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CONTRIBUTION TO THE PROBLEM OF THE CHARACTER OF THE C—Li BOND IN SOME ALPHA-LITHIUM ESTERS

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Abstract—In α-lithium esters of the type $R_1R_2C(Li)COOR_3$, prepared *in situ* in solution, the C=O stretching vibration is shifted in varying degrees with respect to the nonmetallated analogues. According to MO LCAO SCF calculations, the magnitude of this shift indicates the degree of the ionic character of the C—Li bond.

The character of the C—Li bond in organolithium compounds is not quite clear.[1] Both experimental[1] and theoretical[1-3] results indicate the covalent character of this bond in alkyllithium compounds, but if the C-Li group is in α-position with respect to a conjugated system (e.g. fluorenyllithium, tritylithium), then only ionic forms are usually considered in polar media (contact and separated ion pairs, free ions and their aggregates).[4] Therefore it might be expected that esters whose pK_a is considerably lower than that of fluorene or triphenylmethane, would yield purely ionic organolithium derivatives by metallation, due to the larger stabilization of the carbanion. However, the present study indicates that this is not the case.

We were particularly interested in lithium esters of propionic and isobutyric acid and their derivatives, because these can be considered as simplified models of reaction centers in anionic polymerization of acrylic and methacrylic esters, as well as in the Claisen condensation of the corresponding saturated esters.

METHOD OF CALCULATION

The calculations in the π-approximation were performed by the semiempirical method MO LCAO SCF according to Pariser, Parr and Pople,[8-10] i.e. the elements of the Hartree-Fock matrix were

$$F_{\mu\mu} = -I_\mu + 0{\cdot}5\,P_{\mu\mu}\,(I_\mu - A_\mu) + \sum_{\sigma \neq \mu} (P_{\sigma\sigma} - Z_{\sigma\sigma})\langle\sigma\sigma|\mu\mu\rangle; \qquad (1)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - 0{\cdot}5P_{\mu\nu}\,\langle\mu\mu|\nu\nu\rangle, \qquad (2)$$

where I_μ is the ionization potential of the valence state (in our calculation 11·42 for C, 13·8 for O=, 33·8 for CH_3O as a heteroatom and 9·5 eV for the hydrogens of the hyperconjugated Me group), $\beta_{\mu\nu}$ is the bonding parameter, having a nonzero value only for neighbouring atoms (C—C 1, C—C ($\equiv H_3$) 0·52, —$C\equiv H_3$ 1·29, C=O 1, C—OCH_3 0·91). A_μ electron affinity (C 0·58 eV, =O 2·20, CH_3O— 10·8, $H_3\equiv$ 0·0 eV). The computation was performed on the Elliot 503 computer.

The calculations for all valence electrons were performed in the SCF-CNDO/2 approximation according to Pople and Segal,[10-11] i.e. the elements of the H–F matrix were

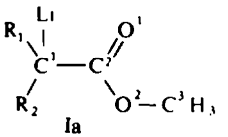
$$F_{\mu\mu} = -\alpha_{\mu\mu} + [(P_{MM} - Z_M) - 0{\cdot}5(P_{MM} - 1)]\,\gamma_{MM} + \sum_{N \neq M} (P_{NN} - Z_N)\,\gamma_{NN} \qquad (3)$$

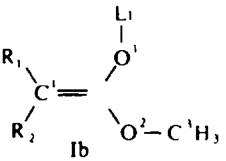
$$F_{\mu\nu} = 0{\cdot}5\, S_{\mu\nu}\,(\beta_M^\circ + \beta_N^\circ) - 0{\cdot}5 P_{\mu\nu}\,\gamma_{MN} \qquad (4)$$

where $\alpha_{\mu\mu}$ is the VSIP of the μ-th AO, β_M° the bonding parameter of the Mth atom (the values of both semiempirical parameters were taken from ref.[11]. The repulsion (γ_{MN}) and overlap ($S_{\mu\nu}$) integrals were calculated from exact formulas.[12] The computation was performed on the IBM 7040 computer.

The results of the computations were in both cases considered as consistent if the maximum difference of the eigen-numbers of the H–F matrix between two iteration steps reached the convergence criterion 10^{-5}.

