used to analyze the products from the reaction of **3** with base. The internal standard for the product analyses, resulting from **2** and **3**, was *n*-butyl alcohol.

Kinetic Method.—Sealed ampoules of the reaction mixture were periodically removed from a thermostated oil bath, quenched in ice–water, warmed to room temperature, shaken, and opened, and a 1.00-ml aliquot was transferred to a 125-ml erlenmeyer flask under a nitrogen atmosphere. The aliquots were titrated to the phenolphthalein end point with standardized hydrochloric acid. The data were processed with standard computer programs.

Registry No.—**2**, 1985-88-2; **3**, 13401-56-4; **6**, 1589-49-7; **8**, 6245-99-4; **10**, 27557-84-2; **11**, 6921-35-3.

Acknowledgment.—This investigation was supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the U. S. Army Research Office (Durham). We thank Mr. R. Cuneo and Mr. W. Koskinen for their assistance.

Mass Spectral Fragmentation of Spiro Ketones and Olefins[1]

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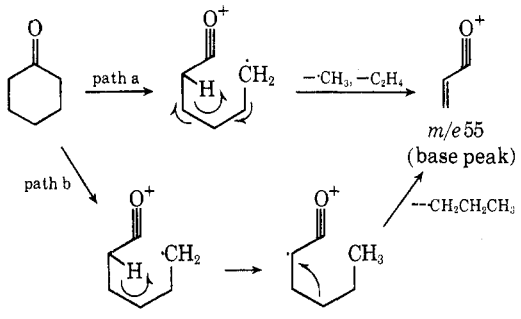
The mass spectra of spiro ketones with varying ring size have been recorded. An unusual fragmentation resulting in the loss of an olefinic radical in a hydrogen-transfer mechanism was observed to be an important decomposition pathway. Deuterium labeling determined the site of the fragmentation to be the nonketone ring. However, in several cases the preferred path of fragmentation was loss of the ketone ring. High-resolution data (Table I) defined the exact composition of the principal fragment peaks. The mass spectra of seven spiro olefins were investigated, and their fragmentation behavior was interpreted in terms of the loss of a series of alkyl radicals correlated with ring size.

Spiro Ketones.—The mass spectra of spiro ketones are found to exhibit a behavior unlike that of simple cycloalkyl ketones such as cyclohexanone or cyclopentanone.[2] The mass spectrum of cyclohexanone, for example, contains significant peaks arising from α cleavage followed by further fragmentation. In particular, the base peak at *m/e* 55 (M − 43) for cyclohexanone arises *via* one or both of the pathways shown in Scheme I. A related scheme can be written for cyclopentanone in which the base peak is also *m/e* 55 (M − 29). It might therefore be expected that a similar mode of fragmentation should occur for the

SCHEME I



spiro ketones which contain a cyclohexanone or a cyclopentanone ring. However, the prominent M − 43 ion (*m/e* 55) from cyclohexanone is extremely weak (*m/e* 123) in the mass spectrum of spiro[5.5]undecan-1-one (**1**) (Figure 1), whereas the M − 55 (*m/e* 111, $C_7H_{11}O$) peak, which is very small in cyclohexanone, is the base peak. Similarly, in the mass spectrum of spiro[4.5]decan-6-one (**2**) (Figure 2) *m/e* 111 ($C_7H_{11}O$) again appears as one of the two significant peaks (70% of the base peak at *m/e* 67, C_5H_7) but now corresponds to the loss of 41 amu. (See Table I.)

In order of establish the structure parameters required for the formation of the intense *m/e* 111 peak, two spiro ketones containing five-membered carbonyl-bearing rings were prepared and analyzed. The mass spectrum of spiro[4.5]decan-1-one (**3**) (Figure 3) exhibits an intense peak (70% of the base peak) corresponding to M − 55 (*m/e* 97, C_6H_9O), and spiro[4.4]nonan-1-one (**4**) (Figure 4) also shows a major peak (50% of the base peak) at *m/e* 97 (C_6H_9O), which corresponds to the loss of 41 amu. The origin of the neutral fragment from the *saturated ring* is consistent with a mass shift of 14 amu (*m/e* 97 going to *m/e* 111) when the carbonyl-bearing ring is increased from five (**3** or **4**) to six carbons (**1** or **2**). Moreover, this correlation is also consistent with the observation that the neutral fragment is 41 amu when the *saturated* ring is five-membered, but 55 amu when the saturated ring is six-membered.

To define more precisely the mechanism and ions involved, the α hydrogens of **2** and **4** were exchanged for deuterium by repeated equilibration with D_2O in the presence of base. In the mass spectra of 7,7-dideuteriospiro[4.5]decan-6-one (**5**) (Figure 5) and 2,2-dideuteriospiro[4.4]nonan-1-one (**6**) (Figure 6), *m/e* 111 and *m/e* 97 are shifted completely to *m/e* 113 and *m/e* 99, respectively. We conclude therefore that the neutral fragments under discussion in the foregoing come entirely from the saturated ring and presumably by similar mechanisms.

One pathway, which is consistent with the data above, for the decomposition leading to the *m/e* 97 or *m/e* 111 peaks is postulated in Scheme II. Thus, the molecular ion undergoes β cleavage at the spiro junction followed by transfer of a δ hydrogen[3] to the carbonyl and C–C bond cleavage with loss of an allylic radical (*m* = 1) or a homoallylic radical (*m* = 2). An alternative mechanism might be written in which the spiro carbon carries the positive charge and abstracts the hydrogen.

(1) We are indebted to the National Science Foundation for financial aid (Grants No. GP-9533 and GP-7193).

(2) For leading references, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 3.

(3) S. D. Sample, D. A. Lightner, O. Buchardt, and C. Djerassi, *J. Org. Chem.*, **32**, 997 (1967).

