Mass Spectrometry in Structural and Stereochemical Problems. CLXXXII.[1] Investigations in the 10-Phenyl-2-decalone System. The Synthesis and Electron Impact Promoted Phenyl Migration of *trans*-10-Phenyl-Δ^3-2-octalone[2]

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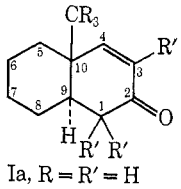
Received July 24, 1969

The synthesis of *trans*-10-phenyl-Δ^3-2-octalone (VI) has been undertaken in order to compare the migration of a phenyl moiety with that of a methyl group in an important electron impact induced 1,2 rearrangement process. The phenyl migration ion (b) from VI carries 25.7 and 28.2% of the ionizing current at 70 and 12 eV, respectively, thus demonstrating that phenyl migration in this system is very facile and preferred to that of methyl. Several apparently anomalous chemical reactions (course of bromination and dehydrobromination as well as stereochemistry of enone reduction products) of the *trans*-10-phenyl-2-decalone system, encountered in the synthetic route to VI, are also reported and the contrasting roles of angular phenyl and methyl substituents are emphasized.

In earlier publications from this laboratory,[4] it was reported that the mass spectrum of *trans*-10-methyl-Δ^3-2-octalone (Ia) contains an important rearrangement peak at *m/e* 69. High-resolution measurements for this fragment ion gave an elemental composition of C_4H_5O, and, although several electron impact induced alkyl and aryl rearrangements had been recognized previously,[5] this represented one of the first authentic 1,2-rearrangement processes in which a neutral moiety is not concomitantly expelled from the molecule. That this fragmentation pathway indeed contained a rearrangement step was demonstrated by the relative shifts of the corresponding peaks from the deuterium-labeled analogs Ib (*m/e* 69 → 72) and Ic (*m/e* 69 → 70). The spectra of Ia–c did not provide information concerning the mechanism of the fragmentation pathway. However,

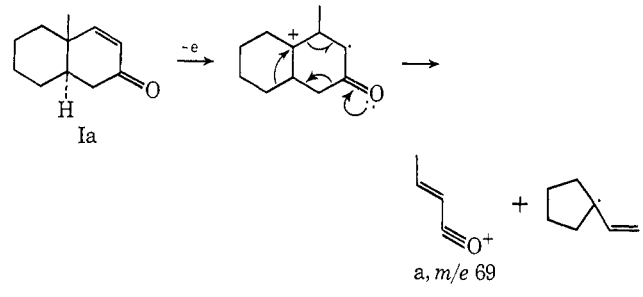


Ia, R = R′ = H
b, R = D, R′ = H
c, R = H, R′ = D

after considering the effect of different structural details in several other α,β-unsaturated ketones, the likely route for the formation of ion a was shown[4b] to be the one reproduced in Scheme I.

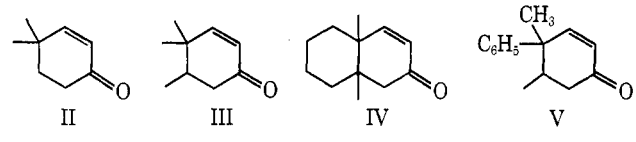
In this regard the spectra of compounds II–V were especially useful in providing information concerning this rearrangement. A fragment ion due to the rearrangement of a methyl group is negligible in the mass spectrum of II, whereas the corresponding ion from III is of a similar abundance to that observed for I. Similarly, substitution of the C-9 hydrogen atom in Ia

SCHEME I



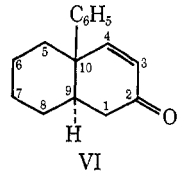
a, *m/e* 69

by a methyl group (to give IV) does not restrict migration of the C-10 methyl substituent.



II III IV V

Of considerable interest was the mass spectrum of 4,5-dimethyl-4-phenyl-Δ^2-cyclohexen-1-one (V), since fragment ions were observed for the rearrangement of both the phenyl and methyl groups. However, a quantitative comparison of migratory aptitudes could not be inferred from the relative intensities of the rearrangement ions, because of the possible influence of stereochemical factors on the rearrangement process and the different subsequent fragmentations of the respective rearrangement ions. We felt that in order to exclude at least any stereochemical uncertainty, a direct comparison of the mass spectra of Ia and *trans*-10-phenyl-Δ^3-2-octalone (VI) was highly desirable so as to shed more light on the relative migratory aptitudes of alkyl and aryl groups after electron impact.



VI

In order to investigate this possibility, we have undertaken a synthesis of VI, and wish to report here a description of this program and a discussion of some anomalous chemistry in the 10-phenyl-2-decalone system, which we have encountered along the synthetic

(1) For paper CLXXXI, see R. T. Gray, R. J. Spangler, and C. Djerassi, *J. Org. Chem.*, in press.

(2) Financial support from the National Institutes of Health (Grants AM-12758 and GM-06840) is gratefully acknowledged.

(3) Postdoctoral Fellow, 1968–1969.

(4) (a) F. Komitsky, Jr., J. E. Gurst, and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 1398 (1965); (b) R. L. N. Harris, F. Komitsky, Jr., and C. Djerassi, *ibid.*, **89**, 4765 (1967).

