Infrared Carbonyl Absorptions and Conformations of Methyl-Substituted Acetones

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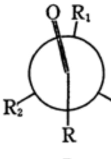
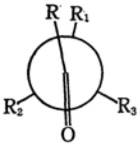
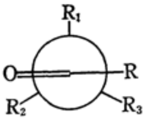
In the course of investigations concerning the stereochemistry of Grignard reactions, information on the conformations of alkyl ketones is required. The conformations of some alkyl carbonyl compounds have been discussed by several authors, and it has been concluded that they take a conformation which has an eclipsed oxo-group to one of the α-substituents (I) among the possible conformations, such as I, II, and III.1-3)



I



II



III

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1) R. W. Kilb, C. C. Lin and E. B. Wilson, *J. Chem. Phys.*, **26**, 1695 (1957).

2) J. D. Swalen and C. C. Costain, *ibid.*, **31**, 1562 (1959).

3) a) L. Pierce and L. C. Krisher, *ibid.*, **31**, 875 (1959); b) L. C. Krisher and E. B. Wilson, *ibid.*, **31**, 882 (1959).

TABLE 1. CARBONYL STRETCHING ABSORPTIONS AND THE CONFORMATIONS OF METHYL SUBSTITUTED ACETONES (RCOR′) IN CARBON TETRACHLORIDE SOLUTION

Alkyl group		Possible conformations			C=O Stretching absorptions (in cm^{-1})		
R	R′	H-H	H-Me	Me-Me	H-H conformation ν_{max} (ε_{max})	H-Me conformation ν_{max} (ε_{max})	Me-Me conformation ν_{max} (ε_{max})
Methyl	Methyl	IV_H-IV_H			1718 (364)		
Methyl	Ethyl	IV_H-V_H	IV_H-V_{Me}		1721 (312)	1712 (36)	
Methyl	Isopropyl	IV_H-VI_H	IV_H-VI_{Me}		1718 (310)	1709 (56)	
Methyl	*t*-Butyl		IV_H-VII_{Me}			1709 (411)	
Ethyl	Ethyl	V_H-V_H	V_H-V_{Me}	V_{Me}-V_{Me}	1720 (346)	1713 (52)	—
Ethyl	Isopropyl	V_H-VI_H	$\begin{cases} V_H\text{-}VI_{Me} \\ V_{Me}\text{-}VI_H \end{cases}$	V_{Me}-VI_{Me}	1718 (403)	1711 (67)	—
Ethyl	*t*-Butyl		V_H-VII_{Me}	V_{Me}-VII_{Me}		1711 (349)	—
Isopropyl	Isopropyl	VI_H-VI_H	VI_H-VI_{Me}	VI_{Me}-VI_{Me}	1716 (436)	1708 (90)	—
Isopropyl	*t*-Butyl		VI_H-VII_{Me}	VI_{Me}-VII_{Me}		1707 (302)	—
t-Butyl	*t*-Butyl			VII_{Me}-VII_{Me}			1687 (256)
		Frequency ranges for conformers			1721—1716	1713—1707	*ca.* 1687

In this report, the favorable conformation about the C–C_α and C–$C_{\alpha'}$ bonds is determined on the basis of the results of observations of the carbonyl-stretching absorptions of methyl-substituted acetones, assuming the results reported above.

Infrared spectral measurements would be a most effective tool for the investigation of the conformational problems, since the potential barrier of the restricted rotation about the C–C(O) bond is low and since the conversion among the conformational isomers is supposed to be too fast for each conformer to be identified by NMR spectroscopy. However, the infrared spectral measurements previously reported did not aim at conformational research, though numerous data are available for simple ketones, such as acetone and methyl ethyl ketone.[4-7)]

It is said that the carbonyl-stretching absorption bands are somewhat asymmetric and that their envelopes cannot be approximated by any simple functions, such as Lorentzian and Gaussian functions. The analysis of the spectra measured by a high-resolution spectrophotometer will also provide some information on this question.

