Spectral Correlations for α,β-Unsaturated Ketones[1a]

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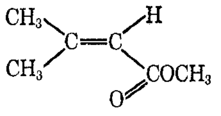
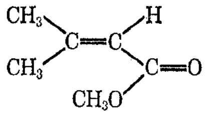
Received March 6, 1969

Preferred conformations of labile alkyl-substituted α,β-unsaturated ketones can be determined quite readily by analysis of nmr and infrared spectra. For the series of ketones studied, correlations of structure with conformation show that the (*S*)-*cis* conformation is favored for those ketones having an α hydrogen and two β-alkyl groups. For methyl ketones with α-methyl and *cis*-β-alkyl groups, steric crowding results in a preferred nonplanar (for C=C and C=O) conformation. For cases where the groups at R and R′ in **25** are as large as a combination of ethyl and methyl, the deviation from planarity is significant, and, where R‴ is also an alkyl group, the data suggest a preferred conformation having the C=O group at or near a 90° angle to the C=C. An attempt is made to approximate the extent of deviation.

It is reported[2] that the COMe group causes a nmr deshielding of the β-methyl group protons in mesityl oxide when they are in the *cis* position. This conclusion was reached on the basis of nmr investigations[3,4] of a series of *cis* and *trans* α,β-unsaturated carboxylic esters. For example, a chemical-shift difference of 0.28 ppm is observed for the two β-methyl groups in methyl β,β-dimethylacrylate. Since this deshielding effect is the average for the three equivalent conformations of the methyl group, it represents a significant shift. To account for a shift of this magnitude, it was suggested that the (*S*)-*cis* conformation (**1a**) is heavily populated. As opposed to the (*S*)-*trans* conformation (**1b**), the (*S*)-*cis* form permits a close approach of the affected protons to the magnetically anisotropic carbonyl group.

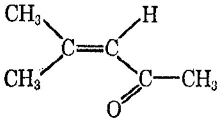


1a



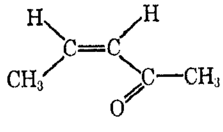
1b

That mesityl oxide (**2**) exists in the (*S*)-*cis* conformation was first demonstrated by dipole-moment measurements[5,6] and subsequently confirmed from infrared,[7,8] Raman,[9] and ultraviolet[5] spectrophotometry. Recently, Baldwin[10] has interpreted the nmr spectrum on the basis of the (*S*)-*cis* conformation. He compared the chemical shifts of the β-methyl groups of mesityl oxide with those of *cis*- (**3**) and *trans*-3-penten-2-one (**4**) and assigned the low-field resonance to the β-methyl group which is *cis* to the carbonyl group.



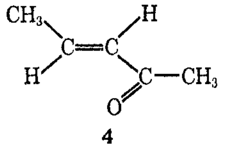
2

δ 2.11 and 1.86 (β CH_3)



3

δ 2.12 (β CH_3)
6.09 (β H)



4

δ 1.90 (β CH_3)
6.71 (β H)

Infrared spectrophotometry differentiates between (*S*)-*cis* and (*S*)-*trans* α,β-unsaturated ketones, since the ratio of the band intensities of the C=O to the C=C stretching vibrations is considerably larger for transoid than for cisoid ketones.[8,9] It was also observed that there is a greater frequency separation between the C=O and the C=C stretching bands of the (*S*)-*cis* conformation than of the (*S*)-*trans*.[9]

The possibility should also be considered that the most stable conformation might be one in which the carbonyl group is rotated out of the carbon–carbon double—plane. The increase in energy due to the decrease in orbital overlap interaction of the two groups might be more than compensated for by a decrease in energy due to a decrease in steric crowding as the two groups rotate away from each other.

In the present work, the preferred conformations of a series of labile (conformationally mobile) α,β-unsaturated ketones have been assigned on the basis of the chemical shifts of hydrogens of β groups. Information from the infrared spectra substantiates the correlations. These results are useful in developing generalizations concerning preferred conformations of α,β-unsaturated ketones from the type of alkyl substituents present.

Nuclear Magnetic Resonance and Infrared Spectroscopy Results.—The chemical shifts observed for the β-methyl, β-methylene, and β-hydrogen moieties for a series of conjugated olefinic ketones are given in Table I, along with the differences in chemical shifts (Δ, ppm) of the protons of a β group *cis* to the carbonyl group relative to a *trans* β group of the same type. With the exception of compound **9**, these chemical-shift differences can be made by direct comparison of identical β groups on the same compound or by comparing *cis* and *trans* isomers. For example, compound **2** has two β-methyl groups. A comparison of the geometric isomers **6** and **7** also permits the determination of chemical-shift differences for *cis* and *trans* β-methyl hydrogens, as well as *cis* and *trans* β-methylene hydrogens. The value for compound **9** is the difference between the observed chemical shift and the average chemical shift (1.84 ppm) of *trans* β-methyl groups (with respect to -COR) in compounds having an α hydrogen. Also listed are the

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[1] (a) Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234; taken from the Ph.D. dissertation of D. D. F. (b) Texas Eastman Fellow, 1964–1965.

[2] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1963, p 121.

[3] L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958).

[4] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2886 (1960).

[5] J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949).

[6] G. K. Estok and J. H. Sikes, *J. Amer. Chem. Soc.*, **75**, 2745 (1953).

[7] R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).

[8] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

[9] K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2201 (1960).

[10] E. Baldwin, *J. Org. Chem.*, **30**, 2423 (1965).

TABLE I

NMR CHEMICAL SHIFTS OF β SUBSTITUENTS AND THE RATIO OF THE C=O TO C=C STRETCHING BAND INTENSITIES OF CONJUGATED OLEFINIC KETONES

