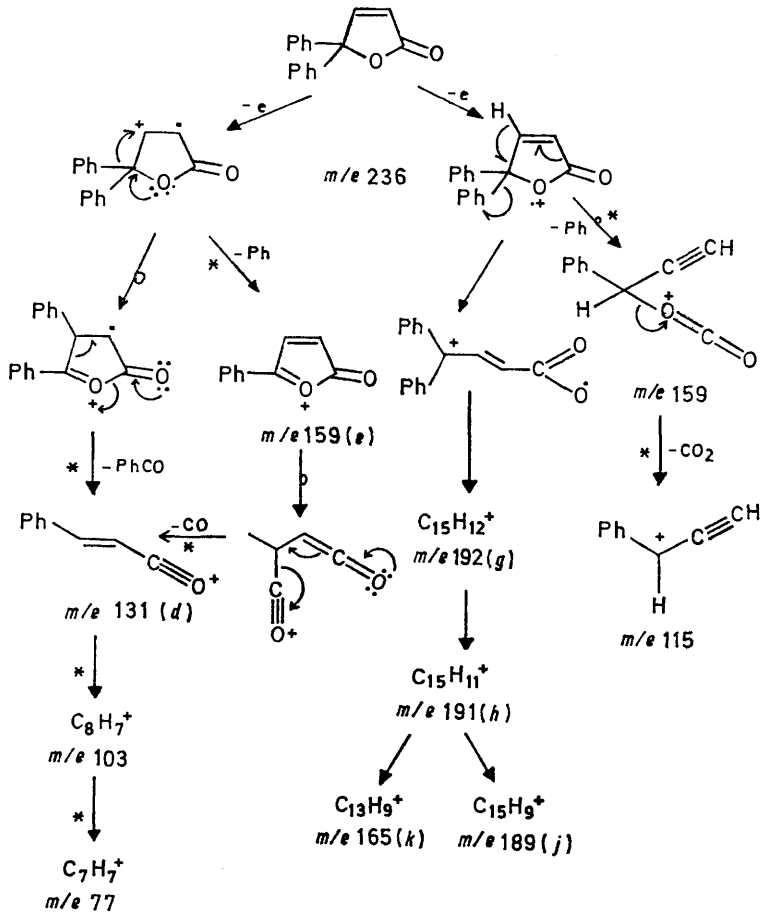
[11] L. J. Haynes and E. R. H. Jones, *J. Chem. Soc.*, 1946, 954.

[12] R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, 1959, **24**, 415.

[13] A. Nobuhara, *Agric. and Biol. Chem. (Japan)*, 1970, **34**, 1745.

[14] M. Franck-Neumann and C. Berger, *Bull. Soc. chim. France*, 1968, 4067.

unsaturated lactones, owing to the addition of hydrogen bromide to the double bond. The 4,4-diphenyl derivative (If) could be obtained by bromination of the saturated lactone with phosphorus and bromine followed by dehydrobromination,[15] but application of this procedure to 4-methyl-4-phenylbutyrolactone (IVb) gave the bromo-compound (Id) in high yield. The iodolactonization method of van Tamelen and Shamma [16] is more satisfactory. This involves treatment of the substituted butenoic acid with iodine in aqueous sodium hydrogen carbonate and potassium iodide followed by treatment with pyridine to remove hydrogen iodide. This synthesis can be more conveniently carried out in one step with 1 equiv. of iodine in pyridine. This method had to be modified slightly to obtain the lactam (III), which was prepared by treatment of the amide (VI) with iodine in *NN*-dimethylacetamide followed by dehydroiodination with pyridine. The product was identical with a sample obtained in very low yield by the published route for 1-(*p*-ethoxyphenyl)-Δ^3-pyrrolin-2-one.[17]



SCHEME 2

TABLE 3

Relative intensities of normal (^{16}O) and isotopic (+2 m.u.) peaks in the spectra of (a) 2,4,4-trimethyl- and (b) 4,4-dimethyl-but-2-enolides

	(a)		(b)	
Peak	Unlabelled	^{18}O-Labelled	Unlabelled	^{18}O-Labelled
M^+	>50 : 1	24 (±3) : 1	>40 : 1	13 (±3) : 1
$M - CH_3$	>50 : 1	25 (±3) : 1	>40 : 1	16 (±3) : 1
$M - CH_3CO$	>50 : 1	26 (±3) : 1	>40 : 1	10 (±3) : 1
$M - CH_3CO - CH_3$	>50 : 1	23 (±3) : 1	>40 : 1	9 (±3) : 1
$C_2H_3O^+$	>100 : 1 *	>100 : 1	>50 : 1	>50 : 1
$C_3H_7O^+$			>50 : 1	>50 : 1

* Doublet: $C_2H_3O + C_3H_7$, relative intensities 50 : 1.

