Nuclear Magnetic Resonance and Mass Spectra of Bicyclo[2.2.2]oct-2-ene Derivatives

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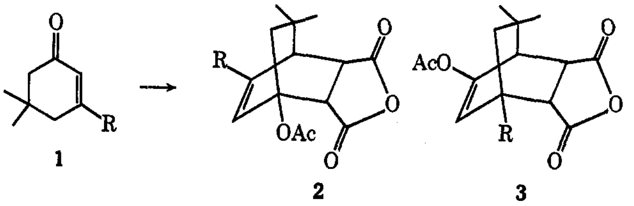
The allylic coupling constants ($J_{2,4}$) in 3-substituted bicyclo[2.2.2]oct-2-enes varies with the nature of the 3 substituent. Substituents capable of electron donation by resonance, as indicated by substituent constant such as σ_R^p, lead to larger coupling constants than those capable of electron withdrawal. The fragmentation of bicyclo[2.2.2]oct-2-ene derivatives on electron impact is dominated by a reverse Diels–Alder reaction with expulsion of an olefin and generation of a cyclohexadienyl radical cation. Enol acetates and bridgehead acetates undergo rearrangement with loss of ketene and transfer of hydrogen. This type of rearrangement occurs more readily than reverse Diels–Alder reactions and directs the fragmentation of members of this particular series.

Our recent observation[2] of the apparent variation of the magnitude of allylic coupling with the 3 substituent in the bicyclo[2.2.2]oct-2-ene system led us to prepare a series of these materials for spectroscopic examination. At this time we would like to discuss the mass spectral fragmentation patterns as well as the allylic coupling exhibited by these substances.

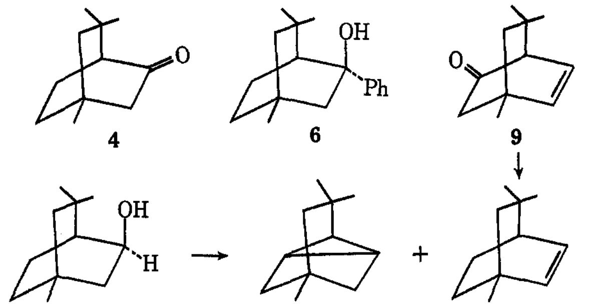
Synthesis.—Having demonstrated[2] the facile conversion of isophorone (**1a**) with maleic anhydride and isopropenyl acetate to the easily separable mixture of adducts **2a** and **3a**, we envisioned preparing a series of 3-(para-substituted phenyl) derivatives of **2a** *via* analogous reactions. The observation[3] that treatment of acetophenone and acetone with base gave **1b** provided a simple, direct route to the required derivatives of **1**. Reaction of acetophenone and mesityl oxide[4] with sodium hydride in dimethylformamide gave **1b** in 18.5% yield. Similar reaction of *p*-methoxyacetophenone gave **1c** (11%), while *p*-nitroacetophenone gave only a brown intractable solid. Nitration of **1a** gave the desired **1d** in 38% yield. Treatment of ketones **1b** and **1c** with maleic anhydride in isopropenyl acetate gave, in each case, a mixture of adducts separable by crystallization. Similar treatment of **1d** gave only the enol acetate **3d**. The olefinic protons of adducts **2b** and **2c**, as well as those of the corresponding dimethyl esters, appeared as broadened singlets precluding a direct measurement of the coupling constant.



1 **2** **3**

a, R = CH_3
b, R = C_6H_5
c, R = p-$CH_3OC_6H_4$
d, R = p-$NO_2C_6H_4$

Having earlier prepared ketone **4** from isophorone,[2] we decided to examine some of its tranformation products. Enamine **5a**, enol acetate **5b**, and vinyl chloride **5c** were prepared by standard methods.[5,6] The lithium reagent derived from chloride **5c** gave iodide **5d** and carboxylic acid **5g** when treated with iodine and carbon dioxide, respectively. Reaction of this lithium reagent with acetaldehyde, followed by Jones oxidation, gave unsaturated ketone **5f**. Acid **5g** gave the methyl ester **5h** when treated with diazomethane. Treatment of ketone **4** with phenyllithium gave alcohol **6** which was dehydrated to olefin **5e** with phosphorus oxychloride in pyridine. Interestingly, dehydration of the secondary alcohol **7** (prepared by sodium borohydride reduction of **4**) under similar conditions gave rise to a 9:1 mixture of tricyclic hydrocarbon **8** and the desired olefin **5i**. A pure sample of **5i** was obtained by Wolff–Kishner reduction of ketone **9**.[2]



4 **6** **9** **7** **8** **5i**

Allylic Coupling.—The values for the allylic coupling constants ($J_{2,4}$) and the chemical shifts of the olefinic protons of olefins **5a–i** are collected in Table I. It is apparent that increased electron density at the double bond, as evidenced by the chemical shift of the olefinic proton, leads to large coupling constants; electron withdrawal results in smaller coupling. Substituent constants such as σ_R^p and σ_R^m, which emphasize the resonance component of substituent effects, predict this trend; the *R* value of Swain and Lupton,[7] however, does not correlate this data as well indicating that the field effect cannot be neglected.

Since these coupling constants are positive,[2,8,9] they should be dominated by σ-bond contributions[10] and can be regarded as occurring through a modified "W" conformation. It is apparent that such coupling, at least when mediated by a double bond, is sensitive to substituent effects.

Mass Spectra.—We have examined the mass spectra of the materials just described as well as others which were available from earlier work in this laboratory.[2] Impetus for this study was provided by the number and

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[1] Hercules, Inc., Fellow, 1967–1968.