For the calculations in the π-approximation (SCF-PPP), the ester carbanions were considered in the idealized planar configuration; in the approximation of all valence electrons (CNDO/2), the geometry for the general formula Ia was varied in the neighbourhood of C^1 from the planar configuration (sp^2-hybridization on C^1) to tetrahedral (sp^3 on C^1); for form Ib, the planar configuration was preserved in both cases, but in one case the Li atom was situated in the axis of the 2p$_z$ orbital of the atom O^1, in the other case the valence angle C^2O^1Li was changed to 111°.


Ia

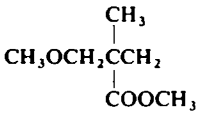
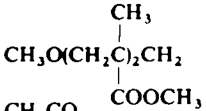

Ib

The standard bond lengths for both approximations were assumed to be the following: in the planar configuration C^1—C^2 1·42 Å, C^2—O^1 1·27 Å, C^2—O^2 = O^2—C^3 = 1·32 Å, in other configurations C—C 1·55 Å, C^1—Li 2·10 Å (Ia), O^1—Li 2·20 Å (Ib), all C—H 1·08 Å: for the tetrahedral configuration C^1—C^2 1·53 Å, C^2—O^1 1·24 Å; bond angles for the sp^2-hybrid always 120°, for sp^3 on carbon 109°, $C^2O^2C^3$ always 111°.

RESULTS AND DISCUSSION

As evident from Table 1, in most of the esters studied, metallation by tritytllithium in THF has been quantitative (as judged from the radioactivity of the ester regenerated by tritiated acetic acid), but the yield of the metallated products differed due to their spontaneous autocondensation, as seen from the yields of ketoesters in Table 1. Substitution of Li by ethyl proceeds invariably into α-position with respect to the ester group. The products IIa and IIb therefore either are not in equilibrium, or, the equilibrium is established very rapidly and IIb is unreactive.

TABLE 1. YIELDS OF THE METALATION OF THE ESTERS $R_1R_2C(H)COOR_3$ BY TRIPHENYLMETHYLLITHIUM IN THF AND OF THE REACTION OF THE PRODUCTS WITH CH_3COO^3H AND $(C_2H_5)_3OBF_4$[*]

No	R_1	R_2	R_3	ME	RE	RKE	Reaction with $(C_2H_5)_3OBF_4$ and CH_3COO^3H α-EE	ENE	α-^{3}H	total
1	CH_3	H	CH_3	88·2	36·5	52·2			--	--
2	CH_3	H	$C(CH_3)_3$	99·8	44·3	51·8	--	--	--	--
3	CH_3	CH_3	CH_3	99·9	48·5	49·2	44·6	0·0	2·5	47·1
4	CH_3	CH_3	$C(CH_3)_3$	100·1	69·2	28·3	61·4	0·0	4·1	66·5
5	CH_3OCH_2	CH_3	CH_3	99·9	52·2	45·3	--		--	--
6	 $CH_3OCH_2\overset{CH_3}{\underset{COOCH_3}{C}}CH_2$	CH_3	CH_3	99·8	85·8	--		-	--	--
7	 $CH_3O(CH_2\overset{CH_3}{\underset{COOCH_3}{C}})_2CH_2$	CH_3	CH_3	99·6	91·2			--	--	--
8	CH_3CO	H	CH_3	100·1	96·5	—	—	—	—	—
9	C_2H_5CO	CH_3	$C(CH_3)_3$	100·1	90·6			--	--	--
10	C_6H_5	H	CH_3	98·9		--	--	--	-	--
11	CH_3OCO	H	CH_3	100·0	98·7	--	81·9	0·0	15·7	97·6
12	CH_3OCO	CH_3	CH_3	100·1	96·9	--	92·3	0·0	5·9	98·2

[*] Yields of products in %: ME-metallated ester, RE-regenerated ketoester (product of autocondensation $R_1R_2C(H)COC(R_1,R_2)COOR_3$), α-EE-ethylderivative of the ester, ENE-enolether of the ester, α-^{3}H-α-^{3}H-derivative of the ester.

