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^{13}C NMR Studies of Dianions of Unsaturated Carboxylic Acids

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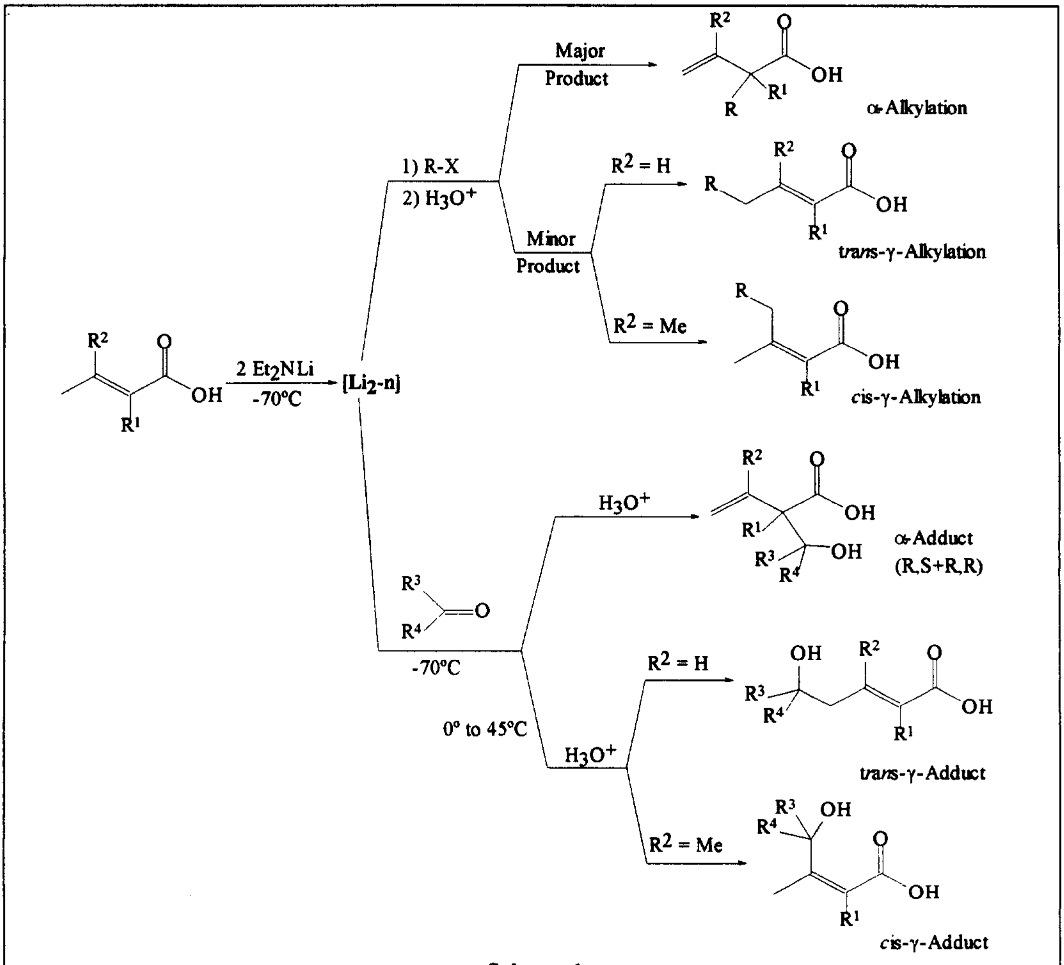
Abstract.- ^{13}C NMR Spectra of the dianions **Li_2-n** resulting from double deprotonation of unsaturated carboxylic acids **1** to **6** by lithium dialkylamides, are examined. Higher field resonance for C_2 than for C_4 atoms are observed, which reveal higher electron density at C_2 than at C_4, in agreement with the kinetic α-regioselectivity exhibited by these dianions on reaction with electrophiles.

