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MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS—CLXXXV*

EFFECT OF PHENYL GROUP IN THE MASS SPECTRA OF *TRANS*-10-PHENYL-2-DECALONE AND *TRANS*-10-PHENYLDECALIN†

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Abstract—With the use of deuterium labeling and metastable ion measurements, the major fragmentation pathways of *trans*-10-phenyl-2-decalone (II) have been deduced. A comparison with *trans*-10-phenyldecalin (IV) demonstrated the almost complete domination of the phenyl group in directing the electron-impact promoted decomposition of II. In fact, in contrast to the spectra of the methylated analogs, only one fragmentation pathway is uniquely associated with the carbonyl function. The substitution of a phenyl group at the ring junction in IV has permitted the recognition of definitive fragmentation pathways for this compound also. Such definition has not previously been possible for unsubstituted alicyclic hydrocarbons. The formation of an abundant tropylium ion from both II and IV has been examined, but its genesis is too complicated to be accurately defined from the labeling data at hand.

A RECENT publication[1] from this laboratory has described the synthesis and mass spectral properties of *trans*-10-phenyl-Δ^3-2-octalone (I). Routine analysis by mass spectrometry of the intermediate products in this preparation led to the interesting discovery that the tropylium ion of mass 91 is a very prominent fragment in the spectrum of each 10-phenyl-substituted compound. The relative abundance (RA) of this ion from each analog is shown in Table 1. For such a fragment ion to be formed two different mechanistic pathways can be envisaged. It may be produced from either (a) an electron-impact induced phenyl migration, similar to that encountered in the spectrum of I,[1] or (b) consecutive carbon-carbon bond cleavages and multiple hydrogen transfer processes. Since the formation and structure of the tropylium ion from different sources has promoted considerable investigation,[2] it seemed worthwhile to study further its genesis from this series of compounds. Although it is possible that the tropylium ion is not formed by the same mechanistic pathway from each 10-phenyl-substituted analog, it was decided to use *trans*-10-phenyl-2-decalone (II) and *trans*-10-phenyldecalin (IV) as model compounds for this investigation. As shown in Table 1 the fragment ion of mass 91 is formed in 71% and 72% RA respectively from these two compounds. These systems were chosen not only because they offered the greatest scope for a deuterium labeling study, but also on the basis that a direct comparison could then be made between their mass spectral characteristics and those of analogous systems such as *trans*-10-methyl-2-decalone,[3] *trans*-decalin[4a] and the isomeric methyldecalins,[4b] whose mass spectra have been described earlier. It was also hoped that the substitution of a phenyl group at the angular

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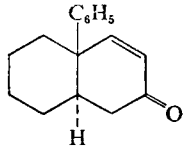
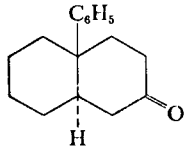
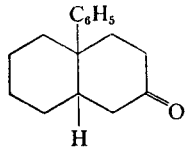
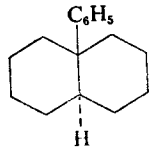
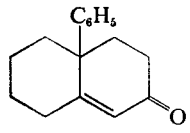
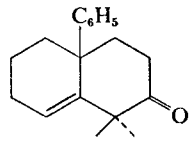
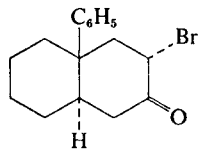
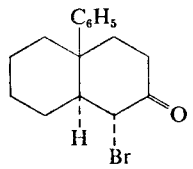
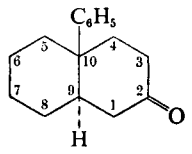
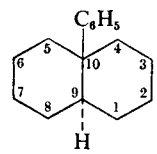
‡ Postdoctoral fellow, 1968 to 1969.

TABLE 1. THE RELATIVE ABUNDANCE (RA) AND PERCENT TOTAL IONIZATION (Σ_{40}) OF THE TROPYLIUM ION IN THE MASS SPECTRA OF 10-PHENYL-2-DECALONES, -OCTALONES AND -DECALIN AT 70 eV

Compound	No.	RA	Σ_{40}
	(I)	15	3·9
	(II)	71	6·2
	(III)	58	5·6
	(IV)	72	8·4
	(V)	36	4·0
	(VI)	58	4·7
	(VII)	75	5·5
	(VIII)	100	7·2



(II)



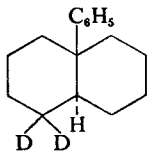
(IV)

position would allow the recognition of definitive fragmentation pathways through deuterium labeling. Such definition generally has not been possible for unsubstituted alicyclic hydrocarbons, for which in many cases structures have not been deduced readily from the mass spectra.[5]

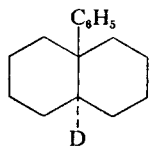
The mass spectra of *trans-* (Fig. 1) and *cis-* (Fig. 2) 10-phenyl-2-decalone are very similar at both 70 eV and 12 eV,* only slight intensity differences being observed. Our discussion will be limited, therefore, to the spectrum of the *trans*-isomer (II) which will be compared to those of several deuterated analogs. Similarly, only *trans*-10-phenyldecalin (IV) and its deuterated derivatives will be described in the present paper.

Unlike the methylated analogs, whose mass spectra have been described in an earlier publication from this laboratory,[3] 10-phenyl-2-decalone would appear to have two potential sites for charge localization, *viz.* the phenyl and carbonyl groups.† Hence it is important to recognize which fragmentation pathways are triggered by each function. One plausible way to separate the two series of cleavages would be to examine each individually, and this is potentially possible if we first consider the mass spectrum of *trans*-10-phenyldecalin (IV). For IV, the principal fragmentation patterns are most likely derived by charge localization in the phenyl nucleus or the benzylic carbon atom. These patterns can then be applied to the spectrum of II, in order to determine which, if any, of the fragment ions from II are directly associated with the carbonyl function.

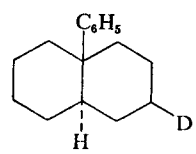
In order to investigate the principal fragmentation patterns derived from the electron-impact promoted cleavage of *trans*-10-phenyldecalin (IV) we have synthesized the deuterium labeled compounds IX to XI. The molecular ion in the mass spectrum (Fig. 3) of IV is the base peak and carries 11·7% of the total ion current at 70 eV.



