

## PREPARATION AND PROPERTIES OF PURE LITHIO ESTERS OF SOME CARBOXYLIC ACIDS

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### SUMMARY

Lithio esters of carboxylic acids have been prepared in pure state and their properties are described. Interaction between the lithio esters with alkali metal alkoxides has been demonstrated, and some adducts have been isolated. The IR and UV spectra of these compounds are described, and their structures are discussed.

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### INTRODUCTION

Carboxylic acid esters substituted at the  $\alpha$ -position by an alkali metal are assumed to be intermediates in a number of important synthetic and polymerization reactions. Thus, *e.g.*, in the anionic polymerization of methacrylic esters the growing centre is thought to be a  $\beta$ -substituted ester of isobutyric acid metalated at the  $\alpha$ -position. These compounds have as yet been prepared and used only "*in situ*", mostly by metalation of esters with various agents, such as organometallic compounds<sup>1,2</sup> or substituted metal amides<sup>3-7</sup>. No esters bearing an alkali metal at the  $\alpha$ -position have been isolated. Our preliminary experiments<sup>2</sup> in this field were only partly successful, but they indicated that such compounds are comparatively stable in hydrocarbons.

The problem of the interaction of the lithio esters with alkali metal alkoxides also seemed of interest, since the latter are catalysts often used in ester condensation reactions; in anionic polymerization too, the participation of lithium alkoxides has been demonstrated<sup>8-12</sup>. Similar complexes have been anticipated<sup>13</sup>, and interactions of other organolithium compounds with lithium alkoxides have already been described<sup>14,15</sup>.

### RESULTS AND DISCUSSION

#### *Preparation and reactions*

It has been found that lithiation of the carboxylic acid esters can be carried out advantageously with a solution of *N*-lithium diisopropylamide in an aliphatic or aromatic hydrocarbon even at room temperature, and that in some cases the lithio esters can be isolated<sup>16</sup>. The metalated ester either separated as an insoluble compound or crystallized at low temperatures after concentration of the solution, usually in a high yield (Table 1). The nitrogen content in these products was low, so

that the amidation of the esters was negligible. *N*-Lithium diisopropylamide also metalated methyl acetate and propionate, as shown by the IR spectra, but in these cases, no separate products could be isolated.

TABLE 1

PREPARATION AND PROPERTIES OF PURE LITHIO ESTERS OF CARBOXYLIC ACIDS AND THEIR ADDUCTS WITH Li ALKOXIDES

Original ester	Amount of <i>t</i> -BuOLi <sup>a</sup>	Yield <sup>b</sup> (%)	Alkalinity <sup>c</sup> of Li (%)	Li content (%)		N content <sup>e</sup> (%)
				Found <sup>d</sup>	Calcd. <sup>f</sup>	
(CH <sub>3</sub> ) <sub>2</sub> CHCOOCH <sub>3</sub>		92	6.27	6.20	6.42	0.22
(CH <sub>3</sub> ) <sub>2</sub> CHCOOC <sub>2</sub> H <sub>5</sub>		69 <sup>f</sup>	5.64		5.68	0.07
(CH <sub>3</sub> ) <sub>2</sub> CHCOOCH(CH <sub>3</sub> ) <sub>2</sub>		62	5.02		5.10	0.14
(CH <sub>3</sub> ) <sub>2</sub> CHCOOCH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>		20			4.62	
(CH <sub>3</sub> ) <sub>2</sub> CHCOOC(CH <sub>3</sub> ) <sub>3</sub>		93	4.70	4.59	4.62	0.2
(CH <sub>3</sub> ) <sub>2</sub> CHCOC(CH <sub>3</sub> ) <sub>2</sub> COOCH <sub>3</sub>		78	3.80		3.89	0.4
(CH <sub>3</sub> ) <sub>2</sub> CHCOC(CH <sub>3</sub> ) <sub>2</sub> COOC(CH <sub>3</sub> ) <sub>3</sub>		70	3.19	3.00	3.15	0.03
(CH <sub>3</sub> ) <sub>2</sub> C-CH <sub>2</sub> -CHCH <sub>3</sub>   COOC(CH <sub>3</sub> ) <sub>3</sub>		59 <sup>g</sup>	1.85		1.907 <sup>g</sup>	
(CH <sub>3</sub> ) <sub>2</sub> CHCOOC(CH <sub>3</sub> ) <sub>3</sub>	1	67 <sup>h</sup>	6.10	5.75	6.03 <sup>h</sup>	0.25
(CH <sub>3</sub> ) <sub>2</sub> CHCOOC(CH <sub>3</sub> ) <sub>3</sub>	2	62 <sup>i</sup>	6.51		6.71 <sup>i</sup>	
(CH <sub>3</sub> ) <sub>2</sub> CHCOC(CH <sub>3</sub> ) <sub>2</sub> COOC(CH <sub>3</sub> ) <sub>3</sub>	1	39 <sup>h,j</sup>	4.64		4.62 <sup>h</sup>	

