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KETONES SUBSTITUTED WITH AN ALKALI METAL. ISOLATION AND SOME PROPERTIES

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Summary

With lithium, sodium, or potassium some derivatives of aliphatic ketones have been isolated. Their IR spectra in various media have been recorded, and in strongly solvating solvents confirm the enolate structures. The interaction of metalated 2,2-dimethyl-3-butanones with t-butoxides of the same alkali metal was demonstrated. Lithio-2,2-dimethyl-3-butanone reacted with alkoxides of heavier alkali metals via a metal—metal exchange reaction with formation of sodio- or potassio-2,2-dimethyl-3-butanone.

Introduction

The majority of papers dealing with ketones substituted with an alkali metal (subsequently referred to as metalloketones irrespective of the true structure) are concerned with their synthetic applications, and only few are devoted to properties of these compounds [1—9]. In synthetic studies metalloketones were prepared "in situ" and used without further purifications, so that participation of other components of the mixture cannot be ruled out. The presence of lithioketones has also been demonstrated in some systems used for the initiation of the anionic polymerization of methacrylate esters [10], and it was desirable to elucidate their role. For this purpose, some aliphatic metalloketones were prepared in the isolated state, and their properties studied. In addition to other questions, we were interested in the interaction of metalloketones with alkali alkoxides. Such an interaction has been observed with other organometallic compounds, and its effect in some reactions of lithioesters has been demonstrated [11—13]. The importance of such investigation is stressed by the fact that in the preparation of lithioketones as described by Gall and House [14], an equivalent of lithium t-butoxide is formed.

Results and discussion

Preparation and spectra of metalloketones

The metalloketones listed in Table 1 were prepared by treating the appropriate ketone with *N*-lithium diisopropyl amide or sodium or potassium hexamethyldisilazane in a hydrocarbon medium at 20°C. The products were isolated from the reaction mixture in good yields by crystallization, filtration, or evaporation of volatile compounds in vacuo. The metalloketones thus obtained decomposed with evolution of heat immediately on exposure to air, while in an inert atmosphere and at +5°C they remained stable for at least a few months. All the metalloketones prepared were soluble in tetrahydrofuran except for lithioacetone. Lithio-2,2-dimethyl-3-butanone reacted exothermally with THF, and a crystalline adduct separated at room temperature from solutions of a concentration higher than ca. 10%. The IR spectrum of its THF solution did not change for 48 h under the conditions used, and thus lithio-2,2-dimethyl-3-butanone does not enter into the autocondensation reaction as readily as lithioesters [12,15].

It is assumed [1—5] that the enolate structure of the metalloketones predominates, according to eq. 1.

$$(CH_3)_3CCOCH_2Li \rightleftharpoons (CH_3)_3CC(OLi){=}CH_2 \qquad (1)$$

As can be seen from Table 2 and Fig. 1, there was evidence in favour of the enolate forms in the IR spectrum of lithio-, sodio- or potassio-2,2-dimethyl-3-

TABLE 1

PREPARATION AND ANALYSIS OF METALATED KETONES

Compound	Reaction medium	Isolation[c]	Yield (%)	Metal content Found (calcd.) (%)[a]	Content of metalloketone[b] (% weight)	Nitrogen content[d] (%)
$(CH_3)_3CCOCH_2Li$	Pentane	C	76	6.44 (6.54)	86	0.23
$(CH_3)_3CCOCH_2Na$	Toluene	F	88.5	19.28 (18.82)	96	0.40
$(CH_3)_3CCOCH_2K$	Toluene	F	54	27.82 (28.28)	—	0.13
$(CH_3)_2CH\text{-}CO\text{-}CLi(CH_3)_2$	Pentane	C	68	5.52 (5.79)	84	0.18
$CH_2CH_2CH_2COCHLiCH_2CH_3$	Pentane	E	100	5.78 (5.79)	80	0.54
$CH_3CH_2COCHLiCH_3$	Pentane	E	100	7.26 (7.55)	56[e]	0.94
$\overline{CH_2CH_2CH_2CH(Li)CO}$	Toluene	F	67	7.52 (7.72)	30[e]	0.70
CH_3COCH_2Li	Toluene	F	62	10.51 (10.85)	32[e]	0.88