TABLE I

HIGH RESOLUTION (1:12,500) MASS MEASUREMENTS OF THE PRINCIPAL FRAGMENT PEAKS OF SPIRO KETONES

Name	m/e	Composition	Multiplet ratio	Obsd mass	Calcd mass
Spiro[5.5]undecan-1-one (1)	111	$C_7H_{11}O$		111.08107	111.08099
	109	C_8H_{13}	9	109.1021	109.10172
	109	C_7H_9O	10	109.06574	109.06534
	98	$C_6H_{10}O$		98.07499	98.07316
	95	C_7H_{11}	1	95.08584	95.08607
	95	C_6H_7O	10	95.04910	95.04969
	81	C_6H_9		81.06999	81.07042
	69	C_5H_9		69.07041	69.07042
Spiro[4.5]decan-6-one (2)	111	$C_7H_{11}O$		111.08085	111.08099
	109	C_8H_{13}	1	109.10207	109.10172
	109	C_7H_9O	5	109.06499	109.06534
	95	C_7H_{11}	5	95.08537	95.08607
	95	C_6H_7O	1	95.04882	95.04969
	81	C_6H_9		81.06999	81.07042
	67	C_5H_7		67.05478	67.05477
Spiro[4.5]decan-1-one (3)	97	C_6H_9O		97.06581	97.06534
	84	C_5H_8O		84.0580	84.05751
	81	C_6H_9		81.07027	81.07042
	79	C_6H_7		79.05457	79.05477
	68	C_5H_8		68.06262	68.06260
	67	C_5H_7		67.05478	67.05477
Spiro[4.4]nonan-1-one (4)	97	C_6H_9O		97.06609	97.06534
	95	C_6H_7O	10	95.04966	95.04969
	95	C_7H_{11}	7	95.08398	95.08607
	94	C_7H_{10}		94.07805	94.07825
	67	C_5H_7		67.05479	67.05477
Spiro[5.6]dodecan-7-one (7)	162	$C_{12}H_{18}$		162.14058	162.14084
	125	$C_8H_{13}O$		125.09660	125.09664
	109	C_8H_{13}		109.10173	109.10172
	96	C_7H_{12}		96.09376	96.09390
	81	C_6H_9		81.07034	81.07042
	79	C_6H_7		79.05450	79.05477
	67	C_5H_7		67.05478	67.05477
Spiro[3.4]octan-5-one (8)	96	C_6H_8O		96.05754	96.05751
	68	C_5H_6		68.06254	68.06260
	67	C_5H_7		67.05478	67.05477
Spiro[2.4]heptan-4-one (9)	68	C_5H_8		68.06261	68.06260
	67	C_5H_7		67.05484	67.05477
	54	C_4H_6		54.04714	54.04695

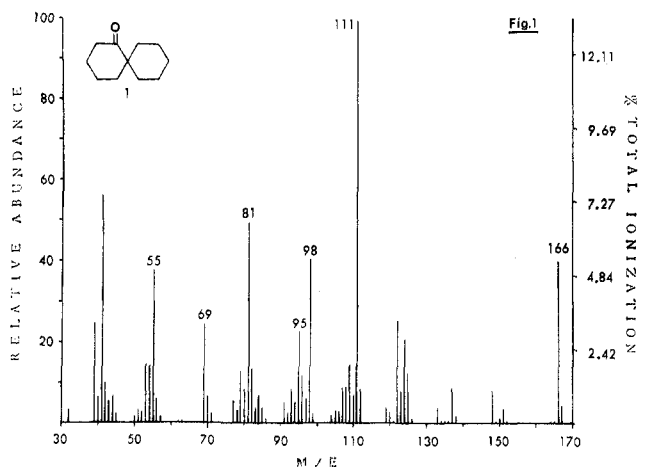


Figure 1.—Mass spectrum of spiro[5.5]undecan-1-one, 70 eV.

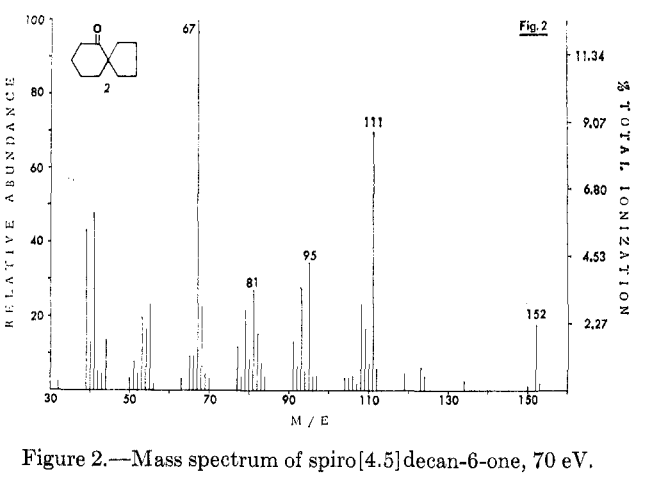
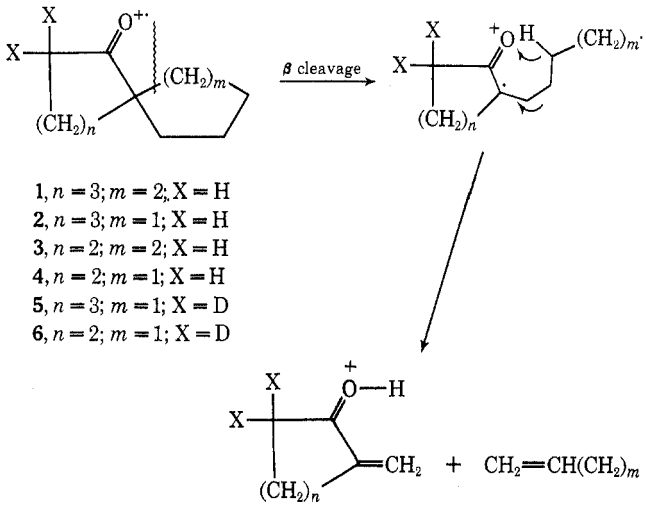


Figure 2.—Mass spectrum of spiro[4.5]decan-6-one, 70 eV.

