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Infrared Spectra of Some Carboxylic Acid Derivatives[1]

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In continuation of the discussion of spectroscopic studies initiated in the preceding paper, and done in connection with penicillin structure, this paper reports the infrared spectra of a series of esters, lactones, chlorides and salts of carboxylic acids.

Experimental details are the same as those given previously,[2] the reproducibility in wave length being better than ± 0.03 μ. The spectra are presented in tabular form in Tables I to IV. As with the previous paper of this series, discussion will be limited to the 3 μ (NH, OH and CH) and 6 μ (double-bond) regions. Thompson and Torkington,[3a] in a much more detailed study of a series of saturated esters, have described many other regularities at longer wave lengths. Recent papers containing some information on carboxylic acid derivatives have been published by Thompson[3b] and Jones, *et al.*[3c]

Esters.—The spectra of a series of esters, studied principally for information on the effects of induction and conjugation on the ester C=O band, are shown in Table I.

Normal aliphatic esters exhibit the C=O band very near 5.75 μ (1739 cm.$^{-1}$), from the work of Thompson and Torkington and others. The spectra of methyl pivalate, ethyl diphenylacetate, and methyl sarcosinate (Table I; 1, 2, 3) have bands so near this position that it is clear that inductive effects due to α-alkyl, α-aryl or α-amino substituents exert no appreciable effect on the C=O force constant. Ethyl cyanoacetate, on the other hand, shows its band at a somewhat shorter wave length (5.71 μ), (1751 cm.$^{-1}$), presumably due to the inductive effect of the C≡N group (Table I; 4). In addition to the C=O bands, the above compounds have the additional expected bands due to phenyl (6.24 and 6.68 μ), (1603 cm.$^{-1}$ and 1497 cm.$^{-1}$), NH (2.985 μ) (3350 cm.$^{-1}$) and C≡N (4.43 μ), (2257 cm.^{1}).

The effect of conjugation of C=O with C=C is illustrated by methyl methacrylate (Table I; 5). The ester C=O band appears at 5.82 μ (1718 cm.$^{-1}$) and the C=C band at 6.11 μ (1637 cm.$^{-1}$) the shift of each to longer wave length being due to the conjugation. Conjugation of the C=O with the phenyl group, as in methyl benzoate (Table I; 7), seems to give a somewhat smaller shift (to 5.80 μ) (1724 cm.$^{-1}$) although Thompson and Torkington[3] found that ethyl benzoate gave the band at 1716 cm.$^{-1}$ (5.83 μ) within the limits of measurability of their published spectrum. Ethyl *o*-, *m*- and *p*-nitrobenzoates (Table I; 8, 9, 10) exhibit a marked lessening of the conjugation shift, the C=O bands occurring near 5.77 μ (1733 cm.$^{-1}$). Evidently the competition of the nitro group for electrons from the ring, through both resonance and induction, accounts for this effect. A similar phenomenon is observed for ethyl β,β-diethoxyacrylate (Table V; 6), where the band appears at 5.76 μ (1736 cm.$^{-1}$). In this case the decrease of conjugation must be attributed to the inductive attraction of the ethoxy groups for electrons, which opposes the ionic resonance structure (+)C—C=C—O(−).

Other bands in the 3 and 6 μ regions of the spectra of these conjugated esters are explicable as follows. Weak bands at 2.70 to 2.90 μ (3704 cm.$^{-1}$ to 3448 cm.$^{-1}$) are due to traces of water or hydroxylic impurities. The strong band of ethyl β,β-diethoxyacrylate at 6.20 μ (1613 cm.$^{-1}$) is attributable to the C=C vibration; the long wave-length shift from the usual C=C position near 6.0 μ (1667 cm.$^{-1}$) need not be attributed to conjugation (see above), but may presumably be due simply to the alkoxy substituents. Weak bands from 4.5 to 5.6 μ (2222 to 1786 cm.$^{-1}$) in spectra of the phenyl-containing compounds are overtones of the ring vibrations. Methyl benzoate exhibits the 6.25 and 6.69 μ (1600 and 1495 cm.$^{-1}$) bands which are common to all mono-substituted phenyl compounds, as well as the band at 6.29 μ (1590 cm.$^{-1}$) given by benzoyl compounds.[2] The nitro compounds have the very strong band near 6.50 μ (1538 cm.$^{-1}$) ascribable, from work on aliphatic nitro compounds, to the NO_2 group, and also show bands near 6.18 μ (1618 cm.$^{-1}$) and 6.75 μ (1481 cm.$^{-1}$) which are presumably the analogs of the 6.25 μ (1600 cm.$^{-1}$) and 6.69 μ (1495 cm.$^{-1}$) bands of simple phenyl compounds. Other weak bands in the 6 μ region do not occur with any regularity in similar compounds, and hence are attributable to impurities.

A further effect noted in ester spectra is to be found in the vinyl ester type of compound. Barnes, *et al.*,[4] give a spectrum of vinyl acetate in which the C=O band appears near 5.65 μ (1770 cm.$^{-1}$). This short wave-length shift is also exhibited by phenyl acetate and *o*-nitrophenyl acetate (Table V; 12, 13), the C=O bands being 5.70 and 5.60 μ (1754 and 1786 cm.$^{-1}$), respectively. The other bands observed are attributable to the phenyl or nitrophenyl groups, or to impurities.