Compd no.	Compd[a]	Chemical shift, δ				Δ, ppm			r_1
		cis β CH$_3$	trans β CH$_3$	cis β CH$_2$	trans β CH$_2$	β CH$_3$	β CH$_2$	β H	(C=O/C=C)
2	CMe$_2$=CHCOMe	2.11	1.85	...	...	0.26	...	...	0.60
5	CMe$_2$=CHCOEt	2.09	1.85	...	...	0.24	...	...	0.70
6	CEtMe=CHCOEt	...	1.85	2.54	...	...	0.40	...	0.88
7	CMeEt=CHCOEt	2.11	...	...	2.14	0.26	...	...	0.66
8	CMe$_2$=CHCOPr	2.05	1.82	...	...	0.23	...	...	0.89
9	CMePr=CHCOMe	2.05	...	...	2.05	0.21	...	...	0.83
10	CMePr=CHCOPr	2.07	...	...	2.08	0.23	...	...	1.01
11	CPrMe=CHCOPr	...	1.84	2.54	...	...	0.46	...	
12	CMe$_2$=CEtCOMe	1.74	1.74	...	...	0.00	...	...	5.09
13	CPrMe=CEtCOMe	...	1.70	2.14	...	...	0.00	...	2.94
14	CMePr=CEtCOMe	1.70	...	...	2.14	0.00	...	...	3.05
15	CMe$_2$=CMeCOEt	1.74	1.74	...	...	0.00	...	...	2.35
16	CEt$_2$=CMeCOEt	...	...	2.10	2.08	...	0.02	...	2.40
17	CEt$_2$=CMeCO-*i*-Pr	...	...	2.04	1.95	...	0.09	...	1.71
18	CMe$_2$=CMeCOMe	1.82	1.76	...	...	0.06	...	...	1.96
19	CEtMe=CMeCOMe	...	1.72	2.25	...	...	0.14	...	1.98
20	CMeEt=CMeCOMe	1.81	...	...	2.11	0.09	...	...	1.69
21	CHEt=CMeCOEt	...	...	2.24	...	...	...	...	5.53
22	CHMe=CMeCOMe	...	1.72	...	...	...	...	...	5.23
23	CH$_2$=CHCOMe	...	...	...	...	...	...	0.3[b]	~5.0
24	CH$_2$=CMeCOMe	...	...	...	...	...	...	0.2[c]	9.0[d]

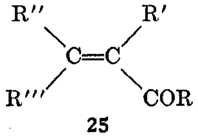
[a] The first alkyl group (or hydrogen) listed is *cis* to the carbonyl group. [b] S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **37**, 1951 (1962). [c] Reference 2, p 123. [d] Reference 8.

ratios (r_1) of the integrated band intensities (determined by cutting and weighing relevant peaks) of the C=O and C=C stretching vibrations.

Discussion

Excluding compounds **21–24**, the α,β-unsaturated ketones in Table I can be divided into three groups: (1) those which show a significant chemical shift of the protons of a β group *cis* to the carbonyl group relative to a *trans* β group of the same type (**2**, **5–11**); (2) those which show an insignificant shift (**12–16**); and (3) those which show a moderate chemical shift (**17–20**).

Consistent with the above discussion, the first group is assigned the (*S*)-*cis* conformation. Infrared data compliment and confirm this assignment, as evidenced by the low ratio of C=O to C=C band intensities. That this ratio would be low for (*S*)-*cis* ketones is well established.[6–8] Considering the general formula **25**,



25

for those cases where R′ = H, R″ = alkyl, and R‴ = alkyl, clearly there will be more steric interference between R and R‴ in the (*S*)-*trans* conformation than between R and H in the (*S*)-*cis* conformation, leading to a preference for the (*S*)-*cis* form.

When R′ is a group other than H, steric repulsions would have a tendency to force the molecule out of the (*S*)-*cis* conformation and into a nonplanar conformation. This would be expected to lead to a reduced deshielding effect on the β-carbon protons as the anisotropic carbonyl group turns away. It seems likely that this deshielding effect would become negligible by the time the carbonyl group has turned 90° away from the (*S*)-*cis* conformation. The question arises as to whether the deshielding effect remains negligible or increases as the carbonyl group continues to turn from the 90° out-of-plane position to the (*S*)-*trans* conformation. Considerable evidence suggests that there is a difference in chemical shifts of *cis* and *trans* β protons for compounds with predominant (*S*)-*trans* conformations. For example, a chemical-shift difference of 0.3 ppm is observed for the β protons of methyl vinyl ketone (**23**) (footnote *b*, Table I). Ronayne, Sargent, and Williams[11] indicate that this compound favors the (*S*)-*trans* conformation at room temperature on the basis of a nmr variable-temperature study. Furthermore, the carbonyl stretching band is *ca.* five times as intense as the C=C stretching band, which is consistent with the (*S*)-*trans* conformation. Similar data for 3-methyl-3-buten-2-one (**24**), *i.e.*, a large ratio (9.0)[8] for the integrated band intensities of the C=O and C=C stretching vibrations and a nmr variable-temperature study,[11] indicate an (*S*)-*trans* conformation, and the β hydrogens show a 0.20-ppm difference in chemical shift (see ref 2, p 123).

This β-hydrogen shift difference of 0.2–0.3 ppm for (*S*)-*trans* compounds is considerably less than the corresponding difference for (*S*)-*cis* compounds, *e.g.*, the β-hydrogen Δ = 0.62 for *cis*- (**3**) and *trans*-3-pentanone (**4**). (However, it is not certain that the conformation of **4** is (*S*)-*cis*; so this comparison may be subject to some uncertainty.) At any rate, compounds **12–16**, which show negligible shifts, must be nonplanar with large angles of rotation of the carbonyl group with respect to the carbon–carbon double bond. Compounds **17–20**, which show intermediate chemical shifts, must have conformations between the planar (*S*)-*cis* or (*S*)-*trans* conformations and the 90° nonplanar form. The ratios

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[11] J. Ronayne, M. V. Sargent, and D. H. Williams, *J. Amer. Chem. Soc.*, **88**, 5288 (1966).

of the C=O to C=C band intensities for the nonplanar ketones (**12–20**) are between the observed values for (*S*)-*cis* ketones (**2**, **5–11**) and (*S*)-*trans* ketones (**21–24**).

From the available data, the effect of structure on conformational preference can be generalized as follows: (1) labile α,β-unsaturated ketones (**25**) with an α hydrogen and alkyl groups at R'' and R''' prefer the (*S*)-*cis* conformation; (2) if R and R' are methyl groups and R''' is an alkyl group, a slight deviation from the planar conformation occurs in order to relieve the moderate steric repulsions between R and R'; (3) if groups at R and R' are as large as a combination of an ethyl and a methyl, steric repulsions become large enough to cause significant deviation from the planar conformation. For those cases where there is also an alkyl group at R''', the data suggest a conformation having the C=O group at or near a 90° angle to the C=C, unless steric repulsions between R and R''' become large. If steric repulsions among R, R', and R''' become large, the molecule assumes a preferred conformation between (*S*)-*cis* or (*S*)-*trans* and 90° out-of-plane. This is well illustrated by 5-ethyl-2,4-dimethyl-4-hepten-3-one (**17**), which has an isopropyl group at R and an ethyl group at R'''. An examination of a molecular model clearly shows that the least sterically hindered conformation has the C=O to C=C angle between 0 and 90° with respect to the planar (*S*)-*cis* conformation. The difference in chemical shifts of the β-methylene hydrogens and an intermediate value for the ratio of C=O to C=C stretching vibrations support this proposition. A smaller effect of this type may be present in compound **16**, which has ethyl groups at R and R'''.