IR spectra of the products of metallation in the range 1600–1800 cm^{-1} are in most cases a superposition of the spectra of the α-lithium ester and of the lithium ketoester formed by autocondensation during measurement, as seen by comparison of Tables 2 and 1. From Table 2 it is seen that the spectra of all the lithium esters measured exhibit a strong band which is not present in the spectra of the hydrolysates, of the parent ester and of the ketoester, and which is evidently characteristic of the α-lithium ester. The fact that the spectra of most lithium esters also exhibit a band of variable intensity corresponding to the C=O vibration of the unmetallated ester was originally interpreted[13] as a manifestation of the keto-enol tautomerism of the esters. However, a number of facts contradict this interpretation:

(i) In crystalline t-butyl-2-lithium isobutyrate practically only the band at 1651 cm^{-1} was found in the characteristic range of the IR spectrum.[14] (ii) The absorbance ratio of both bands exhibits only an insignificant temperature dependence.[13] (iii) A comparison of the calculated electron distribution for methylisobutyrate and methyl-2-lithium isobutyrate in the same space configuration indicates a marked change of bond order of the CO group by substitution of hydrogen by lithium in α-position (Table 4, see below). (iv) The ground state energy of the keto-form of methyl-2-lithium isobutyrate is according to the CNDO/2 calculation, considerably lower than the ground state energy of the enol-form of the same molecule. (v) The spectra of some esters (nos. 8, 9, 10 in Table 2) exhibit practically only the new strong band. (vi) As shown above, the reaction of metallated esters with the highly reactive alkylating agents does not lead to an appreciable yield of the enol ether. Based on this evidence it is necessary to assign the band at the frequency identical with that of the nonmetallated ester to a product of spontaneous hydrolysis or autocondensation of the metallated product, and the new band, appearing only in the spectrum of the metallated ester, to the vibration of an ester group in the vicinity of a C–Li group.

In a purely ionic C–Li bond, conjugation of the carbanion with the ester group and possibly with further substituents may be expected, as indicated by the two canonical formulas IIIa, b:

IIIa IIIb

A linear correlation between the frequency of the CO bound to a conjugated system, and the π-bond order obtained from a MO-calculation, even in a HMO-approximation, has been described in the literature.[15, 16] In our case, no correlation with a HMO-calculation has been found. The results of the calculations for the carbanion of methylpropionate (IV), methyl isobutyrate (V), methylacetoacetate (VI), dimethylmalonate (VII) and dimethylmethylmalonate (VIII) in the MO LCAO SCF (PPP) approximation are given in Table 3.

From Table 3 it is evident that no correlation between the frequency of the CO group of the studied lithium esters and the order of the same group of the hypothetical carbanion according to a MO— calculation in π-approximation can be found. Similarly no correlation was found for the square of the frequency with bond order[17] or with the force constant calculated from bond polarizabilities.[18] A possible polarizing effect of the lithium cation upon the π-system via classical Coulomb

TABLE 2. OBSERVED BAND (cm^{-1}) IN THE RANGE 1600–1800 cm^{-1} OF THE INFRARED SPECTRUM[a] OF THE SOLUTIONS OF α-LITHIUM ESTERS (LiE), THEIR HYDROLYSATES (H), PURE PARENT ESTERS (E) AND α-LITHIUM-KETOESTERS (LiKE)[b]

No[c]	LiE	H	E	KE	LiKE
2		1742m		1742s	1742w
	1736m	1736s	1736s		
		1718s		1718s	1718w
	1615s				1659m
					1651s
	1609m				1609s
3	1746m	1746m		1746s	1746s
	1742m	1742s	1742s		
		1715s		1715s	
	1678s				
	1619m				1619m
	1608m				1608s
4	1741m	1741m	1741s	1742s	
	1738w	1738s	1738s		
		1716s		1716s	1716w
	1674s				
	1618m				1618m
	1609m				1609s
5	1746m	1746m		1746s	1746s
	1742w	1742s	1742s		
		1715s		1715s	
	1678s				
	1618m				1618m
	1608m				1608s
8	1742w	1742s		1742s	
	1718w	1718s		1718s	
	1659m				
	1651s				
	1609s				
11	1753w	1753s	1753s		
	1737w	1737s	1737s		
	1659s				
12		1753s	1753s		
		1736s	1736s		
	1658s				