(1) Most of this work was done under contract between the Office of Scientific Research and Development and the Shell Development Company (Contract OEM-cmr-445).

(2) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

(3a) H. W. Thompson and P. Torkington *J. Chem. Soc.*, 640 (1945).

(3b) H. W. Thompson, *ibid.*, 328 (1948).

(3c) R. N. Jones, V. Z. Williams, M. J. Whalen and K. Dobriner, THIS JOURNAL, **70**, 2024 (1948).

(4) R. B. Barnes, R. C. Gore, U. Liddel and V. Z. Williams, "Infrared Spectroscopy," Reinhold Publ. Corp., New York, N. Y., 1944.

The unusual compound 1,1-diacetoxypropane, $CH_3CH_2CH(OOCCH_3)_2$ (Table I; 11), also exhibits its ester C=O band at shorter wave length (5.68 μ) (1761 cm.$^{-1}$) than normal. This indicates that there may be some inductive effect on the ester C=O band position due to negative α-substituents on the alcohol part of the molecule, the substituent in this case being another acetoxy group. A similar effect has been noted with α-cyano substituents (acetates of cyanohydrins).

In Table II are shown spectra of several esters which illustrate the effect of conjugated chelation.[2] Ethyl α,α-dimethylacetoacetate (Table II; 1) which has no possibility of enolizing to give a

TABLE I

INFRARED SPECTRA OF ESTERS, ILLUSTRATING INDUCTION AND CONJUGATION EFFECTS

1. Methyl pivalate (methyl trimethylacetate), 0.15 mm. 5% soln. in CCl_4.
2. Ethyl diphenylacetate, 0.15 mm. 5% soln. in $CHCl_3$.
3. Ethyl cyanoacetate, 0.15 mm. 5% soln. in CCl_4.
4. Phenyl acetate, 0.02 mm. pure liquid.
5. Ethyl β,β-diethoxyacrylate, 0.02 mm. pure liquid.
6. Methyl sarcosinate (N-methylglycine methyl ester), 0.02 mm. pure liquid.
7. Methyl methacrylate, 0.02 mm. pure liquid.
8. 1,1-Diacetoxypropane, 0.03 mm. pure liquid.
9. Methyl benzoate, 0.02 mm. pure liquid.
10. Ethyl *o*-nitrobenzoate, 0.02 mm. pure liquid.
11. Ethyl *m*-nitrobenzoate, 0.15 mm. 10% soln. in CCl_4.
12. Ethyl *p*-nitrobenzoate, 0.15 mm. 10% soln. in CCl_4.
13. *o*-Nitrophenyl acetate, 0.15 mm. 10% soln. in CCl_4.

(Wave lengths in μ; intensity in units of 10% absorptions; S = solvent interference.)
Bands due to ester C=O stretching vibrations are underlined.

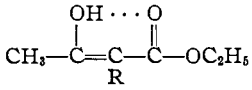
1	2	3	4	4	5
3.35(6)	3.2-3.4 S	3.345(4)	2.90(2)	7.76(2)	2.90(1)
5.76(8)	5.785(8)	4.43(1)	3.28(4)	8.1-8.5(10)	3.34(8)
6.755(4)	6.24(2)	5.71(9)	3.42(1)	8.60(9)	5.76(10)
6.85(3)	6.68(3)	6.81(3)	4.78(1)	9.34(5)	5.97(1)
6.97(3)	6.89(2)	6.915(2)	5.00(1)	9.57(4)	6.20(9)
7.165(2)	7.295(3)	7.15(4)	5.14(2)	9.795(4)	6.48(1)
7.31(3)	7.45(2)	7.30(5)	5.54(1)	9.895(7)	6.86(10)
7.77(7)	7.65(2)	7.52(7)	~5.70(9)	10.38(1)	~7.15(10)
8.37(5)	7.86(1)	7.71(1)	6.09(1)	10.795(8)	7.5-9.7(10)
8.64(9)	7.9-8.4 S	7.95(9)	6.285(7)	11.205(6)	10.45(3)
9.65(2)	8.64(6)	8.40(9)	6.50(2)	12.06(1)	10.65(4)
10.13(4)	8.69(1)	8.98(1)	6.725(8)	12.255(7)	11.51(4)
10.64(1)	9.11(1)	9.085(2)	6.885(2)	12.63(1)	11.81(3)
11.585(4)	9.25(1)	9.71(7)	7.00(4)	13.33(8)	Not
>12.0 S	9.725(6)	10.69(3)	7.30(8)	14.42(7)	contd.
	10.46(1)	11.745(3)	7.59(1)		further
	>12.0 S	>12.0 S			

