γ-Phenyl-α,α-dimethylisocrotonic Acid.—A mixture of 23.0 g. (0.18 mole) of α,α-dimethylsuccinic anhydride, 12 g. (0.07 mole) of sodium α,α-dimethylsuccinate and 26.0 g. (0.24 mole) of freshly distilled benzaldehyde was heated at 190–200° for 60 hours. The reaction mixture was poured into 100 ml. of water and the whole made alkaline to litmus and submitted to steam distillation. The aqueous residue was heated with Norite, filtered and the filtrate acidified with concentrated hydrochloric acid. A light brown precipitate formed and was isolated by suction filtration. After being recrystallized from 50% aqueous ethanol the acid melted at 113–114°; yield 26 g. (75%); neut. equiv., calcd., 190; found, 194.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.64; H, 7.26.

The acid chloride, prepared in 92% yield by reaction with thionyl chloride, boils at 140–142° (11 mm.). When the acid chloride was added to an ether solution of aniline the anilide was produced. After being recrystallized from aqueous ethanol this derivative melted at 113–114°. A mixture of the acid and the anilide melts at 94–99°.

Anal. Calcd. for $C_{18}H_{19}ON$: C, 81.48; H, 7.22. Found: C, 81.23; H, 7.42.

γ-Phenyl-γ-bromo-α,α-dimethylbutyric Acid.—One gram of the above acid was dissolved in 10 ml. of glacial acetic acid. This solution was cooled in an ice-bath while dry hydrogen bromide was passed into the solution for one-half hour. The solid product was isolated by suction filtration and recrystallized from chloroform, m.p. 110–111°. A mixture of this product and the original acid melted at 94–97°. This material is not stable and loses hydrogen bromide during storage. It is readily hydrolyzed to γ-phenyl-α,α-dimethyl-γ-butyrolactone and the structure was assigned on that evidence. The acid could not be purified so as to give a satisfactory analysis.

The same acid was obtained when γ-phenyl-α,α-dimethyl-γ-butyrolactone (from β-benzoyl-α,α-dimethylpropionic acid) was treated with dry hydrogen bromide. Prepared by that method the acid melts at 107–109°.

γ-Phenyl-α,α-dimethyl-γ-butyrolactone.—A mixture of 500 mg. of palladium-on-charcoal and 10.3 g. (0.05 mole) of β-benzoyl-α,α-dimethylpropionic acid dissolved in 175 ml. of dioxane was shaken for 19 hours using 30.5 p.s.i. initial hydrogen pressure. Approximately 0.05 mole of hydrogen was taken up. The catalyst was removed by filtration, the solvent by distillation under reduced pressure and the oil residue shaken with 100 ml. of cold saturated sodium bicarbonate solution. The insoluble solid was recovered by filtration and recrystallized from petroleum ether; m.p. 49–50°; yield 7.9 g. (80%).

Anal. Calcd. for $C_{12}H_{14}O$: C, 75.76; H, 7.42. Found: C, 75.54; H, 7.60.

A sample of the unstable, bromine-containing acid was heated with water for five minutes. When the mixture was cooled a white solid separated which was recrystallized from petroleum ether; m.p. 49–50°. A mixture of this product with the above lactone melted at 49–50°.

CORVALLIS, OREGON

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Infrared Spectra of (Trichloromethyl)-carbinols

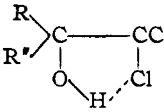
BY ERNST D. BERGMANN AND S. PINCHAS

The infrared spectra of acetonechloroform and four aryltrichloromethylcarbinols have been measured in the O–H and the C–Cl regions and compared with the spectrum of phenylmethylcarbinol. An assignment for the bands observed is suggested. The hydroxyl group in the chlorinated alcohols shows only a very slight tendency to participation in hydrogen bonds. This fact is related to the extreme resistance of acetonechloroform to, *e.g.*, esterification reactions.

