

scribed in ref 2.

(54) A. Hassner, N. H. Cromwell, and S. J. Davis, *J. Am. Chem. Soc.*, **79**, 230 (1957).(55) N. H. Cromwell, R. E. Bambray, and R. P. Barkley, *J. Am. Chem. Soc.*, **81**, 4294 (1959).(56) S. A. G. de Graaf and U. K. Pandit, *Tetrahedron*, **29**, 2141 (1973).(57) G. Haberland, *Chem. Ber.*, **69**, 1380 (1936).(58) R. Cornubert, R. Joly, and A. Strébel, *Bull. Soc. Chim. Fr.*, **5**, 1501 (1938).(59) N. J. Leonard and G. C. Robinson, *J. Am. Chem. Soc.*, **75**, 2143 (1953).

Mass Spectrometric Fragmentation of Some Arylidencycloalkanones

Zeev Aizenshtat, Michael Hausmann, Yechiel Pickholtz, Daniel Tal, and Jochanan Blum*

Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

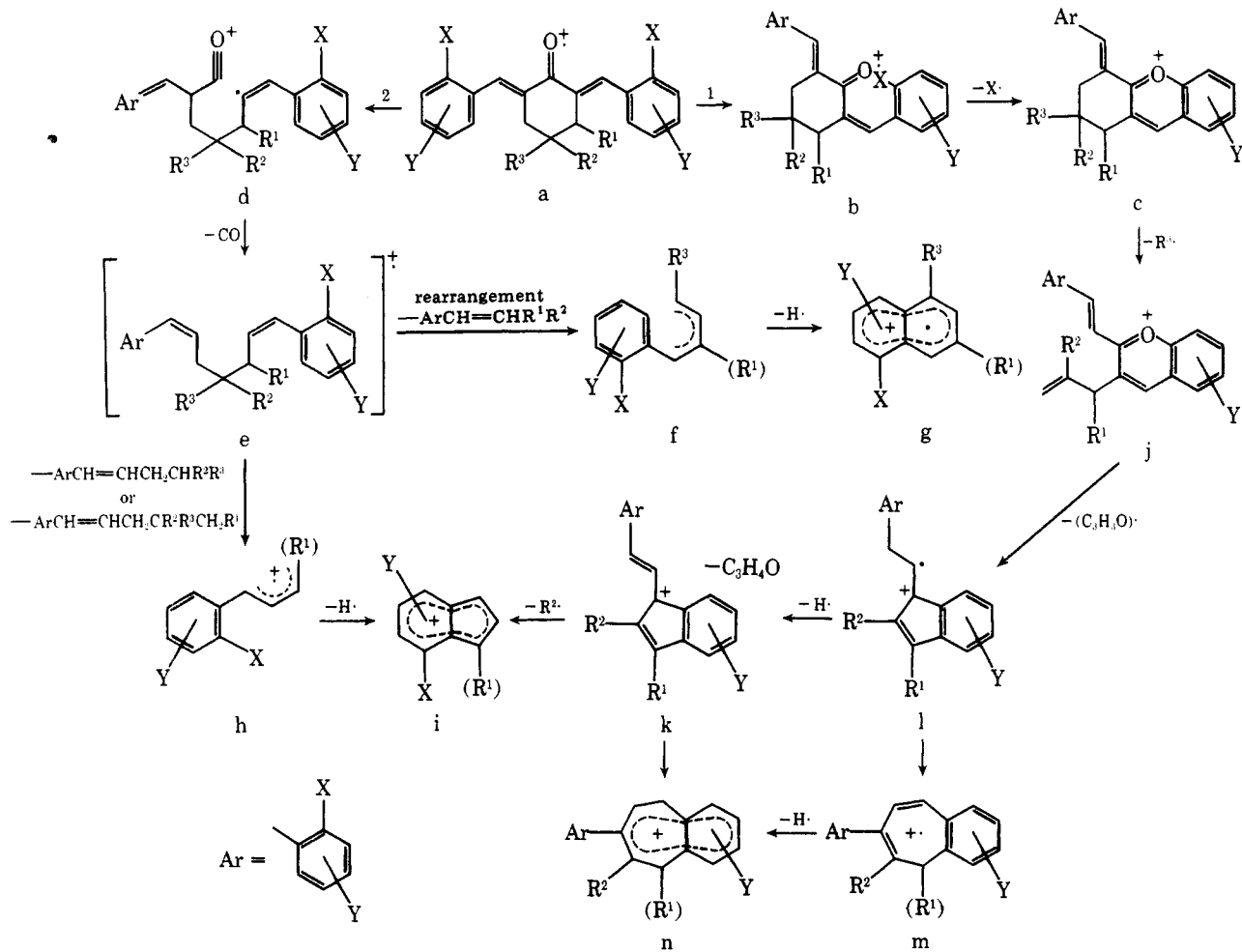
Received August 10, 1976

The mass spectra of (*E,E*)- α,α' -dibenzylidencyclopentanone, -hexanone, -heptanone, and (*E*)-2-benzylidene-1-tetralone are reported. The main feature in these spectra is *E-Z* isomerization of the parent ions followed by production of stable benzopyrylium ions. A competing but less important fragmentation mode involves α -cleavage and CO extrusion as initial steps. The latter route dominates in the mass spectrum of (*E,E*)-3,5-dibenzylidene-tetrahydro-4*H*-pyran-4-one. The mass spectrum of (*E,E*)-3,7-dibenzylidencycloheptane-1,2-dione differs from that of the lower cyclohexanone derivative only by *M* and *M* - CO ions. At 70 eV benzopyrylium ion formation is virtually independent of the electronic nature of the benzylidene moieties, but is promoted by electron-donating groups and reduced by electron-attracting substituents attached to the fused aromatic ring in 2-arylidene-1-tetralones.

In the course of our study on $\text{IrCl(CO)(PPh}_3)_2$ -catalyzed isomerization, isoaromatization, and disproportionation of arylidencycloalkanones,¹ we found that the mass spectra of these ketones may be utilized not only for unequivocal location of the double bonds, but also as a convenient method for estimation of the exo- to endocyclic $\text{C}=\text{C}$ bond migration in these systems.

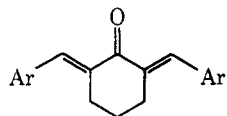