6	7	8	9	9
2.985(3)	3.37(5)	2.30(1)	2.76(1)	8.20(1)
3.37(7)	5.04(1)	2.50(1)	2.91(1)	8.37(5)
3.54(2)	5.82(10)	2.885(2)	3.25(2)	8.48(5)
5.74(8)	6.11(7)	3.35(8)	3.29(4)	8.61(2)
6.75(1)	6.91(7)	3.62(1)	3.35(3)	~ 9.00(10)
6.88(6)	6.96(7)	4.71(1)	3.48(1)	9.305(8)
6.95(8)	7.13(2)	5.68(10)	4.77(1)	9.725(9)
7.06(2)	7.265(3)	~6.50(1)	5.18(2)	9.965(1)
7.30(5)	7.555(8)	6.84(6)	5.59(1)	10.32(8)
7.81(2)	7.685(8)	6.96(6)	5.80(9)	10.645(4)
8.25(10)	8.34(10)	7.28(9)	5.94(3)	11.755(1)
8.51(9)	8.59(10)	7.9-8.3(10)	6.06(1)	12.125(6)
8.86(6)	9.84(5)	8.55(3)	6.245(2)	12.325(3)
9.94(7)	10.02(1)	8.98(10)	6.29(2)	13.135(1)
10.33(5)	10.155(2)	9.27(9)	6.69(2)	~14.0(10)
10.68(2)	10.61(9)	9.6-10.0(10)	6.92(8)	14.52(5)
11.23(2)	10.74(2)	10.33(10)	7.59(5)	14.79(4)
11.36(2)	12.03(3)	10.80(8)	~7.80(10)	
11.92(1)	12.265(8)	11.02(8)		
~13.1(10)		11.36(2)		
~14.4(5)		12.82(4)		

TABLE I (*Continued*)

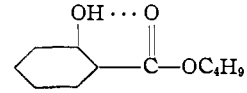
10	11	12	13
2.77(1)	3.205(1)	3.295(4)	3.21(1)
3.24(2)	3.315(4)	5.12(1)	3.39(2)
3.34(5)	5.77(8)	5.51(1)	5.48(1)
5.78(9)	6.16(4)	5.76(8)	5.60(8)
6.19(5)	6.48(8)	6.02(1)	5.77(1)
6.32(2)	6.75(5)	6.185(5)	6.195(6)
6.50(10)	6.915(4)	6.485(8)	6.25(2)
6.76(5)	7.17(3)	6.74(3)	6.495(8)
6.91(4)	7.29(3)	6.80(3)	6.73(4)
~7.37(10)	7.385(6)	6.89(3)	6.86(1)
~7.82(10)	7.585(3)	7.06(4)	6.965(2)
8.51(5)	7.73(7)	7.16(2)	7.28(4)
8.84(9)	7.90(8)	7.29(1)	7.38(7)
9.09(1)	8.49(3)	7.385(9)	7.51(1)
9.295(8)	8.80(8)	7.56(3)	8.40(10)
9.625(5)	8.96(1)	7.82(10)	8.575(4)
9.87(7)	9.095(3)	8.00(2)	8.705(2)
10.38(2)	9.305(6)	8.19(2)	9.145(7)
11.28(1)	9.81(7)	8.50(4)	9.58(4)
11.51(3)	10.62(1)	~9.0(9)	9.895(7)
11.64(3)	10.80(4)	9.20(1)	10.17(2)
11.805(5)	10.96(3)	9.81(7)	10.455(4)
12.64(7)	11.55(5)	11.42(7)	11.00(8)
12.84(5)	11.92(4)	11.87(8)	11.44(5)
13.58(8)	12.0–14.0 S	12.0–14.0 S	11.75(6)
14.28(5)	13.86(9)	13.85(9)	12.0–14.0 S
			14.275(8)
			14.83(4)

conjugated chelate ring, shows only a single band in the double-bond region, at 5.79 μ (1727 cm.$^{-1}$). Examined in more dilute solution, this band is found to have a strong component at 5.82 μ (1718 cm.$^{-1}$), and a weaker one, appearing as a shoulder, at 5.74 μ (1742 cm.$^{-1}$). These are clearly to be ascribed to the ketone and ester groups, respectively. Ethyl α-methylacetoacetate and ethyl acetoacetate (Table II; 2, 3) each exhibit an additional band near 6.06 μ (1650 cm.$^{-1}$), ascribable to the C=O of the conjugated chelate ring:



That the enolization is only partial is seen from the persistence of a strong 5.78 μ (1730 cm.$^{-1}$) band. This result is essentially identical with that from Raman work.[5] However, as with acetylacetone,[2] the 6.06 μ (1650 cm.$^{-1}$) band is more reasonably ascribed to the C=O rather than the C=C vibration in contradistinction to the assignment given by Kohlrausch and Pongratz. The 3.7 μ (2703 cm.$^{-1}$) band expected from the OH of the enol was not observed, very probably because the concentration of enol was not high enough to bring it out. Diethyl α,β-diacetylsuccinate (Table II; 4) exhibits only the unmodified ester and ketone bands, with no evidence of enolization or chelation.

As an example of an aromatic conjugated chelate system, *n*-butyl salicylate was examined (Table II; 5). Bands are found at 3.14 μ (3185 cm.$^{-1}$) and 5.97 μ (1675 cm.$^{-1}$) attributable, respectively, to OH and to ester C=O in the conjugated chelate system:



Both bands are shifted considerably beyond their "normal" positions (hydrogen-bonded OH, 3.0 μ (3333 cm.$^{-1}$); conjugated ester, 5.82 μ (1718 cm.$^{-1}$)), but are not shifted as much as in enolized chelate β-diketones or β-ketoesters (OH = *circa* 3.7 μ (2703 cm.$^{-1}$) C=O, 6.05 μ (1653 cm.$^{-1}$) or more). Hence the chelation is apparently not quite so strong as with this latter class, probably due to the only partial double-bond character of the CC bonds of the ring. That conjugated chelation nevertheless has influenced the spectrum markedly is attested to by an examination of acetylated *n*-butyl salicylate (Table II; 6). The OH band disappears, and the salicylate C=O band returns to the usual conjugated ester position, appearing at 5.805 μ (1723 cm.$^{-1}$). The acetate C=O band, arising from the vinyl ester type of system, appears at a shorter wave length (5.65 μ) (1770 cm.$^{-1}$) than normal unconjugated esters, as discussed above.