Unsaturated carboxylic acids are synthetically useful building blocks. On deprotonation by two equivalents of lithium dialkylamides they afford dianions (**Li_2-n**) that react as ambident nucleophiles through their α or γ carbon atoms leading to single or clearly predominant compounds when allowed to react with electrophiles under adequate conditions [1-3]. Regioselectivity trends depend on the electrophile as well as on reaction conditions (see Scheme 1 for butenoic acids). Thus, α attack predominates in the irreversible reaction with alkyl halides and hydronium ion [4,5], and in reversible additions to aldehydes and ketones under kinetic conditions, but γ-adducts are obtained when these additions are carried out under equilibrium conditions [6-10]. Stereoselectivity for γ-attack is usually very high, and most frequently one single *cis*-γ or *trans*-γ compound is obtained, although the minor isomer may be occasionally observed and isolated [2,7]. The stereoselectivity trend is determined by the substituents at C_3. Thus, unsaturated acids **1** to **3**, with one single alkyl substituent at C_3, afford *trans*-γ compounds, whereas acids **4** and **5**, which bear a methyl group as the second substituent at the same atom lead to *cis*-γ isomers. 1,4-γ-Additions are obtained on reaction with unsaturated ketones [7], and exceptional α-regioselectivities found for some bezylidene ketones have been shown to be the outcome of a *tandem*-1,2-addition-anionic oxy-Cope rearrangement mechanism [11]. Reactions through the α-carbon with prochiral carbonyl compounds are susceptible to diastereofacial selectivity, and moderate selectivities (3:1 to 3:2 *R,S/R,R*) have been found for α-addition of crotonic acid dianion to aldehydes, although no systematic study has been done in order to establish a general trend [10].

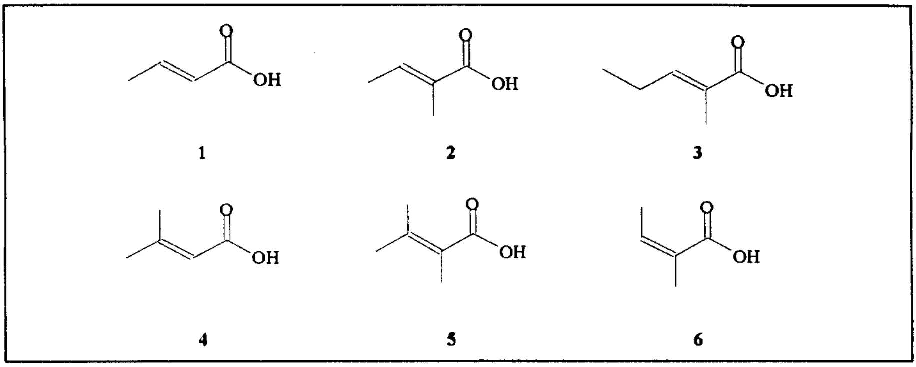
We wish to report here our study on the ^{13}C NMR spectra of the dianions of unsaturated carboxylic acids **1** to **6**. The main purpose of recording these spectra was to find out to what extent the selectivities shown by these dianions are dominated by their structures: whether the common α-regioselectivity is justified by the π electron density charges at C_2 and C_4 atoms, and if the *cis* or *trans*-γ-selectivities are the outcome of stereoconservative processes by which products have the same configuration as the dianions.

The structures of the dianions of unsaturated carboxylic acids can be simply formulated here as lithium dienediolates **A** or as lithiumoxycarbonyl substituted allyl anions **B**. Any one of these formulations provide an oversimplified view of the structures of these dianions, which are expected to form ion pairs and aggregates in weakly polar solvents such as THF [12]. A good number of studies have been published on the structure of lithium or other metal enolates, but little attention has been focused on the spectra and structure of dienolates of unsaturated aldehydes or ketones.[12] As far as we know, the structure of the dienediolates of unsaturated carboxylic acids has been studied only by Bongini, [13] who found that the ^{13}C NMR spectrum of the dianion **Li_2-4** of dimethylacrylic acid **4** is consistent with a delocalized π system. An allyl anion structure like *endo* **B** was assumed by that author for *ab initio* STO/3G calculations, which led to an optimized structure with the lithium atom placed above the sp^2 plane and coordinated to one O atom and to the C_2 and C_4 atoms. The model described by Bongini does not explain the almost exclusive protonation or alkylation at C_2 of the dianion as his calculations find higher net charge at C_4 than at C_2.