(IX)



(X)



(XI)

* The mass spectra of II and III are identical at low voltage, the molecular ion in each case carrying >43% of the total ion current.

† A comparison of the ionization potentials of *t*-butylbenzene (8·68 eV) and cyclohexanone (9·14 eV)[6] suggests that fragmentations associated with the phenyl ring should be more facile than those triggered by the ketone function.

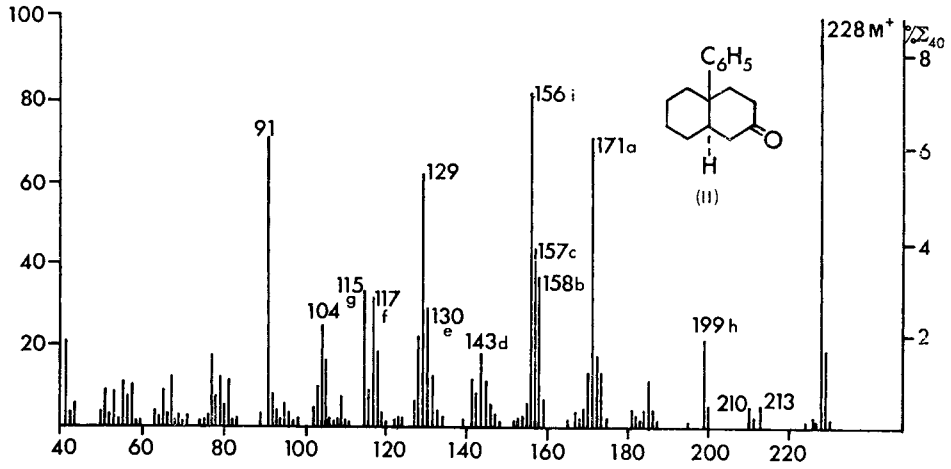


FIG. 1. Mass spectrum of *trans*-10-phenyl-2-decalone (II).

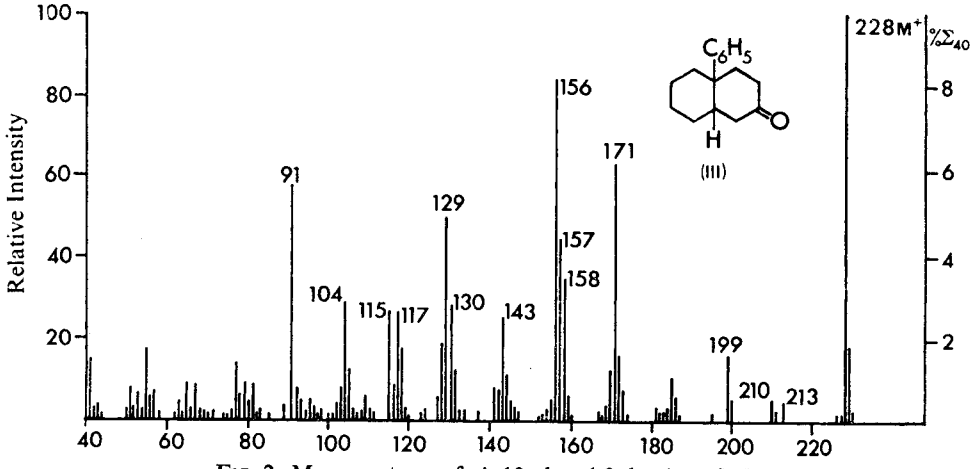


FIG. 2. Mass spectrum of *cis*-10-phenyl-2-decalone (III).

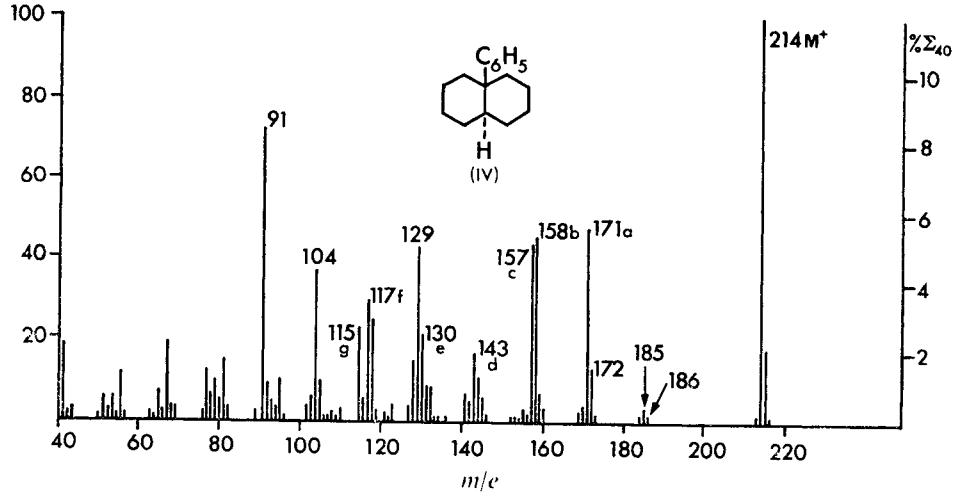
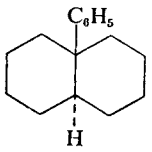
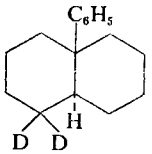
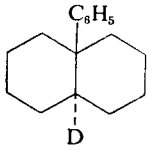
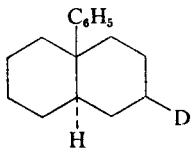


FIG. 3. Mass spectrum of *trans*-10-phenyldecalin (IV).

Very small fragment ion peaks are observed at *m/e* 186 [M − C_2H_4], *m/e* 185 [M − C_2H_5] and *m/e* 172 [M − C_3H_6]. These fragments are relatively insignificant, however, when compared to the corresponding ions from hydrindane[5] and *trans*-decalin,[4a] suggesting that the major ions from IV are only derived by direct assistance from the phenyl group. A consideration of the genesis of each of the major fragment ions (*vide infra*) gives added confirmation to this hypothesis. Where possible each proposed pathway will be supported by deuterium labeling (Table 2) and metastable ion peaks.