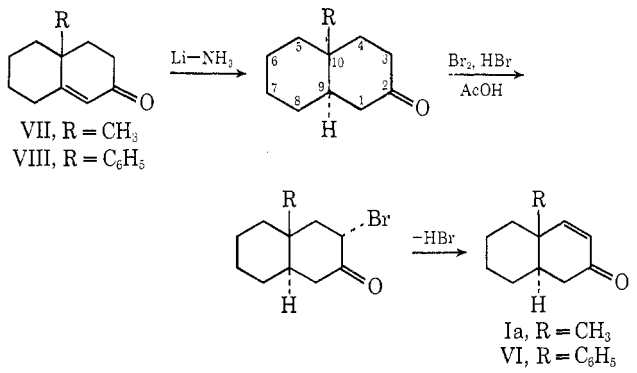
(5) For recent reviews, see (a) P. Brown and C. Djerassi, *Angew. Chem.*, **79**, 481 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 477 (1967); (b) G. W. Cooks, *Org. Mass Spectrom.*, **2**, 481 (1969).

pathway to this compound. Finally, a description of the pertinent mass spectral data will be presented, with particular emphasis being placed on the rearrangement process described above.

Results and Discussion

In devising a feasible synthetic pathway for the preparation of *trans*-10-phenyl-Δ^3-2-octalone (VI), the most plausible method seemed to be one patterned after that of the 10-methylated analog (Ia),[6] *viz.*, metal–liquid ammonia reduction of the corresponding Δ^1-2-octalone (VIII), followed by acid-catalyzed bromination and mild dehydrobromination of the resulting α-bromo ketone (Scheme II).

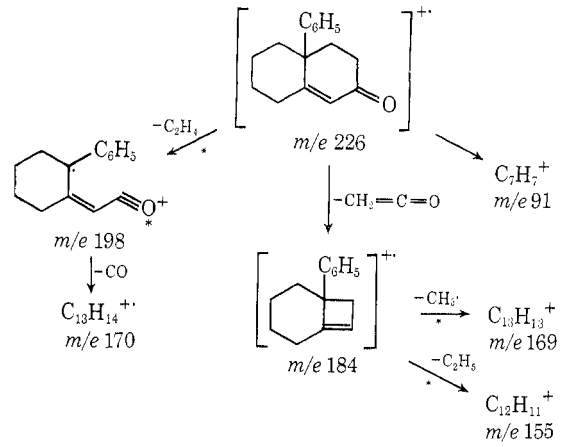
SCHEME II



This procedure seemed particularly attractive in view of the fact that Boekelheide had earlier reported[7] a preparation of 10-phenyl-Δ^1-2-octalone (VIII), albeit in low yield, by the Michael condensation of 2-phenylcyclohexanone with 1-diethylamino-3-butanone. We have repeated this synthesis, using sodium hydride as the condensing agent, and have obtained VIII in moderate yield following purification by thin layer chromatography (tlc) on silica gel. The spectral properties of VIII are consistent with its structure. The nuclear magnetic resonance (nmr) spectrum displays a broad singlet at 6.12 ppm for the single olefinic proton at C-1, and the mass spectrum is characteristic of α,β-unsaturated ketones.[8] Loss of ketene (M − 42) accounts for the largest fragment ion of mass 184, and other important fragmentations, whose genesis have been traced using high-resolution and metastable ion data, are shown in Scheme III. The formation of the peak at *m/e* 91 (tropylium ion) is not well understood at this time.

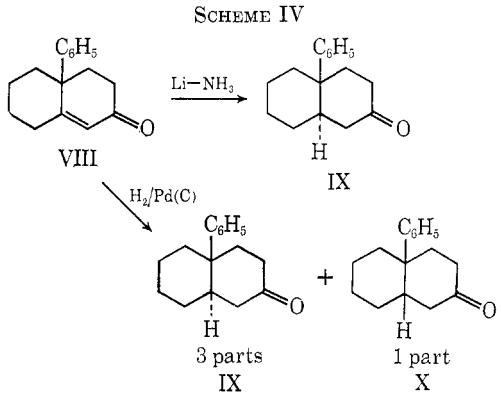
As shown in Scheme II, it was anticipated that a lithium–liquid ammonia reduction of VIII would result in the formation of *trans*-10-phenyl-2-decalone (IX), and indeed, following Jones oxidation[9] of the crude reaction product and final purification by preparative tlc on silica gel, a 10-phenyl-2-decalone was isolated as the only product. That this compound is in fact the *trans* isomer can only be speculative at the moment,

SCHEME III



because, as discussed recently by Marshall,[10] metal–ammonia reductions do not *a priori* give the isomer with the *trans* ring function. However, the usual product from such reductions is the more stable of the two isomers, having the newly introduced hydrogen atom axial to the ketone ring,[11] and, as in most other documented cases of metal–ammonia reductions in similar systems,[12] it will be shown below that the correct assignment for the ring junction of IX is the *trans* configuration (Scheme IV). The structural assignment

SCHEME IV



for this compound is confirmed by its infrared ($\nu_{C=O}$ 1700 cm^{-1}), nmr, and mass spectra. The mass spectrum of IX, together with those of several deuterated analogs of IX and the related decalins, will be described elsewhere.[13]

Catalytic reduction of VIII, using hydrogen over 10% palladium on charcoal, resulted in a mixture of 10-phenyl-2-decalones, identified by vpc as the *trans* (IX, 75%) and *cis* (X, 25%) isomers, together with a small amount of hydrogenolysis products. That the isomer distribution is heavily in favor of the *trans*-decalone is quite surprising, in view of the fact that 10-methyl-Δ^1-2-octalone (VII) itself gives 80% *cis* isomer on catalytic hydrogenation.[6,14] Also, attempts to change this distribution by varying the pH of the medium and