[2] C. M. Cimarusti and J. Wolinsky, *J. Amer. Chem. Soc.*, **90**, 113 (1968).

[3] J. Wolinsky and H. Hauer, unpublished observation.

[4] A reasonable mechanism for the formation of **1b** from acetone and acetophenone involves Michael addition of acetophenone to mesityl oxide (formed *in situ* from acetone) followed by intramolecular aldol condensation.

[5] W. A. White and H. Weingarten, *J. Org. Chem.*, **32**, 213 (1967).

[6] (a) R. Villotti, H. J. Ringold, and C. Djerassi, *J. Amer. Chem. Soc.*, **82**, 5693 (1960); (b) R. N. McDonald and T. E. Tabor, *ibid.*, **89**, 6573 (1967).

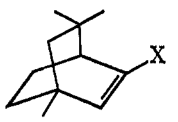
[7] C. G. Swain and E. C. Lupton, Jr., *ibid.*, **90**, 4328 (1968).

[8] R. G. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963).

[9] E. W. Garbisch, Jr., *Chem. Ind. (London)*, 1715 (1964).

[10] M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

TABLE I
NMR SPECTRA OF 3-SUBSTITUTED
1,8,8-TRIMETHYLBICYCLO[2.2.2]OCT-2-ENE DERIVATIVES



No. 5	X	$J_{2,4}$, Hz[a]	δ, ppm[b]	$\sigma_R{}^p$ [c]
a	$(CH_3)_2N-$	1.90	4.74	−0.76[d]
b	AcO−	1.85	5.29	−0.09
c	Cl−	1.75	5.72	−0.24
d	I−	1.63	6.32	−0.11
e	C_6H_5-	*Ca.* 1.4[e]	5.99	−0.09[f]
f	$CH_3\overset{O}{\overset{\|}{C}}-$	1.40	6.73	+0.15
g	HO_2C-	1.30	7.13	
h	CH_3O_2C-	1.30	6.83	+0.11[g]
i	H−		5.93	

[a] All coupling constants were measured at a sweep width of 50 Hz and are the average of several determinations. [b] Measured in CCl_4 except **5g** which was examined in $CDCl_3$ for solubility considerations. [c] Values from L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, p 421. [d] Value for $-NH_2$. [e] Broadening of this signal, although not so extensive as observed for **2b** and **2c**, rendered the measurement very difficult. [f] Value from R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 595. [g] Value for $-CO_2Et$.

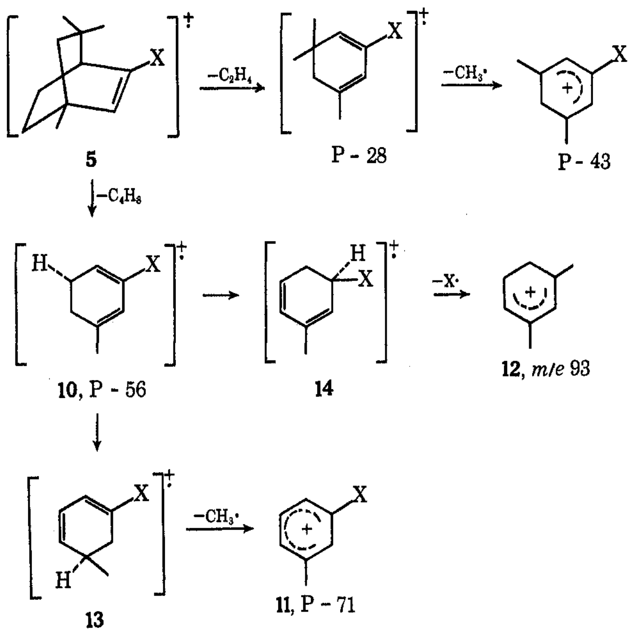
variety of functional groups present in these compounds. It was of interest to determine whether such diverse materials could be accommodated by a general fragmentation scheme for bicyclo[2.2.2]oct-2-ene derivatives.

Certain trends are evident from inspection of the principal ions in the spectra of 3-substituted 1,8,8-trimethylbicyclo[2.2.2]oct-2-enes (**5c–i**) collected in Table II. The fragmentation is dominated by a reverse Diels–Alder reaction proceeding from the initially formed radical cation **5** (Scheme I). Loss of isobutylene to give a P − 56 ion, **10**, is prominent in all cases except the enol acetate **5b**. An alternate, but less significant, pathway involves the loss of ethylene to give a P − 28 radical cation which then loses a methyl radical affording a P − 43 cation. This type of fragmentation is documented by appropriate metastable ions in the spectra of compounds **5i**, **5c**, and **5e**.

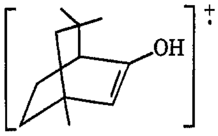
The remaining important ions can be accounted for by the fragmentation pattern shown in Scheme I. The radical cation **10**, through ejection of a methyl radical or the substituent X, gives rise to cations **11** (P − 71) and **12** (*m/e* 93), respectively. Metastable ions corresponding to one or both of these processes are shown by most of the compounds in this series; for example, vinyl chloride **5c** exhibits metastable peaks at *m/e* 99.8 (**10** → **11**) and *m/e* 67.6 (**10** → **12**). A reasonable pathway for the fragmentation of **10** visualizes 1,5-hydrogen shifts[11] to give radical cations **13** and **14** followed by loss of methyl or X radicals to produce the cyclohexadienyl cations **11** or **12**.

It is apparent that the fragmentation of enol acetate **5b** does not fit Scheme I. The absence of significant ions at P − 56, P − 71, and *m/e* 93 attest to this fact.

