

Physical and Chemical Properties of a New Series of Carboxylic Acids, $\text{Cl}(\text{CF}_2\text{CFCl})_x\text{CF}_2\text{CO}_2\text{H}$

W. S. BARNHART,¹ R. J. SEFFL,² R. H. WADE,³ F. W. WEST,⁴ AND J. L. ZOLLINGER⁵
The M. W. Kellogg Co., Jersey City, N. J.

The announcement of the electrochemical fluorination process in 1949 (6) has made available, or potentially so, a whole series of perfluorinated alkanic acids. Somewhat later, Perry (2) described a process for converting α, α, ω -trihydroperfluoro alcohols into the corresponding ω -hydroperfluoro acids. This process, which utilizes liquid polymers of tetrafluoroethylene, is limited to ω -hydroperfluoro acids having an odd number of carbon atoms. In this article a new series of perhalogenated alkanic acids having the general formula $\text{Cl}(\text{CF}_2\text{CFCl})_x\text{CF}_2\text{CO}_2\text{H}$ is described. These acids, which contain an even number of carbon atoms, are prepared by the hydrolysis of the corresponding alkanes, $\text{Cl}(\text{CF}_2\text{CFCl})_{x+1}\text{Cl}$.

Nomenclature. The International system of nomenclature is cumbersome to use for describing chlorofluorocarbons. Hence, in this article the compound is described by the number of carbon atoms present and the nature of the functional group. Thus, 3,4-dichloropentafluorobutyric acid, $\text{ClCF}_2\text{CFClCF}_2\text{CO}_2\text{H}$, is designated as the C_4 chlorofluorocarboxylic acid. These acids are commercially available under the trade name of KEL-F acids (registered trade-mark of the M. W. Kellogg Co. for its fluorocarbon polymers).

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Solubility and Surface Activity. The chlorofluorocarboxylic acids are soluble in most organic liquids: aromatics, aliphatics, ethers, ketones, esters, and chlorinated hydrocarbons.

The solubility of the chlorofluorocarboxylic acids in water depends markedly on the chain length. The C_4 chlorofluorocarboxylic acid is completely miscible with water, whereas the C_6 and higher acids have very limited solubility. Determination of the exact solubility limits of these acids in water is complicated by the fact that they probably exist as ions only in very dilute solution. As the acid concentration is increased, small spherical micelles are formed, which undergo further development into laminar micelles in which the degree of order is very great. This behavior has been extensively investigated for the ω -hydroperfluoro acids by Arrington and Patterson (1). The concentration at which critical micelle formation occurs corresponds approximately to the break in the surface tension vs. concentration curve. This break occurs, as can be seen in Figure 1, at 15 grams per 100 ml. for the C_4 chlorofluorocarboxylic acid, at 0.5 gram per 100 ml. for the C_6 compound, and at 0.002 gram per 100 ml. for the C_{12} compound. All surface tensions were determined on a precision model DuNouy tensiometer.

The surface activity of the chlorofluorocarboxylic acids develops even with very short chain lengths—that is, C_6 or C_8 —whereas the hydrocarbon analogs do not develop

maximum surface activity until the chain contains 16 or 18 carbon atoms. It may be seen in Figure 1 that the longer chain chlorofluorocarboxylic acids are many times more efficient in reducing the surface tension of aqueous solutions than are the lower members of the series. Thus, despite the poorer solubility of the higher homologs, the addition of a few hundredths of 1% of the C_{10} chlorofluorocarboxylic acid is sufficient to lower the surface tension of water to a level suitable for many applications. The lowest surface tension observed for aqueous solutions of the chlorofluorocarboxylic acids is 24 dynes per cm. This value is higher than the lowest value observed for perfluorinated acids or their derivatives which is about 17 dynes per cm. (5).

The chlorofluorocarboxylic acids are highly resistant to oxidation and, hence, can be used to reduce the surface tension of strong oxidizing solutions such as chromic acid.

Table I. Effect of Temperature on Surface Tension of Aqueous C_6 Chlorofluorocarboxylic Acid Solutions

(Acid concentration = 0.695 gram/100ml.)