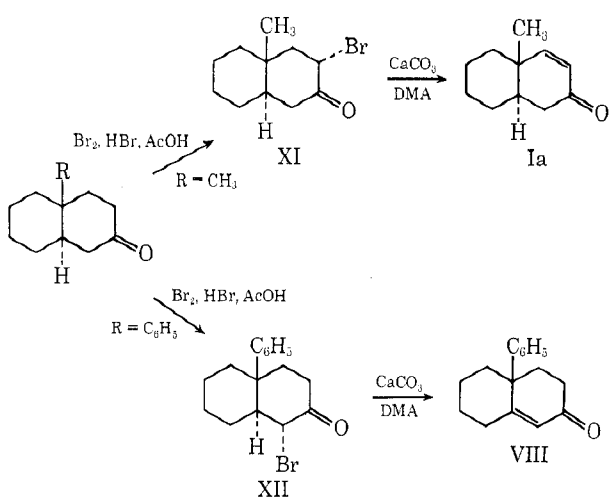
(6) C. Djerassi and D. Marshall, *J. Amer. Chem. Soc.*, **80**, 3986 (1958).
(7) V. Boekelheide, *ibid.*, **69**, 790 (1947).
(8) (a) R. H. Shapiro, J. M. Wilson, and C. Djerassi, *Steroids*, **1**, 1 (1963); (b) R. H. Shapiro and C. Djerassi, *J. Amer. Chem. Soc.*, **86**, 2825 (1964); (c) C. Fenselau, W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *ibid.*, **91**, 112 (1969).
(9) C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).
(10) J. A. Marshall, Seminar, Stanford University, Feb 14, 1969.
(11) G. Stork and S. D. Darling, *J. Amer. Chem. Soc.*, **86**, 1761 (1964).
(12) For examples, see L. H. Zalkow and R. L. Hale, *Chem. Commun.*, 1249 (1968); G. Stork and S. D. Darling, *J. Amer. Chem. Soc.*, **82**, 1512 (1960); G. Stork and J. Tsuji, *ibid.*, **83**, 2783 (1961).
(13) R. T. Gray and C. Djerassi, *Org. Mass Spectrom.*, submitted for publication.
(14) F. Sondheimer and D. Rosenthal, *J. Amer. Chem. Soc.*, **80**, 3995 (1958).

the catalyst/substrate ratio increased the *cis* isomer to only 30% of the total product in this system. Since such techniques have proved highly successful for other related octalones,[15] it appears that the bulky phenyl ring in VIII provides a substantial steric interaction to the catalyst from attacking the top side of the molecule. Hence the predominant product from catalytic hydrogenation of VIII is the same as that from metal–ammonia reduction, *i.e.* the *trans*-decalone IX (Scheme IV).

Fractional crystallization of the catalytic reduction product gave mother liquors enriched to 60% in the *cis*-decalone X, and, since this mixture produced only one spot by tlc, separation of the two isomers had to be accomplished by vapor phase chromatography (vpc). *cis*-10-Phenyl-2-decalone was characterized by the usual spectroscopic methods. Its ir spectrum displayed a carbonyl absorption at 1700 cm^{-1} and the mass spectrum is virtually identical with that of the *trans* isomer. Of particular interest is a comparison of the nmr spectra of the two isomeric 10-phenyl-2-decalones. Whereas the crystalline, conformationally rigid *trans* isomer IX shows a spectrum containing very sharp signals in both the aromatic and methylene regions, that of the *cis* isomer X, an oil, is very broad and ill-defined, as might be expected for a compound with such a flexible carbon skeleton.

The next step in our proposed synthesis of *trans*-10-phenyl-Δ³-2-octalone (VI) involved acid-catalyzed bromination of IX (Scheme I). This reaction has been used extensively for the preparation of α,β-unsaturated ketones and is well documented for analogous compounds containing a methyl group at the ring function. In both the *trans*-decalone[16] and 3-keto steroid[17] series, the result is exclusive equatorial bromination at the 3 position (C-2 in the steroid system, Scheme V, R = CH_3).

SCHEME V



Dehydrobromination of XI has been accomplished with several reagents, including hexamethylphosphoramide (HMPA),[18] calcium carbonate in dimethylacetamide,[16c,19] and 2,4-dinitrophenylhydrazine, all giving the expected Δ³-2-octalone (Ia) as the only product. Other reagents, such as collidine,[16a,b,20] have also been used, but these result in undesired rearrangement products.

Bromination of *trans*-10-phenyl-2-decalone (IX) with bromine–hydrogen bromide in acetic acid, followed by dehydrobromination with $CaCO_3$ in DMA[21] or with HMPA, resulted in a mixture of several products, including recovered starting material (IX), 10-phenyl-Δ¹-2-octalone (VIII), and 1-bromo-10-phenyl-Δ¹-2-octalone. The identity of these products suggested that initial bromination had occurred at C-1, instead of at the expected C-3 position. This postulation was confirmed when, on treatment with calcium carbonate in DMA, a pure sample of the major component of the bromination product gave 10-phenyl-Δ¹-2-octalone (VI) as its only dehydrobromination product.

That this bromide was indeed *trans*-1-bromo-10-phenyl-2-decalone (XII) was demonstrated unambiguously from its physical and spectral properties. The mass spectrum and elemental analysis were consistent with a monobromide formulation, and a shift of 15 cm^{-1} in the infrared carbonyl absorption from that of the unsubstituted decalone (X) indicated an equatorial configuration for the bromine atom.[22] A doublet at 5.20 ppm for the C-1 hydrogen atom in XII confirmed the location of the bromine atom. Also, the value of its coupling constant ($J_{1(ax)-9(ax)}$ = 12 cps) with the ring-junction hydrogen at C-9 is only consistent for an axial–axial coupling,[23] thus giving unambiguous evidence for the *trans* configuration of the ring function in this series of compounds.