<sup>a</sup> Molar ratio lithium tert-butoxide/ester used. <sup>b</sup> Metalated ester related to the ester used. <sup>c</sup> Acidimetrically. <sup>d</sup> Determined by AAS. <sup>e</sup> According to Kjeldahl. <sup>f</sup> Product was very soluble. Heptane medium for metalation preferred. <sup>g</sup> Calcd. for monotetrahydrofuranate. <sup>h</sup> Calcd. for the alkoxide/metal ester ratio equal to 1. <sup>i</sup> Calcd. for the alkoxide/metal ester ratio equal 2. <sup>j</sup> Prepared by shaking a suspension of metalated ester with benzene solution of alkoxide.

All the lithio esters prepared were colourless compounds. They are fairly soluble in aromatic hydrocarbons, except for methyl and tert-butyl  $\alpha$ -lithioisobutyrate and  $\alpha$ -(lithioisobutryl)isobutyrate, the solubilities of which in common hydrocarbons are very poor. The solubilities are increased, however, by the presence of interacting compounds, such as lithium alkoxides. The lithio esters we examined were surprisingly stable in the solid state or in a hydrocarbon medium: thus, *e.g.*, a 5% solution of isopropyl  $\alpha$ -lithioisobutyrate in benzene did not exhibit any changes in the IR spectrum even after 10 days at room temperature. Similar behaviour was observed with tert-butyl  $\alpha$ -lithioisobutyrate in a Nujol suspension after 7 days, and with methyl  $\alpha$ -lithioisobutyrate in the solid state after 30 days at +5°.

The above compounds were mostly very soluble in a strongly solvating solvent, such as tetrahydrofuran (THF); tert-butyl  $\alpha$ -lithioisobutyrate could even be readily recrystallized from THF at -70°. However, auto-condensations occurred in these solutions at room temperature, the rates being very dependent on the structure of the alkoxy group; the half-lives varied from 50 to 1500 min<sup>17</sup>.

In accordance with the suggested structure, tert-butyl  $\alpha$ -lithioisobutyrate reacted with methyl benzoate or benzoyl chloride to give tert-butyl  $\alpha$ -benzoylisobutyrate in 70 or 78% yield, respectively. The structure of methyl  $\alpha$ -lithioisobutyrate was also shown by deuterolysis, which gave 84% (GLC) of methyl isobutyrate-*d*<sub>2</sub> with 99% D.