The generality of this mechanism was examined for spiro ketones containing rings which varied in size from cyclopropane to cycloheptane. As the size of the ketone ring increases, the mass spectrum becomes somewhat more complex, *e.g.*, spiro[5.6]dodecan-7-one (**7**) (Figure 7). However, the prominent (M − 55) fragmentation of the five- (**3**) and six- (**1**) membered ring ketones is found to be a major contributor to the mass spectrum (*cf.* *m/e* 125) of the seven-membered ring ketone (**7**). The effect of decreasing the size of the *hydrocarbon* ring may be seen in the mass spectra of spiro[3.4]octan-5-one (**8**) (Figure 8) and spiro[2.4]-heptan-4-one (**9**) (Figure 9). Spiro[3.4]octan-5-one (**8**) gives only an extremely weak peak at *m/e* 97. The mechanism of Scheme II is unlikely to contribute

SCHEME II



1, $n = 3; m = 2;$ X = H
2, $n = 3; m = 1;$ X = H
3, $n = 2; m = 2;$ X = H
4, $n = 2; m = 1;$ X = H
5, $n = 3; m = 1;$ X = D
6, $n = 2; m = 1;$ X = D

m/e 111 (from **1** and **2**)
m/e 113 (from **5**)
m/e 97 (from **3** and **4**)
m/e 99 (from **6**)

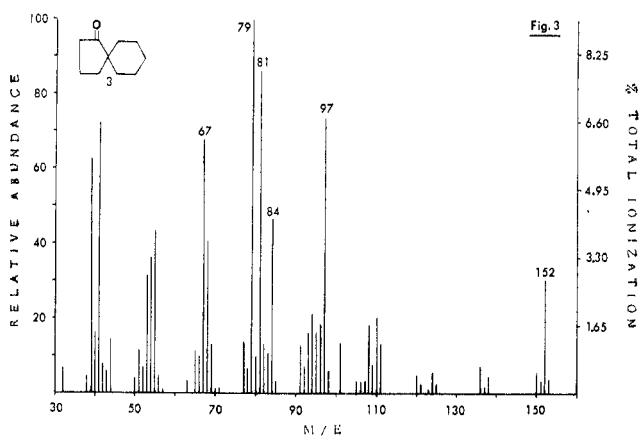


Figure 3.—Mass spectrum of spiro[4.5]decan-1-one, 70 eV.

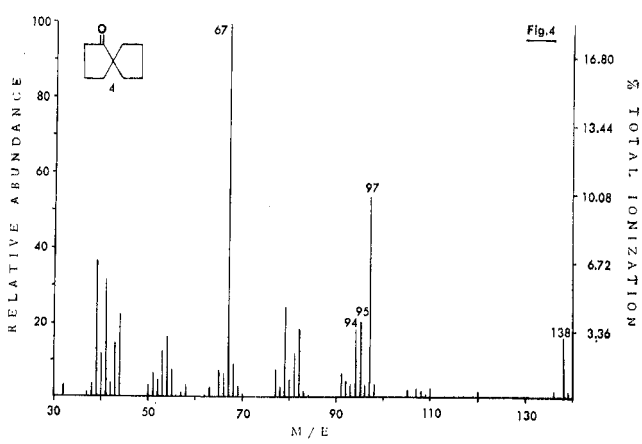


Figure 4.—Mass spectrum of spiro[4.4]nonan-1-one, 70 eV.

greatly in the mass spectrum of **8** for such a mechanism in this instance requires the expulsion of a vinylic and not an allylic or homoallylic radical and is presumably a higher energy pathway than that in **3** or **4**. Spirocyclopropyl ketone **9** can provide no δ hydrogen for the mechanism of Scheme II. However, the mechanism can be successfully invoked to explain

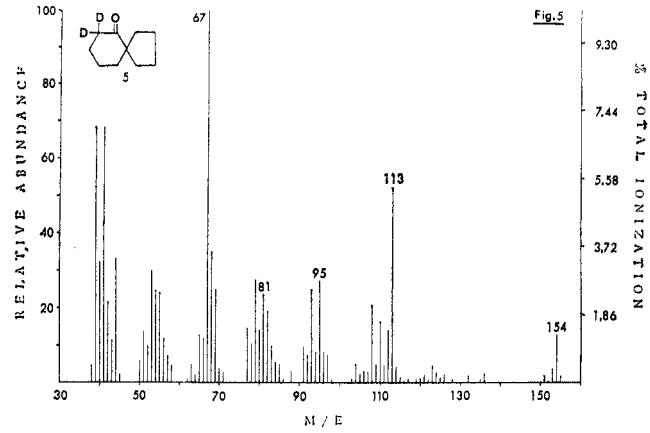


Figure 5.—Mass spectrum of 7,7-dideuteriospiro[4.5]decan-6-one, 70 eV.

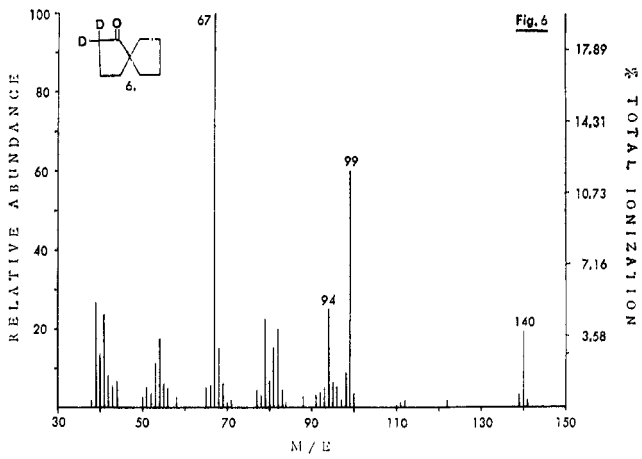


Figure 6.—Mass spectrum of 2,2-dideuteriospiro[4.4]nonan-1-one, 70 eV.