EXPERIMENTAL

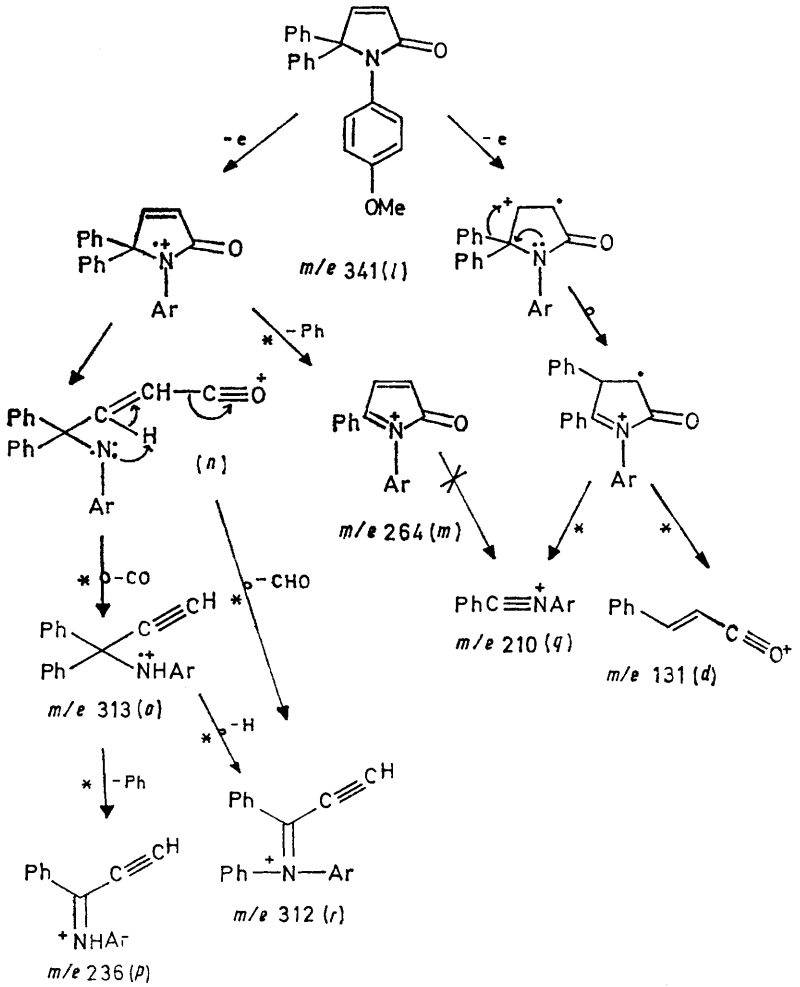
Mass spectra were determined with an A.E.I. MS9, Perkin-Elmer 270, or L.K.B. 9000S instrument. High resolution data were obtained (MS9) at 70 eV ionizing

[15] C. C. Price and J. M. Judge, *Org. Synth.*, 1965, **45**, 22.
[16] E. E. van Tamelen and M. Shamma, *J. Amer. Chem. Soc.*, 1954, **76**, 2315.
[17] H. Otomasu, Jap. P. 7,137,339 (*Chem. Abs.*, 1972, **76**, 14,330p).

voltage and 100 μA trap current at a resolution of about 15,000, with perfluorokerosene or heptacosafluorotri-n-butylamine as mass standard. A few mass measurements on molecular ions were made with the L.K.B. instrument by using the multiple ion detector/peak matcher unit at 60 μA trap current and 16 V sweep voltage at a resolution of about 1500. Metastable transitions in the first field-free region of the MS9 were detected by the standard A.E.I. refocusing technique. N.m.r. spectra were obtained for solutions in deuteriochloroform with a Varian A60 spectrometer.

4,4-Diphenylbutyrolactone (IVc).—This was formed together with 4,4-diphenylbut-3-enoic acid, m.p. 115—116°, by the condensation of benzophenone with diethyl succinate [20] followed by decarboxylation in hydrobromic and acetic acids.[21] It had m.p. 90—91° (Found: C, 80·55; H, 5·8. Calc. for $C_{16}H_{14}O_2$: C, 80·65; H, 5·9%).