Lithium alkoxide adducts were obtained by metalation of esters in the presence of alkoxides. They were also formed by the action of a benzene solution of lithium tert-butoxide on methyl or tert-butyl  $\alpha$ -lithioisobutyrate, or on tert-butyl  $\alpha$ -(lithioisobutryl) isobutyrate (Table 1, or IR spectra). Lithium methoxide was less effective than the tert-butoxide in these reactions. Sodium tert-butoxide formed an adduct with tert-butyl  $\alpha$ -lithioisobutyrate analogous to that formed with lithium alkoxide, and its IR spectrum exhibited even more clearly the features characteristic of this interaction. The effect of different amounts of lithium tert-butoxide on the composition of the interaction product was examined for the metalation of tert-butyl isobutyrate. From a reaction mixture containing a three-molar excess of alkoxide compared to the lithio ester, only alkoxide was isolated successfully, the adducts remaining in the mother liquor. In the case of a two-fold or equimolar alkoxide/ester ratio, crystalline adducts were isolated, as shown in Table 1. It was possible to recrystallize both adducts from toluene without any pronounced change in their lithium content. In contrast, at alkoxide/ester molar ratio of 0.6 or 0.3 the isolated precipitates contained predominantly tert-butyl  $\alpha$ -lithioisobutyrate, in approximately 30 and 60% yields, respectively, thus the formation of a benzene soluble adduct requires an at least equimolar ratio of both components.

### Spectra and structure

The IR spectra of some of the lithio esters and their adducts are described in the Experimental and illustrated in Fig. 1. Comparison with the spectra of the original esters shows that the introduction of the Li atom leads to pronounced changes of the whole spectrum, and to new intense absorptions between 700 and 250  $\text{cm}^{-1}$ . The interpretation of the spectra is complicated by the fact that the  $\alpha$ -lithio esters give oligomeric aggregates in solution (the degree of aggregation being higher than 2), probably by coordination between the oxygen and lithium atoms of different molecules<sup>18</sup>.

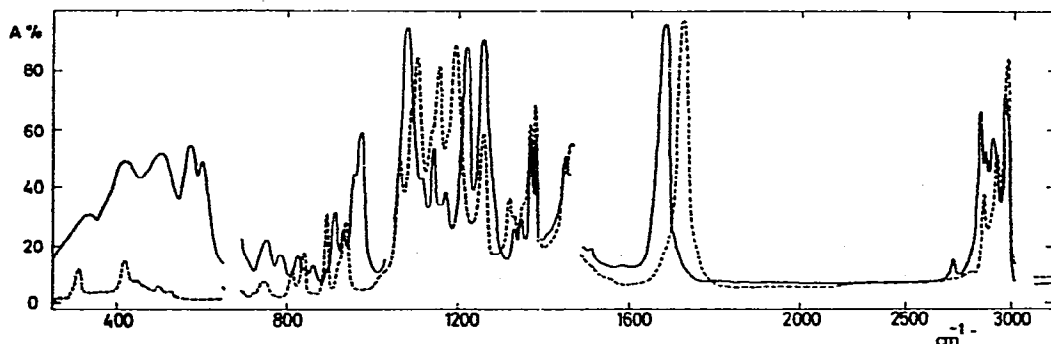


Fig. 1. IR spectrum of 10% solutions in benzene; full line, isopropyl  $\alpha$ -lithioisobutyrate; broken line, isopropyl isobutyrate.

(a). *Esters of  $\alpha$ -lithio carboxylic acids.* The individual esters of  $\alpha$ -lithioisobutyric acid showed a band in the region from 1700 to 1650  $\text{cm}^{-1}$ , instead of the absorption of the non-metalated ester carbonyl group, *cf.*<sup>13</sup>; the intensity of the band