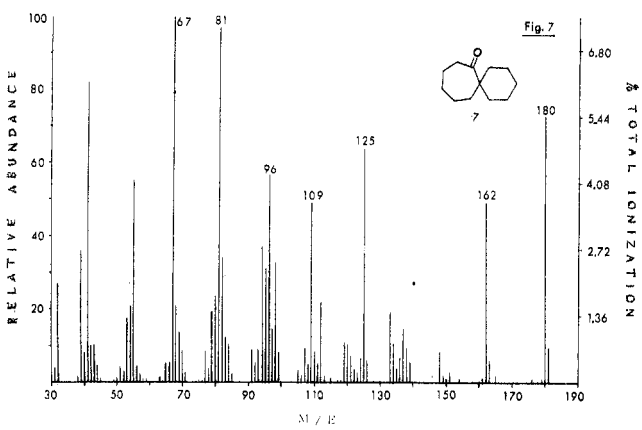


Figure 7.—Mass spectrum of spiro[5.6]dodecan-7-one, 70 eV.

the base peak (*m/e* 97) in the spectrum of spiro[4.4]-nona-1,6-dione (**10**) (Figure 10). For this compound the structure of the fragment expelled is $CH_2{=}CHC{\equiv}O$.

The mass spectra of the various spiro ketones also display several other intense peaks. An ion at *m/e* 67 appears as a major contributor to the total ion current (in some cases, the base peak) in the spectra of **2**, **4**, **5**, and **6**, all of which contain a five-membered saturated ring. The homologous ion at *m/e* 81 appears in the spectra of **1**, **3**, and **7**, all of which contain a six-membered saturated ring. It may be noted, however,

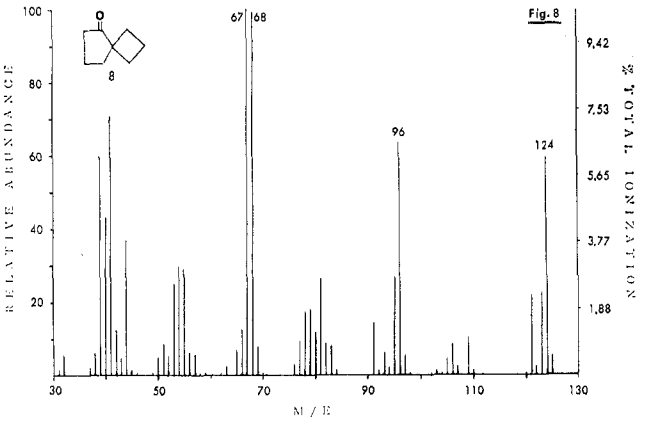


Figure 8.—Mass spectrum of spiro[3.4]octane-5-one, 70 eV.

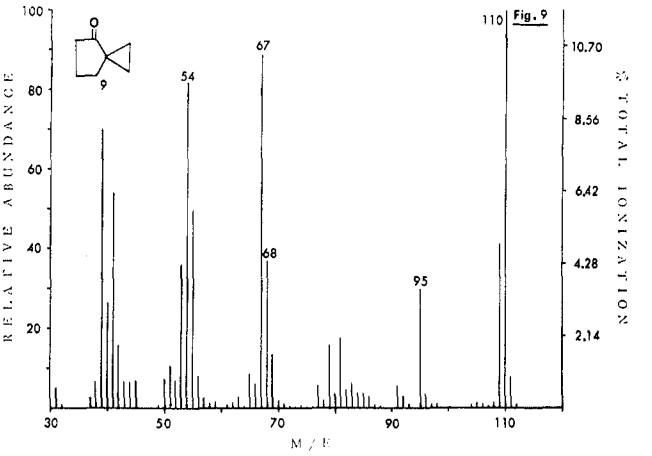


Figure 9.—Mass spectrum of spiro[2.4]heptane-4-one, 70 eV.

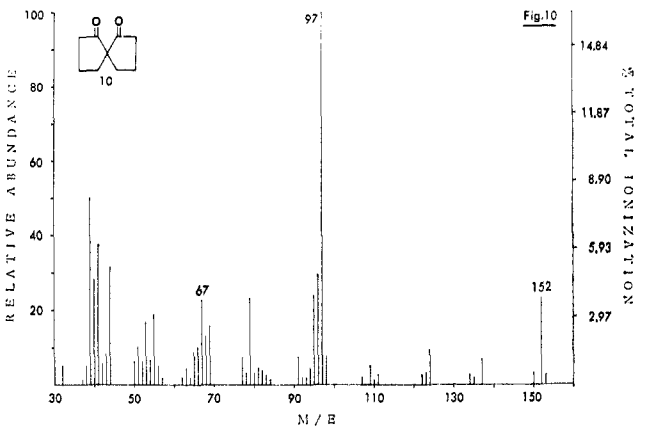
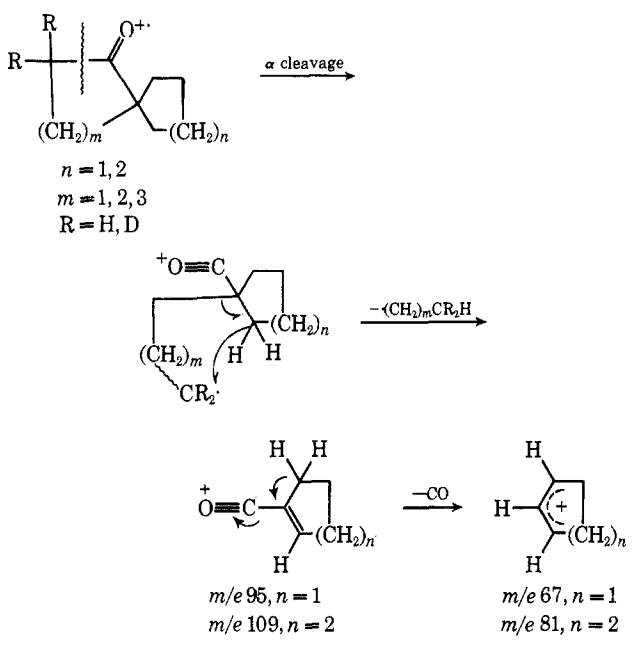


Figure 10.—Mass spectrum of spiro[4.4]nona-1,6-dione, 70 eV.

that m/e 67 as well as m/e 81 appears in the mass spectra of **1** and **7**. The fragment of m/e 67 is assigned $C_5H_7^+$ and that at m/e 81 is assigned $C_6H_9^+$ by high resolution measurements (see Table I). Based on the fact that the peak remains at m/e 67 when **2** and **4** are deuterated α to the carbonyl group, it is assumed that the fragment originated from the saturated ring.