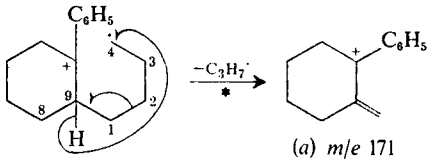
TABLE 2. THE PRINCIPAL FRAGMENT IONS IN THE MASS SPECTRA OF *trans*-10-PHENYLDECALIN AND ITS DEUTERATED DERIVATIVES (% RELATIVE ABUNDANCE)

	 (IV)	 (IX)	 (X)	 (XI)
$[M]^+$	214(100)	216(100)	215(100)	215(100)
[M − 43]	171(48)	173(42)	171(39)	172(26) 171(26)
[M − 56]	158(39)	160(19) 158(21)*	159(36)	159(25) 158(38)*
[M − 57]	157(44)	159(18) 158(21)* 157(22)	158(23) 157(38)	158(38)* 157(26)
[M − 110]	104(36)	105(12) 104(26)	105(20) 104(29)	104(38)
[M − 123]	91(72)	92(19) 91(50)	92(25) 91(56)	91(76)

* By high resolution this ion includes contributions from $C_{12}H_{14}$ and $C_{12}H_{12}D$.

Peak at m/e 171†

A large metastable ion peak at *m/e* 136·7 indicates that this, the second largest fragment ion in the spectrum of IV (Fig. 3), is derived from the molecular ion by loss of a propyl radical. Initial benzylic cleavage, followed by a six-centered specific



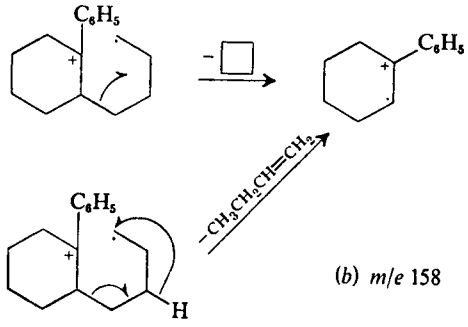
(*a*) *m/e* 171

† The sample peak values have been taken from the mass spectrum of IV. The corresponding *m/e* values from the deuterium-labeled analogs are shown in Table 2.

transfer of the C-9 hydrogen atom and concomitant loss of C-2, C-3 and C-4 provides a species (*a*) containing a highly stabilized positive charge.* This mechanism is confirmed by the labeling data, complete retention of both deuterium atoms in the corresponding ion from IX indicating that both C-1 and C-8 are retained in the ionized fragment. Similarly the corresponding peak from X is found only at *m/e* 171, supporting a specific hydrogen transfer from C-9 for this fragmentation, and showing that for this pathway at least, no hydrogen scrambling occurs prior to fragmentation.

Peak at m/e 158

Two plausible mechanisms can be drawn for the formation of this fragment ion, the difference being only in the structure of the expelled neutral species (*i.e.* the elements of cyclobutane or 1-butene). Although no differentiation can be made



(*b*) *m/e* 158

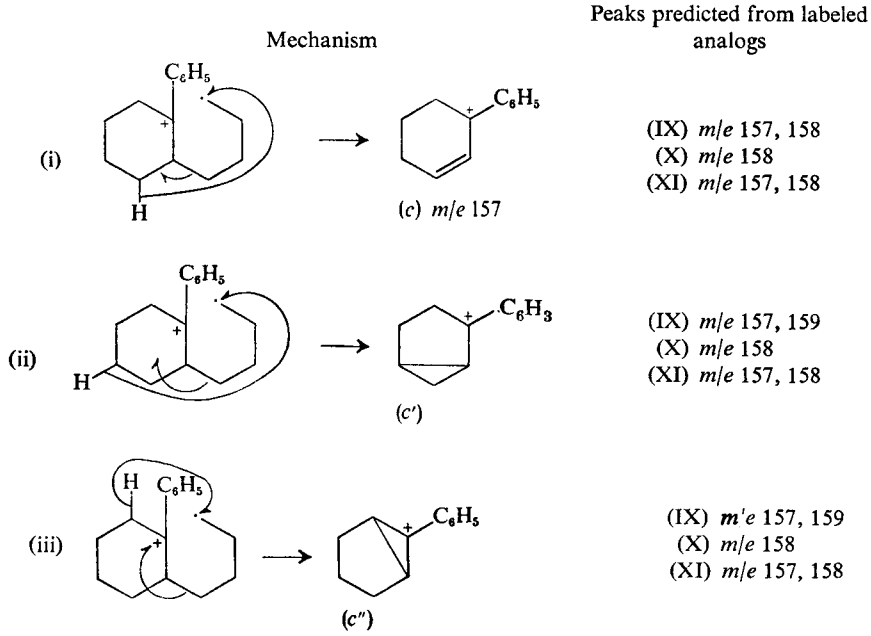
between these two possible pathways, the observation of an appropriate metastable peak at *m/e* 116·7 gives added confirmation to the overall scheme. Further support is obtained from the corresponding shifts of this fragment in the spectra of the labeled compounds. Since the parent molecule IV is symmetrical, the substitution of one ring with deuterium will cause fragments derived from a non-symmetrical cleavage of the molecule to occur at two (or more) different values. Hence, as predicted by the proposed mechanism, the corresponding peaks from IX and XI occur at *m/e* 158 and *m/e* 160, and at *m/e* 158 and *m/e* 159, respectively. In contrast, the fragment ion from X, which contains a deuterium atom symmetrically disposed to both rings, occurs only at *m/e* 159.