was similar to that of the carbonyl group. The spectra were recorded under various conditions; in all cases only a single intense absorption appeared in this region, so that the simultaneous existence of both (keto and enol) tautomeric forms in substantial concentrations was not confirmed. The observed frequency and intensity instead indicates a "keto" structure for  $\alpha$ -lithioisobutyrate (*cf.* IR spectrum of lithium vinyl oxide<sup>19</sup>, and the theoretical analysis of the C-Li bond in the lithio esters<sup>20</sup>). The lithio esters exhibited at least one intense band in the region 1300-900  $\text{cm}^{-1}$ , with a frequency higher than that of the original ester. In this range are found valence vibrations of the C(O)-O-C group interacting with the bond vibrations of C-C<sup>21</sup>; for esters, a relation has been observed between the decrease in the carbonyl frequency and the increase in the frequency of the intense band between 1270 and 1200  $\text{cm}^{-1}$ <sup>22</sup>, and the properties of the lithio esters observed here are in accordance with those expected. A comparatively intense absorption of the lithio esters below 700  $\text{cm}^{-1}$  is evidence in favour of the lithium bond, because the valence and deformation vibrations of the C-Li and (C)-O-Li bonds are situated in the region 600-300  $\text{cm}^{-1}$ <sup>23,24</sup>, and the esters themselves exhibit only a weak absorption here. In the spectra of the THF solutions of the  $\alpha$ -lithioisobutyrate esters, a further decrease in the carbonyl frequency was found, as well as a considerably diffuse character in the spectrum below 700  $\text{cm}^{-1}$  compared with that in the hydrocarbon medium. These changes can be attributed to solvation of lithium by THF, which results in a higher polarity of the C-Li bond (*cf.* ref. 20).

The interaction with lithium or sodium tert-butoxide was reflected in the spectra of tert-butyl  $\alpha$ -lithioisobutyrate by a decrease mainly in the carbonyl frequency. In the part of the spectrum corresponding to tert-butoxides a decrease in the band frequency around 970  $\text{cm}^{-1}$  of about 10  $\text{cm}^{-1}$  was always observed. This band is assigned to a skeletal vibration involving the C-O-(Li) bond<sup>25</sup>, and indicates the participation of the oxygen atom of the alkoxide in the interaction. The spectra of adducts of tert-butyl  $\alpha$ -lithioisobutyrate and lithium tert-butoxide in equimolar ratio, or with an excess of alkoxide, differed from each other only very slightly.

The UV spectrum of a heptane solution of ethyl  $\alpha$ -lithioisobutyrate was found to exhibit an absorption with a maximum below 200 nm ( $\epsilon_{203}$  3100). A weak absorption observed in the region of 290 nm was attributed to traces of impurities, since it did not change when ethanol was added. The tetrahydrofuran solution exhibited an absorption, the maximum of which was below 203 nm ( $\epsilon_{203}$  3800). Ethyl isobutyrate had an absorption maximum at 214 nm ( $\epsilon$  65) which was assigned to the  $n \rightarrow \pi^*$  transition.

In the IR spectrum of the  $\alpha$ -lithio ester of a dicarboxylic acid, di-tert-butyl  $\alpha$ -lithio- $\alpha, \alpha', \alpha'$ -trimethyl glutarate tetrahydrofuranate, two intense bands were observed in the region 1750-1550 at 1700 and 1630  $\text{cm}^{-1}$ , along with two weak bands at 1725 (inflexion) and 1570  $\text{cm}^{-1}$ . A pronounced decrease in the 1630  $\text{cm}^{-1}$  band occurred at room temperature during 48 h, with simultaneous increase in the extinction values of both bands of low intensity, indicating decomposition of the lithio ester. Since no intense absorption of the ester group of the original ester could be found in the spectrum of the lithio ester, an interaction between the  $\gamma$ -ester and the  $\alpha$ -lithio ester group (of the intra- or inter-molecular type) must be assumed. The distance between the two groups is too large to give rise to significant inductive effects. A similar decrease in the carbonyl frequency of the ester group caused by an inter-

action between esters of carboxylic acids and organometallic compounds has been observed previously<sup>26</sup>.

(b). *Esters of  $\alpha$ -(lithioisobutyryl) isobutyric acid.* These esters do not contain hydrogen atom at the  $\alpha$ -position, and so their reaction with *N*-lithium diisopropylamide leads to metalation at the  $\gamma$ -position only. The IR spectrum of this lithiomethyl or tert-butyl ester, recorded in a hydrocarbon medium (and also that of its adduct with lithium tert-butoxide) was characterized in the region 1750–1600  $\text{cm}^{-1}$  in each case by two bands of high and medium intensities. The absorption corresponding to the original ester group was not observed, so that it had clearly reacted again with lithium, like the lithio esters of dicarboxylic acids.