A mechanisms is suggested in Scheme III which

SCHEME III

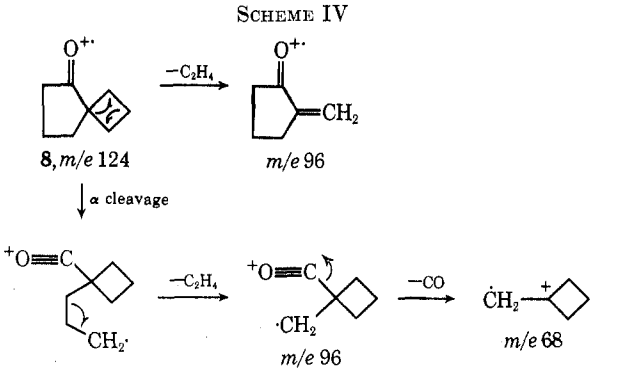


explains the origin of both the m/e 67 and m/e 81 fragments and involves α cleavage of the parent ion followed by hydrogen abstraction from the saturated ring and loss of an alkyl radical. The ion that is formed at this stage is observed at m/e 95 or 109 (Table I) in the mass spectrum, albeit to a small extent (*ca.* 20% of the base peak). The next step is shown as a concerted 1,2-hydrogen shift with loss of carbon monoxide to leave an allylic carbonium ion (m/e 67 or 81). Unfortunately, the paucity of metastable ions in all the mass spectra of our spiro ketones precludes the customary method of confirming the mechanism in this instance.

The mechanism shown in Scheme III is consistent with the observation that per cent ionization at m/e 67 in **4** (18.5%) is greater than that at m/e 81 in **2** (12.5%). In **4** the ketone-containing ring is five membered and, in its opened form following α cleavage, the cyclic transition state for hydrogen abstraction is a six-membered ring. In **2**, however, the hydrogen abstraction step involves a less favorable seven-membered transition state.[4]

The more strained spiro ketones **8** and **9** [as well as the seven-membered ring ketone (**7**)] display a unique behavior. The mass spectrum of spiro[3.4]-octan-5-one (**8**) exhibits two major contributors to the total ion current at m/e 68 (C_5H_8) and m/e 96 (C_6H_8O) which do not appear to any large extent in the spectra of the other spiro ketones. The peak at m/e 96 is readily interpreted (Scheme IV) as the

SCHEME IV



(4) P. Brown, A. H. Albert, and G. R. Pettit, *J. Amer. Chem. Soc.*, **92**, 3212 (1970); D. A. Lightner, unpublished results.

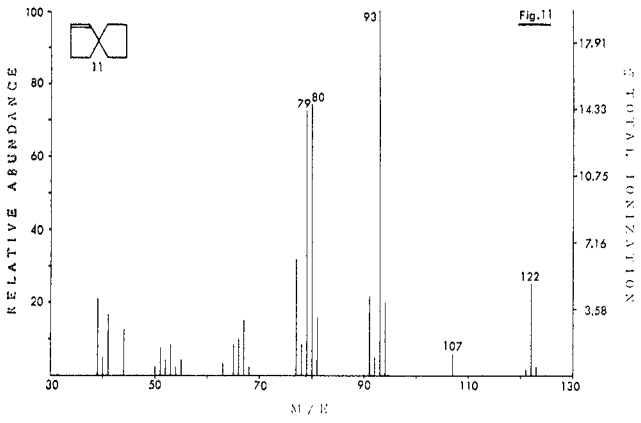


Figure 11.—Mass spectrum of spiro[4.4]non-1-ene, 70 eV.

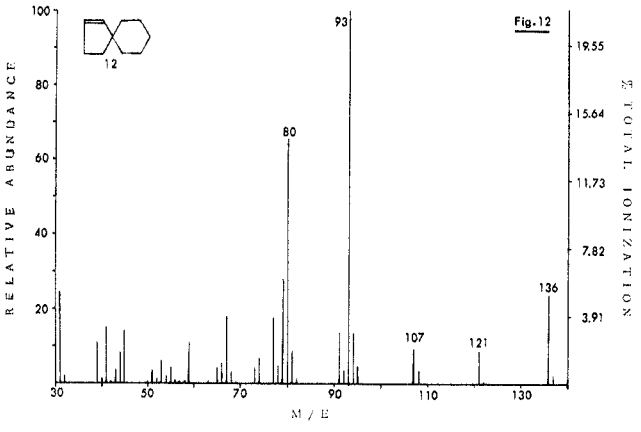
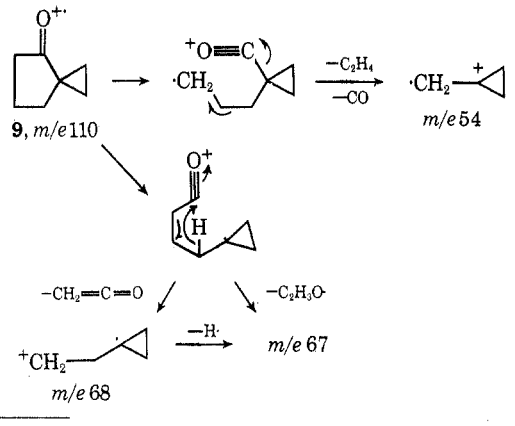


Figure 12.—Mass spectrum of spiro[4.5]dec-1-ene, 70 eV.

expulsion of ethylene, a common decomposition route for cyclobutane rings.[2,5] An alternative pathway to *m/e* 96 involves α cleavage followed by the loss of ethylene from the five-membered ring. Subsequent expulsion of carbon monoxide from this ion leads to *m/e* 68. Again, the absence of metastable ions in the mass spectrum of **8** renders the correlation between *m/e* 96 and 68 tenuous.

Spiro[2.4]heptan-4-one (**9**) (Figure 9) exhibits a peak at *m/e* 67 of the same composition (C_5H_7) as that of the *m/e* peaks found in the spectra of the less highly strained spiro ketones (Scheme III). A rational pathway leading to the *m/e* 67 fragment is shown in Scheme V. Here α cleavage occurs followed by loss of ketene

SCHEME V



(5) "Catalog of Mass Spectral Data," American Petroleum Institute, Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., spectrum no. 416.