The introduction of a bromine atom at C-3 in IX was accomplished through prior formylation of this position with ethyl formate. Utilizing a modification of a previously described procedure,[24] *trans*-10-phenyl-2-decalone (IX) was treated with ethyl formate in sodium hydroxide at ambient temperature, followed by addition of bromine and further sodium hydroxide solution. The position of enolization of IX in basic medium appears to be exclusively at C-3, since the monobromide XIII was the only product of the reaction (Scheme VI). This was confirmed by the ir, nmr, and mass spectra of the crystalline product. Similarly to that observed for bromide XII, the carbonyl absorption for XIII was shifted 18 cm^{-1} from that of the parent ketone, indicating an equatorial configuration for the bromine atom.[22] Also, the nmr coupling pattern for the downfield proton on the bromine-containing carbon ($J_{3(ax)-4(ax)} \cong 14$ cps, $J_{3(ax)-4(eq)} \cong 6$ cps; $J_{AX} + J_{BX} = 20$ cps) is characteristic of the axial X proton of

(15) R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, N. Y., 1965, p. 47; *J. Org. Chem.*, **28**, 152 (1963); *ibid.*, **34**, 1075 (1969).

(16) (a) M. Yanagita and A. Tahara, *ibid.*, **18**, 792 (1953); (b) M. Yanagita and K. Yamakawa, *ibid.*, **21**, 500 (1956); (c) J. A. Marshall, G. L. Bundy, and W. I. Fanta, *ibid.*, **33**, 3913 (1968).

(17) A. Butenandt and A. Wolff, *Chem. Ber.*, **68**, 2091 (1935); E. J. Corey, *J. Amer. Chem. Soc.*, **75**, 4832 (1953). For additional references, see P. A. Hart in "Steroid Reactions," C. Djerassi, Ed., Holden-Day, Inc., San Francisco, Calif., 1963, Chapter 4.

(18) R. Hanna, *Tetrahedron Lett.*, 2103 (1968).

(19) G. F. H. Green and A. G. Long, *J. Chem. Soc.*, 2532 (1961).

(20) C. Djerassi and C. R. Scholz, *J. Amer. Chem. Soc.*, **69**, 2404 (1947).

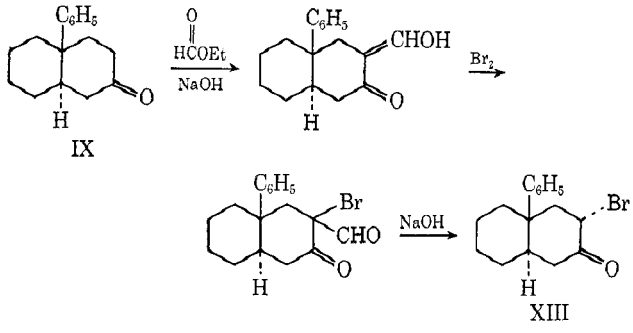
(21) This reaction was performed by Dr. M. Ikeda of this laboratory.

(22) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p 170.

(23) N. S. Baccha and D. S. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 51.

(24) (a) M. Kuehne, *J. Amer. Chem. Soc.*, **83**, 1492 (1961); (b) K. Mori, M. Shiozaki, N. Itaya, T. Ogawa, M. Matsui, and Y. Sumiki, *Tetrahedron Lett.*, 2183 (1968).

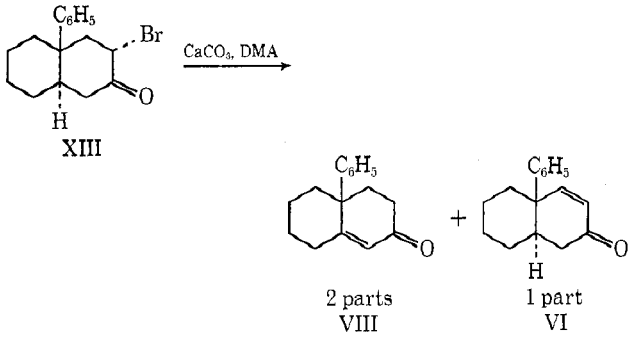
SCHEME VI



an ABX-type system,[25] thus confirming C-3 as the location of the bromine atom. The corresponding signal of a C-1 bromide (*e.g.*, XII) was completely absent, even in the spectrum of the crude reaction product, demonstrating that reaction had occurred exclusively at the C-3 position.

Since the C-3 bromide XIII was now available, it appeared that only treatment with a mild dehydrobrominating agent would be required to obtain VI, especially since reaction of the analogous 2-bromo-3-cholestanone with calcium carbonate in DMA results in the exclusive formation of the Δ^1-3-enone.[19] The anomalous behavior of the 10-phenyldecalone system was again evident, however, because reaction of XIII under identical conditions led to a mixture of Δ^1- and Δ^3-octalones in a 2:1 ratio by nmr (Scheme VII). For