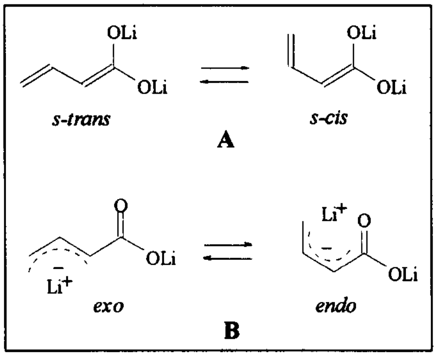
It may be expected that *endo* and *exo* (or s-*cis* and s-*trans*) geometries of these dianions (shown for formulations **A** and **B**) equilibrate fairly rapidly in solution, but previous reports do not entirely clarify. Thus, Katzenellenbogen found that γ alkylation of the two isomeric 2-methylbutenoic acids tiglic and angelic acids **2** and **6** by allylic halides led to identical γ-*trans* allyl compounds. However these results included lithium/copper(I) counterion exchange, and under the same conditions allylation of dimethylacrylic acid afforded nearly 1:1 *cis/trans* mixtures[5], an observation which shows that counterion exchange is causing significant modifications either in the structures of the dianions or on the reaction paths for their alkylation. On the other hand, earlier findings by Pfeffer and Silbert showed that protonation or alkylation of the dianions of *cis*- and *trans*-2-hexenoic



Scheme 1



acids did not afford the same deconjugated acids, but *trans* and *cis/trans* mixtures, of 3-hexenoic acids, respectively [3a]. The same authors reported that methylation of dianions derived from *cis* and *trans* 3-hexenoic acids led to the respective 2-methyl-3-hexenoic acids with configurations retained [3a]. These observations cannot be understood, but through stereoselective deprotonation of acids leading to dianions deprived of free rotation. It is interesting to note that Weiler has proved that the lithium salt of dimethylacrylic acid **4** is selectively deprotonated at the methyl group *cis* referred to the carboxyl group [14].



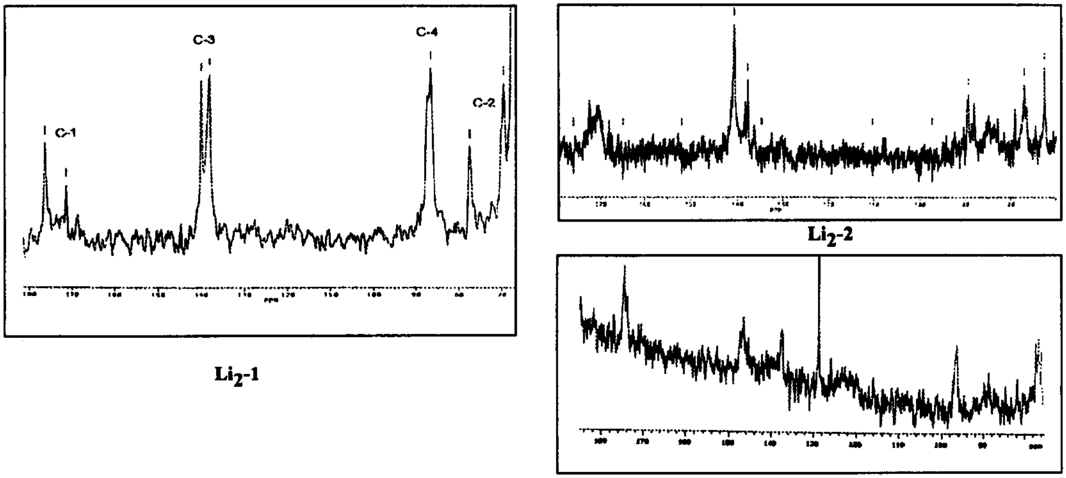
The NMR spectra of the dianions **Li$_2$-1** to **Li$_2$-6** resulting from double deprotonation of butenoic acids **1** to **6** by two equivalents of LDE at -70°C have been mostly recorded at 295°K, for 0.2 to 0.5 M THF solutions, which contained the diethylamine resulting from deprotonation. Occasionally the amine has been removed under a flush of argon and final vacuum, and the residue dissolved again in THF. On a few occasions DMSO has been added as co-solvent. Signals for the lithium carboxylates are occasionally observed, but easily identified from the rest. Long accumulations did not always improve intensities due to instability of the dianions. This has been especially noticeable for the ^{13}C spectra of dimethylacrylic and crotonic acid dianions **Li$_2$-4** and **Li$_2$-1**, for which accumulation times above 2 and 8 h, respectively led to poorer intensities.

Conformations of the dianions could not be established from the ^1H NMR spectra of the dianions of acids **1** to **6**, as these showed a limited number of broad signals, which are indicative of substantial exchange. Other signals are hidden by those due to the solvent, amine or co-solvent. Unfortunately THF-d_8 as solvent did not improve the spectra. Though disappointing, this feature is not surprising in view of the number of peaks observed for each atom in the ^{13}C spectra (see below).