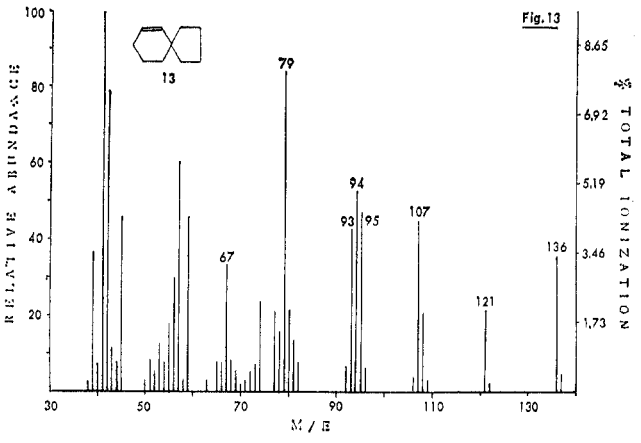


Figure 13.—Mass spectrum of spiro[4.5]dec-6-ene, 70 eV.

leads to *m/e* 68 (C_5H_8) which may in turn lose a hydrogen atom. Alternatively, the concerted loss of C_2H_3O *via* hydrogen transfer may account for *m/e* 67 directly. Another important contributor is the ion at *m/e* 54 whose occurrence might be explained by α cleavage followed by loss of ethylene and carbon monoxide.

Spiro[5.6]dodecan-7-one (**7**) (Figure 7) shows a moderately intense fragment ion at *m/e* 162 (loss of H_2O). The loss of H_2O is found to a smaller extent in the mass spectra of **1** and **2** and is extremely weak or absent in the other ketones presented here. Moreover, the (M − 18) fragmentation is much stronger in the mass spectrum of **7** than that of cycloheptanone.[6] The fragment ion at *m/e* 96 might arise by loss of five carbons of the ketone ring, including the carbonyl group, in a manner akin to the formation of *m/e* 68 from **8** (see Scheme IV). Subsequent losses of hydrogen atoms would lead to *m/e* 95 and 94.

Spiro Olefins.—The mass spectra of spiro olefins exhibited a behavior typical of cyclic alkenes.[7] Two general types of spiro olefins were studied and included olefins containing an exocyclic methylene group and those containing an endocyclic double bond. The *exo*-methylene olefins were prepared in a Wittig reaction from the corresponding ketones and the methylene triphenylphosphine.[8] The endocyclic olefins were prepared by decomposition of the tosylhydrazones of the corresponding ketones with methyllithium.[9] Where the carbon–carbon double bond is in a five-membered ring, as in spiro[4.4]non-1-ene (**11**) and spiro[4.5]dec-1-ene (**12**), the mass spectra are relatively uncomplicated by large numbers of fragmentation peaks (see Figures 11 and 12). The origin of the major fragment peaks, *m/e* 93, 80, and 79, is interpreted in Scheme VI, which also accounts for the homologous fragment ions (*m/e* 107, 94, and 93) in the mass spectra (see Figures 13 and 14) of spiro[4.5]dec-6-ene (**13**) and spiro[5.5]undec-1-ene (**14**). Thus, initial allylic cleavage followed by a second carbon–carbon cleavage, route a, yields *m/e* 80 (or 94), whereas the alternative second step involving a hydrogen transfer, route b, yields

(6) R. T. Aplin, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 3180 (1965).
(7) See ref 2, Chapter 1.
(8) R. Greenwald, M. Chaykowsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).
(9) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Amer. Chem. Soc.*, **90**, 4762 (1968).

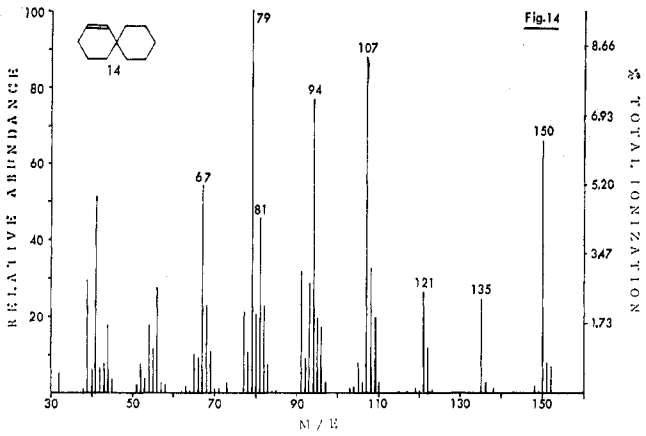


Figure 14.—Mass spectrum of spiro[5.5]undec-1-ene, 70 eV.

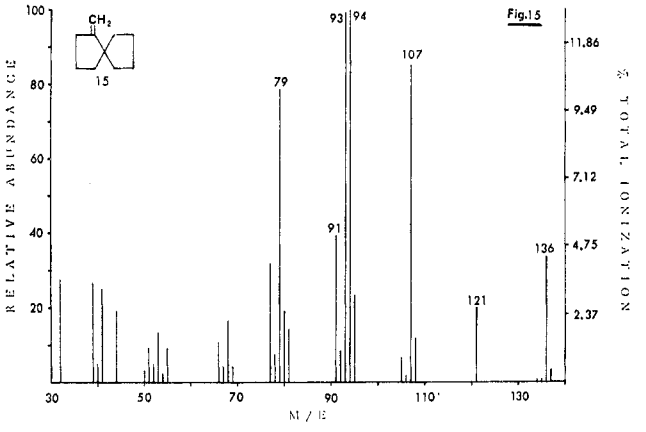
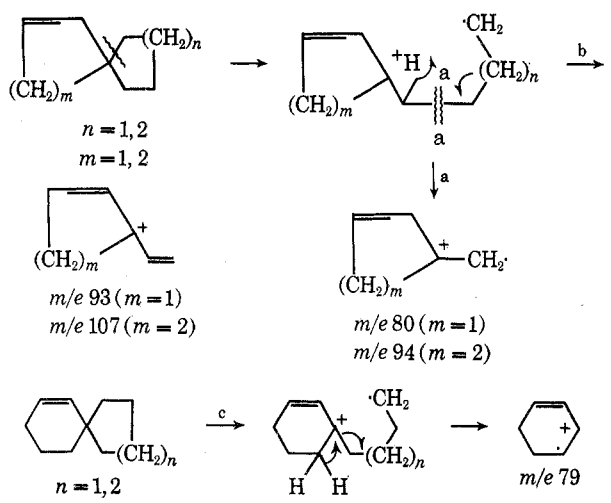


Figure 15.—Mass spectrum of 1-methylenospiro[4.4]nonane, 70 eV.