SCHEME I



Enol acetate **5b** first loses ketene with transfer of a hydrogen atom to afford radical cation **16**. Further



16

fragmentation of enol **16** then proceeds in a manner analogous to that of the other bicyclooctene derivatives.

The possibility of transfer of hydrogen *via* a four-membered transition state finds analogy in the rearrangements of benzyl and furfuryl acetates on electron impact.[12] Transfer of hydrogen to carbon *via* a six-membered transition state does not appear to compete favorably, since certain of the major ions produced in the fragmentation of 1,5,5-trimethylbicyclo[2.2.2]-octan-3-one (**4**), *m/e* 151 (34), 112 (41.6), 107 (68.2), 82 (56.2), 81 (52), 69 (64), 67 (89), and 55 (100), are not found to any appreciable extent in the mass spectrum of enol acetate **5b**, and the *m/e* 138 ion of **5b** is not an important ion in the mass spectrum of **4**.

We turn next to a consideration of the principal ions in the mass spectra of enol acetate anhydrides **3a–e** collected in Table III. Inspection of this information supports the conclusion that the enol acetate moiety directs the fragmentation pattern, just as it did for enol acetate **5b**, by transfering a hydrogen atom and losing ketene to give radical cation **17** as shown in Scheme II. Compounds **3a–d** exhibit metastable peaks which document the loss of 42 mass units from the parent ion. Compounds **3a** and **3b** also display metastable peaks for loss of 98 mass units from the parent ion, indicating a competing cleavage of maleic anhydride by a reverse Diels–Alder reaction, or the loss of ketene and isobutylene. A high-resolution study of the *m/e* 242 ion produced from compound **3b** demonstrated that the loss of maleic anhydride occurred with twice the frequency of the loss of ketene and isobutylene.

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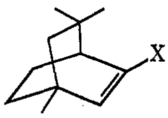
[11] *Cf.* J. Wolinsky, B. Chollar, and M. Baird, *J. Amer. Chem. Soc.*, **84**, 2275 (1962), and references cited therein.

[12] K. Biemann, "Mass Spectroscopy," McGraw-Hill, New York, N. Y., 1962, p 111.

TABLE II

PRINCIPAL PEAKS IN THE MASS SPECTRA OF 3-SUBSTITUTED 1,8,8-TRIMETHYLBICYCLO[2.2.2]OCT-2-ENES (**5b–i**)

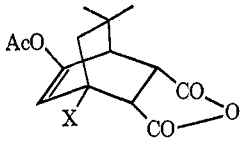


	X =							
Peak	$-OCOCH_3$ (**5b**)[a]	Cl (**5c**)	I (**5d**)	C_6H_5 (**5e**)	$-COCH_3$ (**5f**)	CO_2H (**5g**)	CO_2Me (**5h**)	H (**5i**)
Parent	4.7	9.2	14.4	24.6	11.5	3.1	2.4	1.38
P − 28	5.7	12.6	7.2	27.6	2.4	1.9	1.8	2.85
P − 43	1.4	37.2	6.9	96.7	17.4	3.8	3.8	18.8
P − 56	8.8	100.0	62.8	100.0	89.0	100.0	100.0	100.0
P − 71	0.5	13.0	17.6	57.0	65.3	19.7	14.3	62.2
P − X	0.5	4.5	20.0	0.1	17.4	1.1	2.4	0.23
m/e 93	4.6	80.4	100.0	4.0	50.8	98.0	76.0	13.1
m/e 91	8.7	27.2	62.7	26.0	38.6	18.6	36.7	22.5
m/e 79	10.5	7.0	44.3	5.0	12.2	48.3	10.4	12.2
m/e 77	10.8	23.6	41.6	20.8	32.1	53.0	29.0	32.1
m/e 43	4.2	4.0	32.7	11.0	100.0	55.2	23.8	2.4
m/e 41	75.7	18.7	4.9	37.9	32.4	11.3	4.5	20.8
m/e 39	24.3	18.4	32.7	20.6	27.0	44.3	17.7	24.8

[a] Principal ions at *m/e* 166 (20.2%, P − 42), 138 (21.6%, P − 70), 110 (100%, P − 98), 95 (22.2%, P − 113).

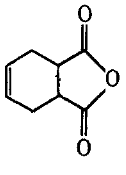
TABLE III

RELATIVE ABUNDANCE OF PRINCIPAL PEAKS IN THE MASS SPECTRA OF 1-SUBSTITUTED 3-ACETOXY-8,8-DIMETHYLBICYCLO[2.2.2]OCT-2-ENE-5,6-DICARBOXYLIC ANHYDRIDES (**3a–e**)



	X =				
Peak	CH_3 (**3a**), %	C_6H_5 (**3b**), %	*p*-MeO-C_6H_4 (**3c**), %	*p*-NO_2-C_6H_4 (**3d**), %	AcO– (**3e**), %
Parent	10.3	12.3	19	4.0	6.1
P − 28	8.3	7.3	4.1	2.4	17.0
P − 42	28.3	22.4	22.0	35.8	13.5
P − 70	24.0	13.5	5.0	9.9	23.0
P − 98	12.7	50.0	75.0	17.6	0.17
P − 140	32.0	28.6	20.0	14.8	68.5
P − 155	69.0	90.9	96.0	42.3	4.0
P − 170	42.8	51.7	39.0	19.0	6.0
m/e 43	100	100	100	100	100

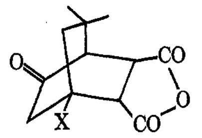
Scheme II suggests a general fragmentation pattern for radical cation **17**. Loss of isobutylene by a reverse Diels–Alder reaction followed by evolution of carbon monoxide and carbon dioxide to give a P − 170 ion **20** finds precedent in the observation that anhydride **21**[13] also loses carbon monoxide and carbon dioxide.