Table 1.- ^{13}C NMR Data of Dianions of Unsaturated Carboxylic Acids

Dianion	C_1	C_2	C_3	C_4
Li$_2$-1	176.4	77.4	139.9	87.1
	171.4	69.3	138.0	86.4
Li$_2$-2	173.4	79.6	141.2	89.8
	173.0	77.4	139.8	88.6
	170.0	73.4	138.4	86
Li$_2$-3	171.7^{br}	77^{br}	135.8^{br}	100.9^{br}
Li$_2$-4	174.9	82.0	146.9	88-91
		76.7	137.5	96.5
Li$_2$-5	171.3	76.3	150.3	93.4
Li$_2$-6	174.0	79.5	141.1	89.9
	173.0	77.3	140.1	88.6
	170.1	73-75	138.4	87.5

^{13}C NMR spectra can be reliably analyzed only at low field for δ values above 68 ppm (see Figure 1 and Table 1), as at higher fields signals are blurred by the those due to THF, diethylamine, and eventually DMSO. Fortunately, signals for the delocalized C_1 to C_4 π system are found at low field , although substituent methyl groups cannot be found. Each carbon is observed as a group of broad signals (Figure 1), that are indicative of several species slowly exchanging in solution. Removal of the amine, or addition of 2 to 6 equivalents of DMSO did not simplify the spectra to a significant extent, except for the signals of dianions **Li_2-2** and **Li_2-4** becoming thinner in the presence of DMSO. Significant change was not observed either on addition of 0.5 equivalents of HMPA, in agreement with Bongini's findings [13], and gelification for higher concentrations of this co-solvent occurred. A similar effect was observed when 1 M or more concentrated solutions of the dianions were employed in order to attain higher intensities. Spectra of the dianions of tiglic and trimethylacrylic acids **2** and **5** were recorded at 233, 273, and 295°K. The lower intensities of the NMR experiment at low temperature, along with the instability of the dianions hampered similar spectra for crotonic and dimethylacrylic acid dianions **Li_2-1** and **Li_2-4** being obtained. Spectra recorded at 233°K showed broader signals, but no further splitting than that observed at room temperature. Unfortunately, spectra below 233°K could not be recorded, and thus it is not possible to discern whether the signals found are in fact promediated values or rather correspond to the shifts for the actual species present in solution. Assignment of signals, or rather groups of signals, was confirmed by DEPT and neighbour selective proton irradiation experiments. In all cases the signals at higher field (70-80 ppm) were shown to correspond to C_2, in contrast with the assignment given by Bongini, who erroneously interchanged signals for C_2 and C_4 in the ^{13}C spectrum of dimethylacrylic acid dianion **Li_2-4** [13].



Li_2-1

Li_2-2

Li_2-4

Figure 1.- ^{13}C NMR spectra of Li_2-1, Li_2-2, Li_2-4.

In view of the above referred literature precedents, which suggested a prevented or slow rotation for the dianions, it was interesting to observe that identical ^{13}C spectra were obtained for dianion solutions obtained by deprotonation of the isomeric tiglic and angelic acids **2** and **6**. This observation is in keeping with findings that tiglic and angelic acids afford identical *trans*-γ-adduct on reaction with benzophenone after ionization at -70°C and immediate addition of the ketone at the same temperature [15]. It should then be recognized that acids **2** and **6** lead to the same dianion, which when allowed to react with a ketone leads to *trans*-γ-adduct, although the composition of conformational equilibrium is not known to us at present.

If attention is now focused on the kinetic α-regioselectivity of the dianions as nucleophiles or as bases, it should be assumed that this is the outcome of a higher π electron density at C_2, than at C_4 in agreement with the shielded position of the peaks assigned to the first carbon. According to Karplus and Pople, the paramagnetic term in the magnetic shielding constant is determined by the electronic density and the multiple bond order, and thus ^{13}C NMR chemical shifts can be correlated with π electron densities, provided comparison is restricted to similar structures where hybridizations for atoms are preserved [16]. This is the basis for the fulfillment of substituent additivity data found in many useful tables for prediction of shift values, and for the establishment of empirical correlations between chemical shifts of carbon atoms and fractional charge distribution in ionic species. Thus, according to the equation formulated by Spiesecke and Schneider [17] (eq. 1), an upfield shift of 160 ppm is