Gerrard and Wyvill[1] have commented upon the unusual inertness of the hydroxyl group of acetonechloroform (dimethyltrichloromethylcarbinol) $(CH_3)_2C(OH)CCl_3$, *e.g.*, in esterification reactions.[2] It seemed interesting to investigate whether this peculiarity is reflected in the infrared absorption of the hydroxyl group in this compound and related substances which have become easily available.[3,4]

Table I summarizes the results obtained; for comparison, the spectrum of phenylmethylcarbinol is included. The apparatus was a Perkin–Elmer Infrared Spectrometer, Model 12 C, with a rock salt prism.

Whilst in phenylmethylcarbinol the band (3330 cm.$^{-1}$) characteristic for the hydrogen-bonded hydroxyl is strong and that of the free hydroxyl group (3640 cm.$^{-1}$) weak, the situation is reversed in the chlorinated alcohols, in which also the location of the hydrogen-bonded hydroxyl frequency is shifted, to shorter wave lengths. It follows that in the chlorinated compounds the hydroxyl hydrogen atom participates only to a slight extent in a hydrogen bond, probably of the intramolecular type



This formula recalls the investigations on the hydrogen bonding in *o*-chlorophenol[5] and in ethylenechlorohydrin.[6] Also in certain substituted 2-aminoethanols, the presence of five-membered hydrogen-bonded rings has been demonstrated by infrared absorption measurements.[7] In the main the hydroxyl group in the trichloroalcohols is free. This may be attributed to the strongly negative inductive effect of the chlorine atoms which causes a firmer bonding of the lone electron pair of the oxygen atom, and thus prevents it from participating in hydrogen bonding. As esterification, in the first stage, also involves this lone electron pair, the difficulty of the esterification of acetonechloroform becomes understandable.

In Table I infrared measurements are also re-

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(1) W. Gerrard and P. L. Wyvill, *C. A.*, **44**, 2440 (1950).

(2) Similar inertness has been observed by C. Willgerodt and F. Duerr (*Ber.*, **20**, 539 (1887)) in the corresponding chloride $(CH_3)_2$-CClCCl$_3$.

(3) Ch. Weizmann, E. Bergmann and M. Sulzbacher, THIS JOURNAL, **70**, 1189 (1948).

(4) E. Bergmann, D. Ginsburg and D. Lavie, *ibid.*, **72**, 5012 (1950).

(5) O. R. Wulf and U. Liddel, *ibid.*, **57**, 1464 (1935); O. R. Wulf, U. Liddel and S. B. Hendricks, *ibid.*, **58**, 2287 (1936).

(6) L. R. Zumwalt and R. M. Badger, *ibid.*, **62**, 305 (1940); compare O. Bastiansen, *Acta Chem. Scand.*, **3**, 415 (1949); J. Glazer and E. E. Turner, *J. Chem. Soc.*, 197 (1951).

(7) E. D. Bergmann, E. Gil-Av and S. Pinchas, unpublished results.

TABLE I

INFRARED SPECTRA OF CHLORINATED ALCOHOLS $RR'C(OH)\cdot CCl_3$ IN THE O–H REGION (CCl_4 AS SOLVENT) AND THE FUNDAMENTAL C–Cl REGION (CS_2 AS SOLVENT)

Cell thickness: 0.1 mm. (The % figures indicate "% transmission.")

			O–H region			C–Cl region				
No.	R	R′	Concentration (g. + 1 cc. of CCl_4)	Bands		Concentration (g. + 1 cc. of CS_2)	Bands			
1	CH_3	CH_3	0.100	3590 (73%)	3480 (82%)[a]	0.100	829 (15%)	796 (2%)	787 (0%)	
2	H	C_6H_5	.117	3600 (47%)	3450 (65%)[b]	.109	823 (1%)	770 (2%)	742 (0%)	
3	H	*o*-$Cl\cdot C_6H_4$	.131	3610 (63%)	3450 (73%)[b]	.124	825 (10%)	773 (14%)	752 (4%)	723 (22%)
4	H	*m*-$Cl\cdot C_6H_4$	.117	3600 (66%)	3430 (73%)	.086	824 (8%)	797 (16%)	774 (7%)	690 (0%)[c]
5	H	*p*-$CH_3\cdot C_6H_4$	.108	3600 (66%)	3480 (81%)[a]	.096	820 (2%)	790 (22%)	729 (14%)	
6	$C_6H_5\cdot CHOH\cdot CH_3$		.102	3640 (70%)	3330 (26%)	.081	757 (0%)	(phenyl absorption)		