The mass spectrum of (*E,E*)-2,6-dibenzylidencyclohexanone (**1**) has been reported previously by Smith, Dimmock, and Turner.² The present investigation extends this study to include various substituted diarylidencyclohexanones and arylidene derivatives of other cyclic structures.

General fragmentation patterns for (*E,E*)-2,6-diarylidencyclohexanones are suggested in Scheme I, and the

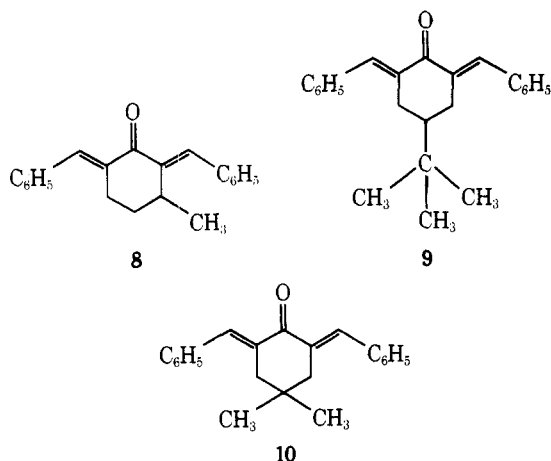
Scheme I^a

^a The fragments shown correspond only to the most intense peaks of the 70-eV spectra. Usually no attempts were made to evaluate peaks of relative intensities lower than 5%.

masses and relative intensities of the principal fragments are assembled in Table I. The most significant fragment in route 1 is the benzopyrilium ion (c), formed by initial *E* to *Z* isomerization of at least one arylidene group (a → b) followed by an intramolecular substitution that involves the ortho function X of the aryl moiety. The *E*-*Z* transformation is temperature dependent, as shown, e.g., by an increase in the (M - 1)/M ratio in 6 from 1.0 to 1.4 upon raising the source tem-



- | | |
|--|---|
| 1, Ar = C ₆ H ₅ | 6, Ar = <i>m</i> -ClC ₆ H ₄ |
| 2, Ar = <i>p</i> -CH ₃ C ₆ H ₄ | 7, Ar = <i>p</i> -ClC ₆ H ₄ |
| 3, Ar = <i>o</i> -CH ₃ OC ₆ H ₄ | 11, Ar = 2-C ₁₀ H ₇ |
| 4, Ar = <i>p</i> -CH ₃ OC ₆ H ₄ | 12, Ar = 2-C ₄ H ₃ O |
| 5, Ar = <i>o</i> -ClC ₆ H ₄ | |



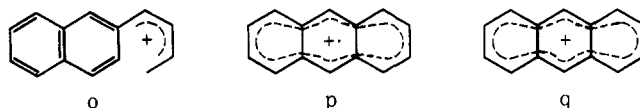
perature from 70 to 130 °C. Cleavage of the α bond to the carbonyl followed by CO extrusion and McLafferty rearrangement (route 2, a → d → e, etc.) ("normal" cyclohexanone fragmentation³) is usually less pronounced than fragmentation 1 or even completely absent (e.g., in ortho-substituted benzylidencyclohexanones). A semiquantitative measure for the relative amount of fragmentation by either route is given by the ratio of ion abundances h/i, since i is formed by both routes and h only by route 2. Compounds that cleave predominantly via benzopyrilium ion have small h peaks, while those that follow mainly the decarbonylation pathway have large ones. (See, e.g., the spectrum of 13 below.)