$$(\delta_n - \delta)/160 = q_c \qquad (1)$$

caused by each charge unit. The difference between shift values for a carbon at a definite site of a neutral molecule (δ_n), and of the corresponding carbanion (δ) enables calculation of the fractional charge (q_c) at that carbon in the latter species. By extension to other carbon atoms, a complete mapping of charge delocalization for the carbanion is obtained. The equation was originally formulated for aromatic carbanionic systems, and assumes that no hybridization changes occur on ionization [17, 12b], and consequently the main difficulty for application of the equation to other structures than aromatic carbanions lies on the choice of the neutral molecule for reference, as Bradamante and Pollack have recently stressed [18,19]. Thus, Lambert and Wharry calculated charge densities for phenylacetic acid dianion, and obtained -0.25 to -0.3 charge unities on C_2, and -0.1 unities scattered along the phenyl ring [20]. However, these authors used the same model as House; namely, the enol acetate of phenylacetone [21], thus disregarding the obvious shielding effect due to the second oxygen atom at C_1 of the phenylacetic enediolate. Bradamante and Polack apply the above equation through a neutral model when an adequate neutral molecule is not available. Shift values δ_n for each carbon of the neutral model are then obtained by addition of shielding contributions A_i of substituents to the chemical shift δ_u of unsubstituted carbons which have the same hybridization (eq 2) as in the carbanion [18,19].

$$\delta_n = \delta_u + \Sigma A_i \qquad (2)$$

Calculation of electron densities q_c at the atoms of the dianions **Li_2-n** from the ^{13}C NMR shifts may be obtained for either a dienediolate or an allyl anion structure, provided adequate neutral molecules or neutral models based on the dienediolate structure **A** or on the carboxyl substituted allyl anion **B** are found. For dienediolate structures **A** vinylketene acetals and 1,3-dienes may constitute two different convenient neutral molecules, which preserve the same sp^2 hybridization for all carbon atoms. The vinylketene acetals should afford the delocalization of the ionic charge, whereas the dienes would afford combined electron densities derived from both the ionic charge and the polar substituent effects.

Ethylene vinylketene acetals **10** to **12** have been prepared from the corresponding β-chloroethyl esters **7** to **9**, according to the method described by Konopelsky [22] (Scheme 2). These ethylene acetals have proved very unstable and volatile, especially for crotonic and dimethylacrylic acid, and NMR spectra (^{13}C and ^1H) have been recorded in 1,2-dimethoxyethane/$CDCl_3$ without isolation of the compounds. Even with these precautions, the ^{13}C spectrum of vinylketene acetal **10** has not been obtained as that of a pure compound. Assignment of signals of ^{13}C spectra has been confirmed by DEPT experiments. Both ^1H and ^{13}C spectra of the intermediate β-chloroethyl esters **7** to **9** and the vinylketene ethylene acetals **10** to **12** are in agreement with their structures (Tables 2 to 4), though signals for C_2 and C_4 protons of the vinylketene acetals cannot be resolved from each other (Table 2).

Carbon charges for dianions **Li_2-1**, **Li_2-2**, **Li_2-4** obtained according to Spiesecke and Schneider's equation and the averaged chemical shift values for the corresponding atoms are shown in Table 4. At the onset of these data the most striking observation is the almost identical chemical shifts shown at C_2 by both the vinylketene acetals and the corresponding dianions, and therefore a negligible negative charge assigned at this carbon. Delocalization of the negative charge is observed only at C_4, and -0.1 to -0.13 charge unities are estimated at this remote carbon. In fact the apparently negligible charge at C_2 is not all that surprising when the structure of dienolates is compared to that of phenolates. Indeed, it has been found that for lithium phenolates proximity effects counterbalance or even outweigh the effects of π-charge density, so that for tetrameric aggregates the *ortho* carbons are actually 5 ppm less shielded than those of the corresponding anisoles, in contrast with the *para* positions which are more shielded by 6 ppm [12d].These proximity effects are probably responsible for the deshielded C_2 observed for lithium carboxylates **Li-1**, **Li-2** and **Li-4** when compared to the corresponding acids **1**, **2**, and **4** or their esters **7** to **9** (Table 3). In any case, the conclusion reached from the present data is that negative ionic charge is mostly localized in the oxygen atoms, in agreement with Lambert's findings [20], and that only a 5% is found at C_4.