SCHEME VI



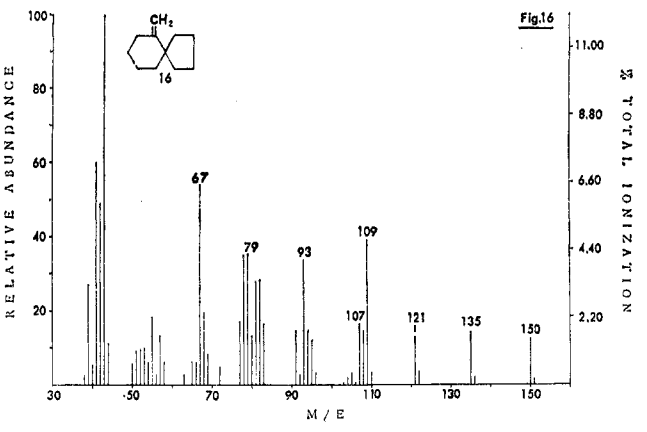


Figure 16.—Mass spectrum of 6-methylenopsiro[4.5]decane, 70 eV.

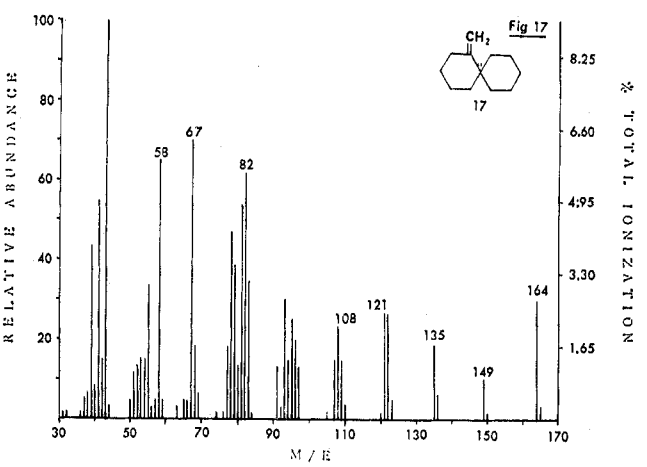


Figure 17.—Mass spectrum of 1-methylenospiro[5.5]undecane, 70 eV.

m/e 93 (or 107). The fragment ions m/e 80 and 94 mentioned above may lose a hydrogen atom to give observed ions at m/e 79 and 93, respectively. The large m/e 79 peak in the cyclohexene spectra (Figures 13 and 14) may be accounted for by route c of Scheme VI. Both cyclohexene derivatives show very weak retro-Diels–Alder fragment ions at m/e 108 (from **13**) and 122 (from **14**).

The *exo*-methylene spiro olefins (**15–17**) display fragment peaks (see Figures 15–17) at similar m/e to the endocyclic olefins (Figures 11–14). The higher mass fragment peaks in the spectra of the exocyclic olefins appear to arise by the loss of a series of alkyl radicals, such as $\cdot CH_3$, $\cdot CH_2CH_3$, $\cdot CH_2CH_2CH_3$, etc. The origin of these alkyl fragments is not well defined and can be postulated to originate from either ring. However, as shown in Scheme VI, one of the most favorable cleavages would be allylic bond breaking at the spiro center. This cleavage could be followed by a hydrogen abstraction from one of several sites and further decomposition would result in ions corresponding to the loss of alkyl radicals. The same general mechanisms shown in Scheme VI might apply also with the exocyclic olefins, and in fact leads to the observed major fragment ions in the high mass region.

In summary, the π-electron groups in both the spiro ketones and spiro olefins serve to direct fragmentation. The ketone fragmentations are unusual, and in one instance a seven-membered cyclic transition state is implicated for hydrogen transfer.

Experimental Section[10]

Synthesis of the Spiro Ketones.—Spiro[2.4]heptan-4-one (**9**), bp 79–81° (50 mm) [lit.[11] 54–55° (14 mm), 160° (760 mm)], was

(10) All gas chromatographic sample purity checks were performed on a Carle Instruments basic gas chromatograph using a 5 ft, 1/8 in. diameter SE-30 column (10% on Chromosorb W). Nmr spectra were measured using a Varian A-60 instrument. All mass spectra were measured on an AEI MS-9 mass spectrometer by Miss E. Irwin. The inlet system and source temperatures were maintained at 180–200°. The ionizing energy was 70 eV and the ionizing current was 100 μA.

prepared in 34% yield from 2-(β-bromoethyl)cyclopentanone by the procedure described by Mayer and Schubert.[11] Spiro[3.4]-octan-5-one (**8**), bp 59–61° (12 mm) [lit.[12] 67–69° (18 mm)], was prepared in 23% yield from 2-(γ-bromopropyl)cyclopentanone, and spiro[4.5] decan-1-one (**3**), bp 120–130° (12 mm) [lit.[12] 105–106° (3 mm)], was prepared in 73% yield from 2-(ω-bromopentyl)cyclopentanone by the method of Mayer, Wenschuh, and Töpelmann.[12] Spiro[4.4]nonan-1-one (**4**), bp 96–97° (25 mm) [lit.[13] 90° (22 mm)], was prepared in 55% yield by the alkylation of 1-piperidone-1-cyclopentene with 1,4-dibromobutane by the method of Krieger, Ruotsalainen, and Montin.[13] Spiro[4.5]-decan-6-one (**2**), bp 94–99° (12 mm) [lit.[14] 120° (45 mm)], was prepared by the rearrangement of 1,1′-dihydroxybicyclopentyl in 57% yield by the method of Zelinski and Elagina.[14] Spiro-[5.5]undecan-1-one (**1**), bp 58–63° (0.3 mm) [lit.[15] 130–132° (25 mm)], was prepared by the alkylation of cyclohexanone with 1,5-dibromopentane in the presence of potassium *tert*-butoxide in 53% yield, and spiro[5.6]dodecan-7-one (**7**), bp 121–122° (12 mm) [lit.[15] 133–135° (18 mm)], was prepared in 50% yield by the rearrangement of 1,1′-dihydroxybicyclohexyl as described by Cristol, Jacquier, and Mousseron.[15] Spiro[4.4]nona-1,6-dione (**10**) was previously prepared by Cram and Steinberg.[16] The deuterated ketones were prepared as follows.