Temp., °C.	Surface Tension, Dynes/Cm.
7.5	26.0
25.5	24.3
41.0	23.5
58.0	23.0

The acids retain their surface activity over a wide range of temperature and in strongly acidic or basic media (Tables I and II). The variation of the surface tension with pH has been reported for fatty acids (3). Thus, when a strong acid is added to a soap solution, the surface tension is lowered because of liberation of the free fatty acid. When alkali is gradually added to a solution of a fatty acid, the surface tension of which is low, the surface tension increases as the free acid lowers the surface tension more than the soap formed on addition of the alkali. Above pH 7 the surface tension again decreases and this is probably due to a "salting-out" effect similar to that found for solutions of sodium nonylate (4).

Table II. Effect of Hydrogen Ion Concentration on Surface Tension of Aqueous C_6 Chlorofluorocarboxylic Acid Solutions

(Acid concentration = 0.25 gram/100 ml.)

pH	Surface Tension, Dynes/Cm.
0.8	24.5
3.1	41.4
3.9	44.3
6.3	49.5
7.3	48.6
10.6	47.8
12.6	29.5

Because of their solubility in many organic liquids, the chlorofluorocarboxylic acids are effective in reducing the interfacial tension between aqueous and nonaqueous systems. Table III illustrates the effect of C_6 chlorofluorocarboxylic acid on the interfacial tension between water and hexane, benzene, carbon tetrachloride, and Freon 113.

¹Present address, Pennsylvania Salt Co., Whitmarsh Laboratories, Philadelphia, Pa.

²Present address, Titan Chemical Co., Boulder, Colo.

³Present address, Stanford Research Institute, Palo Alto, Calif.

⁴Present address, J. C. Chemical Division, Minnesota Mining & Manufacturing Co., Jersey City 3, N. J.

⁵Present address, Central Research Laboratory, Minnesota Mining & Manufacturing Co., St. Paul, Minn.