SCHEME VII

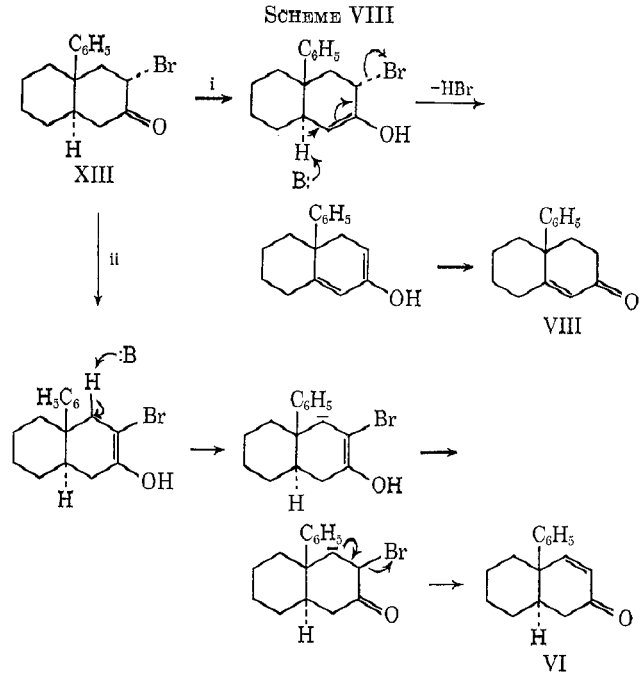


such a distribution of products to be formed under mild conditions it is necessary for a reaction pathway such as shown in Scheme VIII (i) to be more facile than the more straightforward one as in Scheme VIII (ii). It should be recognized, however, that, although Scheme VIII shows a likely representation for these transformations, from the data on hand an additional mechanism involving prior bromine migration in the formation of VIII cannot be totally excluded.

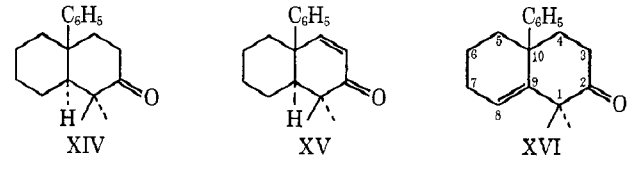
Separation of the enone mixture was accomplished using preparative tlc, with 5% ethyl acetate–benzene as the eluting solvent. *trans*-10-Phenyl-Δ^3-2-octalone (VI) was obtained as a colorless oil, whose elemental analysis and spectral properties were consistent with the proposed structure. The position of the C=C double bond was confirmed by the nmr spectrum, which displayed an AB-type doublet of doublets at 5.85 and 6.97 ppm (J_{AB} = 11 cps) for the two olefinic protons, and by the mass spectrum (*vide infra*), which was very characteristic of this particular compound.

(25) Reference 23, p 46.

SCHEME VIII



Although the required Δ^3-octalone VI had been successfully synthesized, owing to the unusual behavior of the 10-phenyl-2-decalone system it was necessarily obtained in poor yield even from the starting octalone VIII, which itself was formed only in moderate yield from 2-phenylcyclohexanone. It was therefore decided to attempt the synthesis of 1,1-dimethyl-10-phenyl-2-decalone (XIV), a compound which would embody all the requirements of VI in that the mass spectrum of the resulting octalone XV should also display a large fragment ion as a result of a 1,2-phenyl migration.



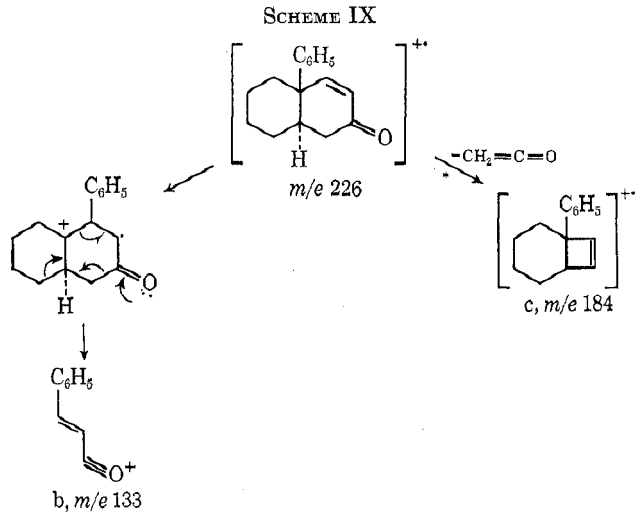
Following a procedure recently described by Marshall for 10-methyl-Δ^1-2-octalone,[26] VIII was smoothly converted into 1,1-dimethyl-10-phenyl-$\Delta^{8(9)}$-2-octalone (XVI) by treatment with potassium *t*-butoxide and methyl iodide in *t*-butyl alcohol. All subsequent attempts to reduce XVI to the decalone XIV were unsuccessful, however, even under such conditions as hydroboration[27] and catalytic reduction with PtO_2 in ethanol–perchloric acid at 3 atm for 18 hr. Such inertia of the $\Delta^{8(9)}$ double bond in XVI is undoubtedly due to the combined steric effects of the phenyl and the *gem*-dimethyl groups, especially since a similar reduction has been accomplished in an analogous system (angular methyl rather than phenyl group) at atmospheric pressure.[28]

The mass spectrum of *trans*-10-phenyl-Δ^3-2-octalone (VI) is shown in Figure 1 and consists essentially of two major peaks at *m/e* 184 and 131. The latter fragment ion, which is the base peak at 70 eV and carries 25.7% of the total ionization, has elemental composition

(26) J. A. Marshall and A. R. Hochstetler, *J. Amer. Chem. Soc.*, **91**, 648 (1969).
(27) H. C. Brown and K. Murray, *ibid.*, **81**, 4108 (1959).
(28) R. E. Ireland and P. W. Scheiss, *J. Org. Chem.*, **28**, 6 (1963).