21

Alternatively, maleic anhydride is eliminated generating radical cation **18** which loses a methyl radical to give the P − 155 cation **19**.

The bridgehead acetate **3e** exhibits additional major ions representing loss of 84, 112, 157, 182, 197, and 212 mass units from the parent ion. The P − 84 ion apparently represents the loss of two molecules of ketene with the accompanying transfer of two hydrogen atoms to give radical cation **17** (X = OH). Most of the remaining ions are derived from radical cation **17** by the fragmentation modes already discussed. The P − 112 ion may represent loss of carbon monoxide from the anhydride group of radical cation **17**. The loss of 28 mass units from anhydride **21**[3] and anhydrides **22a** and **22b** have also been observed. The P − 157 ion may arise from ion **19** by loss of a hydrogen molecule.



22a, X = CH_3
b, X = OAc

Finally, the mass spectra of several bicyclo[2.2.2]oct-2-en-5-ones were examined (Table IV). The most abundant ion produced on electron impact of keto olefin **24** (see Scheme III) involves loss of ketene. Loss of ethylene from the parent ion **24** is negligible (less than 0.1%). On the other hand, loss of isobutylene from the radical cation derived from keto olefin **9** to give radical cation **25** competes favorably with loss of ketene forming **26**. Carbon monoxide is ejected from **25**, in a manner which is probably analogous to the loss of carbon monoxide from phenols,[14] to give a *m/e* 80 radical cation, which then loses a hydrogen atom to form a *m/e* 79 cation. The *m/e* 79 cation ejects a hydrogen molecule generating a *m/e* 77 cation.

The bridgehead acetates **27** and **28** lose ketene from the bridgehead acetate group and then exhibit essentially the same fragmentation pattern shown by compounds **24** and **9**. In addition, there is observed a significant loss of acetic acid from the parent radical cation, followed by ejection of a carbon monoxide molecule. This observation suggests that the frag-

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[13] S. T. Weininger, V. T. Mai, and E. R. Thornton, *J. Amer. Chem. Soc.*, **86**, 3732 (1964).

[14] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra," Holden-Day, San Francisco, Calif., 1964, pp 20, 21.

SCHEME II

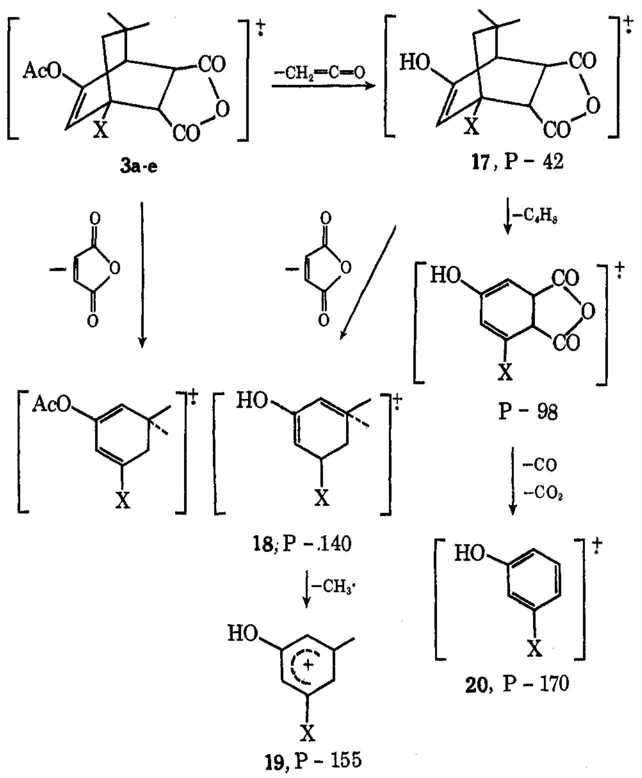
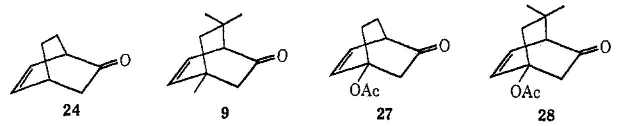


TABLE IV

PRINCIPAL IONS IN THE MASS SPECTRA OF BICYCLO[2.2.2]OCT-2-EN-3-ONES



24		9		27		28	
m/e	% rel abundance	*m/e*	% rel abundance	*m/e*	% rel abundance	*m/e*	% rel abundance
122	14.6	164	10.2	180	0.8	208	0.7
80	100.0	122	63.2	120	27.4	148	39.1
79	63.3	108	24.4	110	5.4	133	15.8
78	8.2	107	100.0	97	7.2	124	45.1
77	44.6	91	29.7	96	100.0	120	32.4
51	7.8	80	27.1	95	24.2	119	26.8
39	21.0	79	21.7	93	7.0	110	23.9
		77	14.8	92	23	109	74.2
		43	13.0	91	30.8	105	29.2
				77	8.5	91	11.3
				43	72.6	82	10.5
				39	17.5	79	11.3
						77	11.3
						43	100
						41	14.1
						39	17.5

mentation of ketene from the bicylooctenone is at least in part a stepwise process generating radical cation **29** from which acetic acid can be eliminated to give radical cation **30**. Radical cation **30** then fragments as shown in Scheme IV.