(5) *E. g.*, K. W. F. Kohlrausch and A. Pongratz, *Z. physik. Chem.*, **B27**, 176 (1934).

TABLE II

INFRARED SPECTRA OF ESTERS, ILLUSTRATING CHELATION EFFECTS

1. Ethyl α,α-dimethylacetoacetate, 0.15 mm. 10% soln. in CCl_4.
2. Ethyl α-methylacetoacetate, 0.15 mm. 10% soln. in CCl_4.
3. Ethyl acetoacetate, 0.15 mm. 10% soln. in CCl_4.
4. Diethyl α,β-diacetylsuccinate, 0.15 mm. 5% soln. in CCl_4.
5. *n*-Butyl salicylate, 0.15 mm. 10% soln. in CCl_4.
6. *n*-Butyl acetylsalicylate, 0.15 mm. 5% soln. in CCl_4.
7. Methyl N-methylanthranilate, 0.15 mm. 10% soln. in CCl_4.
8. Methyl N,N-dimethylanthranilate, 0.15 mm. 10% soln. in CCl_4.
9. Methyl N-methyl-N-acetylanthranilate, 0.15 mm. 10% soln. in CCl_4.

(Wave lengths in μ; intensity in units of 10% absorption; S = solvent interference.) Bands due to ester C=O stretching vibration are underlined.

1	2	3	4
3.33(6)	3.345(5)	3.34(5)	3.37(3)
5.79(10)	5.79(10)	5.78(10)	5.775(5)
6.82(8)	6.05(2)	6.07(9)	5.83(4)
6.92(2)	6.875(6)	6.80(2)	6.83(2)
7.205(4)	7.04(2)	6.915(3)	6.94(1)
7.365(6)	7.355(5)	7.05(4)	7.045(2)
7.69(2)	7.57(4)	7.20(1)	7.20(1)
7.89(9)	7.91(2)	7.32(5)	7.38(6)
8.08(1)	8.045(6)	7.62(6)	7.81(8)
8.47(2)	8.34(7)	8.09(10)	8.00(8)
8.64(7)	8.66(6)	8.42(4)	8.535(8)
8.94(8)	9.08(3)	8.68(9)	8.76(3)
9.09(1)	9.275(4)	8.97(1)	8.965(1)
9.30(1)	9.51(3)	9.095(4)	9.115(2)
9.725(5)	9.74(4)	9.58(8)	9.635(3)
10.315(2)	11.09(2)	9.87(3)	9.80(3)
11.62(2)	11.62(4)	10.68(4)	10.74(1)
>12.0 S	>12.0 S	>12.0 S	11.50(2)
			>12.0 S

5	5	7	8	9
3.14(5)	10.54(2)	2.975(6)	3.345(5)	3.35(5)
3.39(6)	11.03(1)	3.39(6)	3.43(2)	5.775(6)
5.21(1)	11.34(2)	4.89(1)	3.51(1)	6.05(8)
5.53(1)	11.57(3)	5.215(1)	5.21(1)	6.23(5)
5.97(9)	11.70(1)	5.935(9)	5.79(6)	6.32(1)
6.195(4)	>12.0 S	6.22(3)	6.22(5)	6.55(2)
6.30(3)		6.31(6)	6.36(3)	6.695(5)
6.65(1)	6	6.585(6)	6.645(6)	6.885(5)
6.75(3)	3.38(5)	6.78(2)	6.87(3)	6.96(3)
6.83(3)	5.65(6)	6.85(2)	6.95(5)	7.04(1)
7.10(2)	5.805(6)	6.965(8)	7.375(5)	7.24(7)
7.165(4)	6.22(3)	7.27(1)	7.71(5)	7.395(2)
7.53(5)	6.33(1)	7.545(8)	7.98(9)	7.73(9)
7.68(6)	6.74(2)	~8.0(10)	8.255(9)	7.96(9)
7.995(6)	6.89(4)	8.395(4)	8.38(1)	8.375(3)
8.11(1)	6.98(1)	8.52(5)	8.575(5)	8.65(1)
8.275(7)	7.31(6)	8.595(3)	8.835(8)	8.73(1)
8.445(3)	7.74(5)	8.855(8)	9.25(8)	8.86(4)
8.625(5)	7.95(8)	9.16(8)	9.485(4)	9.07(4)
8.78(5)	8.37(9)	9.375(6)	10.31(3)	9.305(7)
9.155(8)	8.62(3)	9.60(3)	10.505(6)	9.595(4)
9.43(2)	8.815(4)	11.52(1)	>12.0 S	10.32(4)
9.68(4)	8.90(1)	11.83(1)		10.81(2)
10.07(2)	9.23(7)	11.98(3)		>12.0 S
10.365(2)	9.59(3)	12.0-14.0 S		
10.48(1)	9.92(5)	14.20(7)		
	10.47(1)			
	10.93(6)			
	11.44(1)			
	>12.0 S			

The final group of esters examined were derivatives of methyl anthranilate, and are of interest in ascertaining whether the NH group can participate in conjugated chelation in the same fashion as does OH.