C_9H_7O by high resolution. This fragment ion is formed by the rearrangement mechanism discussed earlier for certain other α,β-unsaturated ketones,[4] and is shown as the 1,2-phenyl migration product (b) in Scheme IX. This same ion carries 28.2% of the ion

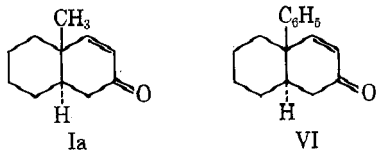
SCHEME IX



current at 12 eV (Table I), but is slightly diminished in relative abundance with respect to the fragment ion of mass 184. The latter ion ($C_{14}H_{16}$, 89%; $C_{13}H_{12}O$, 11%)

TABLE I

PER CENT TOTAL IONIZATION OF THE MAJOR FRAGMENT IONS IN THE MASS SPECTRA OF *trans*-10-METHYL- (Ia) AND *trans*-10-PHENYL-Δ^8-2-OCTALONE[a] (VI)

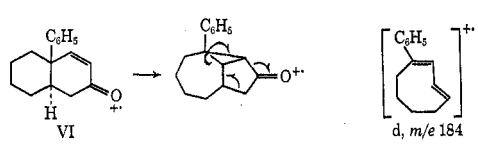


	Ia Σ_{40}[b] 70 eV	Ia Σ_{40}[b] 12 eV	VI Σ_{40}[b] 70 eV	VI Σ_{40}[b] 12 eV
M^+	3.8	14.9	3.6	16.5
M-ketene	12.6	41.3	11.8	37.6
Rearrangement	8.7	9.9	25.7	28.2

[a] These spectra were obtained using an Atlas CH-4 spectrometer. [b] This refers to that region of the spectrum above *m/e* 40.

is formed predominantly through loss of the elements of ketene from the molecular ion, and is characteristic of cyclic α,β-unsaturated ketones.[4,8] A convenient representation for this ion may be c, as shown in Scheme IX. Since direct vinyl cleavage is an unlikely cleavage,[29] a prior rearrangement of the molecular ion probably occurs, as discussed in an earlier communication[4] from this laboratory.

(29) Similar ions formed by loss of ketene from the molecular ions of α,β-unsaturated ketones have recently been postulated as having been formed through a bicyclo[3.1.0]hexan-2-one intermediate.[8c] According to such a mechanism, the representation of this fragment ion would be as in d. No differentiation between c and d is possible with the data at hand.



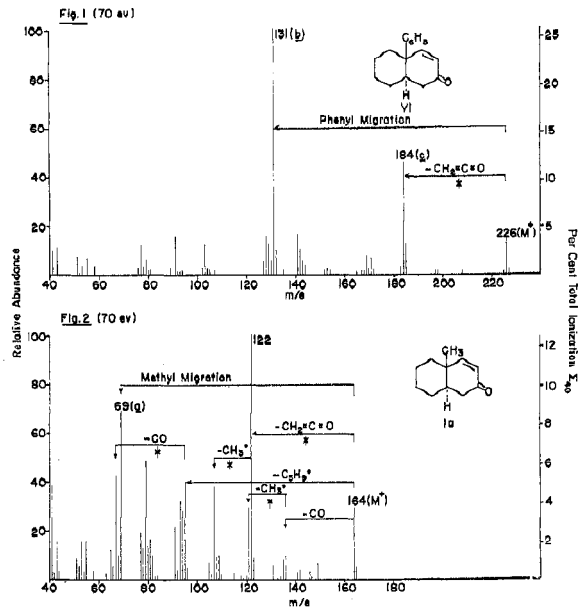


Figure 1.—Mass spectrum of *trans*-10-phenyl-Δ^8-2-octalone (VI).
Figure 2.—Mass spectrum of *trans*-10-methyl-Δ^8-2-octalone (Ia).

A direct comparison of the abundance of the phenyl migration ion b from VI may now be made with the corresponding ions from both *trans*-10-methyl-Δ^8-2-octalone Ia (a in Scheme I) and from 4,5-dimethyl-4-phenyl-Δ^2-cyclohexen-1-one (V). The mass spectrum of Ia is shown in Figure 2 and it can be seen that the rearrangement ion carries only 8.7% of the total ionization at 70 eV. For V, the ions from methyl and phenyl migration carry 0.8 and 8.0%, respectively, of the ionizing current.[4b] It may be argued that the occurrence of other important fragmentation pathways in the high-voltage spectra of I and V prevent a quantitative determination of relative migratory aptitudes for methyl and phenyl groups. A somewhat better comparison of these aptitudes may be obtained from the low-voltage spectra (Table I), especially since in these spectra the rearrangement ion is in each case the fragment of lowest mass, thus precluding any further decomposition products. In fact, for both I and VI at 12 eV the only important navigable pathways are loss of ketene and migration of the angular substituent. Even at low voltage, however, the percentage of total ionization carried by the phenyl rearrangement ion b (28.2%) is still much greater than the 9.9% carried by a, thus confirming that aryl migration is by far the preferred mode of rearrangement in these systems.

Experimental Section

Low-resolution mass spectra were obtained by Mr. C. Carroll using an Atlas CH-4 spectrometer, or by Mr. R. G. Ross using an A.E.I. MS-9 spectrometer. The high-resolution data were secured by Mr. R. G. Ross with the MS-9 instrument. All compounds for mass spectral analysis were purified and checked for purity by vpc.

Infrared spectral data were recorded with a Perkin-Elmer Model 700 or 421 spectrophotometer. Nmr spectra were secured with a Varian Model T-60 or HA-100 spectrometer. All nmr measurements were made on $CDCl_3$ solutions with TMS as the internal standard. Chemical shifts are reported in parts per million downfield from the standard. Coupling constants are reported in cycles per second.