In summary, the fragmentation of bicyclo[2.2.2]oct-2-ene derivatives on electron impact is dominated by reverse Diels–Alder reactions with expulsion of olefins such as ketene, maleic anhydride, isobutylene, and ethylene (to a much less significant extent). Loss of radicals from the odd-electron ions which are produced gives relatively stable cyclohexadienyl cations.

Enol acetates and bridgehead acetates have been found to undergo rearrangement with loss of ketene and transfer of hydrogen to oxygen *via* a four-membered transition state. Such rearrangements generally occur more readily than reverse Diels–Alder reactions and tend to direct the fragmentation of derivatives in this series.

Experimental Section[15]

3-Phenyl-5,5-dimethyl-2-cyclohexen-1-one (1b).—The mineral oil was removed from 23.05 g (0.5 mol) of 53.4% sodium hydride dispersion and 200 ml of dimethylformamide (DMF) was added under nitrogen. A solution of 60 g (0.5 mol) of acetophenone in 60 ml of DMF was added over 8 hr and the mixture stirred overnight. A solution of 49 g (0.5 mol) of mesityl oxide in 40 ml of DMF was added and the mixture stirred at 95–100° for 23 hr, cooled, and poured into a mixture of ice and 175 ml of concentrated hydrochloric acid. Ether extraction gave an oil which was distilled *in vacuo* to give 24 g (40%) of recovered acetophenone and a fraction (18.3 g) with bp 121–155° (1 mm). Two crystallizations from pentane gave 11.1 g (18.5%) of **1b**, mp 54–55° (lit.[16] mp 53.8–54.8°).

3-*p*-Methoxyphenyl-5,5-dimethyl-2-cyclohexen-1-one (1c).—A mixture, prepared as described above, from 16.5 g (0.33 mol) of sodium hydride dispersion, 50 g (0.33 mol) of *p*-methoxyacetophenone, 32 g (0.33 mol) of mesityl oxide, and 220 ml of DMF was stirred for 16 hr and processed as above. The resulting oil (72 g) exhibited hydroxyl absorption in the infrared. A 57-g sample was refluxed for 4 hr with 300 mg of *p*-toluenesulfonic acid in 200 ml of benzene and then distilled to give 23 g (46%) of recovered *p*-methoxyacetophenone and 15.6 g, bp 131–168° (0.3 mm). Two crystallizations from 10% ether in pentane gave 7.1 g (11.6%) of **1c**: mp 49.5–50.5°; ir (CCl_4) 6.0 and 6.2 μ; nmr (CCl_4) 1.3 (s, 6), 6.41 (m, 1), and 6.96 and 7.57 ppm (A_2B_2 q, J = 9 Hz, 4).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.07; H, 8.02.

3-*p*-Nitrophenyl-5,5-dimethyl-2-cyclohexen-1-one (1d).—A 8.7-g (0.0435 mol) sample of **1b** was added over 4 min to 35 ml of concentrated sulfuric acid at −15° under nitrogen. A mixture of 7 ml of sulfuric acid and 8.9 ml of nitric acid was added over 3 min and after a further 10 min the solution was poured into a mixture of ice and ether. The ether was washed with 10% sodium bicarbonate, dried, and evaporated to give an oily solid. Several recrystallizations from hexane–ethyl acetate gave 14.1 g (38.3%) of **1d**: mp 134.5–135°; ir ($CHCl_3$) 5.95 and 6.15 μ; nmr ($CDCl_3$) 1.17 (s, 6), 6.57 (m, 1), and 7.84 and 8.25 ppm (A_2B_2 q, J = 9 Hz, 4).

Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16. Found: C, 68.63; H, 6.41.

1-Phenyl-3-acetoxy-8,8-dimethylbicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (3b).[17]—A solution of 7.0 g (0.035 mol) of **1b**, 5.0 g of maleic anhydride, and 50 mg of *p*-toluenesulfonic acid in 26 ml of isopropenyl acetate was refluxed for 66 hr, cooled, and diluted with 25 ml of ether. The resulting solid (10.7 g, 90.6%) was fractionally recrystallized from hexane–ethyl acetate. The less soluble fractions were combined and recrystallized several times to give **3b**: mp 176–177°; ir (Nujol) 5.35, 5.55, 5.70, and 6.05 μ; nmr ($CDCl_3$) 1.07, 1.19, and 2.19 (s, 3 each), 1.35 and 1.72 (AB q, J = 14 Hz, 2), 2.80 (m, 1), 3.69 (m, 2), 6.54 (d, J = 2 Hz, 1), 7.55 ppm (m, 5).

Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.69; H, 6.14.