Methyl N-methylanthranilate (Table II; 7) exhibits a C=O band at 5.935 μ (1685 cm.$^{-1}$) indicating some chelation effect of almost the same magnitude as with the salicylates. The NH band at 2.975 μ (3361 cm.$^{-1}$), however, appears not to be shifted from its usual position in simple hydrogen-bonding. Removal of the chelating hydrogen, as in methyl N,N-dimethylanthranilate or in methyl N-methyl-N-acetylanthranilate (Table II; 8, 9) results in disappearance of the NH band and in return of the ester C=O band to ~5.78 μ (1730 cm.$^{-1}$), near the usual position for conjugated esters. Actually, the shift due to conjugation with the phenyl ring is smaller than for other similar compounds (*e. g.*, *n*-butyl acetylsalicylate above), but the reason for this is not clear. The N-acetyl compound also shows the 6.05 μ (1653 cm.$^{-1}$) band due to amide C=O.

All the salicylic and anthranilic derivatives discussed above (Table II; 5, 6, 7, 8, 9) exhibit in the main the bands expected from the phenyl ring. These are: (1) the bands near 6.20 μ (1613 cm.$^{-1}$) and 6.6 to 6.7 μ (1515 to 1493 cm.$^{-1}$) found regularly with simple phenyl compounds, and (2) that near 6.30 μ (1587 cm.$^{-1}$) found also in benzoyl compounds. The 6.20 μ (1613 cm.$^{-1}$) bands, which are weak for phenyl rings with carbon substituents, are enhanced in intensity for O- or N-substituted rings, as noted from unpublished work of this Laboratory on phenols and anilines; this effect is to be seen also in the above described salicylate and anthranilate spectra. Two anomalies in the above explanation are: (1) the enhanced intensity of the 6.31 μ (1585 cm.$^{-1}$) band in methyl N-methylanthranilate as compared with the other compounds, and (2) the unexplained band at 6.55 μ (1527 cm.$^{-1}$) in the spectrum of methyl N-methyl-N-acetylanthranilate. Both of these may be due to impurities.

Lactones.—Spectra of some lactones are given in Table III.

As an exemplar of the simple saturated 5-membered lactones, γ-valerolactone was studied (Table III; 1). The sample was evidently considerably impure, as attested to by unexplainable bands at 5.76 and 6.12 μ (1736 and 1634 cm.$^{-1}$) (2.80 μ (3571 cm.$^{-1}$) is due to adventitious water). However, the strong 5.65 μ (1770 cm.$^{-1}$) band is certainly ascribable to the lactone C=O stretching vibration. The reason for this shift from the open chain ester position must be sought in ring strain, but the exact mechanism is unclear. Taufen and Murray[6] give the Raman spectrum of β-butyrolactone, from which it is apparent that the C=O band of this compound would appear near 5.50 μ (1818 cm.$^{-1}$), even further shifted from the open-chain position. On the other hand, δ-valerolactone

(6) H. J. Taufen and M. J. Murray, THIS JOURNAL, **67**, 754 (1945).

TABLE III

INFRARED SPECTRA OF LACTONES

1. γ-Valerolactone, 0.02 mm. pure liquid.
2. β,γ-Angelica lactone (4-hydroxy-3-pentenoic acid γ-lactone), 0.02 mm. pure liquid.
3. Acetate of lactone form of levulinic acid (γ-acetoxy-γ-valerolactone), 0.15 mm. 10% soln. in $CHCl_3$.
4. α-Acetyl-γ-butyrolactone, 0.02 mm. pure liquid.
5. δ-Valerolactone, 0.02 mm. pure liquid.
6. Coumarin (*o*-hydroxycinnamic acid δ-lactone), 0.15 mm. 10% soln. in $CHCl_3$.

(Wave lengths in μ; intensity in units of 10% absorption; S = solvent interference). Bands due to the lactone C=O stretching vibrations are underlined.

1	2	3	4	5	6
2.80(1)	2.59(1)	2.365(1)	2.865(1)	2.89(3)	3.2–3.4 S
3.35(6)	2.79(1)	3.2–3.4 S	2.925(1)	3.38(9)	~5.80(10)
5.65(9)	3.19(1)	5.565(5)	3.33(3)	5.75(10)	5.96(2)
5.76(3)	3.375(3)	5.715(5)	3.40(3)	6.77(3)	6.15(4)
6.12(1)	4.51(1)	7.195(3)	5.64(6)	6.84(4)	6.19(6)
6.85(5)	4.905(1)	7.27(3)	5.82(6)	6.92(3)	6.37(5)
7.025(5)	5.56(10)	Not contd.	6.04(3)	7.13(6)	6.77(2)
7.20(6)	5.945(5)	further	6.74(2)	7.45(5)	6.88(5)
7.42(6)	6.92(3)		6.875(3)	7.83(4)	7.13(5)
7.67(3)	6.96(2)		7.025(4)	~8.04(10)	7.505(1)
7.80(2)	7.15(1)		7.28(6)	~8.62(10)	7.825(3)
8.17(5)	7.20(5)		7.35(6)	9.28(3)	7.925(3)
8.35(3)	7.36(1)		7.51(2)	9.48(9)	7.9–8.4 S
8.52(9)	7.745(4)		7.75(3)	10.16(3)	8.45(8)
8.90(5)	7.875(7)		8.07(2)	10.75(6)	8.90(6)
9.02(2)	8.10(1)		8.205(6)	11.39(2)	9.03(7)
9.11(3)	8.46(7)		8.66(10)	12.09(3)	9.70(1)
9.44(8)	8.99(10)		9.01(1)	12.50(2)	10.14(1)
9.60(2)	9.61(2)		9.185(3)	13.36(3)	10.57(2)
10.00(5)	9.88(4)		9.765(7)		10.71(8)
10.39(2)	10.30(7)		9.98(5)		11.185(7)
10.60(8)	10.71(8)		10.25(1)		11.53(3)
11.14(7)	11.955(6)		10.64(4)		12.025(8)
12.09(2)	13.41(7)		11.54(1)		>12.0 S
12.42(4)	14.305(4)		12.72(4)		
13.45(1)			14.305(4)		