Elemental analyses were done by Mr. E. Meier and Mr. J. Consul of the Stanford microanalytical laboratory. Melting points were obtained on a Kofler hot stage and are uncorrected.

10-Phenyl-Δ^1-2-octalone (VIII).—Using a modification of a previously described procedure,[7] a mixture of 15.41 g (0.089 mol) of 2-phenylcyclohexanone and 7.35 g (0.31 mol) of sodium hydride in 40 ml of dry benzene was heated at reflux for 40 hr. To this suspension was then added 14.56 g (0.10 mol) of 1-diethylamino-3-butanone, and heating was continued for a further 3 hr. Distillation of the mixture through a spinning-band column gave 5.79 g of 2-phenylcyclohexanone and 6.78 g of a mixture of VIII and starting material. Final separation was effected by preparative tlc on silica gel HF_{254}, using 5% ethyl acetate–benzene as the eluting solvent. This procedure gave 5.78 g (29%) of VIII as a colorless oil: bp 165–166° (2.5 mm) [lit.[7] bp 135–140° (0.5 mm)]; ir (film) 1615 (C=C) and 1670 cm^{-1} (C=O); nmr δ 7.30 (br s, 5 H, aromatic protons) and 6.12 (br s, 1 H, C-1 proton); mass spectrum (70 eV) *m/e* (rel intensity) 226 (100), 198 (40), 184 (96), 170 (39), 169 (69), 155 (27), 141 (59), and 91 (36).

Anal. Calcd for $C_{16}H_{18}O$: mol wt, 226. Found: mol wt, 226 (mass spectrum).

***trans*-10-Phenyl-2-decalone (IX) by Li–Liquid NH_3 Reduction of VIII.**—To a solution of 0.75 g (0.11 g-atom) of lithium metal in 100 ml of predistilled liquid ammonia was added dropwise a solution of 1.48 g (0.0065 mol) of VIII in 50 ml of dry ether. The mixture was stirred under a Dry Ice condenser for 2 hr, 12 ml of methanol was added, and the ammonia was allowed to evaporate. A 60-ml portion of water was added and the product was taken into ether, washed with dilute hydrochloric acid, water, and saturated NaCl solution, and dried ($MgSO_4$). Evaporation of the solvent gave 1.40 g of a yellow oil which crystallized on standing. Jones oxidation,[9] followed by preparative tlc on silica gel HF_{254} using 5% ethyl acetate–benzene as the eluent, gave IX as a white solid. Recrystallization from ether–pentane yielded 0.94 g (63%) of IX as white needles: mp 88–89°; ir ($CHCl_3$) 710, 760, 1120, 1240, 1420, 1450, 1500, and 1700 cm^{-1} (C=O); mass spectrum *m/e* 228 (M^+).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.40; H, 8.74.

The tosylhydrazone of IX was obtained from methanol as a white solid, mp 182–183° dec.

***trans*-10-Phenyl-2-decalone (IX) and *cis*-10-Phenyl-2-decalone (X) by Catalytic Reduction of VIII.**—A solution of 0.70 g (0.0031 mol) of VIII in 30 ml of ethanol was reduced with H_2 over 0.26 g of 10% Pd–C in a Parr hydrogenator at 3 atm for 3 hr. After filtration of the catalyst, the solvent was evaporated at reduced pressure to give 0.69 g of a mixture of IX (3 parts) and X (1 part) as a colorless oil. Fractional crystallization of this mixture in ether–pentane gave 0.12 g of IX as white needles, mp 89–91°. The resulting mother liquors, thereby enriched to 60% in X, were subjected to vpc on a 10-ft column of 15% JXR silicone rubber on Chromosorb W. With difficulty, the two isomeric decalones were separated, giving X as a colorless oil: ir (film) 695, 755, 1030, 1115, 1190, 1410, 1440, 1470, 1495, and 1700 cm^{-1} (C=O); mass spectrum *m/e* 228 (M^+).

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.00; H, 8.71.

***trans*-1-Bromo-10-phenyl-2-decalone (XII) by Bromination of IX.**—To a solution of 0.20 g (0.84 mmol) of IX in 6 ml of glacial acetic acid containing 6 drops of acetic acid saturated with anhydrous HBr gas was added dropwise a solution of 0.14 g (0.87 mmole) of bromine in 5 ml of acetic acid. The solution was stirred at room temperature for 5 min and poured into 15 ml of water. The product was taken into ether, and the combined ethereal extracts were washed with water and saturated Na_2CO_3 solution and dried ($MgSO_4$). Evaporation of the solvent gave a yellow oil which partially crystallized on trituration with ether–pentane. The major product XII was separated from traces of starting decalone and dibromides by preparative tlc on silica gel HF_{254} using 3% ethyl acetate–benzene as eluent. This procedure yielded 0.148 g (58%) of XII as colorless platelets: mp 133–135°; ir ($CHCl_3$) 1715 cm^{-1} (C=O); nmr δ 7.60–7.10 (m, 5 H, assigned to aromatic protons) and 5.20 (d, 2 H, J = 12 Hz, assigned to C-1 proton); mass spectrum (70 ev) *m/e* (rel intensity) 306, 308 (25), 251, 253 (52), 227 (61), 226 (18), 171 (65), and 91 (100).

Anal. Calcd for $C_{16}H_{19}BrO$: C, 62.53; H, 6.23; Br, 26.00. Found: C, 62.77; H, 6.31; Br, 26.30.