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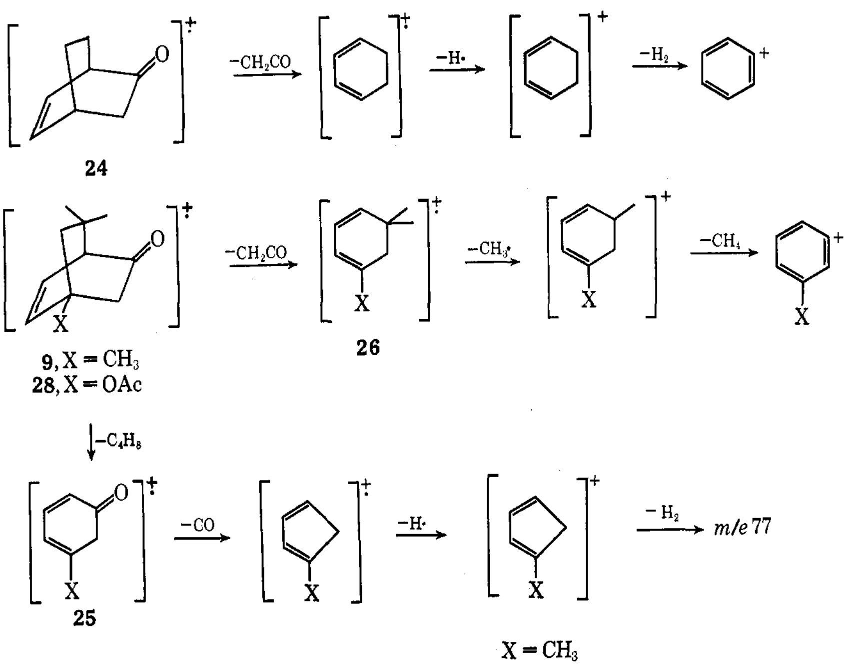
[15] All boiling points and melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer, Model 137-B. Nuclear magnetic resonance spectra were determined at 60 Mc on Varian Associates A-60 and A-60A spectrometers. Chemical shifts are recorded in parts per million with reference to tetramethylsilane as internal standard. Mass spectra were recorded on a Hitachi RMU-6A instrument by the Purdue University Spectral Service Department. Microanalyses were performed by Dr. C. S. Yeh and associates. Gas–liquid chromatography was performed mainly on an Aerograph 90-P instrument (column A: 5-ft 20% SE-30 on Chromosorb; column B: 9-ft 30% β,β'-oxydipropionitrile on Chromosorb).

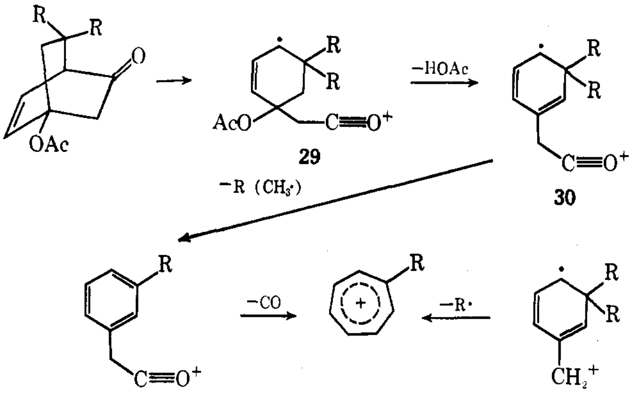
[16] M. Beringer and I. Kuntz, *J. Amer. Chem. Soc.*, **73**, 364 (1951).

[17] The styrene derivatives **2b**, **2c**, and **2d** were distinguished from the isomeric enol acetates **3b** and **3c** by their infrared spectra and by the paramagnetic shift of the C-6 methine caused by the proximity of the C-1 acetoxy group.

SCHEME III



SCHEME IV



1-Acetoxy-3-phenyl-8,8-dimethylbicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (2b).—The more soluble fractions from the reaction of **1b** with maleic anhydride were recrystallized several times to give **2b**: mp 169–169.5°; ir (Nujol) 5.4, 5.6, 5.75, and 6.2 μ; nmr ($CDCl_3$) 0.94, 1.26, and 2.22 (s, 3 each), 1.57 and 2.37 (AB q, J = 12 Hz, 2), 3.33 (m, 1), 3.75 (d of d, $J_{5,6}$ = 9 Hz, $J_{4,5}$ = 3.5 Hz, 1) 4.48 (d, J = 9 Hz, 1), 6.57 (m, 1), and 7.53 ppm (m, 5).

1-(*p*-Methoxyphenyl)-3-acetoxy-8,8-dimethylbicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (3c).—From 6.0 g (0.027 mol) of **1c** was obtained 9.73 g (*ca.* 100%) of crude adduct by treatment with maleic anhydride and isopropenyl acetate. Fractional crystallization from hexane–ethyl acetate gave, as the least soluble component, **3c**: mp 169–169.5°; ir (Nujol) 5.35, 5.6, and 6.05 μ; nmr ($CDCl_3$) 1.03, 1.17, 2.13 (s, 3 each), 6.32 (d, J = 2 Hz, 1), and 6.91 and 7.32 ppm (A_2B_2 q, 4, J = 9 Hz).

Anal. Calcd for $C_{21}H_{22}O_6$: C, 68.09; H, 5.99. Found: C, 67.97; H, 6.13.

1-Acetoxy-3-(*p*-methoxyphenyl)-8,8-dimethylbicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (2c).—The more soluble component from reaction of **1c** proved to be **2c**: mp 161–162.5°; ir (Nujol) 5.35, 5.6, 5.75, and 6.2 μ; nmr ($CDCl_3$) 0.90, 1.20, 2.15 (s, 3 each), 4.28 (d, 1, J = 9 Hz), 6.42 (m, 1), and 6.74 and 7.36 ppm (A_2B_2 q, 4, J = 9 Hz).

Anal. Calcd for $C_{21}H_{22}O_6$: C, 68.09; H, 5.99. Found: C, 68.09; H, 6.21.

1-(*p*-Nitrophenyl)-3-acetoxy-8,8-dimethylbicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride.—From 3.2 g (0.013 mol) of **1d** was obtained 2.85 g (63%) of crude adduct. Recrystallization from hexane–ethyl acetate gave only **3d**: mp 198–199°; ir (Nujol) 5.35, 5.5, 5.6, and 6.0 μ; nmr ($CDCl_3$) 1.07, 1.22, and 2.16 (s, 3 each), 6.35 (d, 1, J = 2 Hz), and 7.62 and 8.22 ppm (A_2B_2 q, 4, J = 9 Hz).

Anal. Calcd for $C_{20}H_{19}NO_7$: C, 62.49; H, 4.72. Found: C, 62.26; H, 5.05.