Sufficient examples are not available to correlate structure with preferred conformations for ketones with a β hydrogen (**21–24**). However, the high ratios of the C=O to C=C stretching bands suggest the (*S*)-*trans* conformation for ketones with a β hydrogen *cis* to the carbonyl group ($R''' = H$). As mentioned earlier, Ronayne, Sargent, and Williams[11] classify methyl vinyl ketone (**23**) as predominantly (*S*)-*trans* from a nmr variable temperature study, and Erskine and Waight[8] show 3-methyl-3-buten-2-one (**24**) to be (*S*)-*trans* from infrared data. On the basis of benzene solvent shifts, Timmons[12] classifies 3-methyl-3-buten-2-one (**24**), 3-penten-2-one, 3-methyl-3-penten-2-one (**22**), and 4-phenyl-3-buten-2-one as (*S*)-*trans*.

Owing to interference from groups other than those of interest, there is some uncertainty in some of the assignments. Two unresolved singlets are present in the spectrum of 3,4-dimethyl-3-penten-2-one (**18**) at 1.82 (6 H) and 1.76 ppm (3 H) which represent the α- and β-methyl groups. An unequivocal assignment cannot be made in this case. A singlet representing *ca.* 0.4 H is also present at 2.09 ppm, which may indicate a small population of the (*S*)-*cis* conformer. A similar difficulty is encountered with 4,5-dimethyl-4-hexen-3-one (**15**), which shows two unresolved singlets at 1.74 (6 H) and 1.72 ppm (3 H) representing the α- and β-methyl groups. Even if the assignment of all six hydrogens of the β-methyl groups at 1.74 ppm is in error, there is only a 0.02-ppm chemical shift caused by the anisotropic carbonyl group.

None of the ketones appears to exist as a mixture of conformers at room temperature to a greater extent than described above, and those with α hydrogens and β-alkyl groups are all present in the (*S*)-*cis* form as far as can be determined.

Correlations by Erskine and Waight[8] based on the ratio of the integrated band intensities of the C=O and C=C stretching vibrations agree with these results for ketones having a hydrogen at R'; however, they would classify 3,4-dimethyl-3-penten-2-one (**18**) as (*S*)-*cis*. The present correlations clearly show that this compound prefers a conformation with the C=O rotated somewhat from the planar (*S*)-*cis* conformation. Similarly, from their infrared data, Noack and Jones[9] report that **18** and *trans*-3,4-dimethyl-3-hexen-2-one (**20**) prefer the (*S*)-*cis* conformation; however, the intensities of the C=C stretching bands are between the values shown for fixed (*S*)-*cis* and fixed (*S*)-*trans* compounds shown in their tabulations. These intermediate values, together with the present nmr results, fit better the assignments to nonplanar conformations made here.

For ketones showing intermediate chemical shifts, it appears that there should be a correlation between the chemical shift of β groups and the dihedral angle formed by the carbonyl group and the carbon–carbon double bond. Although an exact angle cannot be calculated from the available data, a function (ϕ) of this angle can be determined as follows.

For (*S*)-*cis* ketones (**2**, **5–11**), an average chemical-shift difference (β-*cis* relative to β-*trans*) of 0.24 ppm is observed for β-methyl groups. Then ϕ for ketone **18** is $0.06/0.24 = 0.25$. For ketones **19** and **20**, ϕ is $0.09/0.24 = 0.37$. Similarly, the average difference in chemical shifts of β-methylene groups is 0.43 for (*S*)-*cis* ketones. Using this value for ketones **19** and **20** leads to the value $\phi = 0.14/0.43 = 0.33$. Table II lists values of ϕ for ketones **2** and **5–20**. A number near unity indicates a (*S*)-*cis* ketone and a value of zero indicates that the carbonyl group is 90° out of the plane of the carbon–carbon double bond. Although sufficient data are not available to evaluate the Δ value for (*S*)-*trans* β groups, it is conceivable that some of the ketones with intermediate chemical-shift values might have preferred conformations between 90° nonplanar and (*S*)-*trans*.

Table II

The Function, ϕ, of α,β-Unsaturated Ketones Listed in Table I

Compd	ϕ
2	1.0
5	1.0
6	0.93
7	1.0
8	0.96
9	0.88
10	0.96
11	1.0
12	0.0
13	0.0
14	0.0
15	0.0
16	0.05
17	0.22
18	0.25
19	0.37,[a] 0.33[b]
20	0.37,[a] 0.33[b]

[a] Calculated from β-methyl groups. [b] Calculated from β-methylene groups.

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[12] C. J. Timmons, *Chem. Commun.*, 576 (1965).

However, it is probable (see the β-hydrogen discussion above) that Δ will be smaller for fixed (*S*)-*trans* than for fixed (*S*)-*cis* compounds; so only those compounds with small, nonzero values of ϕ suffer from this uncertainty. The relatively low values for the ratios of C=O to C=C stretching frequencies for these compounds indicate that the preferred conformations certainly are not very near (*S*)-*trans*.

Experimental Section

Almost all of the olefinic ketones were separated and purified by preparative gas chromatography, and a Wilkins Model A-700 Autoprep chromatograph was used for this purpose. All of the mass spectra and the nmr spectra of some of the compounds were taken by Mr. H. T. Ford and Dr. P. Flannigan, respectively, of Continental Oil Co., for which assistance the authors are most grateful. The mass spectra were recorded on a CEC 103 mass spectrometer using an ionization voltage of 70 eV. The nmr spectra taken by Dr. Flannigan were recorded at room temperature on a Varian HA-100 spectrometer. The remainder were recorded in this laboratory at room temperature on a Varian A-60 spectrometer.

Infrared spectra were obtained on a Perkin-Elmer Model 337 grating infrared spectrophotometer and a Perkin-Elmer Model 21 spectrophotometer using neat samples between sodium chloride windows.