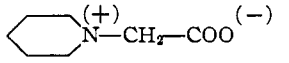
exhibits its band at 5.75 μ (1739 cm.$^{-1}$), the same position as open-chain esters (Table III; 5). Hence the strain is sufficiently reduced in the six-membered ring to exert no effect spectroscopically. Similar shifts from the open-chain position are to be observed in five- and four-membered cycloketone and lactam rings.

The remaining lactones discussed here demonstrate further effects on the lactone C=O band position which are identical with effects described above for the open-chain esters. Thus β,γ-angelica lactone (Table III; 2) is essentially a vinyl ester type of compound. The shift of its C=O band to 5.56 μ (1799 cm.$^{-1}$), a short wave-length shift from the saturated 5-ring lactone position (5.65 μ), (1770 cm.$^{-1}$), parallels the shift of open-chain vinyl esters from the saturated open-chain ester position (see preceding section). The C=C band appears at 5.945 μ (1682 cm.$^{-1}$). Similarly, γ-acetoxy-γ-valerolactone (Table III; 3) exhibits its lactone C=O band at 5.565 μ (1797 cm.$^{-1}$) and its acetate group C=O band at 5.715 μ (1750 cm.$^{-1}$), the short wave-length shifts here paralleling the ones observed for 1,1-diacetoxypropane (see preceding section of this paper).

The β-ketoester type of lactone is represented by α-acetyl-γ-butyrolactone (Table III; 4). The non-enolized form is evidenced by a normal 5-ring lactone band at 5.64 μ (1773 cm.$^{-1}$) and a normal ketone band at 5.82 μ (1718 cm.$^{-1}$), whereas the rather weak band at 6.04 μ (1656 cm.$^{-1}$) indicates a small amount of enolization to a conjugated chelate system (see discussion of acetoacetic esters in preceding section).

A more complex lactone is illustrated by coumarin (Table III; 6). The multiple conjugation here makes it useless to attempt a specific assignment of the double-bond bands until such systems are further studied.

Salts.—Two examples of spectra of salts of carboxylic acids are given in Table IV. Sodium acetate possesses as its only absorption in the 6 μ region a band at 6.33 μ (1580 cm.$^{-1}$). This must be attributed to one of the vibrations of the COO^- group. Work of other laboratories in the penicillin project on spectra of salts indicated considerable variability in the infrared band position, but it generally falls in the range 6.20 to 6.35 μ (1613 to 1575 cm.$^{-1}$). An example of an extreme shift in position is found in pyridine betaine (Table III; 2),



The band attributable to COO^- occurs at 6.055 μ (1652 cm.$^{-1}$), indicating a powerful inductive or electrostatic effect of the positive nitrogen on the COO^- group.

TABLE IV

INFRARED SPECTRA OF SALTS AND ACID CHLORIDES OF CARBOXYLIC ACIDS

1. Sodium acetate, 0.02 mm. 5% soln. in CH_3OH.
2. Pyridine betaine, 0.02 mm. 20% soln. in CH_3OH.
3. Acetyl chloride, 0.15 mm. 10% soln. in CCl_4.
4. Phenylacetyl chloride, 0.15 mm. 10% soln. in CCl_4.
5. Benzoyl chloride, 0.15 mm. 5% soln. in CCl_4.

(Wave lengths in μ; intensity in units of 10% absorption; S = solvent interference.) Bands due to the C=O stretching vibration are underlined.

1	2	3	4	5
6.33(6)	6.055(7)	2.75(1)	3.265(3)	3.245(1)
(studied	6.75(4)	3.27(2)	3.40(1)	5.64(6)
from	7.27(6)	3.35(2)	5.13(1)	5.76(5)
5-7μ	7.67(3)	4.86(1)	5.23(1)	6.255(2)
only)	8.19(1)	5.23(3)	5.56(9)	6.305(2)
	8.40(2)	~5.50(10)	5.84(1)	~6.70(2)
	(studied	5.71(5)	6.05(1)	6.895(4)
	from	7.01(7)	6.28(2)	7.05(1)
	5-9μ	7.325(7)	6.675(4)	7.21(1)
	only)	7.725(4)	6.875(4)	7.44(1)
		~9.07(10)	7.02(1)	7.60(2)
		9.78(3)	7.125(3)	7.67(1)
		10.46(9)	7.635(1)	8.305(9)
		>12.0 S	8.43(5)	8.50(6)
			8.62(1)	9.075(1)
			9.03(1)	9.27(1)
			9.275(3)	9.73(1)
			9.71(3)	9.975(2)
			9.885(7)	10.68(1)
			10.015(6)	11.41(10)
			10.44(10)	12.0-14.0 S
			12.0-14.0 S	14.56(8)
			14.09(8)	14.83(8)
			14.30(5)	