[a] Acidimetrically. [b] From GLC of the hydrolysed product. [c] Isolation procedure: C, after filtration and concentration of the reaction mixture in vacuo crystallization at —70°C, then recrystallization under similar conditions; F, filtration (centrifugation) of the precipitate; E, after filtration of the reaction mixture evaporation to dryness in vacuo. [d] According to Kjeldahl. [e] The values varied strongly with the mode of hydrolysis.

TABLE 2

IR SPECTRA OF LITHIO-, SODIO- AND POTASSIO-2,2-DIMETHYL-3-BUTANONE, IN SOME CASES IN THE PRESENCE OF t-BUTOXIDES OF ALKALI METALS

System[a]	Important absorption bands in the spectrum range[b] (cm^{-1})			
	3150—3050	1650—1500	850—650	650—250
Li-Pin heptane	3118w	1615s, 1586m, 1540m	791m, 733w, 711w	560s, 530in, 484m, 428m, 352vw
Li-Pin + t-BuOLi heptane	3112w	1605s, 1583m, 1525m	793m, 730w, 708w	c
Li-Pin THF	3108m	1599s, 1557w	778m, 707m	553m, 517m, 425s, 382in, 357m
Li-Pin HMPT + heptane	3098m	1585s	≈760m, 690m	557s, 524m, 439m, 395m, 305vw
Na-P in nujol	3112vw, 3081w	1589s, 1555in	775m, 765in, 725in, 709m	543w, 499w, 400vw, 364w, 313w, 281w
Na-Pin + 2 t-BuONa heptane	3107w	1579s, 1555in	782m, 733m, 722in, 700w	c
Na-Pin in THF	3101m	1577s, 1555in	762m, 696m	549w, 498w, 396w, 365w, 308w, 281w
K-Pin nujol	3090w	1560s, 1526w	762w, 703m, 695m	544w, 489w, 387w, 361w, 303w, 279w
K-Pin + t-BuOK benzene?	?	1565s, 1542in	760w, ?	c
K-Pin THF	3094w	1565s, 1545in	762w, 694m, 659m	545w, 492w, 389w, 361w, 301w, 277w

[a] Li-, Na-, K-Pin: Lithio-, sodio-, potassio-2,2-dimethyl-3-butanone; t-BuOLi (Na, K) = lithium (sodium, potassium) t-butoxide. [b] vw, very weak, w, weak, m, medium, s, strong, in inflexion. [c] Overlaps with the bands of the alkoxide.