Although the formation of the relatively stable ion c is associated with intramolecular aromatic substitution, the data given in Table I indicate no Hammett-like correlation. E.g., both the electron-attracting Cl and the electron-donating OCH₃ cause the (M - X)/M ratio to be larger than that obtained by introduction of a CH₃ group. In fact this is not unexpected as previous studies^{4,5} have shown that at 70 eV (M - fragment)/M is not an exact reflection of the formation of the two ions. With the exception of the anisyl derivative 4, 1 < (M - 1)/M > 2 at 70 °C and 70 eV. The parent ion M in the spectrum of 4 is somewhat less abundant than M - 1. Smith et al.² suggested two possible explanations for the low (M - 1)/M ratio in the spectrum of the related 2-(*p*-dimethylaminophenylmethylene)cyclohexanone: (a) The stabilizing effect of the electron-donating group on the parent ion is making the attack of the carbonyl oxygen onto the aromatic ring less favored. (b) Charge location on either of the heteroatoms may stabilize pseudoquinone structures which do not tend to undergo much further fragmentations. Neither of these suggestions can be employed in our system. Compound 2, e.g., which has an electron-donating CH₃ group, exhibits the highest (M - 1)/M ratio recorded, and the frag-

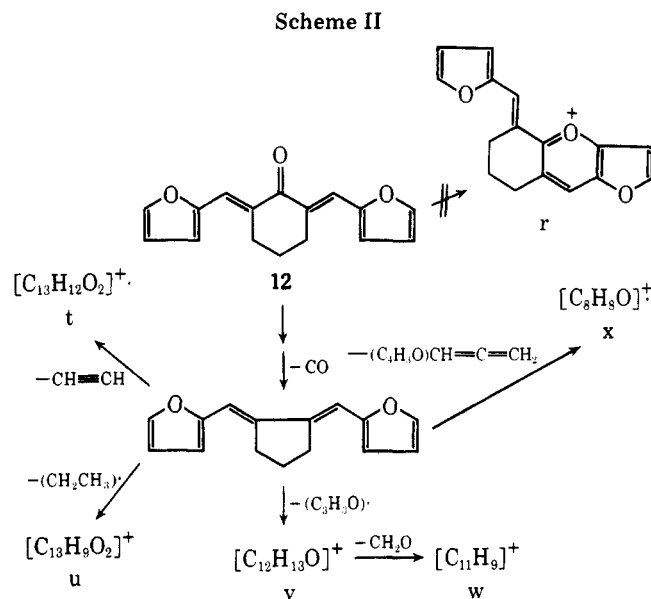
mentation of methoxyl containing 4 is not less than that of unsubstituted 1.

When one ortho position in each aromatic ring in 1 is substituted by either electronegative Cl or electropositive OCH₃, elimination of the substituents, rather than the ortho hydrogen atom, takes place. The ortho-substituted compounds undergo very little fragmentation and the abundance of any but the benzopyrilium ion is very low.

Fragmentation of (*E,E*)-2,6-bis(2-naphthylmethylene)cyclohexanone (11) follows the same patterns outlined for the lower benzologs. However, apart from the intense M and M - 1 peaks [*m/e* 375 (92), 373 (100)] the peaks of the low energy species o, p, and q (that correspond to f, g, and i in Scheme I) are unusually strong [*m/e* 179 (98), 178 (64), and 165 (68), respectively].



Substitution of the aryl groups of 1 by a function which is not strictly aromatic suppresses the formation of stable oxonium ions and route 1 describes no longer the fragmentation of the dienone. Thus, (*E,E*)-2,6-bis(2-furfurylidene)cyclohexanone (12) does not form a furanopyrilium ion, but undergoes, instead, rapid decarbonylation followed by "normal" furfurylidene-cycloketone cleavages⁶ (Scheme II).



The corresponding masses and relative intensities of the parent ion and fragments s and t-x (70 °C, 70 eV) are *m/e* 254 (100), 226 (28), 200 (14), 197 (17), 171 (13), 141 (15), 120 (10).