A mixture of 0.077 g (0.25 mmol) of XII and 0.050 g of calcium carbonate in 5 ml of dimethyl acetamide were heated at reflux for 16 hr. The mixture was then poured into 10 ml of water and extracted with ether. The extracts were thoroughly washed with dilute hydrochloric acid and water, dried ($MgSO_4$), and evaporated, giving 0.054 g (95%) of **10-phenyl-Δ^1-2-octalone** (VIII) as a pale yellow oil. The ir, nmr, and mass spectra of this material were identical with those of VIII prepared as described earlier.

Treatment of the crude bromination product with $CaCO_3$ in DMA as described above,[21] or with hexamethylphosphoramide at 120° for 3 hr, resulted in a complex mixture of compounds. Separation was attempted with preparative tlc on silica gel HF_{254} using 4:1 pentane–ether as the eluent. Apart from the starting material IX and the major product VIII, **1-bromo-10-phenyl-Δ^1-2-octalone** was also tentatively identified as a product of this reaction: ir (film) 1615 (C=C) and 1680 cm^{-1} (C=O); mass spectrum (70 ev) *m/e* (rel intensity) 304, 306 (16), 225 (58), 198 (100), 170 (31), and 91 (31).

Anal. Calcd for $C_{16}H_{17}BrO$: mol wt, 305. Found: mol wt, 304, 306 (mass spectrum).

***trans*-3-Bromo-10-phenyl-2-decalone (XIII) by Formylation and Bromination of IX.**—To a mixture of 0.62 g (0.011 mol) of sodium methoxide and 0.70 g (0.0032 mol) of IX in 30 ml of dry benzene was added 0.70 g (0.0097 mol) of ethyl formate in 5 ml of benzene. The mixture was allowed to stir under nitrogen at room temperature for 17 hr and poured into 30 ml of ice-water, and the product was taken up in ether. A conventional work-up procedure gave 0.78 g (98%) of ***trans*-3-hydroxymethylene-10-phenyl-2-decalone** as a pale yellow, crystalline residue.

Using a previously described procedure,[24] this total product was dissolved in sodium hydroxide solution and treated with a solution of Br_2 in aqueous KBr. There was thus obtained 0.67 g of crude XIII as a pale yellow oil. Purification was effected with preparative tlc on silica gel HF_{254} using 5% ethyl acetate–benzene as the eluent, which gave 0.28 g (29% from IX) of XIII as unstable, colorless platelets: mp 95–97°; ir ($CHCl_3$) 1718 cm^{-1} (C=O); nmr δ 7.70–7.00 (m, 5 H, aromatic protons) and 4.23 (d of d, 1 H, $J_{AX} + J_{BX}$ = 20 cps, C-3 proton); mass spectrum (70 eV) *m/e* (rel intensity) 306, 308 (19), 227 (87), 226 (14), 171 (27), 158 (62), 157 (100), and 91 (75).

Anal. Calcd for $C_{16}H_{19}BrO$: mol wt, 307. Found: mol wt, 306, 308 (mass spectrum).

***trans*-10-Phenyl-Δ^3-2-octalone (VI) and 10-Phenyl-Δ^1-2-octalone (VIII) by Dehydrobromination of XIII.**—A mixture of 0.25 g (0.82 mmol) of XIII and 0.20 g of $CaCO_3$ in 15 ml of DMA was heated at reflux for 2 hr. After cooling, the suspension was poured into 20 ml of water and the product was extracted into ether. A conventional work-up procedure gave 0.18 g (98% crude yield) of a mixture of VI and VIII in a 1:2 ratio by nmr. The total product was subjected to repetitive preparative tlc on silica gel HF_{254}, using 4% ethyl acetate–benzene as the eluent. There was thus obtained 0.100 g of VIII, slightly contaminated with XIII, and 0.040 g of pure VI as a colorless oil: ir (film) 1600 (C=C) and 1680 cm^{-1} (C=O); nmr δ 7.60–7.10 (m, 5 H, aromatic protons), 6.97 (d, 1 H, J = 11 cps, C-4 proton), and 5.85 (d, 1 H, J = 11 cps, C-3 proton); mass spectrum *m/e* 226 (M^+).

Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.71; H, 8.06.

1,1-Dimethyl-10-phenyl-$\Delta^{8(9)}$-2-octalone (XVI) by Methylation of VIII.—Using a modification of a previously described procedure,[26] from 0.63 g (0.0028 mol) of VIII, 4.5 g (0.04 mol) of potassium *t*-butoxide, and 10 ml of methyl iodide there was obtained 0.67 g (94% crude yield) of XVI as a yellow oil. Final purification by vpc (5-ft column of 5% SE-30 on Chromosorb W) gave XVI as a colorless oil: ir (film) 1600 (C=C) and 1715 cm^{-1} (C=O); nmr δ 7.25 (s, 5 H, assigned to aromatic protons), 5.98 (t, 1 H, J = 4 cps, C-8 proton), 1.32 (s, 3 H, C-11 or C-12 protons), and 1.25 (s, 3 H, C-11 or C-12 protons); mass spectrum (70 eV) *m/e* (rel intensity) 254 (100), 239 (31), 197 (34), 183 (41), 155 (39), 141 (36), and 91 (58).

Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.79; H, 8.65.

Attempts to reduce XVI, using hydroboration[27] and catalytic hydrogenation with PtO_2 in glacial acetic acid[28] or ethanol containing perchloric acid, resulted in a quantitative recovery of starting material.

Registry No.—Ia, 22844-34-4; VI, 22844-35-5; VIII, 18943-13-0; IX, 22844-36-6; X, 22844-37-7; XII, 22844-38-8; XIII, 22844-39-9; XVI, 22837-84-9.