In contrast to the results in the hydrocarbon medium, new very intense bands at 1713, 1275 and 518  $\text{cm}^{-1}$  appeared in the IR spectrum in the THF solution of tert-butyl  $\alpha$ -(lithioisobutyryl) isobutyrate, with a simultaneous decrease in the intensity of the 1682, 1298, 1258  $\text{cm}^{-1}$ , and other bands. The extent of changes in the spectrum of this lithio ketoester depended on the THF concentration, as was found for the mixtures THF/heptane. However, the frequencies of all the bands varied only slightly with the THF concentration, and the intensity of the 1621  $\text{cm}^{-1}$  band also did not change very much (Table 2). It is possible to explain these results in terms of the existence of a solvated form of tert-butyl  $\alpha$ -(lithioisobutyryl) isobutyrate, which is formed in the THF solution to an extent of about 50%. The presence of both forms could also be observed in the spectra of methyl  $\alpha$ -(lithioisobutyryl) isobutyrate.

TABLE 2

EXTINCTION COEFFICIENTS OF SOME BANDS IN THE IR SPECTRUM OF TERT-BUTYL  $\alpha$ -(LITHIOSOBUTYRYL) ISOBUTYRATE (I) AND OF ITS ADDUCT WITH LITHIUM TERT-BUTOXIDE (II) UNDER VARIOUS CONDITIONS

	(I)				(II)	
	THF	THF + heptane 1+1	THF + heptane 1+2	Nujol	THF	Benzene
$E_{1713}/E_{1393}$	4.0	2.9	2.0	0	1.85	0
$E_{\approx 1680}/E_{1393}$	2.75	3.6	3.6	3.9	3.0	3.5
$E_{\approx 1620}/E_{1393}$	2.1	2.05	2.0	1.95	1.32	1.31

The concentration of the solvated form was considerably lower in the THF solution of an adduct of tert-butyl  $\alpha$ -(lithioisobutyryl) isobutyrate with lithium tert-butoxide than in the same solution of the lithio ester alone (Table 2). In a benzene solution, the IR spectrum of this adduct differed from the sum of the spectra of the components by virtually only a decrease in the frequency of the alkoxide bands at 974 and 586  $\text{cm}^{-1}$ . (For their assignments see refs. 24 and 25).

## EXPERIMENTAL

All operations with organic compounds of the alkali metals were carried out under pure argon (oxygen content lower than 15 ppm). The alkalinity of the products

was determined acidimetrically in methanol or in water. The lithium content was determined by atomic absorption spectrometry, with a Perkin-Elmer 303 apparatus. The absorption spectra were recorded in the IR region on a Perkin-Elmer 457 spectrometer with CsI cells 0.1–0.05 mm thick, and in the UV region on a Cary 14 apparatus with quartz cells, 0.1–0.01 mm thick.

### Chemicals

The isobutyric acid esters were prepared by usual methods and distilled. *tert*-Butyl and methyl isobutyryl isobutyrate were obtained by treatment of the appropriate  $\alpha$ -lithioisobutyrate for 2 h with isobutyryl chloride in pentane at 10° with stirring. The yields of crude esters were 64.5% for the methyl ester (b.p. 91–93°/31 mmHg) and 72.5% for the *tert*-butyl ester (b.p. 121–121.5°/41 mmHg). Since they also always contained approx. 5% of impurity (GLC), they were crystallized from a pentane solution (1 + 1–2 by vol.) at –70°. The crystals were washed and distilled. All the pure (GLC) esters thus prepared were dried by boiling for several hours with calcium hydride (under reduced pressure where necessary) and by distillation. Diisopropylamine was distilled twice and dried with barium oxide. The hydrocarbon solvents were distilled and dried with lithium aluminium hydride. Nujol for the IR spectra was stirred at 200° 1 h with sodium metal and distilled *in vacuo* after filtration. THF was distilled, dried with lithium aluminium hydride, and re-distilled in the presence of sodium anthracene immediately before use. *N*-Lithium diisopropylamide was obtained from a heptane solution of butyllithium ( $c = 1$  mol/l) by the addition of an equivalent amount of diisopropylamine with cooling, and crystallized out (taking up to 24 h) at room temperature. The white microcrystals were recrystallized at –70° from THF, and the crystals thus obtained were dried to constant weight at 50°/1 mmHg. The yield was 79% of the theoretical yield (slightly yellowish). Alkalinity: found (after removal of amine by boiling) 6.79% Li; lithium content: found 6.33; calcd.: 6.48%. The hydrocarbon solutions of butyllithium were prepared from butyl chloride and lithium powder. Lithium<sup>15</sup> and sodium<sup>27</sup> *tert*-butoxides were prepared by literature methods.