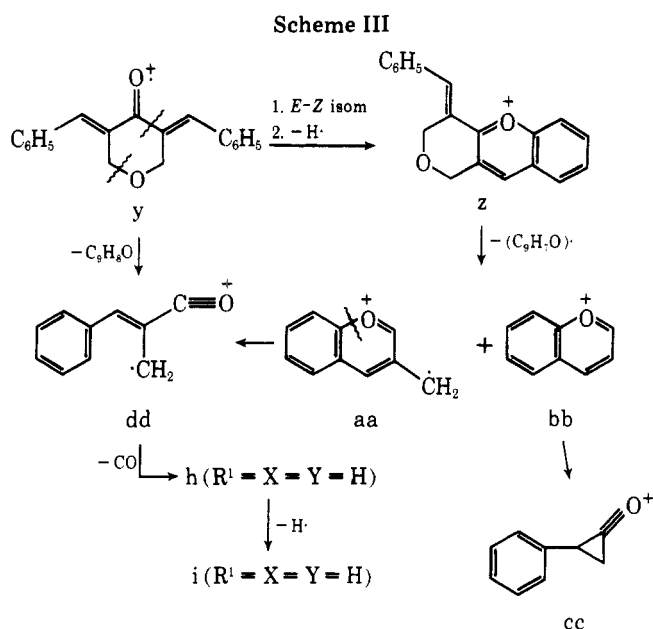
When an oxygen atom is introduced into the central cycloalkanone ring as, e.g., in (*E,E*)-3,5-dibenzylidene-tetrahydro-4*H*-pyran-4-one (13), the formation of a benzopyrilium ion (z) is greatly diminished by the existing of a competing fragmentation pathway which involves cleavage of the C₂-C₃ (α to carbonyl) and the etheric C₂-O bonds. Carbon monoxide extrusion from ion dd, so formed, followed by loss of H· gives fragments h and i as shown in Scheme III.

The benzopyrilium ion z cleaves at the α position to the carbonyl group, and to the ring oxygen to yield aa and bb. The latter may rearrange into the relatively stable phenylcyclopropanonium ion cc. Ion aa may open up to dd and thus contribute to the abundances of h and i. The major peaks in the mass spectrum of 13 are *m/e* y 276 (79), z 275 (44), aa and dd 144 (12), bb and cc 131 (8), h (R¹ = X = Y = H) 116 (100), i (R¹ = X = Y = H) 115 (60). All other peaks are extremely weak,

Table I. Summary of Major Fragment Ions of (*E, E*)-2,6-Diarylidencyclohexanones^a