Ultraviolet spectra for all compounds were obtained in 95% ethanol on a Beckman Model DK-1 recording spectrophotometer. α,β-Unsaturated ketones show a weak R band of the carbonyl group between 300 and 350 mμ and a strong K band of the α,β-conjugated system between 215 and 250 mμ.[13] The empirical generalizations derived by Woodward[14] for the effect of substitution upon the position of the K band were used with excellent results as an aid in assigning the structures of some of the ketones.

Complete details of all syntheses are given in the Ph.D. dissertation of D. D. F.[15]

5-Methyl-4-hexen-3-one (5) and 3,4-Dimethyl-3-penten-2-one (18).[16]—Phosphorus oxychloride (376 g) was distilled into a mixture of 200 g (3.49 mol) of acetone and 251 g (3.49 mol) of butanone contained in a round-bottomed flask. The reaction mixture was left for 48 hr in a water bath cooled by tap water to 28°. The solution was orange at the beginning of the reaction and became progressively darker until a dark brown mixture resulted after 48 hr. The reaction mixture was treated with 1400 ml of water, and the dark brown chloro ketone layer was separated, washed with water, and dried over sodium sulfate. Dehydrochlorination was effected by refluxing with 350 g of dimethylaniline for 30 min. The resulting mixture had two distinct layers. After the mixture was cooled in an ice bath, 235 g of a light brown oil was decanted from the solid dimethylaniline hydrochloride. This crude product was washed with dilute hydrochloric acid followed by sodium bicarbonate solution, and then distilled through a short Vigreux column to give 116 g of colorless product boiling at 130–175°; 116 g of residue remained in the distillation flask. Gc analysis (at 110 and 138°, respectively) of the crude distillate using a 10 ft × 0.25 in. column packed with 20% Carbowax coated on firebrick and a 20 ft × 0.375 in. column packed with 30% SE-30 coated on Chromosorb P showed *ca.* 9.5% mesityl oxide, 48.7% C_7 olefinic ketones, and 41.8% C_8 olefinic ketones.

The desired C_7 homologs could not be separated by preparative gc in a one-step operation [the mixture was complicated by the presence of mesityl oxide, 3,4-dimethyl-4-penten-2-one (**26**), and 4-methyl-4-hexen-2-one (**27**)]. However, at 138°, a 20 ft × 0.375 in. column packed with 30% SE-30 coated on Chromosorb P conveniently separated the desired compounds into groups A and B. Group A was further separated at 80° using a 6 ft × 0.375 in. 20% Carbowax column and was shown to contain 45% **26**, 50% mesityl oxide, and 5% impurities. Similarly, group B contained 12% **5**, 11% **27**, 74% **18**, and 3% impurities. At 115° an 8 ft × 0.375 in., 20% silicone fluid XF-1150 (Varian Aerograph) column achieved resolution sufficient to isolate pure **5** and a mixture of **18** and **27**. The mixture containing 15.7% **27** and 84.3% **18** was separated conveniently at 100° using the 20 ft × 0.375 in., 30% SE-30 column.

Spectral data of compound **5** follow: nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.98 [s, fine splitting, 1 H, $CH_3C{=}C\mathbf{H}$ (for simplicity, this type of long-range spin–spin coupling between an olefinic proton and protons of an olefinic alkyl group is referred to as a singlet with fine splitting)], 2.34 (q, 2 H, $COC\mathbf{H}_2CH_3$), 2.09 (s, fine splitting, *cis* to carbonyl, 3 H, $HC{=}CC\mathbf{H}_3$), 1.85 (s, fine splitting, *trans* to carbonyl, 3 H, $HC{=}CC\mathbf{H})_3$, and 1.01 (t, 3 H, $CH_2C\mathbf{H}_3$); ir (neat) $\nu_{\max}^{\mathrm{NaCl}}$ 1690 (s, C=O), 1623 (s, C=C), 1413 (m, CH_2 bend of CH_2CO), and 837 cm^{-1} (s, CH bend on trisubstituted double bond); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 312 (w, R band) and 237 mμ (s, K band); mass spectrum *m/e* (rel intensity) 112 (16) (parent peak), 83 (100), 57 (51), 55 (82), 43 (15), 41 (19), 39 (43), 29 (93), 28 (25), 27 (63), and 15 (10).

Spectral data of compound **18** follow: nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 2.14 (s, 3 H, $COC\mathbf{H}_3$), 1.82 (s, 6 H, *trans* $C\mathbf{H}_3C{=}CC\mathbf{H}_3$), and 1.76 (s, 3 H, $C{=}CC\mathbf{H}_3$ *trans* to carbonyl); ir $\nu_{\max}^{\mathrm{NaCl}}$ 1690 (s, C=O), 1618 (s, C=C), and 1348 cm^{-1} (s, CH_3 bend of a methyl ketone); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 305 (w, R band) and 247 mμ (s, K band); mass spectrum *m/e* (rel intensity) 112 (16) (parent peak), 97 (14), 69 (36), 55 (11), 43 (100), 41 (75), 39 (27), 28 (14), 27 (20), and 15 (21).

***cis*-5-Methyl-4-hepten-3-one (6), *trans*-5-Methyl-4-hepten-3-one (7), *cis*-3,4-Dimethyl-3-hexen-2-one (19), and *trans*-3,4-Dimethyl-3-hexen-2-one (20).**—Phosphorus oxychloride (378 g), bp 104°, was distilled into 504 g (7.0 mol) of butanone contained in a round-bottomed flask. The reaction mixture was left in a water bath cooled by tap water to 15–20°. The crude olefinic ketone mixture obtained by the procedure described above was distilled through a short Vigreux column to give 210.8 g of colorless product, bp 52–78° (225 mm), leaving 56 g of high-boiling residue. Gc analysis indicated the presence of 6.5% **6**, 19.9% **7**, 19.8% **19**, 5.3% **20**, and 46.5% 3,4-dimethyl-4-hexen-2-one (**28**) (mixture of *cis* and *trans*). The preparative gc separation of these ketones is described elsewhere.[17]

Spectral data of compound **6** follow: nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.96 (s, fine splitting, 1 H, $CH_3C{=}C\mathbf{H}$), 2.54 (q, fine splitting, 2 H, $HC{=}CC\mathbf{H}_2CH_3$), 2.35 (q, 2 H, $COC\mathbf{H}_2CH_3$), 1.85 (s, fine splitting, 3 H, $HC{=}CC\mathbf{H}_3$), and 1.04 and 1.02 (overlapping t, 6 H, $CH_2C\mathbf{H}_3$); ir (neat) $\nu_{\max}^{\mathrm{NaCl}}$ 1690 (s, C=O), 1620 (s, C=C), 1413 (m, CH_2 bend of CH_2CO), and 800 cm^{-1} (m, CH bend on trisubstituted double bond); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 310–315 (w, R band) and 238 mμ (s, K band); mass spectrum *m/e* (rel intensity) 126 (11) (parent peak), 97 (46), 69 (16), 57 (100), 55 (12), 53 (12), 43 (12), 41 (71), 39 (30), 29 (78), 28 (14), and 27 (43). The compound gave a negative iodoform test; the semicarbazone derivative had a melting point of 127.5–128.5°.