### Metalation of esters

To 0.1 mol *N*-lithium diisopropylamide in a benzene or toluene solution ( $c = 0.4$  mol/l), 0.095 mol of ester (diluted 1 + 1 with the same solvent) was added during approx. 30 min with stirring and cooling to approx. 10°. In the case of ketoester the addition was reversed. The mixture was stirred at room temperature for 30 min, and the lithio ester was then isolated: the insoluble ester was removed by centrifugation, while the soluble one crystallized at –70° (sometimes with difficulty) after the solution had been concentrated. The products were dried at room temperature for at least 5 h at 1 mmHg. In the lithiation reactions of isobutyrate, a similar result was obtained when the reaction mixture butyllithium/diisopropylamine was used without isolation of amide (butyllithium/amine/ester 1/1.05/0.9 mol). After lithiation of di-*tert*-butyl  $\alpha, \alpha', \alpha'$ -trimethyl glutarate at –20° the crystalline product could be isolated only after THF had been added (in an amount 1/5 of the reaction mixture volume) at –70° a microcrystalline tetrahydrofuranate then being formed, which had only limited stability (decomposing at 5° after several days). The product was dried only for 1/2 h, since it was losing THF *in vacuo*.

TABLE 3

INFRARED SPECTRA IN THE REGION 2000–250  $\text{cm}^{-1}$ <sup>a</sup>*tert*-Butyl  $\alpha$ -lithioisobutyrate

(a). *Nujol*. (1736 s), 1677 s, ?, 1272 s, 1260 m(sh), 1227 m, 1180 m, 1145 w, 1075 s, 953 m, 866 m, 791 w, 768 w, 686 w, 606 w, 561 m, 512 m, 494 m, 450 w, 417 w, 338 w.

(b). *THF* (measured 4 min after dissolution). (1736 s), 1659 s, 1470 w, 1449 w, 1374 w, 1360 m, 1227 s, 1256 m(sh), 1226 m, 1183 m, ?, 970 m, 953 w(sh), 870 w, 790 w, 768 w, 690 w, 599 w, 566 w, diffusion band m, 452 m, 410 m, 340 w.

*Adduct of tert-butyl  $\alpha$ -lithioisobutyrate and lithium tert-butoxide (Nujol)*

1670 s, ?, 1364 w, 1350 m, 1262 s, 1240 w, 1219 s, 1178 m, 1148 w, 1078 s, 964 s<sup>b</sup> 955 m(sh), 869 m, 787 w, 763 s, 752 w, 674 w, 584 m(dif.)<sup>b</sup>, 514 m(dif.), 468 w, 400 m(dif.), 340 w, 300 w.

*Methyl  $\alpha$ -lithioisobutyrate*

(a). *Nujol*. (1750 s), 1694 s, ?, 1263 s, 1220 s, 1194 w, 1150 w, 1089 s, 1070 s, 1037 m, 930 m, 735 w, 710 m, 676 w, 579 m, 548 m, 453 m, 412 m, 362 m.

(b). *THF*. (1750 s), 1676 s, ?, 1433 m, 1290 i, w, 1264 s, 1221 s, 1180 w, ?, 740 w, 710 w, 676 w, 553 m, 435 s(dif.).