Peak at m/e 157

The occurrence of an appropriate metastable peak at *m/e* 115·2 in the spectrum of IV suggests that this fragment is generated from the molecular ion by the loss of a butyl radical. Although the expected ions at *m/e* 157 and *m/e* 159 are evident in the spectrum of the C_1-d_2 analog (IX), however, high resolution measurements indicate

* Although cyclic structures are given for the major product ions, ring-expanded structures should not be excluded as possible formulations for the products from the fragmentation of IV.

that the fragment ion of mass 158 from IX also contains a deuterated species. Since this latter moiety must also be equivalent to the ion of mass 157 from IV, more than one mechanistic pathway is suggested for the formation of the ion in question. The difference between these mechanisms can only reside in the ring carbon from which the hydrogen atom is transferred, which in turn will govern the formal structure of the product ion (Scheme 1). Since the contribution of each mechanism to the actual

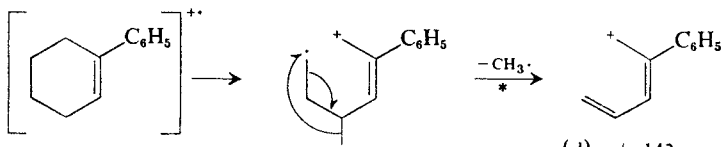


SCHEME 1

mode of formation of the fragment at *m/e* 157 is not known, no quantitative interpretation can be made. With the proposed mechanism in Scheme 1 are also shown the resulting labels in the fragment ions, however, and with the exception of one peak these proposed mechanisms match the observed isotopic shifts. A further mechanistic pathway is needed to account for the residue of this peak at *m/e* 157 from the C_9-d_1 analog X. This apparently anomalous observation may possibly be explained by an initial cleavage of the C_9—C_{10} bond followed by hydrogen transfer and bond scission, or by hydrogen-deuterium exchange at C-9 prior to fragmentation.

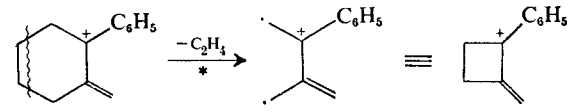
Peak at m/e 143

The observation of two pertinent metastable ions (m* 158 → 143, calcd. 129·42, observed 129·5; m* 171 → 143, calcd. 119·58, observed 119·6) suggest that this fragment ion is formed by several navigable pathways. Hence the use of labeling data is not feasible in this case. The loss of a methyl group from the fragment ion of mass 158 is conveniently represented, however, by a similar mechanism to that discussed earlier in the mass spectrum of cyclohexene.[7] The mechanism for the loss of the elements of ethylene from fragment *a* is not clear, but may involve simple ring



(*b*) *m/e* 158 (*d*) *m/e* 143

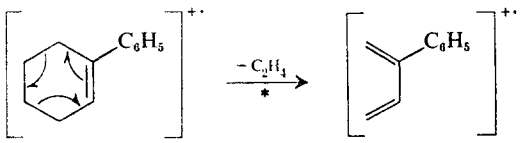
contraction with the formation of a stable ionic species such as *d'*.



(*a*) *m/e* 171 (*d'*) *m/e* 143

Peaks at m/e 130 *and m/e* 129

Due to the close proximity of these peaks, no trustworthy data can be obtained from the shifts of the corresponding ions from the labeled analogs. A metastable ion at *m/e* 106·8 is observed, however for the fragmentation of ion *b* with concomitant loss of ethylene. This is best explained by a retro-Diels-Alder reaction, to give *e*, in a similar fashion to that observed in other cyclohexenes.[7] Other metastable ion measurements suggest the formation of the ion at *m/e* 129 to be from at least two distinct precursors, *viz.* ions *a* and *b*, with the concomitant losses of propene and an ethyl radical respectively. Although rational mechanisms could possibly be drawn

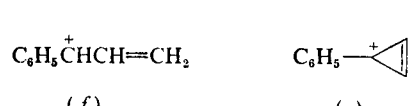


(*b*) *m/e* 158 (*e*) *m/e* 130

for these transformations, as discussed earlier for other alicyclic hydrocarbons several hydrogen transfers must be involved and the structures of the product ions would not be meaningful.

Peaks at m/e 117, *m/e* 115 *and m/e* 104

Fragment ions of similar *m/e* values have been reported as important peaks in the mass spectra of 1-phenylheptenes,[8] phenylcyclopropane[9] and phenylpropenes. Thus, although the relative shifts of the ion of mass 117 in the labeled compounds IX to IX do not provide information concerning the involvement of particular carbon atoms in its formation, structures such as *f* are plausible candidates. This is especially likely on the basis that a metastable ion is observed for its decomposition to an ion of mass



(*f*) (*g*) (*g'*)

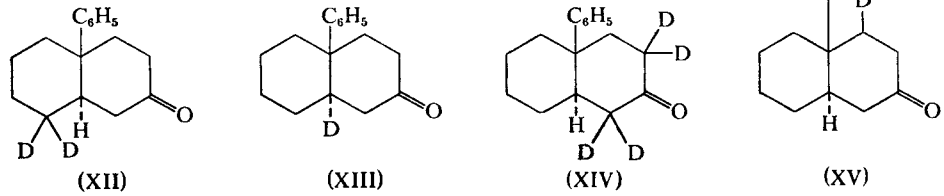
115, as reported earlier in the mass spectrum of each isomeric 1-phenylheptene.[8] This latter fragment is also formed from ion *a*(*m/e* 171) and probably has a structure such as *g* or *g'*.

The fragment ion of mass 104, which corresponds to the elements of ionized styrene, is formed, at least in part, by the loss of $C_5H_7^{\cdot}$ from the ion of mass 171 (*a*), as evidenced by the occurrence of the appropriate metastable ion at *m/e* 63·2. Although the labeling data suggest the involvement of hydrogen atoms from C-1 and C-8 in its genesis, a quantitative shift is not observed in the spectra of IX or X. Hence, consecutive hydrogen transfers rather than a phenyl migration are indicated as the method of its formation.