Table 2.- ^1H NMR Data of β-Chloroethylesters and Vinylketene Acetals of Crotonic, Tiglic and Dimethylacrylic Acids.

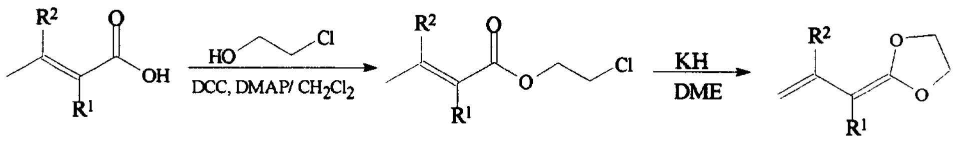
	co-solvent	chemical shift ($CDCl_3$) 3-H	2-H & 4-H	CH_2	CH_3
7	-	7.03	5.87	3.69 &4.35	1.89
8	-	6.81	-	4.27 &3.63	1.75 & 1.69
9	-	-	5.65	4.27&3.63	2.11 &1.84
10	DME	5.75	4.7-4.4	3.95	-
11	DME	6.60	4.60	4.11	1.52
12	DME	-	4.30	3.69	1.84

Table 3.- ^{13}C NMR Data for Crotonic, Tiglic and Dimethylacrylic acids[a], their β-chloroethylesters[b] and their lithium salts[a]

	C_1	C_2	C_3	C_4	Me
1	167.7	124.5	143.8	17.8	
7	166.0	121.9	145.8	18.0	
Li-1	173.0	132.0	136.5	17.5	
2	169.4	129.9	136.2	14.2	12.0
8	167.2	127.9	137.9	14.1	11.7
Li-2	174.3	135.2	130.1	13.9	13.4
4	168.1	117.6	155.2	27.1	19.1
9	165.8	115.2	157.9	27.2	20.1
Li-4	174.3	126.2	143.7	26.7	19.7

a.- In THF/DMSO.
b.- In $CDCl_3$.

When dienes are used as neutral molecules, equation 1 is applied through the chemical shifts of the carbon atoms of the dianions **Li_2-1**, **Li_2-2**, and **Li_2-4** and literature data [16] for the carbon atoms of 1,3-butadiene and isoprene located at the same position and with the same alkyl substitution as in the corresponding dienediolate



1 $R^1 = R^2 = H$
2 $R^1 = Me, R^2 = H$
4 $R^1 = H, R^2 = Me$

7 $R^1 = R^2 = H$
8 $R^1 = Me, R^2 = H$
9 $R^1 = H, R^2 = Me$

10 $R^1 = R^2 = H$
11 $R^1 = Me, R^2 = H$
12 $R^1 = H, R^2 = Me$

Scheme 2

Table 4.- ^{13}C NMR Data of Vinylketene Acetals, Averaged ^{13}C NMR shifts of Crotonic, Tiglic and Dimethylacrylic Acid Dianions and Electron Densities Based on ^{13}C NMR Shifts of Vinylketene Acetals and Dienes as Neutral Molecules for Dienolate Structure of the Dianions.

	C_1				C_2				C_3				C_4				Me
	δ	q_c^{i}	q_c^{ii}	q_c^{iii}	δ	q_c^{i}	q_c^{ii}	q_c^{iii}	δ	q_c^{i}	q_c^{ii}	q_c^{iii}	δ	q_c^{i}	q_c^{ii}	q_c^{iii}	δ
Ethylene[a]	123.5																
Butadiene[a]	116.6				137.2												
Isoprene[a]	113.0				142.9				140.3				116.4				
Ethyl acrylate[a]	165.9				129.3				130.1								
10	156.7		0.25	0.004	77.2		-0.38	-0.41	139.8		0.016	-0.06	106.7		-0.06	-0.06	
Li_2-1[c]	173.9	0.11	0.36	0.127	73.4	-0.02	-0.40	-0.41	139.0	0.00	0.010	-0.067	86.8	-0.13	-0.19	-0.18	
11	157.3		0.28	0.010	80.5		-0.39	-0.42	133.4		-0.040	-0.08	104.2		-0.08	-0.08	9.5
Li_2-2[c]	172.0	0.09	0.37	0.11	76.8	-0.02	-0.41	-0.43	139.8	0.04	-0.003	-0.003	88.1	-0.10	-0.18	-0.16	
12[b]	158.5		0.26	-0.001	74.8		-0.41	-0.44	131.6		-0.070	-0.11	105.0		-0.05	-0.05	18.2
Li_2-4[b,c]	174.9	0.10	0.37	0.1	79.4	0.03	-0.38	-0.43	142.2	0.07	-0.004	-0.001	93.3	-0.07	-0.12	-0.15	