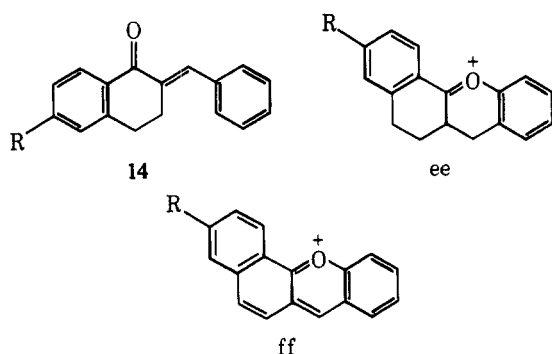
Compd	Substituents as referred to Scheme I	<i>m/e</i> values for fragment ions (rel intensity, %)										Other significant ions
		a (M)	c (M - X)	e (M - CO)	f ^b	g ^b	i ^b	l and/or m ^c	k and/or n ^c	Y - C ₇ H ₆ ⁺ , C ₇ H ₇ ⁺		
1	R ¹ = R ² = R ³ = X = Y = H	274 (65)	273 (100)	246 (7)	129 (12)	128 (13)	115 (27)	218 (11)	217 (22)	91 (13)	C ₆ H ₅ -c-C ₃ H ₃ =O ⁺ , 131 (13), d h, 116 (7)	
2	R ¹ = R ² = R ³ = X = H; Y = <i>p</i> -CH ₃	302 (26)	301 (50)	274 (2)	143 (5) 129 (16) ^e	142 (7) 128 (21)	115 (21)	246 (4) 232 (4)	245 (9) 231 (16)	105 (14) 91 (14)	M - CH ₃ , 288 (26); M - CH ₃ , 287 (100); e - CH ₃ , 259 (10); C ₁₁ H ₉ ⁺ , 141 (8)	
3	R ¹ = R ² = R ³ = Y = H; X = OCH ₃	334 (<1) ^f	303 (100)				115 (2)		277 (1) 247 (1)	121 (4) 91 (8)	c - O, 287 (4); c - CH ₃ OC ₆ H ₄ , 297 (8)	
4	R ¹ = R ² = R ³ = X = H; Y = <i>p</i> -OCH ₃	334 (100)	333 (72)	306 (9)	159 (16) 129 (19)	128 (74)	145 (26) 115 (32) 149 (10)	277 (16) 247 (18)	277 (16) 247 (18)	121 (10) 91 (43)	M - OCH ₃ , 303 (16); e - OCH ₃ , 275 (14); c - HCl, 271 (19)	
5	R ¹ = R ² = R ³ = Y = H; X = Cl	344 (<1) 342 (<1)	309 (33) 307 (100)				115 (29) 252 (19)		287 (1) 285 (2)	91 (5)	M - Cl, 309 (33); 307 (100); e - Cl, 281 (9), 279 (26); e - 2Cl, 244 (30)	
6	R ¹ = R ² = R ³ = X = H; Y = <i>m</i> -Cl	344 (13) 342 (38)	343 (13) 341 (39)	316 (<1) 314 (<1)	155 (4) 153 (13) 129 (10)	154 (8) 152 (13) 128 (30)	151 (6) 149 (10) 115 (50)	287 (11) 285 (11) 253 (11)	287 (11) 285 (11) 253 (11)	91 (48)	M - Cl, 309 (33); 307 (100); e - Cl, 281 (21), 279 (62); e - 2Cl, 244 (56)	
7	R ¹ = R ² = R ³ = X = H; Y = <i>p</i> -Cl	344 (36) 342 (55)	343 (57) 341 (86)	316 (3) 314 (5)	155 (9) 153 (27) 129 (38)	154 (16) 152 (43) 128 (55)	151 (23) 149 (35) 115 (100)	288 (7) 286 (22) 254 (4)	287 (11) 285 (11) 251 (32)	91 (35)	M - Cl, 309 (33); 307 (100); e - Cl, 281 (21), 279 (62); e - 2Cl, 244 (56)	
8	R ¹ = CH ₃ ; R ² = R ³ = X = Y = H	288 (79)	287 (100)	260 (5)	143 (6) 129 (30) ^e	142 (6) 128 (28)	115 (44)	218 (20)	217 (28)	91 (78)	h, 116 (20)	
9	R ¹ = R ³ = X = Y = H; R ² = C(CH ₃) ₃	330 (62)	329 (100)	302 (10)	129 (28)	128 (24)	115 (59)	218 (18)	273 (10) ^g 217 (28)	91 (78)	M - CH ₃ , 316 (9); M - CH ₃ - CH ₃ , 301 (11); h, 116 (21); C(CH ₃) ₃ ⁺ , 57 (51)	
10	R ¹ = X = Y = H; R ² = R ³ = CH ₃	302 (60)	301 (100)	274 (4)	143 (13) 129 (14)	142 (14) 128 (15)	115 (42)	233 (7)		91 (50)	e - CH ₃ , 259 (9); l or m - CH ₃ + H, 218 (10); k or n - CH ₃ + H, 217 (12), h, 116 (15)	

^a All spectra were recorded at 70 °C; electron energy 70 eV. ^b Also this fragment -Y and H transfer. ^c Also these ions -Y, -2Y, and -R³ coupled with H transfer. ^d For the formation of this ion see Scheme III. ^e *m/e* 129 corresponds to i as well. ^f Ratio of intensities of M (*m/e* 334): M - 1 (*m/e* 333) is 4:5. ^g *m/e* 273 is also M - C(CH₃)₃.



thus indicating that **13** hardly cleaves to give the analogous of ions j-n of Scheme I.

(*E*)-2-Arylidene-1-tetralones (**14**) were included in our study¹ as representative cyclohexanone derivatives with one exocyclic and one endocyclic bond. These compounds readily undergo *E-Z* isomerization and produce benzopyrylium ions ee, and the even more stable naphthobenzopyrylium ions ff,