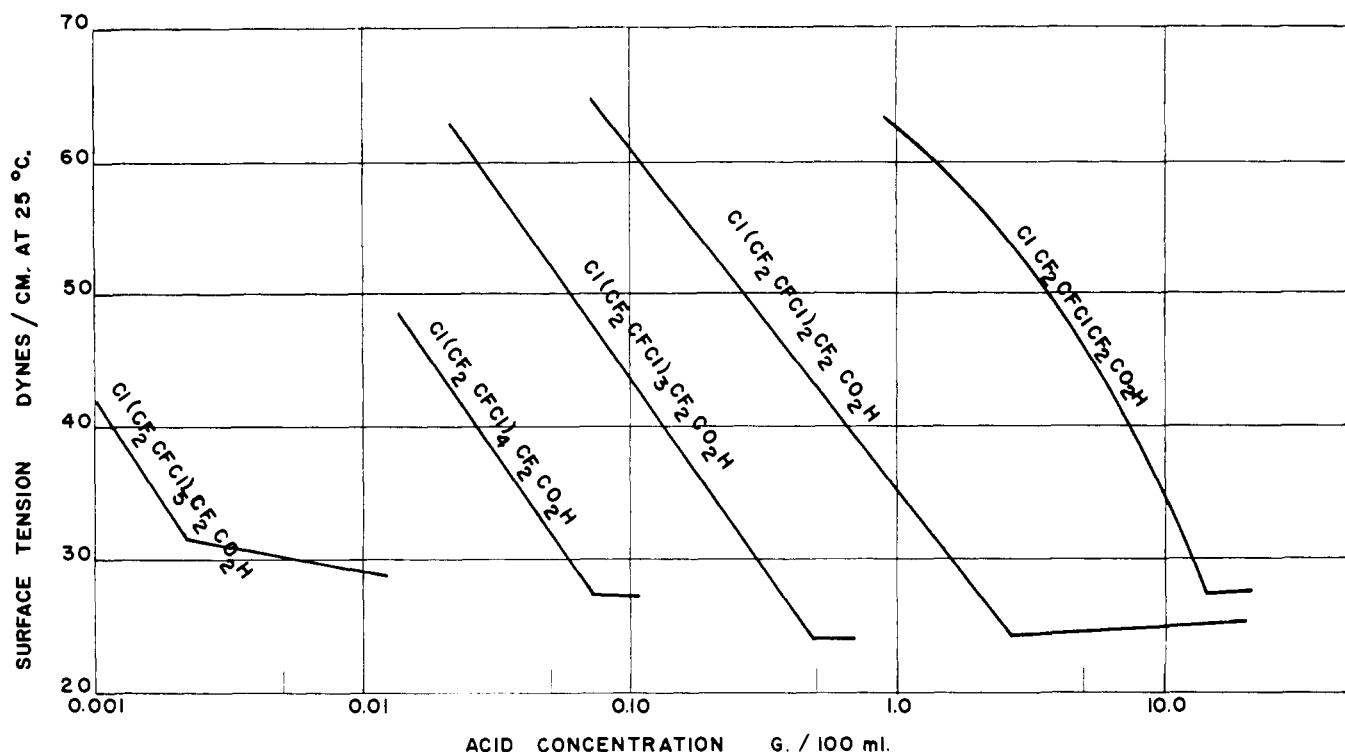


Figure 1. Surface Tension of Chlorofluorocarboxylic Acid Solutions

Table III. Effect of C_6 Chlorofluorocarboxylic Acid on the Interfacial Tension between Organic Solvents and Water

Acid Concn., Gram/100 Ml.	Interfacial Tension between Organic Solvent and Water, Dynes/Cm.			
	CCl_4	$n-C_6H_{14}$	C_6H_6	$CF_2ClCFCl_2$
0.000	40.9	41.1	33.4	44.2
0.0112	35.6	35.5	30.5	36.1
0.0336	30.6	30.8	30.1	29.8
0.112	21.2	20.6	27.8	22.5
0.440	13.4	9.3	24.6	13.7
0.650	9.9	5.5	20.6	11.5

Boiling Points. Because of their higher molecular weight, the chlorofluorocarboxylic acids have higher boiling points and densities than the corresponding perfluoro and hydrocarbon fatty acids.

Miscellaneous Properties. Detailed physical properties of the chlorofluorocarboxylic acids are given in Table IV.

The chlorofluorocarboxylic acids have excellent thermal stability, as is evidenced by the fact that the C_6 compound has been heated at between 220° and 230°C. for 24 hours with no apparent degradation.

CHEMICAL PROPERTIES

A large number of derivatives of the chlorofluorocarboxylic acids have been prepared. These include esters, amides, acid chlorides, olefins, ketones, alcohols, nitriles, organic salts, and inorganic salts. A list of derivatives and their physical properties is given in Table V. The actual preparation of some typical derivatives is given below.

EXPERIMENTAL

Methyl Ester of C_6 Chlorofluorocarboxylic Acid. A solution of 363.4 grams (1.0 mole) of the C_6 chlorofluorocarboxylic acid and 404 ml. (10 moles) of methanol was refluxed for 5 hours. The refluxing alcohol was recycled to the reaction flask after passing through Drierite. After the

Table IV. Physical Properties of Chlorofluorocarboxylic Acids

Formula	$ClCF_2CFCICF_2CO_2H$	$Cl(CF_2CFCl)_2CF_2COOH$	$Cl(CF_2CFCl)_3CF_2COOH$	$Cl(CF_2CFCl)_4CF_2COOH$
Physical state	Colorless liquid	Colorless liquid	Colorless liquid	Colorless liquid
Odor	Sharp	Sharp	Sharp	Sharp
Formula weight	247	363	480	596
Boiling point, °C.	183	232	280	305
Freezing point, °C.	-30
Density, 20 °C., grams/ml.	1.732	1.833	1.894	1.935
Viscosity, 20 °C., cs.	15	125	1619	264 at 60 °C.
Surface tension, 25 °C., dynes/cm.	...	27.6	28.7	31.4
Vapor pressure, mm. Hg./t °C.	29.5/100 250/150	3.4/100 39.4/150	0.4/100 6.8/150	0.07/100 1.6/150
Constants for vapor pressure equation ^a				
A	9.156	9.5258	9.5534	10.162
B	2863	3356	3690	4209
Index of refraction, n_D^{20}	1.377	1.389	1.397	1.404
Dielectric constant, 25 °C.	4.17 at 22 °C.	3.65	3.39	3.19 at 22 °C.
Heat of vaporization, kcal./mole	13.1	15.4	16.9	19.3
Trouton ratio	28.7	30.5	30.6	33.4