*Adduct of methyl  $\alpha$ -lithioisobutyrate and lithium tert-butoxide (Benzene)*

1683 s, ?, 1374 w, 1350 m, 1260 m, 1215 s, 1190 w(sh), 1080 s, 1020 w, 962 m<sup>b</sup>, 940 m, 920 w, 745 w(dif.), 705 w, 680 w(sh), 576 s(dif.)<sup>b</sup>, 508 m, 458 w, 405 w(dif.).

*di*-*tert*-Butyl  $\alpha$ -lithio- $\alpha,\alpha',\alpha'$ -trimethyl glutarate (tetrahydrofuranate) (Benzene)

(1733 s), 1725 m(sh)<sup>f</sup>, 1700 s, 1630 s, 1580 w<sup>c</sup>, ?, 1388 m, 1368 s, 1330 w, 1316 w, 1257 s, 1210 s, 1165 m(sh), 1142 s, 1072 s<sup>d</sup>, 1038 w, 1010 w, 975 w, 960 w, 900 w, 848 m, 768 w, 750 w, 725 w<sup>e</sup>, 620 w, 597 w, 585 w, 524 w(sh), 510 m, 470 w(dif.), 404 m.

*tert*-Butyl  $\alpha$ -(lithioisobutyryl) isobutyrate

(a). *Nujol*. (1743 s, 1718 s), 1677 s, 1616 m, 1495 m, ?, 1393 m, 1367 s, 1298 s, 1258 s, 1200 s, 1162 s(sh), 1140 s, 1060 m, 1034 w, 1011 w, 966 w, 946 w, 906 w, 867 w, 846 m, 782 w, 767 w, 726 w, 677 m, 605 m, 568 w, 532 w, 479 m, 425 m, 355 w, 307 w.

(b). *THF*. (1742 s, 1717 s), 1713 s, 1682 s, 1621 m, 1458 m, 1391 m, 1367 s, 1298 m(sh), 1275 s, 1258 m(sh), 1208 s, 1135 s, ?, 846 m, 770 w(dif.), 731 w, 695 w, 650 w(dif.)<sup>f</sup>, 620 w(sh), 565 w, 535 w(sh), 518 m, 476 w, 450 w, 385 w, 360 w, 335 w.

*Adduct of tert-butyl  $\alpha$ -(lithioisobutyryl) isobutyrate and lithium tert-butoxide (THF)*

1713 w, 1680 s, 1613 m, ?, 1392 m, 1369 m, 1348 m, 1292 s, 1254 s, 1206 s, 1140 s, ?, 976 s<sup>b</sup>, ?, 782 w, 765 w, 753 w, 723 w, 690 w, 670 w, 616 w, 567 w, 535 m(sh), 517 m, 417 m(dif.), 385 w(sh), 337 w.

<sup>a</sup> In the list of wave numbers for the lithio esters, the wave numbers of the unmetalated ester in the region 1750–1700  $\text{cm}^{-1}$  are shown in parentheses. Characteristics of bands: s strong, m medium, w weak, sh shoulder, dif. diffuse. Regions covered by the solvent are indicated by a question mark. <sup>b</sup> Bands of lithium tert-butoxide are at 974 and 586  $\text{cm}^{-1}$ . <sup>c</sup> Probably arising from decomposition. <sup>d</sup> Intense band of THF at 1070  $\text{cm}^{-1}$ . <sup>e</sup> The spectrum between 750 and 250  $\text{cm}^{-1}$  has a diffuse character; only visible maxima are given.

The adducts of lithio esters with alkoxides were prepared either by the metalation of the ester as described above but in the presence of lithium alkoxide, or by shaking a suspension of lithio ester with lithium or sodium tert-butoxide in toluene at room temperature for 8 h. The insoluble fraction was removed from the reaction mixture and the adduct was isolated by crystallization at  $-70^\circ$  after concentration of the solution.

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