3-(*N*,*N*-Dimethylamino)-1,8,8-trimethylbicyclo[2.2.2]oct-2-ene (5a).—A solution of 0.52 g (0.0055 mol) of titanium tetrachloride in 10 ml of pentane was added to 0.88 g (0.005 mol) of **4** and 1.98 ml (0.03 mol) of dimethylamine in 30 ml of pentane at 0°. After 4 hr the mixture was filtered and the filtrate evaporated *in vacuo* to give an oil. Examination by glc (column A) showed two components in a 1:1 ratio. The first of these was unreacted **4** while the second proved to be the desired enamine. Preparative glc gave a sample of **5a** contaminated by *ca.* 20% of **4**: ir (CCl_4) 6.2 μ; nmr (CCl_4) 0.80 (s, 3), 1.01 and 2.51 (s, 6 each), and 4.28 ppm (d, 1, J = 1.90 Hz).

3-Acetoxy-1,8,8-trimethylbicyclo[2.2.2]oct-2-ene (5b).—A solution of 0.3 ml of **4** in 10 ml of isopropenyl acetate was refluxed with 30 mg of *p*-toluenesulfonic acid for 43 hr and distilled to leave a volume of *ca.* 3 ml. The residue was partitioned between ether and dilute sodium bicarbonate solution. Solvent removal gave an oil which contained one major component in addition to **4** and was purified by preparative glc: ir (film) 5.60, 6.0, and 14.6 μ; nmr (CCl_4) 0.87, 1.03, 1.08, and 2.02 (s, 3 each), and 5.31 ppm (d, 1, J = 1.85 Hz).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.55; H, 9.68.

3-Chloro-1,8,8-trimethylbicyclo[2.2.2]oct-2-ene (5c).—A solution of 1.50 g (0.009 mol) of **4** and 2.2 g (0.011 mol) of phosphorus pentachloride in 20 ml of dichloromethane was refluxed for 22 hr, cooled, and added dropwise to 100 ml of ice–water. The ether extract was washed with saturated sodium carbonate solution. Solvent removal followed by distillation gave 1.14 g (68.5%) of **5c**: bp 45–46° (0.3 mm); ir (film) 6.15 and 13.4 μ; nmr (CCl_4) 0.92, 1.03, and 1.06 (s, 3 each), and 5.72 ppm (d, 1, J = 1.75 Hz). The analytical sample was secured by glc collection.

Anal. Calcd for $C_{11}H_{17}Cl$: C, 71.53; H, 9.27. Found: C, 71.51; H, 9.51.

3-Iodo-1,8,8-trimethylbicyclo[2.2.2]oct-2-ene (5d).—A solution of 1.95 g (0.0105 mol) of chloride **5c** in 10 ml of ether was added to a slurry of 0.75 g (0.107 g-atom) of finely cut lithium wire (high sodium content) in 15 ml of ether. After refluxing for 1 hr, hydrolysis of an aliquot showed only olefin **5i** by glc; *ca.* one-third of this solution was added to a solution of 2.54 g (0.01 mol) of iodine in 10 ml of ether. After 30 min the solution was washed with 100 ml of 5% sodium bisulfite. Solvent removal gave 632 mg (*ca.* 60%) of an oil which showed one peak in addition to solvent on glc (column A). Preparative glc gave a pure sample of

5d: ir (film) 6.28 and 14.1 μ; nmr (CCl_4) 1.00 (s, 6), 1.05 (s, 3), and 6.23 ppm (d, 1, J = 1.63 Hz).

Anal. Calcd for $C_{11}H_{17}I$: C, 47.85; H, 6.20. Found: C, 47.87; H, 6.21.

3-Phenyl-1,8,8-trimethylbicyclo[2.2.2]oct-2-ene (5e).—From the reaction of 1.68 g (0.01 mol) of **4** and phenyllithium (prepared from 18.5 g (0.12 mol) of bromobenzene and 2.1 g (0.3 g-atom) of lithium there was isolated a crude product which was chromatographed over alumina. A total of 0.6 g of alcohol **6** was obtained which was contaminated with unreacted ketone **4**. This material was dissolved in 5 ml of pyridine at 0° and stirred with 0.7 ml of phosphorus oxychloride for 2 hr. This mixture was poured into ether and dilute hydrochloric acid. The ether layer was separated and evaporated to give 430 mg of oil which contained one major component in addition to *ca.* 10% of ketone **4**. Preparative glc gave a pure sample of **5e**: ir (film) 6.24, 6.71, and 6.9 μ; nmr (CCl_4) 0.92, 1.10, and 1.13 (s, 3 each), 5.99 (d, 1, J = 14 Hz), and 7.0–7.5 ppm (m, 5).

Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.10; H, 9.98.

3-Acetyl-1,8,8-trimethylbicyclo[2.2.2]oct-2-ene (5f).—A solution of 2.0 ml (large excess) of acetaldehyde in 10 ml of ether was added to a solution of lithium reagent prepared from 910 mg (5 mmol) of chloride **5c** and 0.7 g (0.1 g-atom) of lithium. After 10 min the solution was decanted from excess lithium and poured into water and ether. The ether solution was evaporated to give an oil which was dissolved in 10 ml of acetone and treated with 2 ml of Jones reagent. After processing in the usual manner 780 mg of oil was obtained which contained olefin **5i** and ketone **4** in addition to the desired **5f**. Preparative glc gave a sample of **5f**: ir (CCl_4) 5.95 and 6.2 μ; nmr (CCl_4) 0.64, 1.08, 1.17, and 2.19 (s, 3 each), and 6.73 ppm (d, 1, J = 1.40 Hz). The analytical sample was secured by preparative glc.