$$^a \text{Log } P (\text{mm. Hg}) = A - \frac{B}{T^\circ K}$$

Table V. Physical Properties of Derivatives of Chlorofluorocarboxylic Acids

Compound ^a	Yield ^b , %	Molecular Weight, Theory	Boiling Point, °C./Mm. Hg	Melting Point, °C.	d ₄ ²⁰	n _D ²⁰	Molar Refraction		Analysis		
							Calcd. ^c	Obsd.	Type	Calcd.	Obsd.
CIM ₂ CF ₂ CO ₂ CH ₃	81.5	377.5	87/10	...	1.735	1.3841	51.12	50.9	Cl	28.2	28.2
									F	40.3	40.6
CIM ₃ CF ₂ CO ₂ CH ₃	...	493.9	131/10	...	1.826	1.3952	65.4	65.0
CIM ₃ CF ₂ CO ₂ (CH ₂) ₃ CH ₃	84.0	536.0	106/0.5	...	1.634	1.4001	79.4	79.5	Sap. No.	536	522
CIM ₂ CF ₂ CO ₂ CH ₂ CH=CH ₂	81.5	403.5	100/10	...	1.620	1.3966	60.0	59.9	Cl	26.4	26.4
									F	37.6	37.4
CIM ₃ CF ₂ CO ₂ CH ₂ CH=CH ₂	93.5	520.0	106/1.0	...	1.704	1.4026	74.3	74.4	Sap. No.	520	513
CIM ₃ CF ₂ CONH ₂	98.0	478.9	...	82-84	N	2.92	2.85
(—CIM ₃ CF ₂ CONHCH ₃ —)	...	984.0	...	148-150	N	2.85	2.81
CIM ₃ CF ₂ CON(CH ₂ CH ₂ OH) ₂	84.0	567.1	...	185-190	N	2.47	2.49
CIM ₃ CF ₂ CONHOH	36.0	494.9	...	84-85	N	2.83	2.78
CIM ₃ CF ₂ COCl	96.0	381.9	180/760	...	1.800	1.3888	49.8	50.2
CIM ₃ CF ₂ COCl	98.0	498.4	145/50	...	1.860	1.3964	64.14	64.4	Neut. Eq.	249	247
CIM ₃ CF ₂ COC ₆ H ₅	43.0	540.0	149/1.3	...	1.732	1.4534	83.7	84.3	Cl	26.25	26.33
CIM ₃ CF ₂ CF=CF ₂	65.0	399.4	156-7/760	...	1.800	1.3639	49.3	49.3
CIM ₃ CF ₂ CN	73.0	460.9	119/50	...	1.793	1.3800	59.1	59.5	N	3.04	3.02
CIM ₃ CF ₂ CH ₂ OH	80.0	465.9	141/14	...	1.863	1.399	60.8	60.5	Cl	30.4	30.2
CIMCF ₂ CO ₂ H·HN=C(NH ₂)SCH ₂ C ₆ H ₅	99	190-91	Cl	17.2	17.4
CIM ₂ CF ₂ CO ₂ H·HN=C(NH ₂)SCH ₂ C ₆ H ₅	99	182	Cl	20.1	20.4
CIM ₃ CF ₂ CO ₂ H·HN=C(NH ₂)SCH ₂ C ₆ H ₅	99	184-5	Cl	21.9	22.2
CIM ₄ CF ₂ CO ₂ H·HN=C(NH ₂)SCH ₂ C ₆ H ₅	99	162-3	Cl	23.2	23.2
CIM ₃ CF ₂ CO ₂ H·HN=C(NH ₂)SCH ₂ C ₆ H ₅	99	162-4	Cl	24.2	24.2
CIM ₃ CF ₂ CO ₂ H·H ₂ NC ₆ H ₁₁	48	119-21	Cl	24.5	24.3

^a M = —CF₂CFCl —.

^b Yield based on limiting reactant.

^c Calculated by using value of 1.10 for atomic refraction of fluorine.

excess alcohol had been removed, the product was distilled at reduced pressure. The ester [yield 306.6 grams (81.5% conversion)] was a colorless liquid with a clovelike odor.