Spectral data of compound **7** follow: nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.96 (s, fine splitting, 1 H, $CH_3C{=}C\mathbf{H}$), 2.40 (q, 2 H, $COC\mathbf{H}_2CH_3$), 2.14 (q, fine splitting, 2 H, $HC{=}CC\mathbf{H}_2CH_3$), 2.11 (s, fine splitting, 3 H, $HC{=}CC\mathbf{H}_3$), and 1.05 and 1.02 (overlapping t, 6 H, $CH_2C\mathbf{H}_3$); ir (neat) $\nu_{\max}^{\mathrm{NaCl}}$ 1690 (s, C=O), 1618 (s, C=C), 1413 (m, CH_2 bend of CH_2CO), and 803 cm^{-1} (m, CH bend on trisubstituted double bond); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 310–315 (w, R band) and 238 mμ (K band); mass spectrum *m/e* (rel intensity) 126 (11) (parent peak), 97 (45), 69 (16), 57 (100), 55 (12), 53 (11), 43 (12), 41 (72), 39 (30), 29 (80), 28 (20), and 27 (44). The compound gave a negative iodoform test; the semicarbazone derivative had a melting point of 155–157°.

Spectral data of compound **19** follow: nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 2.25 (q, 2 H, $C{=}CC\mathbf{H}_2CH_3$), 2.13 (s, 3 H, $COC\mathbf{H}_3$), 1.81 (s, 3 H, α methyl), 1.72 (s, 3 H, β methyl), and 1.01 (t, 3 H, $CH_2C\mathbf{H}_3$); ir (neat) $\nu_{\max}^{\mathrm{NaCl}}$ 1690 (s, C=O) and 1615 cm^{-1} (m, C=C); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 305 (w, R band) and 247 mμ (s, K band); mass spectrum *m/e* (rel intensity) 126 (12) (parent peak), 111 (15), 83 (35), 67 (10), 55 (74), 53 (12), 43 (100), 41 (56), 39 (29), 29 (28), 28 (11), 27 (37), and 15 (23). The compound gave a positive iodoform test.

Spectra data of compound **20** follow: nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 2.15 (s, 3H, $COC\mathbf{H}_3$), 2.11 (q, 2 H, $C{=}CC\mathbf{H}_2CH_3$), 1.81 (s, 6 H, α and β methyls), and 1.01 (t, 3 H, $CH_2C\mathbf{H}_3$); ir (neat) $\nu_{\max}^{\mathrm{NaCl}}$ 1690 (s, C=O), 1615 (m, C=C), and 1349 cm^{-1} (s, CH_3 bend of $COC\mathbf{H}_3$); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 305 (w, R band) and 247 mμ (s, K band); mass spectrum *m/e* (rel intensity) 126 (11) (parent peak), 111 (16), 83 (37),

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55 (76), 53 (12), 43 (100), 41 (48), 39 (26), 29 (17), 28 (10), 27 (32), and 15 (23). The compound gave a positive iodoform test.

2-Methyl-2-hepten-4-one (**8**), **4-Methyl-3-hepten-2-one** (**9**), **and 3-Ethyl-4-methyl-3-penten-2-one** (**12**).—Analogous to the condensation of a mixture of acetone and butanone by phosphorus oxychloride, 500 g (5.814 mol) of 2-pentanone and 337.2 g (5.814 mol) of acetone were condensed by means of 624.7 g (4.07 mol) of phosphorus oxychloride. After the mixture had stood for 48 hr at room temperature (*ca.* 25°), 790 g (4.85 mol) of crude chloroketone was isolated, which represents 83.4% of the theoretical yield. The chloro ketone was dehydrochlorinated by refluxing for 2 hr with alcoholic potassium hydroxide, which was prepared by dissolving 444.5 g (8.52 mol) of potassium hydroxide in 2000 g of 95% ethanol. After treatment with a large volume of water, the upper ketonic layer was separated and distilled through a short Vigreux column to give a mixture of olefinic ketones boiling at 115–190°.

Gc analysis showed the relative yield of products to be 7.3% mesityl oxide, 47.1% C_8 olefinic ketones, and 45.6% C_{10} ketones. The mixture of C_8 olefinic ketones consists of 21.5% **8**, 12.5% **9**, 45.5% **12**, and 20.5% 3-ethyl-4-methyl-4-penten-2-one (**29**). The C_8 ketones were separated to give **29**, a mixture of **8** and **12**, and pure **9** on a 12 ft × 0.375 in., 30% Carbowax column at 145°. Ketones **8** and **12** were separated on a 20 ft × 0.375 in., 20% polyethylene glycol distearate column at 120°.

Spectral data of compound **8** follow: nmr $\delta^{CCl_4}_{TMS}$ 5.99 (s, fine splitting, 1 H, $CH_3C{=}C\mathbf{H}$), 2.26 (t, 2 H, $COC\mathbf{H}_2CH_2$), 2.05 (s, fine splitting, *cis* to carbonyl, 3 H, $HC{=}CC\mathbf{H}_3$), 1.82 (s, fine splitting, *trans* to carbonyl, 3 H, $HC{=}CC\mathbf{H}_3$), *ca.* 1.54 (m, 2 H, $CH_2C\mathbf{H}_2CH_3$), and 0.87 (t, 3 H, $CH_2C\mathbf{H}_3$); ir (neat) 1681 (s, C=O), 1613 (s, C=C), and 813 cm^{-1} (w, CH bend on a trisubstituted double bond); uv λ^{EtOH}_{max} 310 (w, R band) and 237 mμ (s, K band); mass spectrum *m/e* (rel intensity) 126 (14) (parent peak), 83 (100), 55 (36), 43 (12), 41 (16), 39 (22), 29 (19), 27 (31), and 15 (10). The compound gave a negative iodoform test.