[a] Solutions in the THF (0·1 mole), KBr or KRS-5 cells, 0·1 mm;
[b] Intensity of bands: s = strong, m = medium, w = weak;
[c] No of compound in Table 1

interactions should in all cases be approximately the same. In compounds VI, VII and VIII the quantum calculation predicts higher $\nu_{C=O}$ than in IV and V, the result of the experiment is just the opposite. This discrepancy with previous experience[15, 16] can be explained only so that the electronic structure of the studied esters deviates

TABLE 3. COMPARISON OF THE WAVENUMBER OF THE ESTER CARBONYL GROUP OF SOME α-LITHIUM DERIVATIVES OF ESTERS WITH THE RESULTS OF MO LCAO SCF (PPP) CALCULATIONS FOR THE CORRESPONDING CARBANIONS

Compound	$\tilde{\nu}_{C=O}$	$\Delta\tilde{\nu}_{C=O}$[a]	$p_{C=O}$[b]	q_{C_1}[c]
IV	1663	80	0·619	1·489
V	1678	64	0·623	1·509
VI	1655	88	0·720	1·418
VII	1660	96	0·713	1·413
VIII	1659	95	0·723	1·434

[a] Difference of the wavenumber of the carbonyl group of the metallated and parent ester.

[b] Order of the carbonyl group—bond order on MO calculation ($p_{rs} = 2\sum C_r C_s$);

[c] π-charge of α-carbon in carbanion according to MO-- calculation.

to a variable degree from the π-approximation on which the calculation is based. In the absence of pronounced steric effects, perturbation of the π-structure of the carbanion can in our case be only caused by the formation of a more or less strong covalent bond of the carbanion with lithium; this bond interferes with conjugation partly by overlap of the molecular orbital with the atomic orbitals of lithium, partly by change of hybridization and consequently also of the relative configuration of substituents on the atom binding lithium. In Table 4, the results of CNDO/2 calculations of six different configurations of methyl-2-lithium isobutyrate are given (configuration Va with a planar carbanion and lithium placed 10 Å above the plane of the molecule; Vb the same but for C—Li 2·10 Å; Vc, d with tetrahedral configuration on C^1, in Vc C--Li 10 Å, Vd C--Li 2·10 Å; Ve with lithium 2·20 Å above O^1 in the axis of the $2p_z$ orbital of O^1, the rest of the molecule as in Va, b; Vf with the LiO^1C^2 plane perpendicular to $C^1C^2O^1$ and the angle LiO^1C^2 111°, the bond C^1—C^2 shortened to 1·38 Å and C^2--O^1 prolonged to 1·32 Å; IX corresponds to methyl isobutyrate with a geometry identical with Vd, with Li substituted by H with a standard bond length). From this table it is mainly evident that substitution of hydrogen by lithium (VI contra Vd) leads to a considerable lowering of the bond order C^2—O^1 and to an overall polarization of the molecule. The ground state energy of the assumed "enol form" (Ve, f) is considerably higher than the ground state energy of the "keto form" with a covalent bond C^1—Li (Vd).

If the C--Li bond is dissociated (Va, c), the planar configuration is energetically favoured; approach of lithium to a bonding distance leads to a preference of the tetragonal configuration. The actual energy minimum will probably correspond to a compromise between these two configurations. The electronic structure of the planar dissociated anion Va is in good agreement with the picture obtained in π-approximation (V). However, both a change of hybridization on α-carbon (Vc compared with Va), and an approach of lithium to a bonding distance (Vb, d) leads to a marked change of the distribution of π-charge as well as of the whole electronic structure. The overall effect of this situation is the appearance of a non-negligible C—Li covalent bond and a decrease of the conjugation between the α-carbon and carbonyl accompanied by a decrease of polarization and increase of the energy of the C=O bond.