Peak at m/e 91

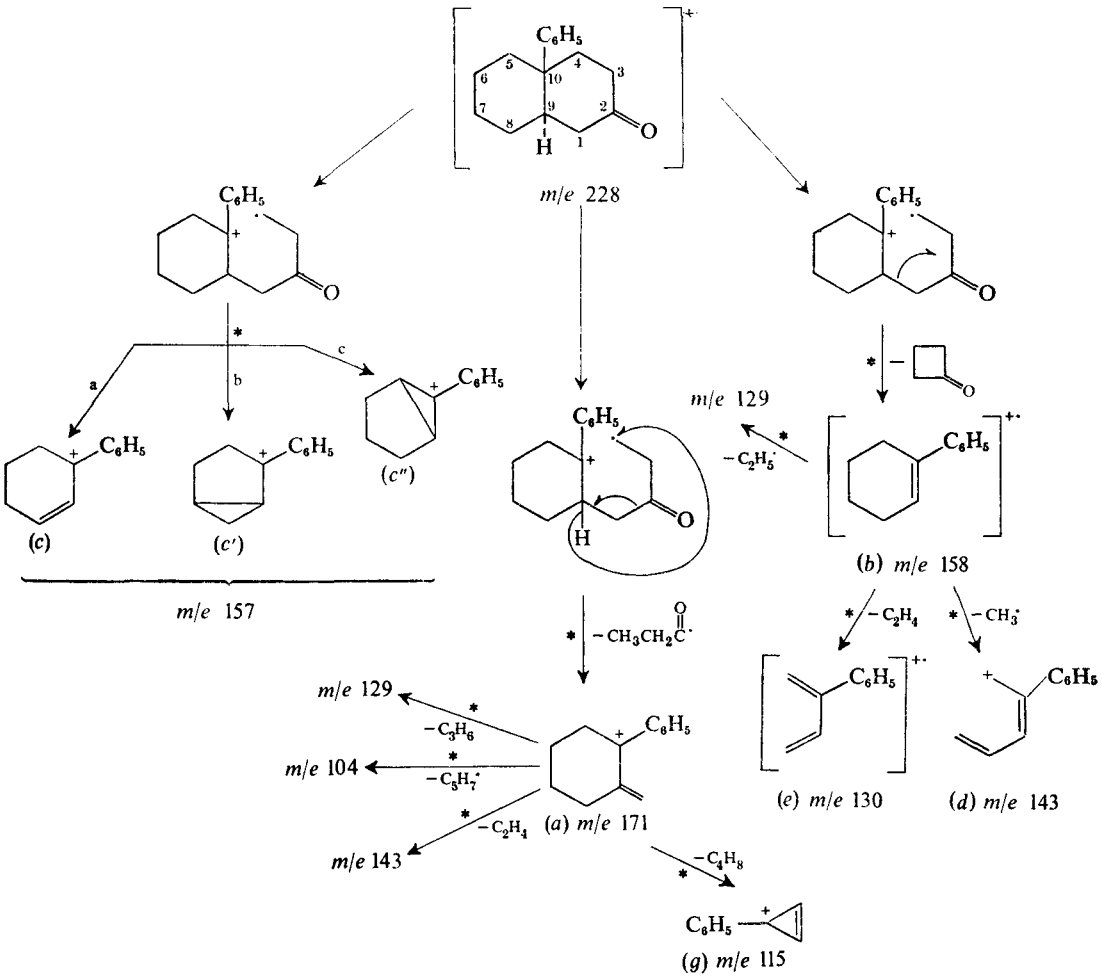
The tropylium or benzyl ion ($[C_7H_7]^+$, *m/e* 91) accounts for 8·4% of the total ion current at 70 eV and is the largest fragmentation peak in the mass spectrum of IV. Metastable ion measurements indicate that this fragment also is formed from several precursors and this is supported by the observed shifts of *m/e* 91 in the spectra of the deuterium labeled analogs. It is formed, at least in part, by loss of C_5H_6 from a species of mass 157 and by the elimination of acetylene from the fragment ion of mass 117 (*f*). Although the partial shift of *m/e* 91 to *m/e* 92 in the spectra of IX and X do indicate that the hydrogen atoms at C-1 and C-9 are involved in its formation, however, on the basis of the data at hand it can only be surmised that C-10 in IV is in fact also the methylene carbon in the resulting ion of mass 91. Labeling with ^{13}C would be required to settle this question unambiguously.

In order to elucidate the major fragmentation pathways in the electron-impact induced decomposition of *trans*-10-phenyl-2-decalone (II) and to compare these routes with those discussed above for the fragmentation of IV, we have synthesized the deuterium-labeled analogs XII to XV.



(XII) (XIII) (XIV) (XV)

A comparison of the mass spectra of the two unlabeled compounds (II and IV) indicate striking similarities between them, the principal difference residing in the



SCHEME 2

a Transfer of C-8 hydrogen to ketonic oxygen, followed by loss of $CH_2{=}C(OH){-}CH_2{-}CH_2^{\cdot}$.

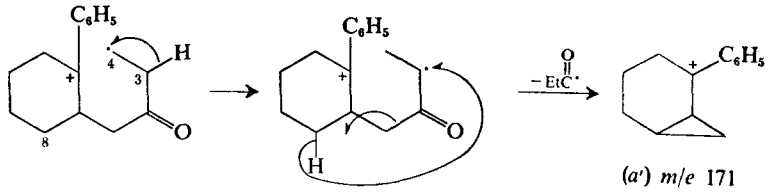
b 3,4-Hydrogen transfer, followed by shift of C-7 hydrogen to ketone and loss of $CH_3{-}CH_2{-}C(=O){-}CH_2^{\cdot}$.

c 3,4-Hydrogen transfer, followed by shift of C-5 hydrogen to ketone and loss of $CH_3{-}CH_2{-}C(=O){-}CH_2^{\cdot}$.

m/e 155 to 160 region. This suggests that a predominance of the navigable pathways in the decomposition of II, as is necessarily the case for IV, also occur through assistance from the phenyl group. As shown in Scheme 2, in order to accommodate the relative shifts of each peak in the mass spectra of the labeled compounds (Table 3), these are in fact best represented by initial benzylic cleavage, followed by various hydrogen transfers and corresponding bond cleavages. The isotopic shifts in the labeled decalones, which are given in Table 3, correspond well to those from the 10-phenyldecalins for the fragment peaks at *m/e* 158 and *m/e* 157. Likewise a diversity

of mechanisms for the formation of those at *m/e* 130, *m/e* 129, *m/e* 117, *m/e* 115 and *m/e* 104 is also indicated. Initial benzylic cleavage apparently always occurs in the oxygenated ring, with the result that charge retention is invariably on the hydrocarbon fragment. Hence the expelled species, radical or neutral, always contains the ketone function (Scheme 2). High resolution measurements on the major peaks in the spectrum of II indicate that only very few ions contain a significant proportion of oxygenated material.