2-Methylbut-2-enolide (Ia).—This was prepared by bromination of 2-methylbut-3-enoic acid followed by dehydrobromination with triethylamine as described in the literature.[14]



SCHEME 3

4,4-Dimethylbutyrolactone (IVa).[18]—Prepared by the action of concentrated hydrochloric acid on 4-methylpent-3-enoic acid, this had b.p. 120° at 30 mmHg.

4-Methyl-4-phenylbutyrolactone (IVb).—4-Phenylpent-3-enoic acid [19] was stirred for 4 h at room temperature with an excess of concentrated hydrochloric acid. After neutralization with aqueous sodium hydroxide the solution was extracted with ether. Distillation of the dried extracts yielded an oil, b.p. 182—186° at 23 mmHg, M^+ 176·0865 (Calc. for $C_{11}H_{12}O_2$: M, 176·0837), shown to be homogenous by g.l.c. (1% OV1 on Chromosorb W at 140°); ν_{CO} 1760 cm^{-1}, τ 2·64 (5H, s), 7·50 (4H, m), and 8·28 (3H, s).

4,4-Diphenylbut-2-enolide (If).—4,4-Diphenylbut-3-enoic acid (0·6 g) was dissolved in aqueous sodium hydrogen carbonate (0·5N; 15 ml) and a solution of iodine (1·27 g) and potassium iodide (2·5 g) in water (8 ml) was added. The mixture was kept in the dark for 24 h and then extracted with chloroform. The extracts were washed with aqueous 5% sodium thiosulphate until they were colourless and then evaporated to dryness, yielding a yellow solid which was dissolved in pyridine (10 ml) and kept at room temperature for 10 min. The pyridine was removed *in vacuo* and the residue crystallized from benzene–petroleum (b.p. 60—80°) giving needles (0·36 g), m.p. 131—132° (lit.,[22] 131—132°),

[18] B. J. Clarke and R. P. Hildebrande, *J. Inst. Brewing*, 1967, **73**, 60.

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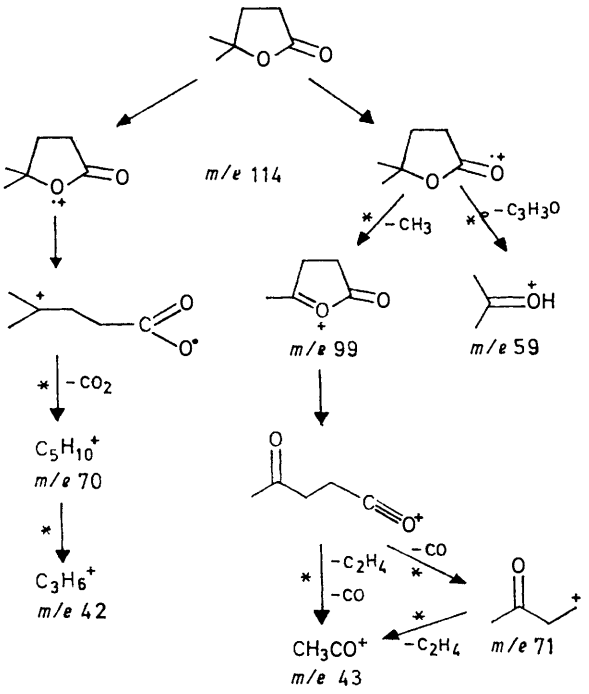
ν_{CO} 1745 cm^{-1}, τ 2·31 (1H, d), 2·65 (5H, s), 3·92 (1H, d), and 8·16 (3H, s) (Found: C, 81·3; H, 5·15. Calc. for $C_{16}H_{12}O_2$: C, 8·3; H, 5·1%).



SCHEME 4

4-Methyl-4-phenylbut-2-enolide (Id).—4-Phenylpent-3-enoic acid [19] (1 g) and iodine (1·4 g) dissolved in dry pyridine (8 ml) were kept in the dark for 16 h. The residue obtained on evaporation was dissolved in chloroform (20 ml) and the solution was washed with portions of aqueous 5% sodium thiosulphate until it was nearly colourless. The dried solution was distilled affording an oil (0·61 g), b.p. 180—186° at 22 mmHg, shown to be homogeneous by g.l.c. (1% OV1 on Chromosorb W at 160°), M^+ 174·0700 (Calc. for $C_{11}H_{10}O_2$: M, 174·0681), ν_{CO} 1750 cm^{-1}, τ 2·31 (1H, d), 2·65 (5H, s), 3·92 (1H, d), and 8·16 (3H, s).