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.33; H, 10.18.

1,8,8-Trimethylbicyclo[2.2.2]oct-2-ene-3-carboxylic Acid (5g).—The remaining two-thirds of the solution of lithium reagent prepared above was added to a stirred slurry of *ca.* 30 g of powdered Dry Ice in 25 ml of ether. After 90 min the mixture was poured into 60 ml of water containing two potassium hydroxide pellets. The aqueous layer was separated, acidified carefully, saturated with salt, and extracted with ether. Solvent removal and recrystallization from pentane gave 838 mg (*ca.* 68%) of acid **5g**: mp 135–136°; ir ($CHCl_3$) 2.8–4.0 (broad), 5.92, and 6.15 μ; nmr ($CDCl_3$) 0.77, 1.07, and 1.15 (s, 3 each), and 7.13 ppm (d, 1, J = 1.30 Hz). Sublimation at 80° (0.1 mm) gave the analytical specimen, mp 135.5–136°.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.45; H, 9.20.

The corresponding methyl ester **5h** was prepared from 300 mg (1.54 mmol) of **5g** and excess ethereal diazomethane. Solvent removal gave 312 mg (97%) of an oil which was purified by preparative glc to give pure **5h**: ir (film) 5.80 and 6.15 μ; nmr (CCl_4) 0.73, 1.08, 1.13, and 3.65 (s, 3 each), and 6.83 ppm (d, 1, J = 1.30 Hz).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.00; H, 9.64.

1,8,8-Trimethylbicyclo[2.2.2]oct-2-ene (5i).—A mixture of 0.83 g (0.005 mol) of **9**,[2] 5 g of hydrazine hydrate, and 5 g of potassium hydroxide was refluxed for 90 min in 25 ml of diethylene glycol and then distilled until the internal temperature reached 190°. The solution was refluxed for 5 hr, cooled, diluted with water, and extracted with ether. Solvent removal gave 307 mg (36%) of oil which showed one peak on glc. Collection of this material gave pure **5i**: ir (film) 6.2 and 14.2 μ; nmr (CCl_4) 0.80, 1.01, and 1.03 (s, 3 each), 5.77 (d, 1, $J_{2,3}$ = 8.5 Hz), and 6.24 ppm (d of d, 1, $J_{2,3}$ = 8.5, $J_{3,4}$ = 6.5 Hz).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 88.16; H, 12.33.

exo-**1,8,8-Trimethylbicyclo[2.2.2]octan-3-ol (7).**[18]—An amount of 1.55 g (0.009 mol) of **4** was reduced with 0.8 g (0.02 mol) of sodium borohydride in 40 ml of cold methanol. After 2 hr the mixture was partitioned between ether and water to give an oil which crystallized from 10 ml of pentane to give 1.42 g (90.5%) of **7**: mp 55.5–56.5°; ir ($CDCl_3$) 2.7 and 2.9 μ; nmr (CCl_4) 0.80, 0.98, and 1.18 (s, 3 each), and 4.07 ppm (m, 1).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.71; H, 12.13.

1,8,8-Trimethyltricyclo[2.2.2.0^{3,5}]octane (8).—A solution of 400 mg (0.00024 mol) of **7** in 4 ml of pyridine was stirred for 3 hr with 0.25 ml of phosphorus oxychloride at ambient temperature and then partitioned between ether and dilute hydrochloric acid. Drying and solvent removal gave 280 mg of oil which showed one peak on glc (column A, 140°). Preparative glc gave a sample of **8** [nmr (CCl_4) 0.88 (s, 3), 1.01 (s, 6), and 0.32–2.15 ppm (m, *ca.* 9)], which also exhibited weak signals in the olefinic region corresponding to those of **5i** (*ca.* 15% by integration). Analytical glc (column B, 85°) indicated that this material contained *ca.* 10% of olefin **5i**. The analytical specimen was secured by preparative glpc: mass spectrum (70 eV) *m/e* (rel intensity) 150 (24), 135 (32), 107 (40), 95 (27), 94 (100), 93 (88), 91 (24), 81 (24), 80 (40), 79 (72), 77 (24), and 41 (32).

Anal. Calcd for $C_{11}H_{18}$: C, 87.95; H, 12.07. Found: C, 88.13; H, 12.34.

Registry No.—**1c**, 29339-44-4; **1d**, 29339-45-5; **2b**, 29339-46-6; **2c**, 29339-47-7; **3a**, 29339-48-8; **3b**, 29339-49-9; **3c**, 29339-50-2; **3d**, 39339-51-3; **3e**, 29453-56-3; **5a**, 29339-52-4; **5b**, 29339-53-5; **5c**, 29339-54-6; **5d**, 29339-55-7; **5e**, 29339-56-8; **5f**, 29339-57-9; **5g**, 29339-58-0; **5h**, 29339-59-1; **5i**, 29339-60-4; **7**, 29339-61-5; **8**, 29339-62-6; **9**, 17760-98-4; **24**, 2220-40-8; **27**, 17761-01-2; **28**, 17761-00-1.

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(18) The *exo*-hydroxyl group is indicated by the paramagnetic shift of 0.10 ppm for one of the *gem*-methyl groups. The reduction of camphor[19] is known to give a predominance (90%) of isoborneol. The *gem*-dimethyl group in **4** should hinder exo attack to a greater degree than in camphor, since it lies closer to the carbonyl groups.

(19) D. S. Noyce and D. B. Denney, *J. Amer. Chem. Soc.*, **72**, 5743 (1950).