Of the fragments that originate from the decomposition of both II and IV, only that at *m/e* 171 ($C_{13}H_{15}$, 96%; $C_{12}H_{11}O$, 4% from II) shows any discrepancy in the deuterium labeling data. The corresponding ions from the C_1-d_2 (IX) and C_9-d_1 (X) decalin analogs appear only at *m/e* 173 and *m/e* 171 respectively (Table 2), whereas those from the similarly labeled decalones (XII and XIII) occur at *m/e* 173 and *m/e* 172, and at *m/e* 172 and *m/e* 171 respectively (Table 3). In order to explain this apparent anomaly it is necessary to invoke a mechanism such as that shown in Scheme 3 for the decomposition of II. Initial benzylic cleavage followed by a 1,2-hydrogen



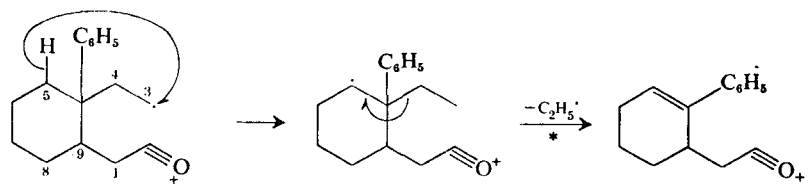
(*a'*) *m/e* 171

SCHEME 3

shift between C-3 and C-4 would result in a secondary α-keto radical. A six-centered hydrogen transfer from C-8 with concomitant loss of a keto radical would then give a species such as *a'*, stabilized through conjugation of the carbonium ion with both a cyclopropyl and a phenyl ring.

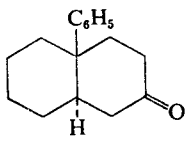
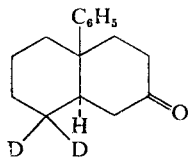
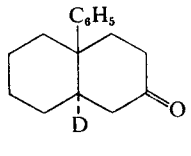
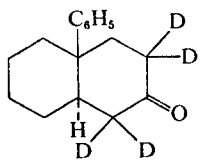
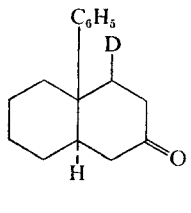
From previous investigations of the mass spectra of α-[10,11] and β-[3] decalones it may have been predicted that several additional fragmentations, resulting from cleavage α to the ionized ketone function,[12] would be present in the spectrum of II. Apart from insignificant peaks at *m/e* 210 and *m/e* 213, formed by loss of water and a methyl radical respectively, however, the only notable additional peaks are found at *m/e* 199 and at *m/e* 156.

The fragment ion of mass 199 in Fig. 1 corresponds to the loss of an ethyl radical from the molecular ion and apparently represents the only major fragment derived directly from initial cleavage α to the carbonyl group. The labeling data (Table 3) suggest that C-3 and C-4 are ejected in the fragmentation process. The following mechanism can be used to accommodate these observations. Complete retention of



(*h*) *m/e* 199

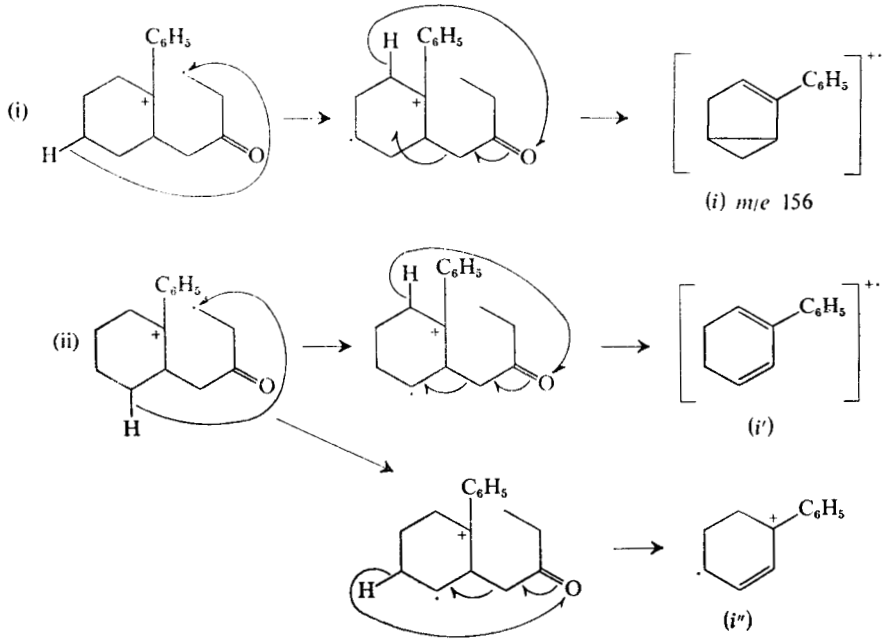
TABLE 3. THE PRINCIPAL FRAGMENT IONS IN THE MASS SPECTRA OF *trans*-10-PHENYL-2-DECALONE AND ITS DEUTERATED DERIVATIVES (% RELATIVE ABUNDANCE)

	 (II)	 (XII)	 (XIII)	 (XIV)	 (XV)
$[M]^+$	228(100)	230(100)	229(100)	232(100)	229(100)
[M − 29]	199(21)	201(22)	200(21)	201(20)	199(23)
[M − 57]	171(68)	173(52) 172(19)	172(38) 171(50)	173(72)	171(83)
[M − 70]	158(30)	160(32)	159(47)	158(41)	158(45)
[M − 71]	157(34)	159(32) 158(81)*	158(49)	157(39)	157(39)
[M − 72]	156(79)	158(81)* 157(16)	157(92)	156(98)	156(89)
[M − 137]	91(71)	93(10) 92(25) 91(62)	92(29) 91(61)	93(10) 92(18) 91(60)	92(32) 91(85)

* Includes contributions from $C_{12}H_{12}D$ and $C_{12}H_{10}D_2$.

deuterium by XII and XIII in the ionized fragment indicate that the transfer of hydrogen prior to decomposition must come from a position other than C-8 or C-9.* The hydrogen atom for C-5 is a likely candidate, resulting in a species (*h*) with a double bond conjugated to the phenyl ring.

