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ONE BOND COUPLING CONSTANTS OF THE α -C-H BOND IN SOME SATURATED AND UNSATURATED DICARBOXYLIC ACIDS AND THEIR CORRESPONDING ANHYDRIDES

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The one bond coupling constants of the α -C-H bond in several saturated and unsaturated dicarboxylic acids and their corresponding cyclic anhydrides have been measured. As expected, cyclization into anhydrides causes significant changes in the one bond C-H coupling constants. These changes have been explained on the basis of electronegativity and ring strain in these compounds.

Key words: Coupling constant, Dicarboxylic acid, Anhydrides.

INTRODUCTION

It is known that the C-H couplings are very much dependent on the electronegativity and angular strain in a molecule [1-10]. Since both these factors are expected to change in converting a dicarboxylic acid into its corresponding anhydride we have studied the α bond C-H couplings in various saturated and α , β -unsaturated dicarboxylic acids and their corresponding anhydrides. The significant differences observed between the ^{13}C shifts in these compounds had been satisfactorily explained on the basis of changes in electronegativity, and the ring strain introduced in a molecule upon cyclization into a cyclic anhydride [11, 12]. In this paper the results of our study on α -bond C-H couplings in various dicarboxylic acids and their corresponding anhydrides are presented.

EXPERIMENTAL









All the compounds used in this study were purchased from Aldrich Chemical Company and were used without any further purification. Proton coupled ^{13}C NMR spectra were recorded on a Varian XL-200 NMR spectrometer operating at 50,3 MHz and using 10 mm samples tubes, solutions for the measurement of the spectra were prepared by dissolving 0.5 g of the sample in 2.5 ml of chloroform-d containing a few drops of TMS as internal reference. The solvent chloroform-d, provided the internal field frequency lock signal. The experimental parameters were as follows: spectral width, 11000 Hz; data points, 32K; temperature, 293K; pulse width 6 μ s, and number of transients, 5000.

RESULTS AND DISCUSSIONS

$^1\text{J C-H}$ in saturated dicarboxylic acids and their cyclic anhydrides. The values for $^1\text{J C-H}$ of the α -bond in some saturated dicarboxylic and their cyclic anhydrides are given in Table 1. The couplings in the saturated dicarboxylic

acids are found to be in the range of 126-130 Hz, while in saturated anhydrides these are in the range of 132-138 Hz. The difference in C-H couplings between the acids and the corresponding alkanes are in the range of 4-5 Hz. This is obviously due to the electronegativity effect of the carboxylic group.

Table 1. C-H coupling constants of the α -bond in some saturated dicarboxylic acids and their corresponding anhydrides.

	Compound	$^1\text{J C-H}$ (Hz)	Δ (Anhydride- acids)
1.		130.0	
2.		137.5	7.5
3.		127.0	
4.		132.3	5.3
5.		126.3	
6.		137.0	10.7
7.		129.5	
8.		1134.3	5.2

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Since six membered-rings are essentially strain free, the difference in the C-H couplings between glutaric anhydride [4] and glutaric acid [3] of 5.3 Hz may be taken as the electronic effect of changing an acid group into anhydride group. This is logical since $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{O}-\text{C}- \end{array}$ group is more electro-negative than the $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$ group.

The difference in coupling between succinic anhydride [2] and succinic acid [1] is 7.5 Hz. This increase is coupling by approximately 2 Hz in comparison to glutaric acid and its anhydride may be due to ring strain in the five membered ring.

The difference in C-H coupling between cis-cyclohexane 1, 2-dicarboxylic acid [5] and its corresponding anhydride [6] is found to be 10.7 Hz. This increase of approximately 5.4 Hz in comparison to the glutaric acid and its anhydride is believed to be due to an excessive ring strain in the formation of cis-anhydride.

Suprisingly the presence of a double bond in compounds 7 and 8 leads to a difference of only 5.2 Hz.



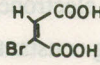

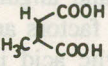

¹J C-H in unsaturated systems. The values for ¹J C-H of the α-bond in some unsaturated dicarboxylic acids and their anhydrides are given in Table 2. The C-H couplings of the olefinic protons of various substituted maleic acids are in the range of 166-172 Hz, while in various substituted maleic anhydrides they are in the range of 189-193 Hz.

The increase in C-H coupling between succinic acid and maleic acid [9] of 36 Hz. is due to the fact that olefins in general have a greater coupling than paraffins. However the difference in coupling between ethane and ethylene is only 31 Hz. This increase of Hz may be attributed to the conjugation of the double bond to the carboxylic group. The difference in C-H coupling between maleic anhydride [10] and succinic anhydride [2] is 52 Hz. This large difference is due to three factors i.e. the olefinic C-H bond has a greater coupling than the paraffinic C-H bond, greater delocalization of olefinic bond in maleic anhydride and the greater ring strain in this compound.

The difference in the coupling between ethylene and maleic acid [9] is approximately 11 Hz. Thus introduction of a carboxyl group in unsaturated systems effects the CH coupling by a greater extent than for the corresponding saturated systems. This is due to greater electron delocalization of electrons in α,β unsaturated systems.