Spectral data of compound **9** follow: nmr $\delta^{CCl_4}_{TMS}$ 5.95 (s, broad, 1 H, $CH_3C{=}C\mathbf{H}$), 2.05 (t, partially obscured, 2 H, $CH_2C\mathbf{H}_2C{=}C$), 2.05 (s, fine splitting, 6 H, $COC\mathbf{H}_3$ and $COCH{=}CC\mathbf{H}_3$ *cis* to carbonyl), 1.47 (sextet 2 H, $CH_3C\mathbf{H}_2CH_2$), and 0.90 (t, 3 H, $CH_2C\mathbf{H}_3$); ir (neat) ν^{NaCl}_{max} 1691 (s, C=O), 1620 (s, C=C), 1352 (m, CH_3 bend of $COCH_3$), and 809 cm^{-1} (w, CH bend on a trisubstituted double bond); uv λ^{EtOH}_{max} 310 (w, R band) and 240 mμ (s, K band); mass spectrum *m/e* (rel intensity) 126 (17) (parent peak), 111 (88), 98 (18), 83 (28), 69 (36), 55 (69), 53 (12), 43 (100), 41 (44), 39 (39), 29 (21), 27 (43), and 15 (45). The compound gave a positive iodoform test. This sample contains an impurity with almost identical properties. In the nmr spectrum there is a singlet with an area representing *ca.* 0.7 H at δ 1.82 which shows second-order splitting by the vinyl proton into a doublet. The chemical shift of this absorption is at the correct position to indicate the presence of a small amount of the geometric isomer of **9**; *i.e.*, this impurity has the carbonyl group and the β-methyl group *trans*. A simple calculation indicates that the *cis–trans* mixture contains about 30% the geometric isomer of **9**.

Spectral data of compound **12** follow: nmr $\delta^{CCl_4}_{TMS}$ 2.26 (q, 2 H, $C{=}CC\mathbf{H}_2CH_3$), 2.13 (s, 3 H, $COC\mathbf{H}_3$), 1.74 (s, 6 H, β methyls), and 0.96 (t, 3 H, $CH_2C\mathbf{H}_3$); ir (neat) ν^{NaCl}_{max} 1688 (s, C=O), 1614 (w, C=C), and 1352 cm^{-1} (m, CH_3 bend of $COCH_3$); uv λ^{EtOH}_{max} 300–305 (w, R band) and 244 mμ (s, K band); mass spectrum *m/e* (rel intensity) 126 (37) (parent peak), 111 (34), 83 (46), 55 (62), 53 (10), 43 (100), 41 (41), 39 (31), 29 (13), 27 (26), and 15 (45). The compound gave a positive iodoform test.

***trans*-6-Methyl-5-nonen-4-one** (**10**).[18]—2-Pentanone (478 g, 5.56 mol) was added to a solution prepared by dissolving 23 g of sodium in 300 ml of methyl alcohol, and the resulting material was refluxed for 3 hr. The basic solution was neutralized with 20% sulfuric acid and diluted with excess water. The insoluble ketonic layer was separated, washed with water, and dried over potassium carbonate. Distillation through a short Vigreux column under reduced pressure yielded 94 g of colorless product, bp 77–79° (8 mm). It was determined that 2-pentanone condenses only at the methyl carbon in the presence of sodium methoxide by comparing the reaction product with authentic samples of olefinic ketones formed from the acid-catalyzed condensation of 2-pentanone at the methylene carbon.

cis- (**11**) and *trans*-6-methyl-5-nonen-4-one (**10**) are formed along with two other compounds which are probably the nonconjugated isomers, *cis*- (**30**) and *trans*-6-methyl-6-nonen-4-one (**31**). Analytical gc results on a 5% FFAP column show that the mixture contains *ca.* 75.8% conjugated and 24.2% nonconjugated olefinic ketones. A satisfactory gc method to separate the nonconjugated olefinic ketones from the conjugated ones was not accomplished; however, a number of gc columns are suitable for the isolation of **10** from the other three compounds. The 20 ft × 0.375 in., 30% SE-30 column was used at 163° for the isolation of **10**. Interestingly, elution over a 20 ft × 0.375 in., 30% FFAP column causes considerable *trans–cis* (**10** to **11**) isomerization to occur. The fact that the *trans* compound had isomerized to the *cis* isomer is readily detectable from the nmr spectrum owing to the difference in chemical shift of the β-methyl group in the two isomers.

Spectral data of compound **10** follow: nmr $\delta^{CCl_4}_{TMS}$ 5.97 (s, fine splitting, 1 H, $CH_3C{=}C\mathbf{H}$), 2.33 (t, 2 H, $COC\mathbf{H}_2CH_2$), *ca.* 2.08 (t, partially obscured, 2 H, $C{=}CC\mathbf{H}_2CH_2$), 2.07 (s, fine splitting, *cis* to carbonyl, 3 H, $CH{=}CC\mathbf{H}_3$), *ca.* 1.56 (m, 4 H, $CH_3C\mathbf{H}_2CH_2$), and 0.93 (t, 6 H, $CH_2C\mathbf{H}_3$); ir (neat) ν^{NaCl}_{max} 1691 (s, C=O) and 1623 cm^{-1} (s, C=C); uv λ^{EtOH}_{max} 310 (w, R band) and 240 mμ (s, K band); mass spectrum *m/e* (rel intensity) 154 (13) (parent peak), 111 (100), 71 (39), 69 (23), 43 (64), 41 (47), 39 (26), 29 (18), and 27 (37). The mixture containing the *cis* isomer (**11**) shows a nmr singlet at δ 1.84, which indicates that the β-methyl group is *trans* to the carbonyl function. Also, a partially obscured triplet is found at δ 2.54 indicating that the β methylene is *cis* to the carbonyl function.