Acid Chlorides.—Spectra of three acid chlorides are given in Table IV. Both acetyl chloride and phenylacetyl chloride exhibit the C=O band near 5.55 μ (1802 cm.$^{-1}$). The moderately intense band of the former at 5.71 μ (1751 cm.$^{-1}$) is ascribable to a hydrolytic impurity of acetic acid, and the same explanation may be applicable for some of the weak bands of phenylacetyl chloride. The spectrum of benzoyl chloride is anomalous in that two bands appear in the double-bond region (5.64, 5.76 μ) (1773, 1736 cm.$^{-1}$), aside from the bands of the phenyl ring (6.255, 6.305, 6.70 μ) (1599, 1586, 1493 cm.$^{-1}$). It is improbable that one of these results from hydrolysis, since benzoic acid C=O bands are found near 5.9 μ (1695 cm.$^{-1}$), and since repeat experiments in which precautions were taken against hydrolysis yielded the same spectrum. Two possible causes of this doubling are partial association into dimers, and inter-action with a low thermally-excited vibration. Aside from this anomaly, the expected long wave-length shift due to conjugation is present, as is evident by a comparison with acetyl and phenylacetyl chlorides.

Experimental

The sources and purities of samples used were as follows (synthetic work carried out by Drs. C. W. Smith and D. S. Melstrom):

Methyl pivalate was prepared by treatment of pivalic acid with diazomethane. The product was washed with bicarbonate, dried over sodium sulfate, and fractionated through a micro still. The heart cut, b. p. 100° (lit. 100 to 102°), $n^{20}D$ 1.3892, was used.

Ethyl diphenylacetate was prepared from diphenylketene and absolute ethanol. The product was recrystallized from absolute ethanol, m. p. 56.5 to 57° (lit., 57 to 59°).

Methyl Sarcosinate.—Methylaminoacetonitrile was prepared from methylamine hydrochloride, formaldehyde and potassium cyanide, according to the method of Lilly.[7] It was converted to methyl sarcosinate hydrochloride with hydrochloric acid in methanol. The ester was liberated from the hydrochloride, and fractionated twice. The final product used had the constants: b. p. (20 mm.) 43.0–43.5°, $n^{20}D$ 1.4154. *Anal.*: C, 46.76, 46.48; H, 8.83, 8.85. (Calcd.: C, 46.59; H, 8.80.)

Ethyl Cyanoacetate.—Eastman Kodak Co. White Label was used without further purification.

Methyl methacrylate was taken from a careful distillation of technical material.

Ethyl β,β-diethoxyacrylate was prepared from ethyl cyanoacetate with ethanol and hydrochloric acid by the method of Reitter and Weindel.[8] The product was distilled from a Claisen flask and a fraction b. p. 80 to 86° (1 mm.) was used for the spectroscopic work (lit. b. p. 127.8 to 128.2° (12 mm.)).

Methyl benzoate, the three ethyl nitrobenzoates, and phenyl acetate were Eastman Kodak Co. White Label products used without further purification. The *o*-nitrophenyl acetate sample was Eastman Yellow Label, with a stated m. p. of 37 to 39°, and was not further purified.

1,1-Diacetoxy-2-propene was prepared from acrolein and acetic anhydride by the method of Wohl and Maag.[9] The product was hydrogenated over nickel (15 p. s. i.) to give the diacetoxypropane, and had the constants: b. p. 62° (5 mm.), $n^{20}D$ 1.4070.

The ethyl acetoacetate used was a commercial sample, b. p. (10 mm.) 78 to 79°.

Ethyl α-methylacetoacetate was prepared by alkylation of acetoacetic ester with methyl iodide according to the method of Folkers and Adkins.[10] The final product had a b. p. (23 mm.) of 81 to 84°. *Anal.*: C, 58.2, 58.45; H, 8.43, 8.43. (Calcd.: C, 58.32, H, 8.39.)

Ethyl α,α-dimethylacetoacetate was prepared by further methylation of the above monomethylated compound. Unreacted monomethylated ester was removed from the product by extraction of a benzene solution with 25% aqueous potassium hydroxide according to the method of Pedersen.[11]

Diethyl α,β-diacetylsuccinate was prepared from sodium acetoacetic ester and iodine according to the procedure of Knorr and Haber[12]; m. p. 85 to 88° (lit. 85–88°).

The *n*-butyl salicylate sample used was Eastman White Label without further purification; b. p. (20 mm.) 145 to 146°. Its acetyl derivative was obtained by treatment with acetic anhydride in pyridine; b. p. (0.9–1 mm.) 128 to 130°; sp. gr. 20/4 1.101, 1.102; $n^{20}D$ 1.4989.

Methyl N-methylanthranilate was prepared from Eastman White Label N-methylanthranilic acid. The N,N-dimethyl compound was obtained from this and methyl iodide according to the method of Kahn.[13] The N-

(7) Lilly, L-XIII-10; Reports of the Penicillin Structure and Synthesis Project.

(8) H. Reitter and A. Weindel. *Ber.*, **40**, 3358 (1907).

(9) A. Wohl and R. Maag, *Ber.*, **43**, 3293 (1910).