Diethanolamide of C₈ Chlorofluorocarboxylic Acid. A charge of 99.7 grams (0.2 mole) of the C₈ chlorofluoro acyl chloride was added to a solution of 47 grams (0.45 mole) of diethanolamine in 150 ml. of water. The hot mixture was stirred intermittently and allowed to stand overnight. Solid ammonium sulfate was added and the mixture was extracted several times with ether. The organic layer was treated with Drierite, filtered, and evaporated in a stream of nitrogen. The crude yield after drying was 96.4 grams (0.17 mole); 84% conversion. Recrystallization of the amide from xylene-dioxane solvent afforded large white flakes, melting point, 185° to 190°C. (dec.).

Acid Chloride of C₈ Chlorofluorocarboxylic Acid. Phosphorus pentachloride (407 grams; 1.95 moles) was added over a 0.5-hour period to 960 grams (2.0 moles) of C₈ chlorofluorocarboxylic acid in a 3-liter flask fitted with a drying tube. There was vigorous hydrogen chloride evolution, but the temperature did not exceed 42°C. After being heated for 1 hour on a steam bath, the phosphorus oxychloride was removed by heating the reaction mixture slowly to 205°C. The clear liquid was transferred to a 1-liter flask and distilled at reduced pressure to give 878 grams (1.76 moles; 97.5% conversion) of a clear colorless liquid.

Chlorofluoro-octyl Phenyl Ketone. A charge of 149.5 grams (0.3 mole) of C₈ chlorofluoro acyl chloride was added dropwise to a stirred mixture of 44 grams (0.33 mole) of anhydrous aluminum chloride and 78 grams (1.0 mole) of benzene maintained at between 3° and 7°C. The mixture was stirred overnight and gradually warmed to room temperature. The resultant dark brown solution was cooled and poured into 200 ml. of 6N hydrochloric acid. After the solution was mixed, the organic layer was washed with 5% sodium bicarbonate solution. An emulsion formed which could not be broken except by removal of the excess benzene by steam distillation. The aqueous layer was decanted and the dark brown organic layer was dissolved in

ether. The ethereal solution was dried over calcium chloride, filtered, and distilled through a short Vigreux column at reduced pressures. The ketone, 68.6 grams (73.5% conversion), was obtained as a colorless liquid boiling at 148° to 149°C. and 1.3 mm. of mercury.

Preparation of C₈ Chlorofluoro Alcohol [(CF₂CFCl)₃-CF₂CH₂OH]. Into a 2-liter, 3-necked flask fitted with a nitrogen inlet, stirrer, condenser, and dropping funnel were placed 420 ml. of ether containing about 14.8 grams (0.4 mole) of lithium aluminum hydride. A solution of 100 grams (0.2 mole) of C₈ chlorofluoro acyl chloride in 150 ml. of ether was added gradually so as to maintain reflux over a 2-hour period. The mixture was stirred for an additional hour; then the excess reagent and the complex were decomposed by the careful addition of 60 ml. of water, with vigorous stirring. The mixture was poured into 1.3 liters of 10% sulfuric acid to dissolve the insoluble hydroxides. The ether layer was separated, and the aqueous layer was saturated with sodium sulfate (300 grams) and extracted three times with ether. The combined ether layers were washed with a saturated sodium chloride solution, 5% sodium bicarbonate solution, again with saturated sodium chloride solution, and finally treated with Drierite. The ether was evaporated and the liquid residue was distilled through a 6-inch Vigreux column. A forerun of 26.9 grams boiling at 117° to 138°C. and 14 mm. of mercury was obtained. This forerun was analyzed for chlorine and 11.9% was found. A total of 52.3 grams of alcohol were obtained boiling at 141° to 141.5°C. and 14 mm. of mercury.

It is apparent from the chlorine determination and physical constants that dehalogenation occurred in the lower boiling fractions.

C₈ Chlorofluoronitrile. A mixture of 47.9 grams (0.1 mole) of C₈ chlorofluoroamide and 14.2 grams (0.1 mole) of phosphorus pentoxide was heated in a 100-ml. flask provided with a short-path distilling head. The product distilled at 200°C. (flask temperature 250° to 286°C.) over a 40-minute period to give 33.6 grams (0.073 mole, 73.2% conversion) of a clear liquid having a pleasant aroma.

The crude acidic product was purified by filtering through a 1-inch layer of anhydrous potassium carbonate and was fractionated to give a neutral product.