i.- Obtained through equation 1 with vinylketene acetals **10** to **12** as neutral molecules.
ii.- Obtained through equation 1 with Dienes as neutral molecules.
iii.- Obtained through equation 2 with ethylene carbon as sp^2 carbon neutral model.
a.- Data obtained from references 16
b.- Isoprene is used as model for both tiglic and dimethylacrylic acid dianions, but correspondence of carbons for the later is inverted.
c.- Averaged shifts are used.

(see Table 4). Although electron densities at C_2 for the dianion are again almost the same as for the corresponding vinylketene acetals, their values are in any case larger than at C_4.

The model based on additive shielding contributions (eq 2) leads to electron densities in very good agreement with the values obtained with dienes as neutral molecules, except for C_1, for which almost negligible positive charges are estimated. (Table 4) For this calculation the dienediolates and the vinylketene acetals are constituted by four sp^2 carbons, and the ^{13}C literature chemical shift of ethylene [16a] is used for the unsubstituted sp^2 carbon (δ_u). This value is then corrected, according to equation 2 by the shielding contributions due to conjugation and alkyl substitution on the one hand, and to two oxygen atoms, or a carboxyl group (as a model for a sp^2 carbon atom bearing two oxygen atoms) on the other. The shielding contributions A_i of conjugation and alkyl substitution are equal to the chemical shift of the corresponding atom in butadiene or isoprene, minus the chemical shift of ethylene. The shielding contribution can be similarly obtained for C_1 from a carboxyl group and for carbons C_2 and C_3 from the chemical shifts of ethylene carbons α and β to a carboxyl group as they are found in an acrylic acid ester.

The application of the equation of Spiesecke and Schneider for calculation of electron density distributions in the dianions **Li_2-n** when these are conceived as carboxyl substituted allyl anions B meets with the difficulty of no adequate neutral molecules being found. However, this estimation can be performed in a simple way for C_2 to C_4 atoms when it is recognized that the basic model of these substituted allyl anions is constituted by the three sp^2 carbon atoms of an allyl structure. When compared to this basic three sp^2 carbon model, the dianion **Li_2-1** of crotonic acid is built up by introduction of a charge and of a lithiumoxycarbonyl substituent. The same would be true for tiglic and dimethylacrylic dianions **Li_2-2** and **Li_2-4** when methyl substitution at the basic model is taken into account. Electron densities for C_2 to C_4 atoms of these dianions can thus be easily calculated (Table 5) through the ^{13}C chemical shifts of ethylene (and C_2 of propylene) and the averaged shifts of the C_2 to C_4 carbons of the dianions.

Table 5.- Electron Densities of Dianions of Crotonic, Tiglic and Dimethylacrylic Acids as Allyl Anions, Based on ^{13}C NMR Shifts of sp^2 Carbons.

	C_1		C_2		C_3		C_4	
	δ	q_c	δ	q_c	δ	q_c	δ	q_c
Ethylene[a]	123.5							
Propylene[a]	115.9		133.4					
Li_2-1	173.9	-	73.35	-0.31	138.95	0.09	86.75	-0.23
Li_2-2	172.0	-	76.8	-0.245	139.80	0.10	88.13	-0.22
Li_2-4	174.9	-	79.35	-0.275	142.20	0.16	93.25	-0.20

a.- Data obtained from references 16

It is interesting to find that electron density at C_2 is consistently higher that at C_4, regardless of a **A** or **B** structure for the dianion being assumed. However, the gap between C_2 and C_4 electron density values is narrower when the allyl anion structure **B** is taken for application of equation 1. This finding would be in keeping with some current unpublished results of this laboratory, according to which regioselectivity for alkylation of dianions **Li_2-2** by alkyl, allyl and benzyl halides is significantly depending on the nature of the leaving group.