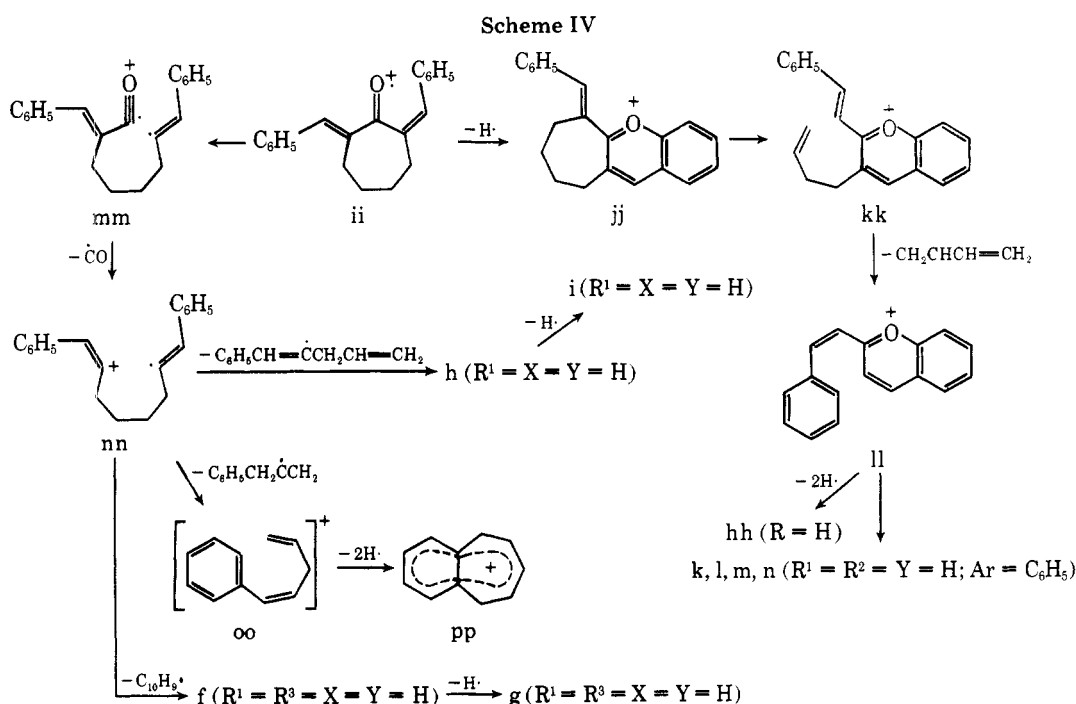
by loss of two hydrogen atoms. Fragmentation via the decarbonylation pathway is extremely small in this series.

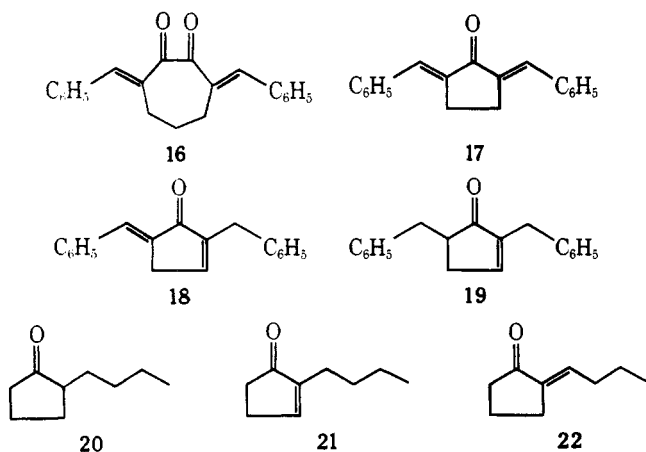
Although no correlation of the substituents with the ratio $(M-1)/M$ could be observed in (*E,E*)-2,6-diarylidencyclohexanones, in **14** the substituents R attached to the fused aromatic ring affect this ratio in accord with expectations. Electron-donating substituents that stabilize structure ee cause the ratio to increase, and vice versa with electron-attracting groups. The corresponding *m/e* values and relative intensities for ions M, M-1, and M-3 of (a) **14**, R = OCH₃; (b) **14**, R = H; (c) **14**, R = OCOCH₃, are (a) 264 (33), 263 (100), 261 (5); (b) 234 (60), 233 (100), 231 (19); (c) 292 (38), 291 (26), 290 (1). [(M-1)/M for (a), (b), and (c) are 3.03, 1.66, and 0.68, respectively]. Two further strong peaks, *m/e* 249 (29) and 248 (100), appear in the mass spectrum of 6-acetoxy-2-benzylidene-1-tetralone (**14**, R = OCOCH₃) owing to loss of acetoxy or acetic acid from the parent ion.

The tendency to form benzopyrylium ions is not limited to derivatives of six-membered cycloalkanones. Expansion of the central ring in **1** by one carbon unit gives (*E,E*)-2,7-dibenzylidencycloheptanone (**15**), which behaves similarly to **1** under electron impact. The fragmentation patterns suggested for **15** in Scheme IV resemble, therefore, those shown in Scheme I except for the features that are associated with the cycloheptane ring. The masses, assignments, and relative abundances (80 eV) are as follows: M⁺· 288 (90), jj 287 (100), nn 260 (14), hh 231 (14), e and m 218 (20), k and n 217 (40), pp 141 (49), f (R¹ = R³ = X = Y = H) 129 (40), g (R¹ = R³ = X = Y = H) 128 (51), i (R¹ = X = Y = H) 115 (81), C₇H₇⁺ 91 (65).

It is most remarkable that the mass spectra of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-**15** are essentially identical for a broad range of electron energies (30–80 eV). This suggests that under electron impact rapid interconversion of the three geometric isomers takes place.