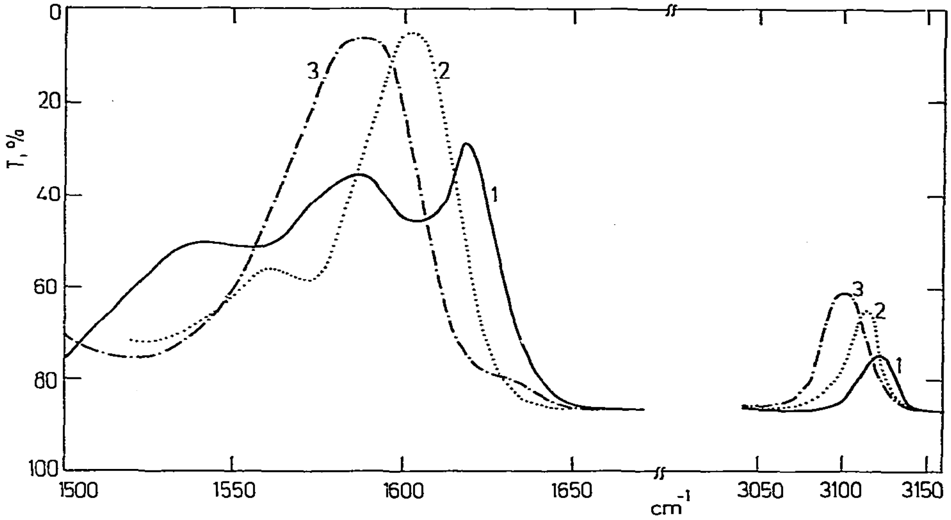


Fig. 1. IR spectra of lithio-2,2-dimethyl-3-butanone in various solvents. (1) Ltihio-2,2-dimethyl-3-butanone (Li-Pin) 0.47 mol/l in heptane, (2) Li-Pin 0.47 mol/l in THF, (3) Li-Pin 0.45 mol/l and 2.2 mol/l hexamethylphosphortriamine in heptane.

butanone (Li-, Na-, K-Pin), dissolved in strongly solvating solvents (THF, hexamethylphosphorotriamine (HMPT). In particular, absorptions in the ranges 3150—3050 and 850—650 cm^{-1}, may be assigned to the stretching or wagging vibrations of the C—H bond in the grouping $RR'C{=}CH_2$, respectively, which are strongly shifted from their usual positions owing to the effect of the enolate ion pair. [cf. 16—18]. In the spectra of the above metallo-2,2-dimethyl-3-butanones, only one intense absorption in the range 1620—1560 cm^{-1} can be observed, in place of the carbonyl absorption of the original ketone; it is usually assigned to the stretching vibration of the C=C bond in the enolate form [2—5]. Besides this, some spectra exhibit a weak band at somewhat lower frequencies (see Table 2). Li-Pin also shows an intense absorption in the range 600—250 cm^{-1}, in which the stretching vibrations of the C—Li and O—Li bonds are found [19,20]. In the case of 2,2-dimethyl-3-butanone derivatives of heavier alkali metals, this intense absorption is obviously shifted to frequencies below 250 cm^{-1}, as can be deduced from the insignificant dependence of bands of these derivatives in the range 600—250 cm^{-1} on the cation and/or solvent, and also by analogy with the IR spectra of sodium and potassium t-butoxide [21].

The IR spectra of metallo-2,2-dimethyl-3-butanones in a weakly solvating medium (hydrocarbons) differed from those in the strongly solvating media in the frequencies and absorbances of bands; the extent of the change decreased in the order from Li-Pin to K-Pin. In a heptane solution of Li-Pin the absorption near 1600 cm^{-1} consisted of at least three bands, one of which exhibited an increased frequency. Their overall intensity was approximately the same as that of bands observed in the solvating solvents in the same range. The stretching and bending vibrations of the $(=)CH_2$ bands also exhibited some shifts of frequency; but more importantly their intensity dropped to ca. 1/2 of that found in strongly solvating solvents like THF. The shape of absorption in the long-wave range below 600 cm^{-1} also depends on solvent. Both Na- and K-Pin showed little solubility in hydrocarbons, and so their spectra were recorded in a nujol suspension. With Na-Pin, two absorption bands were observed in the range between 3120 and 3080 cm^{-1}, whereas after interaction with sodium t-butoxide (cf. below), or after dissolution in THF there was only one. Since the intensity of absorption in a nujol suspension cannot be compared with absorption in solutions, in the case of Na-Pin the heptane and THF solutions of its adduct with sodium t-butoxide were compared. In this case, too, the absorptions assigned to the stretching and bending vibrations of the (=) CH_2 groups in heptane were much weaker than in THF. The absorption curve of Na-Pin in nujol near 1600 cm^{-1} contains fewer bands than that of Li-Pin; the frequency of the intense band was again higher than in THF. Compared with the spectrum of the THF solution, the only rather important change in frequency exhibited by the nujol spectrum of K-Pin was a displacement of the two bands in the range of bending vibrations of the (=)CH_2 bonds towards higher frequencies.