As a conclusion, we think that the ^{13}C NMR spectra of the dianions of unsaturated carboxylic acids justify the kinetic α-regioselectivity exhibited by these dianions when they react as nuclophiles or as bases, by showing higher electron density at carbon C_2 than at C_4. Several ways for estimation of these electron densities from chemical shifts agree in this assignment, but values vary according to the structure assumed for the dianion; namely, a dienediolate A or a lithiumoxycarbonyl substituted allyanion B. Observation of identical ^{13}C NMR spectra being obtained for the isomeric tiglic and angelic acids **2** and **6** show that dianions have easy rotation around C_2-C_3 bond, although at the present state of the research it is not possible to tell at what extent complexity found in the ^{13}C spectra is due to aggregation states or/and at stereoisomeric conversions. No answer is thus obtained to the origin of the stereoselectivity of the reactions through C_4, leading to either *cis* or *trans* γ-adducts. Molecular model calculations currently in progress will most certainly shed some light on the structure of these dianions and the selectivities shown by them.

EXPERIMENTAL SECTION

Materials. Unless otherwise indicate, reagents were purchased from Aldrich and used without further purification. Anhydrous THF and DME were refluxed over blue sodium-benzophenone ketyl, followed by distillation prior to use. Anhydrous Et_2NH was bidestilled from CaH_2 and stored over CaH_2. 99% Anhydrous DMSO stored under Ar was purchased from Aldrich. Anhydrous CH_2Cl_2 was dried over $CaCl_2$ followed by distillation and storage over 4 Å molecular sieves

NMR Measurements.- ^1H and ^{13}C NMR shifts were recorded at 25° on a Varian Unity 400 spectrometer, operating at, respectively, 400 and 100 MHz. ^1H and ^{13}C NMR shifts were measured relative to TMS as external standard. ^{13}C NMR shifts were recorded using 0.5 M solutions in the solvents stated. When no deuterated solvent was used, solutions (in 10-mm o.d. tubes), were provided with an internal 5 mm coaxial tube containing D_2O. Variable temperature experiments, were recorded on a Brucker AC-200 spectrometer at 233 and 273°K under cooling by stream of cold N_2 gas coming from liquid N_2. In these cases a coaxial tube containing CD_3COCD_3 was used. The tube with the dianion solution was then kept under Ar atm. in a long flask inside a CO_2-acetone bath before transferring the tube to the spectrometer.

Standard pulse sequences were used for running DEPT and selective irradiation experiments.

General Procedure for Preparation of Dianion Solutions.- BuLi in hexane (5 mmol) was concentrated by a flush of Ar and the residue dissolved in THF (2 ml) at -70°C. After 10 min at 0°C, Et_2NH (0.5 ml) was added dropwise at -70°C and the solution was stirred for 1 h at 0°C. The unsaturated acid (2.25 mmol) in THF (2 ml) was then added dropwise at -70°C. After 1 h at -70°C, or at 0°C, a portion of the solution was transferred through a *cannula* to the NMR tube, previously purged with Ar (at least by 5 cycles of vacuum-Ar), placed inside a long flask flushed with Ar during transfer of the solution and inserting the coaxial tube.

Monoanions of acids were prepared with 1 equivalent of $LiNEt_2$ by the same procedure.

2-Methyl-2-vinylketene ethylene acetal (11).- DCC (912 mg, 4.4 mmol) was added in three portions to a solution of tiglic acid **2** (400 mg, 4 mmol), 2-chloroethanol (972 mg, 16 mmol) and DMAP (40 mg, 0,33 mmol) in dry CH_2Cl_2 (4 ml), at 0°C. The mixture was stirred for 4 h at rt, and filtered. Hexane (35 ml) was added, the solution washed with 0.5 M aqueous HCl (2 x 20 ml), aqueous $NaHCO_3$ (2 x 20 ml), and brine, and dried ($MgSO_4$). Evaporation of solvent, gave a crude oil (571 mg, 3.5 mmol, 88%) which was purified by silica gel column chromatography with hexane-ether (9:1) as eluant to yield chromatographic and spectroscopically pure 2-chloroethyl (E)-2-methyl-2-butenoate **8**.

HK (50 mg) in a round bottomed flask, under Ar atm., was washed with dry THF (3 x 5 ml) and dry DME (2 x 5 ml), and **8** (190 mg, 1.17 mmol) in dry DME (5 ml) was added, and the mixture stirred overnight. After filtration under Ar atm using an Shlenck apparatus, the solution was partly concentrated, under Ar atm, to yield a solution of **11** which was diluted with $CDCl_3$ and used to run the NMR experiments.

Following this procedure the β-chloroethyl esters **7** and **9** and the vinylketene acetals **11** and **12** were similarly prepared.

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