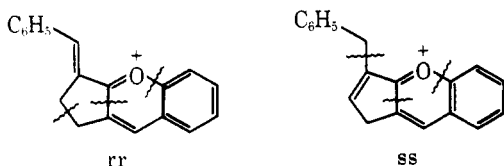
(*E,E*)-3,7-Dibenzylidencycloheptane-1,2-dione (**16**), as a typical 1,2-diketone, ejects one molecule of CO prior to further fragmentation.⁷ By this process the parent ion of 2,6-dibenzylidencyclohexanone is formed (not necessarily as the closed structure a). One could, therefore, anticipate the resemblance of the mass spectra of **16** and **1** and expect a small parent peak for **16**. The recorded masses and relative inten-





sities [m/e (120 °C, 70 eV) 302 (<1), 274 (73), 273 (100), 218 (14), 217 (24), 129 (20), 128 (27), 115 (59), 91 (25)] confirm these assumptions.

(*E,E*)-2,5-Dibenzylidenecyclopentanone (17) follows almost entirely the "benzopyrylium" mode of fragmentation. The mass spectrum [m/e (70 eV) M^+ 260 (33), rr 259 (56.5), $C_{11}H_9^+$ 141 (7.5), i 115 (100), $C_7H_7^+$ 91 (20)] indicates no α -cleavage of the parent ion and CO abstraction. The intense indenyl ion i (m/e 115) may be produced by two independent routes from the benzopyrylium ion rr : one involves α - and β -cleavage followed by hydrogen transfer, and the other route proceeds via ion dd as shown in Scheme III.



An isomer of 17 with only one exocyclic double bond, 2-benzyl-5-benzylidenecyclopent-2-enone (18), has the following mass spectrum: m/e (70 eV) M^+ 260 (65), ss 259 (50), [$M - C_7H_7$] $^+$ 169 (21), [$M - C_7H_7 - CO$] $^+$ 141 (20), i 115 (44), $C_7H_7^+$ 91 (100), $C_6H_5^+$ 77 (20). The spectrum differs from that of 17 in two respects: (a) The intensities of ion M and $M - 1$ are no longer in favor of $M - 1$. (b) The base peak corresponds to the tropylium ion (m/e 91) due to facile benzyl ion abstraction from the parent ion and from ss . The latter fragment may, however, undergo α - and β -cleavage in the same manner as rr and give some indenyl cation i as well.

When the exocyclic double bond in 18 is selectively reduced to form 2,5-dibenzylcyclopent-2-enone (19), naturally, the $M - 1$ peak disappears. The base peak (m/e 91) results from the *two* available benzyl groups. The only other intense peaks correspond to M [m/e 262 (36)], $M - C_7H_7$ [m/e 171 (30)], and $M - C_7H_7 - H_2O$ [m/e 153 (19)].

It may thus be concluded that benzopyrylium ion production is feasible only when *exocyclic* double bonds are available, and that the ratio of intensities ($M - 1$)/ M is proportional to the number of benzylidene functions. On the basis of these features we were able to locate by mass spectrometry the position of double bonds in the various reaction products obtained from 17 and $IrCl(CO)(PPh_3)_2$ described in the preceding paper.¹ Moreover, upon recording the intensities of peaks m/e 260, 259, 115, and 91 throughout the catalytic process, we could calculate the rate of disappearance of 17 and rate of product formation in accuracy comparable with the usual GLC method.^{1,8}

Finally, the mass spectra of 2-alkyl- and 2-alkylidenecycloalkanones 20–22 were recorded for comparison with those of the aryl-containing compounds. The spectrum of 2-*n*-butylcyclopentanone (20) resembles that of the lower homo-

logue.^{9–11} The molecular ion [m/e 140 (7)] undergoes McLafferty rearrangements, mainly with γ -hydrogen shift, to give cyclopentanol ion [m/e 84 (100)] that reketonizes to $C_5H_7O^+$ [m/e 83 (26)]. McLafferty rearrangement with δ -hydrogen shift is less important. It yields the 2-methylcyclopentanol ion [m/e 97 (15)].

The cyclopentenone derivative (21) undergoes likewise McLafferty rearrangements; however, the main feature of this compound is α -cleavage (side chain) and H-transfer to give an unsaturated enol ion m/e 96 (100) which reketonizes [m/e 95 (50)]. Other intense peaks in the spectrum of 21 result from ethyl abstraction and the complete rupture (α -cleavage) of the side chain [m/e 109 (44) and 81 (45), respectively].