Cyclohexylamine Salt of C₈ Chlorofluorocarboxylic Acid. A solution of 24 grams (0.05 mole) of C₈ chlorofluorocarboxylic acid in 25 ml. of ethyl ether was added to 5 grams (0.05 mole) of cyclohexylamine in 15 ml. of ethyl ether. The solvent was evaporated and the remaining solid was recrystallized from cyclohexane to give 14 grams (48%) of white solid.

Decarboxylation of C₈ Chlorofluorocarboxylic Acid. A 27-gram charge of C₈ chlorofluorocarboxylic acid was neutralized with sodium hydroxide, concentrated under a stream of nitrogen, and dried at 105°C. in a vacuum oven. A 10.7-gram (0.0214 mole) sample of the dry sodium salt was heated in a small distillation apparatus. A liquid product (8.3 grams) distilled at ca. 160°C. as the pot temperature rose from 160° to 300°C. and gave a positive unsaturation test with aqueous potassium permanganate. A redistilled portion had a molar refractivity confirming the structure $\text{CF}_2\text{Cl}(\text{CFCICF}_2)_2\text{CF}=\text{CF}_2$. $\text{CF}_2\text{Cl}(\text{CFCICF}_2)_2\text{CCl}=\text{CF}_2$ is indicated by the presence of fluoride in the pyrolysis residue.

APPLICATIONS

The chlorofluorocarboxylic acids are resistant to thermal decomposition and are very stable toward strong acids,

bases, and oxidants. This stability indicates that the acids or their derivatives will be excellent surfactants in some environments where hydrocarbon surfactants fail.

The large number of derivatives of the chlorofluorocarboxylic acids potentially available should provide new classes of materials useful as hydraulic fluids, lubricants, plasticizers, and for other applications where a non-flammable, stable material is required.

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Pyrolytic Degradation Products of Cellulose

ROBERT F. SCHWENKER, JR., AND EUGENE PACSU
Textile Research Institute, Princeton, N. J.

This work represents the first phase of a study designed to elucidate the nature of the pyrolytic degradation of cellulose and the mechanism by which the reaction proceeds, in order to understand better the larger problem of the flame and glow resistance of cellulosic materials. This is of high priority in the Department of Defense for clothing purposes. A knowledge of the degradation of cellulose may ultimately give a solution of the problem.

The decomposition of the cellulose polymer in the solid state at temperatures greater than 250°C. has been studied extensively (3, 4, 6, 7, 9-11, 20-22, 25-28). The products of decomposition have usually been divided into three main categories (7).

1. **Gas Phase Products.** This phase consists of carbon monoxide, carbon dioxide, methane, and hydrogen, usually constituting 20 to 25% of the total products of pyrolysis (3, 6, 7, 20, 25, 26).

2. **Solid Phase Products.** A carbonaceous residue or char is produced in approximately 15% yield (9, 11, 17, 20, 26).

3. **Liquid Phase Products.** An aqueous distillate (the pyrolyzate) is obtained, consisting of tars, water, and volatiles condensable at 0°C., and comprising approximately 65% of the total products. According to Coppick (7), the aqueous distillate obtained from the pyrolysis or controlled combustion of cellulose contains the tarry primary dissociation products which appear to be critically related to the flaming characteristics of fabrics.

At elevated temperatures then, cellulose decomposes to form considerable amounts of flammable products. It has been suggested that when a cellulosic material burns, the volatile decomposition products arising from pyrolytic decomposition of the cellulose actually cause flaming (4).

A mechanistic theory of the pyrolytic degradation of cellulose (21) suggests that the reaction proceeds through a common intermediate, 1,6-anhydro-β-D-glucopyranose (levoglucosan), resulting from initial depolymerization. Levoglucosan is then thought to participate in two competing reactions: repolymerization in a dehydration process to form char and decomposition to volatile, flammable products. The degradation reactions of cellulose at temperatures of pyrolysis are not clearly understood at present, and the chemical literature lacks information and data as to the nature of the products in the cellulose pyrolyzate.

Gillet and Urlings (9-11) have made a thorough investigation of the pyrolysis of wood and cellulose. True pyrolysis was found to begin at 250°C. and adjudged complete at 360°C. Glyoxal and glycolic aldehyde were suggested as products from the pyrolysis of cellulose, but no experimental data were presented. Coppick (7) reports the existence of hydroxyl, methylene, methyl, carbonyl, ethylene, and