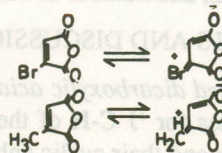
The difference in C-H coupling of the α-bond between unsaturated dicarboxylic acids and their corresponding anhydrides is found to be in the range of 18-22.5 Hz. This is due to a combination of both electronic and steric effects. In the unsaturated 5 membered cyclic anhydrides there is a much greater electron delocalization due to resonance, as well as ring strain, in comparison to the corresponding saturated systems. Since the normal bond angle of a tetrahedral carbon atom is 109.5° which is changed 105° in a five membered ring, the ring strain is 4.5°. In comparison to the

Table 2. C-H coupling constants of the α-bond in some unsaturated dicarboxylic acids and their corresponding anhydrides.

Compound	¹ J C-H (Hz)	Δ (Anhydride-acid)
9. 	166.7	
10. 	189.2	22.5
11. 	171.5	
12. 	193.3	21.8
13. 	170.6	
14. 	189.0	18.4

normal bond angle of Sp² carbon atom is 120° which is reduced to 105° in a five membered ring causing a ring strain of 15°. Thus the ring strain is much greater in unsaturated systems.

The degree of C-H coupling in 2-bromo maleic acid [11] and its anhydride [12] and in 2-methyl maleic acid [13] and its anhydride [14] is found to be greater than for the unsubstituted compounds. This may be explained by the greater electronegative inductive effect of bromine and methyl groups. However the difference in the C-H coupling between bromo maleic anhydride and acid is less in magnitude (21.8 Hz). Similarly the difference in C-H coupling between methyl maleic anhydride [14] and its acid [13] is even smaller (18.4 Hz). This can be explained by the following resonance form for bromo maleic anhydride, and hyperconjugation in methyl maleic anhydride. This explanation seems reasonable since ¹J C-H are known to be dependent on electron donation [6] and hyperconjugative effects [13] of the substituents.



These effects are expected to be greater in the anhydrides than their corresponding acids due to greater planarity of the five membered ring in anhydrides.

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heated at 100° for 4 hours. After the required reaction time the tubes were broken open. The product so obtained was first dissolved in ethyl acetate and then precipitated with distilled water or petroleum ether. Finally it was dried under reduced pressure to a constant weight. In place of precipitating with distilled water, it may be recommended to distilled off the solvent and the unreacted monomers for getting water free final product. The product thus obtained was found soluble in most of the organic solvents. It is white solid substance that softens at 69-70°. The IR spectra of the product poly(MMA) poly(EHA) and poly(AA) were recorded (Table 2) for comparison and to ensure polymer formation. The viscosity of the solutions of terpolymer samples prepared in acetone was measured by Oswald's viscometer at 30° by following the procedure given elsewhere [4]. The refractive index was measured on refractometer No. 123894 of Zeiss Opton (Germany). The terpolymer samples were estimated for C and H.

RESULTS AND DISCUSSION

The detailed results of the free terpolymerization of MMA, AA and EHA are summarized in Table 1.

Table 1. Benzoyl peroxide (1%) initiated terpolymerization of MMA, AA and EHA using ethyl acetate as a diluent for 4 hours (expt. No. 7 with diluent for 2 1/2 hours).

Expt. No.	Feed in		Yield (%)	Elemental analysis (%)		
	MMA (%)	AA (%)		C	H	O
1	63.12	16.90	19.97	4.80	61.81	8.45
2	33.73	36.79	17.47	4.93	61.89	8.24
3	31.36	23.80	24.85	4.87	62.30	8.22
4	49.10	22.64	28.25	4.78	62.25	8.63
5	48.34	20.14	31.25	4.25	62.20	8.69
6	24.88	34.26	40.22	4.8	64.73	9.19
7	22.73	28.29	17.47	4.92	61.24	8.31

INTRODUCTION

The versatility of the multicomponent copolymerization is now well known. It helps in synthesizing an unlimited different products of varying properties. In recent years the copolymers and terpolymers with of certain molecular weight (10⁴-10⁶) have been used in the preparation of different cosmetic products like nail varnishes, shampoos, lotions, hair colourants etc. Researchers have been trying their best to replace cellulose nitrate and low molecular weight sulphuramide or formaldehyde resin used to plasticize the nitrocellulose by these polymers [1]. Survey of the literature provides reference that terpolymers based on unsaturated polar and methacrylate monomers are becoming familiar to cosmetic products [2, 3]. Attempts have been made to prepare some useful multicomponent copolymers of vinyl monomers. This paper deals with the benzoyl peroxide-initiated terpolymerization of acrylic acid, methyl methacrylate and 2-ethylhexyl acrylate using ethyl acetate as diluent.

MATERIAL AND METHODS

Methyl methacrylate (E. Merck) and 2-ethylhexyl acrylate (E. Merck) were washed with sodium hydroxide to remove inhibitor and dried over calcium chloride. These monomers were then distilled. Acrylic acid (Sasak Haru) was distilled and the fraction boiling at 141.5° was collected. Solvents like ethyl acetate, acetone, ethyl alcohol, methyl ethyl ketone (E. Merck) were used. Benzoyl peroxide (BPO) was recrystallized in chloroform twice.

Procedure of terpolymerization. All copolymerization reactions were carried out in sealed pyrex tubes. The required amount of methyl-acrylate (MMA), 2-ethylhexyl acrylate (EHA), acrylic acid (AA) and benzoyl peroxide (1%) was transferred in the reaction ampules already containing 2 ml ethyl acetate. The ampules were then cooled and sealed at construction. The contents of tubes were