The covalent bond of the carbonion with the lithium cation can therefore be

TABLE 4. CHARGES OF ATOMS[a] (q_r), π-BOND ORDERS (π_{rs}), OVERLAP POPULATIONS (p_{rs}) AND GROUND STATE ENERGIES (ELECTRONIC E_{el} and TOTAL E_{tot}) OF VARIOUS CONFIGURATIONS OF METHYL-2-LITHIUM ISOBUTYRATE AND METHYL-ISOBUTYRATE (CNDO/2)

Configuration	q_{Li}	q_{C^1}	q_{C^2}	q_{O^1}	$\pi_{C^1C^2}$	$\pi_{C^2O^1}$	p_{LiC^1}	$p_{C^1C^2}$	$p_{C^2O^1}$	E_{el} −eV	E_{tot} −eV
Va	+0·82	−0·38	+0·47	−0·69	0·708	0·621	0·012	1·826	1·309	7268·13	2410·01
Vb	+0·58	−0·29	+0·49	−0·55	0·613	0·703	0·585	1·771	1·364	7272·43	2415·31
Vc	+0·81	−0·49	+0·42	−0·56	0·631	0·686	0·018	1·613	1·523	7264·21	2408·97
Vd	+0·51	−0·26	+0·40	−0·45	0·524	0·876	0·639	1·372	1·594	7278·13	2417·12
Ve	+0·68	−0·24	+0·48	−0·71	0·715	0·618	0·042	1·823	1·306	7273·62	2415·82
Vf	+0·62	−0·21	+0·46	−0·70	0·732	0·607	0·059	1·865	1·294	7275·13	2415·44
IX	--	−0·08	+0·17	−0·31	0·083	0·898	--	1·128	1·785	6892·11	2004·32

[a] Numbering of atoms as in the general formulas $I_{a,b}$.

expected to lead to an increase of the frequency of the C═O vibration of the ester group, as compared with a free anion or an ion pair. Our experimental results are in good agreement with this prediction. In carbanions where, according to the SCF (PPP) calculation the α-carbon carries a lower charge due to the inductive and mesomeric effect of the substituents (the charge is more delocalized and the carbanion stabilized), a weaker tendency to the formation of a covalent bond with lithium can be expected. In agreement with this, the lowering of the frequency of the CO group by metallation into α-position is more pronounced than in those cases, where the bond between the carbanion and the lithium ion is more covalent.

The lowering of the frequency of the CO group caused by metallation of the studied esters by lithium into α-position can serve, according to our interpretation, as an indirect measure of the ionic character of their C—Li bond in various media. Differences in the magnitude and sense of the CO frequency shift indicate differences in the character of the C—Li bond in various compounds. Our results thus confirm the model of the strongly polarized covalent C—Li bond, as opposed to the simple ionic picture.

EXPERIMENTAL

1. *Preparation of α-lithium esters.* Due to their low stability, these compounds were prepared *in situ* in THF at − 10° and under inert conditions by metallation with an equimolar amount of trityllithium by a procedure adapted from ref.[5] For studies in other media, 5 ml toluene were added to the original soln, the solvent was evaporated at 0° and 0·1 Torr, and the appropriate amount of the respective dry solvent was distilled onto the residue. The content of THF in the resulting soln was checked by gas chromatography of the hydrolysate and was less than 0·01%.

2. *Reactions of organolithium with* CH_3COO^3H. The soln of the substance (0·1 mole/l) in toluene or in a mixture of toluene with THF reacted at 0° for 10 min with a 10-fold excess of 90% CH_3COO^3H (10^{-2} Ci/l), the product was washed 4 times in a large excess of water and dried. After analysis on a gas chromatograph (PYE) and IR spectroscopy (Perkin-Elmer), the ester regenerated from the raw product was isolated by rectification and double crystallization and its radioactivity measured on the liquid scintillation counter Mark 2 (Nuclear Chicago).

3. *Reactions of organolithium compounds with* $(C_2H_5)_3OBF_4$. A soln of the compound (0·1 mole/l) in THF was mixed with a 50% excess triethyloxoniumboron tetrafluoride (0·5 mole/l, prepared according to ref. [6]) in THF at room temp and under inert conditions; after 2 min a twofold excess of CH_3COO^3H (10 Ci/mole) was added. The product was isolated and analysed as in section (2).

4. The IR spectra of organolithium compounds were measured in an inert atmosphere of pure argon (max 15 ppm of O_2) in 0·1 mm cells with KBr or KRS-5 windows, specially adapted according to ref. [7] Prior to measurement, the cell was rinsed 3 times with a soln uf the measured compound.

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