The side chain of 2-butylidenecyclopentanone (22) is gradually cleaved off to give fragment ions m/e 123 (40), 109 (15), and 95 (60). α -Cleavage of the parent ion [m/e 138 (65)] followed by decarbonylation affords ion m/e 110 (11), which, upon α -cleavage, gives the base ion $C_5H_7^+$ (m/e 67). As no significant $M - 1$ ion appears in the spectrum, it may be concluded that stable perylum ion formation from cycloalkanones is conditioned by the presence of an *arylidene* group at the α position.

Experimental Section

The preparations of compounds 1–12 and 14–19 are described or referred to in the preceding paper.¹ 3,5-Dibenzylidenetetrahydro-4H-pyran-4-one¹² and 2-butylidenecyclopentanone¹³ were synthesized according to the literature. The latter was isomerized and reduced to 2-butylcyclopent-2-enone and 2-butylcyclopentanone, respectively, by $IrCl(CO)(PPh_3)_2$ under the condition described for 2,5-dibenzylidenecyclopentanone.¹ All liquid samples were purified by gas chromatography and solids by recrystallization prior to mass spectrometric analysis.

The mass spectra were measured with a double focusing Varian MAT-311 spectrometer. The exact masses of all ambiguous ions were determined by high resolution, $R = M/\Delta M > 10\,000$.

Acknowledgments. We wish to thank Professor Seymour Meyerson for reading the manuscript and for helpful suggestions. Y.P. is also indebted to the Albert and Kathleen Casali Foundation for a Research Fellowship.

Registry No.—1, 42052-61-9; 2, 42792-79-0; 3, 62085-70-5; 4, 62085-71-6; 5, 62085-72-7; 6, 62085-73-8; 7, 42792-80-3; 8, 62085-69-2; 9, 42792-77-8; 10, 62085-90-9; 11, 62085-77-2; 12, 62085-75-0; 13, 62085-91-0; 14a, 50558-94-6; 14b, 57558-64-2; 14c, 62085-37-4; 15, 62085-48-7; 16, 62085-26-1; 17, 34611-43-3; 18, 62085-32-9; 19, 23923-54-8; 20, 934-42-9; 21, 5561-05-7; 22, 56292-42-3.

References and Notes

- Z. Aizenshtat, M. Hausmann, Y. Pickholtz, D. Tal and J. Blum, *J. Org. Chem.*, preceding paper in this issue.
- P. S. Smith, J. R. Dimmock, and W. A. Turner, *Can. J. Chem.*, **51**, 1458 (1973).
- See, e.g., J. H. Bowie in "The Chemistry of the Carbonyl Group", Vol. II, J. Zabicky, Ed., Interscience, New York, N.Y., 1970, pp 292–294.
- Cf. M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 4484 (1966).
- Cf. I. Howe, D. H. Williams, and R. G. Cooke, *Org. Mass Spectrom.*, **2**, 137 (1969).
- R. L. N. Harris, F. Komitsky, and C. Djerassi, *J. Am. Chem. Soc.*, **89**, 4775 (1967).
- Cf., e.g., J. H. Bowie, R. G. Cooks, G. E. Gream, and M. H. Laffer, *Aust. J. Chem.*, **21**, 1247 (1968).
- Similarly we measured by mass spectrometry kinetics of transfer hydrogenation of 2,7-dibenzylidene- to 2,7-dibenzylcycloheptanone (ref 1). The major fragmentations of the latter compound are m/e (85 °C, 70 eV) M^+ 292 (3), [$M - H_2O$] $^+$ 274 (4), [$PhCH_2CH(CH_2)_2CH=CH_2$] $^+$ or [Ph -cyclohexyl] $^+$ 159 (67), [PhC_3H_5] $^+$ 146 (72), [$PhCH_2CHCH_2CH=CH_2$] $^+$ 145 (48), [$PhCH_2CHCH=CH_2$] $^+$ 131 (67), [PhC_3H_5] $^+$ 117 (69), [C_6H_6] $^+$ 104 (66), [C_6H_5O] $^+$ 97 (48), [C_7H_7] $^+$ 91 (100).
- J. R. Haas, M. M. Bursey, D. G. I. Kingston, and H. P. Tannenbaum, *J. Am. Chem. Soc.*, **94**, 5095 (1972).
- D. G. I. Kingston, J. T. Bursey, and M. M. Bursey, *Chem. Rev.*, **74**, 215 (1974).
- Cf. also G. Eadon and C. Djerassi, *J. Am. Chem. Soc.*, **91**, 2724 (1969).
- R. Cornubert, R. Delmas, S. Monteil, and J. Vrirot, *Bull. Soc. Chim. Fr.*, **17**, 36 (1950).
- L. Birkofer, S. M. Kim, and H. D. Engels, *Chem. Ber.*, **95**, 1495 (1962).