7,7-Dideuteriospiro[4.5]decan-6-one (**5**).—To a mixture of 10 ml of D_2O and 1.2 g of sodium methoxide was added 1.50 g (0.010 mol) of spiro[4.5]decan-6-one (**2**). The mixture was refluxed 3 hr and then cooled and extracted three times with ether. The ether extracts were combined, washed with D_2O, dried, and filtered. The ether was removed by distillation through a 6 in. Vigreux column and the residual ketone was treated as described four more times. Distillation of the product afforded 0.71 g (46% yield) of a colorless liquid which showed no α hydrogens in the nmr and was found to be 95% dideuterated and about 5% monodeuterated by mass spectrometric analysis.

2,2-Dideuteriospiro[4.4]nonan-1-one (**6**).—The deuteration of 2.40 g (0.0174 mol) of spiro[4.4]nonan-1-one (**4**) was accomplished by mixing the ketone with 10 ml of dioxane and 2.0 g of sodium methoxide and refluxing the mixture for 3 hr. The reaction mixture was cooled and extracted three times with ether. The ether extracts were combined and washed once with D_2O, dried with magnesium sulfate, and filtered, and the ether was removed by distillation through a 6 in. Vigreux column. This process was repeated three more times on the residual ketone. The deuterated ketone was vacuum distilled to give 0.907 g (37% yield) of product which showed no α hydrogen in the nmr spectrum and was found to be 88% dideuterated, 12% monodeuterated, and less than 1% nondeuterated by mass spectrometric analysis.

(11) R. Mayer and H. J. Schubert, *Chem. Ber.*, **91**, 768 (1958).
(12) R. Mayer, G. Wenschuh, and W. Töpelmann, *ibid.*, **91**, 1616 (1958).
(13) H. Krieger, H. Ruotsalainen, and J. Montin, *ibid.*, **99**, 3715 (1966).
(14) N. D. Zelinski and H. V. Elagina, *C. R. Acad. Sci., URSS*, **49**, 568 (1945); *Chem. Abstr.*, **40**, 6058 (1946).
(15) H. Cristol, R. Jacquier, and M. Mousseron, *Bull. Chim. Soc. Fr.*, 346 (1957).
(16) D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, **76**, 2753 (1954).

Synthesis of the Endocyclic Spiro Olefins.—These olefins were prepared by decomposing the tosylhydrazones of the corresponding spiro ketones by the method of Dauben, *et al.*[8] The olefins prepared in this manner were found to have identical physical properties with those prepared by Krapcho and Donn.[17] Those prepared for this study were spiro[4.4]non-1-ene (**11**), bp 139–143° (760 mm) (lit.[17] bath temperature 140°), spiro[4.5]dec-1-ene (**12**), bath temperature 200° [lit.[17] bp 177° (740 mm)], spiro[4.5]-dec-6-ene (**13**), bp 178–179° (760 mm) [lit.[17] bp 181° (740 mm)], and spiro[5.5]undec-1-ene (**14**), bath temperature 210° [lit.[17] bp 205–207° (740 mm)].

Synthesis of the *exo*-Methylene Spiro Olefins.—These olefins were prepared from the corresponding spiro ketones by the Corey modification[7] of the Wittig reaction.[18] A typical preparation follows.

6-Methylenospiro[4.5]decane (**16**).—To 25 ml of dry dimethyl sulfoxide (DMSO) was added 1.5 g of sodium hydride followed by 8.0 (0.0225 mol) of methyltripenylphosphonium bromide. This mixture was stirred at 50–55° for 1 hr before 3.04 g (0.020 mol) of spiro[4.5]decan-6-one (**2**) was added as a solution in 20 ml of DMSO. After the mixture had stirred at 55° overnight, it was added to 50 ml of water and extracted four times with pentane. The pentane extracts were combined, washed with 1:1 DMSO–water and saturated NaCl solution, and then dried and filtered. The pentane was removed by distillation. The residue was distilled in a Hickman distillation apparatus at a bath temperature of 200° to give 1.08 g (36% yield) of colorless liquid: infrared (neat, NaCl plates) 3.6 μ (s), 6.2 (m), and 7.0 (s); nmr (CCl_4 solution) δ 4.60 (singlet, olefinic protons), 2.16 (broad singlet, allylic protons), and 1.7–1.4 (broad multiplet, aliphatic protons) in the ratio 1:1:7. The vpc analysis on a 5 ft SE-30 column showed only one component.

Also prepared by this procedure were 1-methylenospiro[4.4]-nonane (**15**) [bp 162–165° (760 nm)] and 1-methylenospiro[5.5]-undecane (**17**) (bath temperature 250°).

Registry No.—**1**, 1781-83-5; **2**, 13388-94-8; **3**, 4728-91-0; **4**, 14727-58-3; **5**, 27723-38-2; **6**, 27723-39-3; **7**, 4728-90-9; **8**, 10468-36-7; **9**, 5771-32-4; **10**, 27723-43-9; **11**, 873-12-1; **12**, 697-27-8; **13**, 697-28-9; **14**, 699-56-9; **15**, 19144-06-0; **16**, 19144-01-5; **17**, 27723-50-8.

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(17) A. P. Krapcho and R. Donn, *J. Org. Chem.*, **30**, 641 (1965).
(18) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).