4-(Bromomethyl)-4-phenylbut-2-enolide (Ie).—To a stirred mixture of 4-methyl-4-phenylbutyrolactone (2·04 g) and red phosphorus (0·133 g) at 0°, bromine (1·95 g) was added dropwise over 30 min. The mixture was then heated to 70° and further bromine (1·95 g) was added dropwise over 30 min. The mixture was stirred at 80° for 4 h, water (3 ml) was added, and the mixture was then refluxed for 3 h. After cooling, the mixture was poured into water (20 ml) and extracted with ether. The extracts were dried (Na_2SO_4) and distilled *in vacuo* affording a yellow oil (1·6 g), b.p. 160—165° at 2×10^{-3} mmHg, shown to be homogeneous by g.l.c. (1% OV1 on Chromosorb W at 180°), ν_{CO}, 1750 cm^{-1}, τ 2·25 (1H, d), 2·55 (5H, s), 3·72 (1H, d), and 3·90 (2H, s).

4,4-Dimethylbut-2-enolide (Ib).—Prepared by the method described for 4,4-diphenylbut-2-enolide, this had b.p. 94° at 14 mmHg (lit.,[11] 80° at 10 mmHg) and was shown to be pure by g.l.c. (3% SE52 on Chromosorb W at 125°), M^+ 112·0524 (Calc. for $C_6H_8O_2$: M, 112·0524), τ 8·48 (6H, s), 3·97 (1H, d), and 2·52 (1H, d).

^{18}O-Labelling Experiments.—The butenolide (Ib or c) (prepared by Dr. H. N. A. Al-Jallo) (5 mg) was added to a solution prepared by the reaction of sodium (10 mg) with ^{18}O-labelled water (100 ml; 11·2% enrichment, normalized) under nitrogen at 0°. The mixture was kept at room temperature for 90 min, acidified with concentrated sulphuric acid (1 drop), and extracted with benzene. After drying, the benzene was evaporated off and the residual oil introduced into the heated inlet system (at 110°) of the mass spectrometer. Alternatively the reaction was performed in a Reactivial and the alkaline solution was injected directly into the gas chromatograph inlet of the mass spectrometer. A number of mass spectra scans, taken at the apex of the gas chromatographic peak, were averaged.

2-Methyl-[4-^{2}H$_2$]but-2-enolide.—2-Methylbut-2-enolide (15 mg) was kept in a solution of sodium deuterioxide in D_2O (2 ml) at 60° for 2 days, after which the n.m.r. signal at τ 5·2 had disappeared.

1-(4-Methoxyphenyl)-5,5-diphenyl-Δ^3-pyrrolin-2-one (III).—(*a*) To 4,4-diphenylbutyrolactone (100 mg) and red phosphorus (15 mg) in refluxing carbon tetrachloride was added bromine (0·25 ml), followed after 1 h by more bromine (0·25 ml). After 1 h under reflux the mixture was evaporated to dryness *in vacuo* at room temperature and *p*-anisidine (0·5 g) in carbon tetrachloride (10 ml) was added. The mixture was stirred at room temperature for 10 min, the solvent was removed *in vacuo*, and the residue was heated at 160—170° under nitrogen for 3 h. A solution of the product in chloroform was washed successively with dilute hydrochloric acid and saturated aqueous sodium hydrogen carbonate. Removal of the solvent left an oily solid which was subjected to t.l.c. on silica gel (GF_{254}). The material of R_F 0·45 in chloroform was rechromatographed and then had m.p. 118°, M^+ 341·1408 (Calc. for $C_{23}H_{19}NO_2$: M, 341·1416), ν_{CO} ($CHCl_3$) 1675 cm^{-1}, $\lambda_{max.}$ (EtOH) 220, 300, 315, and 325 nm (log ε 4·02, 3·61, 3·62, and 3·59).

(*b*) *N*-(4-Methoxyphenyl)-4,4-diphenylbut-3-enamide (VI) (30 mg; m.p. 130°; from 4,4-diphenylbut-3-enoic acid [20]) and iodine (300 mg) in *NN*-dimethylacetamide were kept in the dark at room temperature for 24 h. The solvent was removed *in vacuo* and the residue dissolved in pyridine (5 ml). After 2 h the pyridine was removed *in vacuo*, the residue was dissolved in chloroform, and the solution was washed successively with aqueous 5% sodium thiosulphate and saturated aqueous sodium hydrogen carbonate. Evaporation of the dried solution afforded an oil which was purified by t.l.c. as in (*a*). The product (6 mg), recrystallized from benzene–petroleum, had m.p. 123·5°, with spectral properties identical with those of the sample from (*a*).

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