(10) K. Folkers and H. Adkins, THIS JOURNAL, **53**, 1416 (1931).

(11) K. J. Pedersen, *ibid.*, **53**, 240 (1936).

(12) L. Knorr and F. Haber, *Ber.*, **27**, 1155 (1894).

(13) R. Willstätter and W. Kahn, *ibid.*, **37**, 401 (1904).

methyl-N-acetyl compound was prepared from methyl N-methylanthranilate by treatment with acetic anhydride in pyridine, and removal of unreacted material under reduced pressure and by hydrochloric acid extraction. The product was an oil which failed to crystallize at the time the infrared spectrum was taken, but which crystallized later.

γ-Valerolactone was produced by catalytic reduction of β,γ-angelica lactone (see below) in absolute ethanol with Raney nickel at 25° and 40 p. s. i. (max.) hydrogen. The product was twice fractionated; b. p. (20 mm.) 93.5. *Anal.:* C, 58.99, 58.74; H, 8.40, 8.29. (Calcd.: C, 59.98; H, 8.06).

β,γ-Angelica lactone was prepared by destructive distillation of levulinic acid (lactone form) acetate (see below), following the method of Thiele, Tischbein, and Lossow.[14] The product was washed with bicarbonate solution and twice distilled; b. p. (12 mm.) 56.2–57.0°. *Anal.:* C, 60.87, 60.76; H, 6.19, 6.14. (Calcd.: C, 61.21; H, 6.17.)

The acetate of the lactone form of levulinic acid was prepared from freshly distilled levulinic acid, acetic anhydride and a trace of acetyl chloride, after the method of Thiele, *et al.*[14] The product was recrystallized twice from ethanol and once from dilute aqueous ethanol: m. p. 74.5 to 75°. *Anal.:* C, 52.94, 53.01; H, 6.45, 6.43. (Calcd.: C, 53.16; H, 6.37.)

α-Acetyl-γ-butyrolactone was prepared from sodium acetoacetic ester and ethylene oxide in absolute ethanol according to the method of Knunyantz, Chelintzev, and Osetrova[15]: b. p. (20 mm.) 135 to 136°; $n^{20}D$ 1.4600. *Anal.:* C, 56.19, 56.17; H, 6.39, 6.43. (Calcd.: C, 56.24; H, 6.29.)

δ-Valerolactone was made by hydrogen peroxide oxidation of δ-hydroxyvaleraldehyde in acetic acid. The product had b. p. 80° (4 mm.); $n^{20}D$ 1.4532. *Anal.:* C, 58.90, 58.89; H, 8.12, 8.13. (Calcd.: C, 59.98; H, 8.05.)

The coumarin used was Eastman White Label with no further purification.

Sodium acetate and acetyl chloride were taken from Baker's C. P. quality materials.

Pyridine betaine hydrochloride and the free betaine were prepared from pyridine and chloroacetic acid by the procedure of Edsall and Wyman.[16] A portion of the free pyridine betaine product was dried for 6.6 hours in a vacuum desiccator over phosphorus pentoxide. *Anal.:* N, 9.8, 9.9. (Calcd.: 10.22.)

Phenylacetyl chloride and benzoyl chloride were Eastman White Label samples.

(14) J. Thiele, R. Tischbein and E. Lossow, *Ann.*, **319**, 180 (1901).

(15) J. L. Knunyantz, G. V. Chelintzev and E. D. Osetrova, *C. r. acad. sci. U. S. S. R. (N. S.)*, 1, 312 (1934); *C. A.*, **28**, 4382 (1934).

(16) J. T. Edsall and J. Wyman, Jr., THIS JOURNAL, **57**, 1964 (1935).

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Summary

1. Infrared absorption maxima in the 2-to-15 μ region are tabulated for a group of carboxylic acid esters, lactones, salts, and acid chlorides.

2. Unconjugated esters exhibit their C=O bands near 5.75 μ (1739 cm.$^{-1}$), although sufficiently electronegative α-substituents may shift the position down as far as 5.70 μ (1754 cm.$^{-1}$).

3. Conjugation of the ester C=O to C=C or phenyl shifts the C=O band position to *circa* 5.81 μ (1721 cm.$^{-1}$). The amount of this shift may be markedly modified by induction or resonance effects due to substituents on the conjugated system.

4. Vinyl ester or phenyl ester compounds exhibit the ester C=O band shifted to *circa* 5.65 μ (1770 cm.$^{-1}$).

5. Enolized β-ketoesters, and salicylic esters, show the enhanced shift in C=O position expected from conjugated chelate systems. The C=O bands appear near 6.0 μ (1667 cm.$^{-1}$) in these cases. An anthranilic ester showed a similar conjugated chelation effect, but the C=O shift was only to 5.935 μ (1685 cm.$^{-1}$).

6. Saturated five-membered lactone rings give a C=O band near 5.65 μ (1770 cm.$^{-1}$). This may be modified by conjugation, vinyl ester and chelation effects as described for open-chain esters. A saturated six-membered lactone gives a band at 5.75 μ (1739 cm.$^{-1}$), *i.e.*, unshifted from the open-chain ester position.

7. Salts of carboxylic acids yield a band near 6.3 μ (1587 cm.$^{-1}$).

8. Unconjugated acid chlorides exhibit the C=O band near 5.55 μ (1802 cm.$^{-1}$).

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