cis- (**13**) **and *trans*-3-Ethyl-4-methyl-3-hepten-2-one** (**14**).—2-Pentanone (250 g) was condensed by phosphorus oxychloride in a reaction similar to the ones described above. The reaction mixture was allowed to stand for 48 hr at 20°. The resulting chloroketone was dehydrochlorinated by refluxing for 2 hr with alcoholic potassium hydroxide, prepared by dissolving 168 g (3 mol) of potassium hydroxide in 945 ml of 95% ethanol. Treatment of the product with a large excess of water separated the desired olefinic ketones. Distillation of the crude product gave 42 g of colorless material, bp 55–65° (5–7 mm). This product consisted of a complex mixture of isomeric C_{10} olefinic ketones which could not be completely resolved by any of the gc columns tried. However, 3-ethyl-4-methyl-4-hepten-2-one (**32**) could easily be separated from the other isomers using a 30% SE-30 column at 167°. Analytical gc showed that the mixture contained about 45.9% **32** and 54.1% a mixture of isomeric ketones. Seven grams of **32** was saturated with dry hydrogen chloride and allowed to stand in a refrigerator at 5° for 12 hr. The chloro ketone was dehydrochlorinated by refluxing for 2 hr with alcoholic potassium hydroxide. The recovered olefinic ketones were distilled under reduced pressure to give 5.2 g of a colorless product, bp 57–58° (10 mm). Gc analysis of the mixture obtained in this reaction showed 83.5% **32**, 8.2% **13**, and 8.3% **14**. These ketones were separated using a 20 ft × 0.375 in., 30% FFAP column at 173°.

Spectral data of compound **13** follow: nmr $\delta^{CCl_4}_{TMS}$ 2.14 (m, 4 H, $CH_2C\mathbf{H}_2C{=}CC\mathbf{H}_2CH_3$), 2.14 (s, 3 H, $COC\mathbf{H}_3$), 1.70 (s, 3 H, β methyl), *ca.* 1.47 (m, 2 H, $CH_3C\mathbf{H}_2CH_2$), and 1.00 (t, 6 H, $CH_2C\mathbf{H}_3$); ir (neat) 1690 (s, C=O) and 1612 cm^{-1} (m, C=C); uv λ^{EtOH}_{max} 305 (w, R band) and 247 mμ (s, K band); mass spectrum *m/e* (rel intensity) 154 (25) (parent peak), 139 (35), 125 (11), 69 (74), 55 (47), 43 (100), 41 (42), 39 (21), 29 (16), 27 (24), and 15 (16).

The spectral properties of compound **14** are almost identical with those of **13**; therefore, the geometric assignments could be in error.

3-Methyl-3-penten-2-one (**23**).[19]—A solution of 265 g (3.7 mol) of butanone and 150 g (3.4 mol) of freshly prepared acetaldehyde was placed in a round-bottomed flask and cooled to −5°. This solution was saturated with dry hydrogen chloride and allowed to stand for 12 hr at −5°. The crude product was washed with dilute sodium hydroxide and dried over sodium sulfate. Distillation through a short Vigreux column gave 68 g of colorless product, bp 135–136°. Isolation of **23** from impurities was achieved using a 20% silicon fluid XF-1150 column at 130°.

Spectral data of compound **23** follow: nmr $\delta^{CCl_4}_{TMS}$ 6.67 (q, fine splitting, 1 H, $CH_3C{=}C\mathbf{H}CH_3$), 2.22 (s, 3 H, $COC\mathbf{H}_3$), 1.86 (d, 3 H, $CHC\mathbf{H}_3$, *trans* to carbonyl), and 1.72 (s, fine splitting, 3 H, $CH{=}CC\mathbf{H}_3$, α-methyl); ir (neat) ν^{NaCl}_{max} 3055 (w, vinyl H),

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1677 (s, $\mathrm{C{=}O}$), 1655 (m, $\mathrm{C{=}C}$), 1365 (s, $\mathrm{CH_3}$ bend of $\mathrm{COCH_3}$), and 822 cm^{-1} (s, CH bend on a trisubstituted double bond); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 305 (w, R band) and 228 mμ (s, K band); mass spectrum *m/e* (rel intensity) 98 (33) (parent peak), 83 (25), 55 (100), 43 (55), 39 (22), 29 (29), 27 (32), and 15 (21). The compound gave a positive iodoform test.

4-Methyl-4-hepten-3-one (22).—This compound was prepared by condensation of propionaldehyde and 3-pentanone in a manner similar to the preparation of **23**.

Spectral data of compound **22** follow: nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 6.46 (t, fine splitting, 1 H, $\mathrm{CH_3C{=}CHCH_2}$), 2.59 (q, 2 H, $\mathrm{COCH_2CH_3}$), 2.24 (quintet, broad, 2 H, $\mathrm{CH_3CH_2CH}$, *trans* to carbonyl), 1.72 (s, fine splitting, 3 H, $\mathrm{CH{=}CCH_3}$, α methyl), and 1.08 and 1.04 (2 t, 6 H, $\mathrm{CH_2CH_3}$); ir (neat) $\nu_{\max}^{\mathrm{NaCl}}$ 3045 (w, vinyl H), 1670 (s, $\mathrm{C{=}O}$), 1642 (w, $\mathrm{C{=}C}$), and 802 cm^{-1} (s, CH bend on a trisubstituted double bond); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 305 (w, R band) and 224 mμ (s, K band); mass spectrum *m/e* (rel intensity) 126 (15) (parent peak), 97 (80), 69 (77), 57 (13), 41 (100), 39 (27), 29 (38), 28 (12), and 27 (38).

5-Ethyl-4-methyl-4-hepten-3-one (16).—Analogous to the condensations described above, 172 g (2 mol) of 3-pentanone was condensed by means of 108 g (0.66 mol) of phosphorus oxychloride. Twenty grams of zinc chloride was used as a catalyst in this reaction. The usual work-up procedure gave 145 g of crude product. Distillation under reduced pressure gave 85 g of colorless product, bp 75–104° (5 mm). Analysis of the product shows the presence of 7.0% **16** and 93.0% 5-ethyl-4-methyl-5-hepten-3-one (**33**). Separation was accomplished by means of a 20 ft × 0.375 in., 30% FFAP column.

Spectral data of compound **16** follow: nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 2.44 (q, 2 H, $\mathrm{COCH_2CH_3}$), 2.10 and 2.08 (pair of quartets, 4 H, $\mathrm{CH_3CH_2}$), 1.79 (s, 3 H, α methyl), and 1.02 (overlapping t, 9 H, $\mathrm{CH_2CH_3}$); ir (neat) $\nu_{\max}^{\mathrm{NaCl}}$ 1689 (s, $\mathrm{C{=}O}$) and 1615 cm^{-1} (w, $\mathrm{C{=}C}$); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 305 (w, R band) and 247 mμ (s, K band).