Experimental

All of the ketones used for this investigation were either commercially available or were prepared by known methods,[8-11)] and they were purified by fractionation or by preparative gas chromatography. Their purity was checked by the measurement of their physical constants and by gas chromatography.

The infrared carbonyl absorptions were measured with a Perkin Elmer 112 G infrared spectrophotometer. The measurements were carried out in a dilute carbon tetrachloride solution by the use of a rock salt cell 25 mm long. Under the conditions described above, the concentration of the solution is about 10^{-3} mol/*l* and the effect of associated species on the spectra is completely negligible. The spectral slit width was kept within 0.9 cm^{-1} throughout the measurements. The overlapping bands were separated by a method previously reported by one of the present authors.[12)]

Results and Discussion

The carbonyl absorption bands of all possible methyl-substituted acetones are shown in Table 1; some of them are illustrated in Figs. 1 and 2. The C=O stretching absorptions of acetone, pinacolone and di-*t*-butyl ketone, illustrated in Fig. 1, possess symmetric band envelopes which can be well approximated by Lorentzian functions. The C=O stretching absorptions of other *t*-butyl ketones are also asymmetric, but other methyl-substituted acetones show asymmetric band envelopes.

Rotational Isomerism about the C–C(O) Bond. Assuming that the reported preference for the I conformation will also be realized with methyl-substituted acetones, half of the ketone molecule ($CR_1R_2R_3CO$-moiety) will take one of the conformations shown below.

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4) A. Pozefsky and N. D. Coggeshall, *Anal. Chem.*, **23**, 1611 (1951).

5) R. A. Friedel and J. A. Queiser, *ibid.*, **29**, 1362 (1957).

6) T. Shimanouchi, "Sekigaisen Kyushu-Supekutoru Kaisekiho," Nanko-do, Tokyo (1963), p. 35.

7) A. R. Katritzky and S. Oksen, *Spectrochim. Acta*, **17**, 1286 (1961).

8) G. A. Hill and E. W. Flosdorf, "Organic Syntheses," Coll. Vol. I, p. 462 (2nd Ed., 1948).

9) F. C. Whitmore and E. E. Stahly, *J. Am. Chem. Soc.*, **55**, 4153 (1933).

10) P. D. Bartlett and A. Schneider, *ibid.*, **67**, 141 (1945).

11) N. C. Cook and W. C. Percival, *ibid.*, **74**, 4141 (1949).

12) Details of the measurement and analysis of the spectra were nearly the same as previously reported by the author. *Cf.* M. Ōki and M. Hirota, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 115 (1965) and papers cited therein.

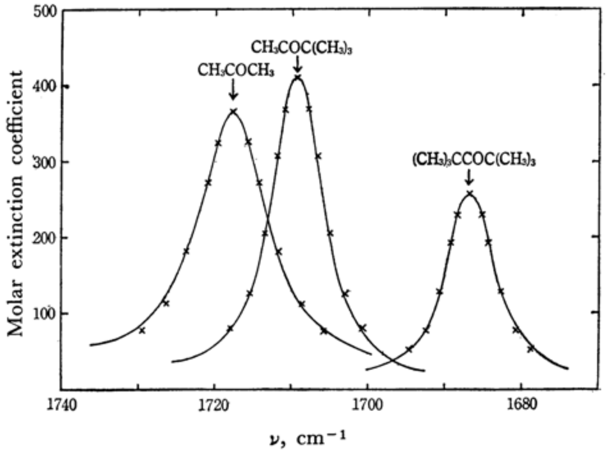


Fig. 1. Carbonyl stretching absorptions of acetone, pinacolone ane di-*t*-butyl ketone in carbon tetrachloride. The band envelopes calculated from the best fit Lorentzian functions are also shown by × in this figure.