[a] Transmission in the 3300 cm.$^{-1}$ region 90–95%. [b] Transmission in the 3300 cm.$^{-1}$ region 80%. [c] Very broad band.

corded in the absorption region characteristic for the CCl_3 groups (normally between 710 and 780 cm.$^{-1}$).[8] (No absorption was observed in this region for phenylmethylcarbinol besides the phenyl band.) In each case, two intense bands were found (at 820–830[9] and 770–800 cm.$^{-1}$, respectively) which are obviously due to the CCl_3 grouping in immediate vicinity of the hydroxyl.

For a number of other bands, observed in the same region, the following assignment seems reasonable. The 742 cm.$^{-1}$ band in the phenyl compound (No. 2) is the typical absorption of monosubstituted benzenes; the 752 cm.$^{-1}$ peak in the *o*-chlorophenyl compound (No. 3) is characteristic for all ortho-substituted, that at 774 and that at 690 cm.$^{-1}$ in the *m*-isomer (No. 4) for all meta-substituted, and that at 729 cm.$^{-1}$ in the *p*-methyl derivative (No. 5), for all para-substituted benzene derivatives.

It is further suggested that the absorption of (*o*-chlorophenyl)-trichloromethylcarbinol (No. 3) at 723 cm.$^{-1}$ is due to the C_{ar}–Cl bond and that this band merges for the meta-isomer into the 690 cm.$^{-1}$ band which, indeed, has been observed to be unusually broad. The existence of a C_{ar}–Cl absorption at about 700 cm.$^{-1}$ has been shown for chlorobenzene (705 cm.$^{-1}$), *m*-chlorotoluene (682 cm.$^{-1}$) and *p*-chlorotoluene (680 cm.$^{-1}$).[10] The same conclusion can be reached from the Raman spectrum of chlorobenzene[11]; equally, the existence of an absorption band in the neighborhood of 680 cm.$^{-1}$ follows from the Raman spectrum of 1,2,4-trichloro-, 1,2,4,5-tetrachloro- and pentachlorobenzene.[12]

Recently, Karplus and Halford[13] observed in the infrared spectrum of methylchloroform (CCl_3CH_3) the following bands: 713, 766 (shoulder), 792 and 830 cm.$^{-1}$ (weak). One might be tempted to identify the last two bands with the two bands of the CCl_3 grouping in the trichloromethylcarbinols. The intensities, however, are quite different in the two cases, and, furthermore, the C–Cl absorption at 713 cm.$^{-1}$ has not been observed in any of the cases studied here so that, obviously, the influence of the surroundings on the CCl_3 group is strongly reflected in the infrared spectra. The vicinity of the hydroxyl groups in the trichloromethylcarbinols both strengthens the C–Cl bonds, because of the negative inductive effect of the hydroxyl, and splits the vibration due to the stretching of a single C–Cl bond, a vibration which, for reasons of symmetry, is degenerate in the molecule of methylchloroform.

REHOVOTH, ISRAEL

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(8) N. B. Colthup, *J. Optical Soc.*, **40**, 397 (1950).

(9) In the case of compound No. 5, this band has probably merged into the characteristic absorption band of a *p*-substituted phenyl group (820 cm.$^{-1}$); hence its exceptional intensity.

(10) J. Lecomte, *Compt. rend.*, **201**, 1341 (1935).

(11) J. W. Murray and D. H. Andrews, *J. Chem. Phys.*, **1**, 406 (1933).

(12) J. W. Murray and D. H. Andrews, *ibid.*, **2**, 119 (1934).

(13) R. Karplus and R. S. Halford, *ibid.*, **18**, 910 (1950). Compare P. Venkateswarlu, *ibid.*, **19**, 298 (1951).