High resolution measurements for the peak at *m/e* 156 in the mass spectrum of II indicate its composition to be entirely hydrocarbon ($C_{12}H_{12}$, 100%). The relative *m/e* values of the corresponding ions from the labeled analogs XIV and XV (Table 3) demonstrate its genesis from the molecular ion (m* 228 → 156, calcd. 106·74, observed 106·8) through loss of C_4H_8O from the oxygenated ring. It follows, therefore, that transfer of two hydrogen atoms from the hydrocarbon portion must occur prior to decomposition. Also, since a similar ion of mass 156 is not observed in the spectrum of IV, the mode of its formation must depend on the presence of the ketone function. A possible mechanism accommodating these observations is shown in Scheme 4 (i). The presence of a significant peak at *m/e* 157 in the spectrum of the



SCHEME 4†

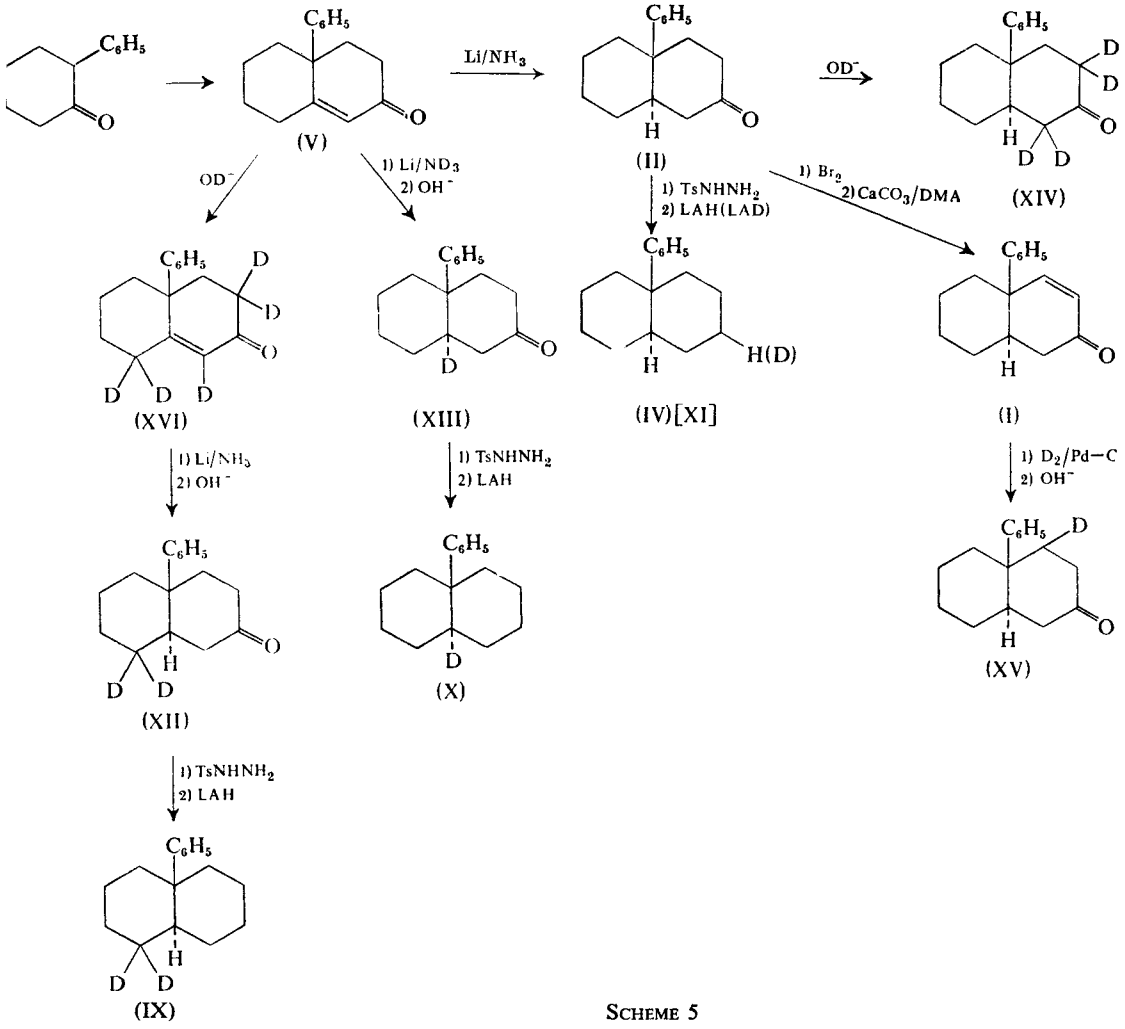
C_8-d_2 analog (XII), however, suggests a secondary mode of formation for this fragment. This fact may be explained by either of the mechanisms shown in Scheme 4 (ii), which both involve transfer of a C-8 hydrogen atom to the expelled neutral species, and still result in stable ionic species (*i'* or *i''*) as the final products.

The genesis of the ion of mass 91 from *trans*-10-phenyl-2-decalone is apparently

* In contrast, the [M − 29] fragment from the methylated analog was shown to originate through transfer of the C–1 hydrogen atom to the ejected ethyl radical.[3] Conjugation of the resulting double bond with the phenyl ring is presumably the driving force for the observed pathway from II.

† It is probable that the two hydrogen transfers postulated in each mechanism occur through chair forms in which the 1,3-substituents are axial and hence can approach each other closely.

even more complicated than that from the corresponding decalin (IV). Although a metastable peak at *m/e* 52·7 is observed for its formation from a precursor of mass 157, this is certainly not the only navigable pathway for its genesis. According to the relative shifts in the spectra of the deuterium-labeled analogs (Table 3), a certain proportion of hydrogen is transferred from each position of labeling during the formation of this ion. On the basis that a quantitative shift to *m/e* 92 is not seen for any one labeled compound, however, a phenyl migration during its formation can be excluded as a mechanistic possibility. It must therefore be concluded that the proven stability of the tropylium ion[2b] provides the driving force for its genesis and that it is formed through multiple carbon-carbon bond cleavages and hydrogen transfer from several, if not all, positions of the decalin skeleton.