4,5-Dimethyl-4-hexen-3-one (15).[20,21]—Propionyl chloride (186 g, 2 mol) was mixed with 210 g (3 mol) of Eastman technical-grade pentene (*ca.* 2:1 ratio of 2-methyl-2-butene and 2-pentene) in a round-bttomed flask fitted with a reflux condenser. Twenty grams of stannic chloride was added slowly through the condenser, causing the temperature to rise to *ca.* 50°. The flask was heated gently for 30 min, at which time the temperature of the reaction mixture had reached *ca.* 100°. The resulting liquid was cooled and then poured into dilute hydrochloric acid prepared with 160 ml of concentrated hydrochloric acid and 600 ml of water. The top ketonic layer was washed with saturated sodium bicarbonate and dried over sodium sulfate. After low-boiling material had been removed, 305 g of crude chloro ketone was refluxed for 2 hr with 90 g of potassium hydroxide dissolved in 405 g of 95% ethanol. Treatment with a large volume of water separated 117 g of olefinic ketone. Although some unidentified products were present, most of the material was a mixture of the condensation products of propionyl chloride and 2-methyl-2-butene. Isolation of the olefinic ketone mixture by preparative gc and subsequent characterization showed the mixture to consist of 84.7% **15** and 15.3% 4,5-dimethyl-5-hexen-3-one (**34**). The two ketones were separated on an 8.5 ft × 0.375 in., 20% TCEP column at 123°.

Spectral data of compound **15** follow: nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 2.42 (q, 2 H, $\mathrm{COCH_2CH_3}$), 1.74 (s, 6 H, β methyls), 1.72 (s, 3 H, α methyl), and 0.99 (t, 3 H, $\mathrm{CH_2CH_3}$); ir (neat) $\nu_{\max}^{\mathrm{NaCl}}$ 1695 (s, $\mathrm{C{=}O}$), 1626 (m, $\mathrm{C{=}C}$), and 1418 cm^{-1} (w, $\mathrm{CH_2}$ bend of $\mathrm{COCH_2}$); $\lambda_{\max}^{\mathrm{EtOH}}$ 300–305 (w, R band) and 244 mμ (s, K band); mass spectrum *m/e* (rel intensity) 126 (20) (parent peak), 97 (88), 69 (92), 57 (18), 53 (13), 41 (100), 39 (28), 29 (36), and 27 (34).

5-Ethyl-2,4-dimethyl-4-hepten-3-one (**17**).—Isobutyryl chloride (7.5 g) and 10.3 g (0.105 mol) of 3-ethyl-2-pentene were condensed in the presence of stannic chloride. The reaction and work-up procedure were similar to that described above. A mixture of **17** and 5-ethyl-2,4-dimethyl-5-hepten-3-one (**35**) was obtained. Separation was accomplished using a 6 ft × 0.375 in., 20% Carbowax column at 155°.

Spectral data of compound **17** follow: nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 2.75 [m, 1 H, $\mathrm{COCH(CH_3)_2}$], 2.04 (q, 2 H, $\mathrm{CH_3CH_2C{=}C}$, *cis* to carbonyl), 1.95 (q, 2 H, $\mathrm{CH_3CH_2C{=}C}$, *trans* to carbonyl), 1.76 (s, 3 H, α methyl), 1.02 [d, 6 H, $\mathrm{CH(CH_3)_2}$], and 0.99 (t, 6 H, $\mathrm{CH_2CH_3}$); ir (neat) $\nu_{\max}^{\mathrm{NaCl}}$ 1678 (s, $\mathrm{C{=}O}$) and 1616 cm^{-1} (w, $\mathrm{C{=}C}$); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 302 (w, R band) and 247 mμ (s, K band); mass spectrum *m/e* (rel intensity) 168 (7) (parent peak), 125 (56), 69 (21), 55 (100), 43 (28), 41 (36), 39 (16), 29 (15), and 27 (25).

Registry No.—**2**, 141-79-7; **5**, 13905-10-7; **6**, 20685-43-2; **7**, 20685-44-3; **8**, 22319-24-0; **9**, 22319-25-1; **10**, 22287-10-1; **11**, 22319-26-2; **12**, 22287-11-2; **13**, 22287-12-3; **14**, 22287-13-4; **15**, 17325-90-5; **16**, 22319-28-4; **17**, 22319-29-5; **18**, 684-94-6; **19**, 20685-45-4; **20**, 20685-46-5; **21**, 22319-31-9; **22**, 565-62-8; **23**, 78-94-4; **24**, 814-78-8.

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Bicyclo[1.1.1]pentane Derivatives[1]

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Received July 1, 1969

The synthesis of a variety of 1- and 2-substituted bicyclo[1.1.1]pentanes is described. Free-radical substitution occurs primarily at the bridgehead, and both types of hydrogens are markedly deactivated toward free-radical attack. The bridgehead radical opens to the methylenecyclobutyl radical at an appreciable rate. The K_a of the bridgehead acid is higher than that for any other simple saturated carboxylic acid, and the K_b of the bridgehead amine is lower than that of any other simple aliphatic amine. The nmr spectra of the compounds are discussed and the coupling constants and chemical shifts are given.

In the case of bicyclo[1.1.1]pentane, the parent hydrocarbon is more easily obtained than its simple derivatives.[3] Bicyclopentane was originally prepared by the reaction of 3-bromomethylcyclobutyl bromide with lithium amalgam.[4] It has also been obtained by the photolysis of bicyclo[2.1.1]hexan-2-one[5] and of 1,4-pentadiene.[6] The Wurtz reaction has been improved using the naphthalene radical anion as the halogen abstractor to give a 6.5% yield of the hydrocarbon. Recently, Rifi has found that the electrochemical dehalogenation[7] also is successful with 3-bromomethylcyclobutyl bromide and gives over twice the yield obtained using the chemical reagents.[8] This

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[1] This investigation was supported by the U. S. Army Research Office (Durham).

[2] Taken from part of the Ph.D. thesis of V. Z. Williams, 1968. Proctor and Gamble Fellow, 1966–1967; Heyl Fellow, 1967–1968.

[3] The only functional bicyclo[1.1.1]pentane derivative which has been obtained from a compound other than the parent hydrocarbon is the 2-phenyl-2-hydroxy compound formed *via* the irradiation of phenyl cyclobutyl ketone [A. Padwa and E. Alexander, *J. Amer. Chem. Soc.*, **89**, 6376 (1967)].

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