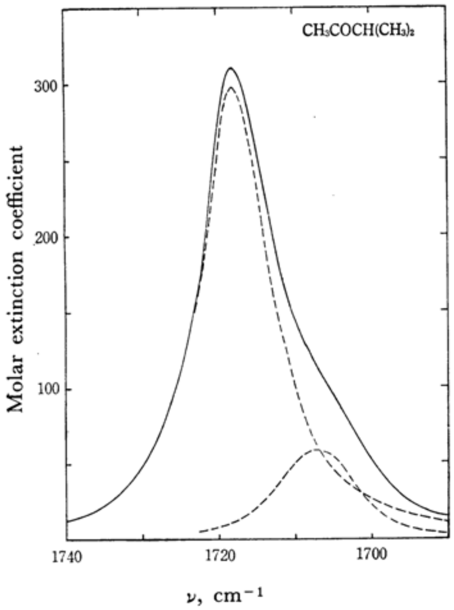
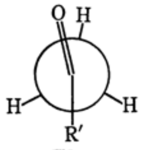
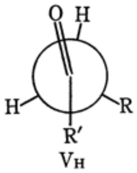


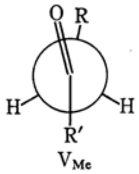
Fig. 2. Carbonyl stretching absorption of methyl isopropyl ketone in carbon tetrachloride. The absorptions of H-H conformer and H-Me conformer were separated and shown by ---- in this figure.



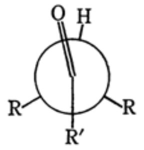
IV_H



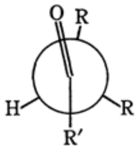
V_H



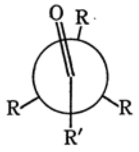
V_{Me}



VI_H



VI_{Me}



VII_{Me}

R = Me, R′ = Alkyl

Here the suffixes H and Me refer to the conformations in which the oxo-groups are eclipsed to the hydrogen atom and the methyl group respectively. The conformation of the whole ketone molecule can then be expressed by a combination of the conformations of the two halves of the moleule; the possible conformations of the methyl-substituted acetones on this assumption are shown in Table 1, together with the observed ν_{max} and ε_{max} values. The term "H–H" conformation in this Table implies a conformation in which the carbonyl group is eclipsed to both α- and α′-hydrogen atoms, "H–Me" corresponds to a conformation in which the carbonyl group is eclipsed to the α-hydrogen atom and the α′-methyl group, and "Me–Me," to a conformation in which the carbonyl group is eclipsed to both α- and α′-methyl groups.

The assumptions that the infrared $\nu_{C=O}$ frequencies of these ketones are controlled mainly by the two eclipsing groups, and that the number of methyl substituents, as well as other factors, affects on the $\nu_{C=O}$ frequencies rather slightly, makes the following discussions possible; these assumptions are very probable, since they have been proven to be true in other series of rotational isomers.[13]

Judging from the intensity data in Table 1, the H–H conformation would be the most favorable and the Me–Me conformation would be the least favorable. The C=O stretching frequencies for

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[13] For example, the conformation of alcohols were discussed assuming similar conformational dependence of the infrared O–H frequency. *Cf.* M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

H–H conformers range from 1716 cm^{-1} to 1721 cm^{-1}, this range being different from the C=O frequency range of H–Me conformers. With a ketone which can exist as either an H–H or an H–Me conformer, the H–H conformer predominates, and so the absorption by the H–Me conformer is characterized as a shoulder of the absorption band of the former. The Me–Me conformer might be unlikely because it causes serious crowding in the ketone molecule; in fact, the absorption assigned to this conformation is observed only with di-*t*-butyl ketone, in which only the Me–Me conformer is possible. The absorption frequency ranges for the H–Me and Me–Me conformations are 1707 cm—1713 cm^{-1} and *ca.* 1687 cm^{-1} respectively. The C–C(O)–C bond angle strain foreseen for the last ketone would be at least partly responsible for the extremely low C=O stretching frequency of the Me–Me conformation.[14]

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14) J. O. Halford, *J. Chem. Phys.*, **24**, 830 (1956).