SCHEME 5

Synthesis of labeled compounds

As described earlier,[1] entry into this series of compounds was made through the Michael condensation of 2-phenylcyclohexanone with 1-diethylamino-3-butanone.[13] The subsequent transformations of the resulting 10-phenyl-Δ^1-2-octalone (V) to the various deuterium-labeled decalones are shown in Scheme 5. Each labeled decalin was prepared from the corresponding decalone by reaction with *p*-toluenesulfonylhydrazide, followed by reduction with lithium aluminum hydride or deuteride.[14]

EXPERIMENTAL

Both high and low resolution spectra were obtained by Mr R. G. Ross using an AEI MS-9 instrument. All compounds for mass spectral analysis were purified and checked for purity by v.p.c. Infrared spectra were recorded with a Perkin-Elmer 700 spectrophotometer. Elemental analyses were done by Messrs E. Meier and J. Consul of the Stanford microanalytical laboratory. Melting points were obtained on a Kofler hot stage and are uncorrected.

The preparation of compounds I to III and V to VIII have been described in detail in an earlier publication,[1] and these experimental details will not be repeated here.

trans-8,8-d_2-10-*Phenyl*-2-*decalone* (XII). Using a previously described procedure,[11] a portion of 10-phenyl-Δ^1-2-octalone (V, 0·30 g, 0·0013 mole) was heated at reflux with a solution of sodium metal in a mixture of deuteriomethanol and deuterium oxide for 16 hrs. A workup procedure using dry ether and deuterium oxide, followed by three repeated equilibrations, gave 0·29 g (95%) of 1,3,3,8,8-d_5-10-*phenyl*-Δ^1-2-*octalone* (XVI) as a pale yellow oil. Purification of a portion of this material by v.p.c.* gave a sample of XVI as a pale yellow oil containing 95% d_5 and 5% d_4 species $[M]^+$ at *m/e* 231.

Reduction of 0·25 g (0·0011 mole) of XVI with lithium in liquid ammonia, as described earlier for II,[1] gave 0·20 g (80%) of *trans*-1,3,3,8,8-d_5-10-*phenyl*-2-*decalone* as a pale yellow oil, which crystallized on standing. A solution of this total product in 15 ml of 50% aqueous methanol containing 0·40 g of sodium hydroxide was heated at reflux for 24 hrs. The methanol was evaporated and the product taken into ether. The ethereal extracts were washed with water, dried ($MgSO_4$) and evaporated, giving 0·18 g (91%) of XII as a pale yellow solid. Final purification with v.p.c. gave XII as a white solid containing 98% of the d_2 species by mass spectrometry: i.r. ($CHCl_3$) 1700 (C=O), 2100 and 2200 cm^{-1} (C—D).

trans-9-d_1-10-*Phenyl*-2-*decalone* (XIII). To a solution of 0·15 g (0·022 g-atom) of lithium metal in 10 ml of deuterioammonia† was added dropwise a solution of 0·15 g (0·66 mmole) of V in 5 ml of dry ether. The mixture was stirred under a Dry-Ice condenser for 30 mins, when deuteriomethanol (5 ml) was added, and the ammonia allowed to evaporate. A conventional workup, followed by oxidation of the resulting alcohol-ketone mixture with standard Jones reagent[16] gave 0·11 g (72%) of *trans*-1,9-d_2-10-*phenyl*-2-*decalone* as colorless needles. Back-exchange with sodium hydroxide in aqueous methanol, as described above for XII, gave 0·10 g (66% from V) of XIII as white needles containing 11% d_2, 82% d_1 and 7% d_0 by mass spectrometry: m.p. 86 to 87°; i.r. ($CHCl_3$) 1700 (C=O) and 2150 cm^{-1} (C—D).

trans-1,1,3,3-d_4-10-*Phenyl*-2-*decalone* (XIV). This compound was prepared by repetitive exchanges of II with a solution of sodium metal in a mixture of deuteriomethanol and deuterium oxide. Four equilibrations gave XIV as white needles containing 7% d_2, 32% d_3 and 61% d_4 species (mass spec).

trans-4-d_1-10-*Phenyl*-2-*decalone* (XV). A solution of 0·020 g (0·089 mmole) of *trans*-10-phenyl-Δ^3-2-octalone (I) in 5 ml of deuteriomethanol was reduced with deuterium gas over 0·010 g of 10% Pd/C. After filtration of the catalyst, the solvent was evaporated to give a mixture of *trans*-3,4-d_2-10-*phenyl*-2-*decalone* and its dimethyl acetal. Treatment of a solution of the total product in 2 ml of methylene chloride with 2 ml of 10% hydrochloric acid for 1 hr,[17] followed by back-exchange

* A 5 ft column of 5% SE-30 on Chromosorb W (oven temp 180 to 200°) was used in each purification.

† Prepared as described earlier[15] by the slow addition of 42 ml of deuterium oxide to 70 g of magnesium nitride.

of the resulting ketone with sodium hydroxide in aqueous methanol gave 0·015 g (74%) of XV as a white solid. Final purification by v.p.c. gave XV as colorless needles containing 3% d_2, 92% d_1 and 5% d_0 species by mass spectrometry.

trans-1,1-d_2-(IX), 9-d_1-(X) *and* 2-d_1-(XI)10-*Phenyldecalin* were prepared from the corresponding decalone by the following general procedure described here for *trans*-10-*phenyldecalin* (IV): A solution of 0·10 g (0·46 mmole) of II and 0·10 g (0·54 mmole) of *p*-toluenesulfonylhydrazide in 5 ml of methanol was heated at reflux for 30 mins. Upon concentration and cooling, a precipitate formed. The solid material was filtered, yielding 0·16 g (92%) of *trans*-10-*phenyl*-2-*decalone p-toluenesulfonylhydrazone* as a white solid. Recrystallization of a portion of this material gave an analytical sample: m.p. 182 to 183° (decomp.).

Using a previously described procedure,[14] a mixture of 0·15 g of the hydrazone and 0·15 g of lithium aluminum hydride in 15 ml of dry tetrahydrofuran was heated at reflux under nitrogen for 12 hrs. After cooling, water was carefully added, followed by 6 ml of 10% hydrochloric acid, and the product extracted into ether. A conventional workup procedure gave 0·070 g (86%) of IV as a pale yellow oil, which partially crystallized upon cooling. Final purification by v.p.c. gave IV as colorless platelets: m.p. 49 to 50°; mass spectrum $[M]^+$ at *m/e* 214. Found: C, 89·93; H, 10·31. $C_{16}H_{22}$ requires C, 89·65; H, 10·35.

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