For comparison, we also recorded the ^{13}C NMR spectra of Li-Pin, and the following chemical shifts (in δ ppm) were found in various solvents: for $C(=CH_2)$ and C(C—OLi): heptane 76.8 and 177.0, THF 75.4 and 176.6 (lit. [3] dimethoxyethane 73.5 and 176.8). The NMR method cannot of course, be used to distinguish two different species present in dynamic equilibrium, and the values of chemical shifts found may represent the weighted average of two or more species present. The UV spectra of Li-Pin exhibited also a shift of the maximum depending on the solvent: heptane λ_{max} 210.0 nm ($\epsilon = 6.3 \times 10^3$), THF λ_{max} 223.2 nm ($\epsilon = 6.3 \times 10^3$). In THF, solvation weakens the interaction of the metallic atom with the organic part of the molecule. This makes possible a greater delocalization of electrons, with a simultaneous increase in electron density at $C_{(=CH_2)}$. The UV and NMR spectra are in agreement with this view.

Overall, the IR spectra confirm the enolate structure of alkaline metallo-2,2-dimethyl-3-butanones suggested earlier on the basis of the NMR spectra [2—5]. Exceptions are seen in Li- and Na-Pin in a weakly solvating medium (K-Pin could not be examined in this manner), for which a much lower absorbance of the stretching and deformation vibrations of the (=)CH_2 groups was observed. Such decrease may be caused either by a change in the extinction coefficient (ϵ), or by a change in the concentration of the respective species. Some papers [22—24] suggest that ϵ of the stretching and bending vibrations of the C—H bonds in variously-substituted olefins may assume considerably different values. If it is unlikely however, that ϵ falls to at least half its value upon change from a THF to a heptane solution of metallo-2,2-dimethyl-3-butanones, the cause of decrease in the intensity of their (=)CH_2 bands must be looked for in a decrease in concentration of the enolate form, which could be best explained by a shift in the direction of the keto structure. The greater number of absorption bands near 1600 cm^{-1} of lithio-2,2-dimethyl-3-butanone is consistent with such a possibility in weakly solvating mediums.

Of the IR spectra of the other lithioketones prepared (Table 3), the spectrum of lithioacetone in nujol exhibited similar bands in the ranges examined as that of the heptane solution of Li-Pin. Owing to the low solubility of lithioacetone, the spectrum of its THF solution could not be obtained. The spectra of lithiodiethyl ketone, lithiodi-n-propyl ketone and lithiocyclopentanone in THF exhibited as intense absorption between 1650—1550 and 650—250 cm^{-1}, as in

TABLE 3

IR SPECTRA OF SOME LITHIOKETONES

System [a]	Absorption bands in the range (cm^{-1})			
	3100—3000	1650—1500	850—650	650—250
Li-Ac, nujol	3086w	1610s, 1572m, 1542w	784m, 726m, 693w, 677vw	550s, (diffuse), 470w, 410m
Li-DEK, heptane	3055 [b]	1640s, 1631s	816m, 800m, 770w, 740vw	diffuse absorption 620—370, max. 580s
Li-DEK, THF	3065 [b]	1628s	819m, 794m, 773w, 727m	581m, 561m, 507s, 409s
Li-CPK, heptane	3035 [b]	1619s, 1602s	774m, 727w, 694vw	500m, 390m
Li-CPK, THF	3045 [b]	1612s	753m, 733vw, 677m	491m, 407m
Li-DNPK, heptane	3035 [b]	1634s, 1617m	822w, 767vw, 700vw	627w, 573s, 527s, 427m, 347w
Li-DNPK, THF	3040 [b]	1621s	837w, 803w, 767vw, 671vw	630w, 560m, 516m, 418s
Li-DIPK, heptane	—	1638s	717m 681w	583m, 525m, 489w, 425m
Li-DIPK, THF	—	1627s	733m, 699vw, 670vw	577m, 542m, 515m, 452m, 359m

[a] Abbreviations: Li-AC, Lithioacetone, Li-DEK, lithiodiethyl ketone, Li-CPK, lithiocyclopentanone, Li-DNPC, lithiodi-n-propyl ketone, Li-DIPK, lithiodiisopropyl ketone. The meaning of the other abbrevations see Table 2. [b] The band is overlapped with the beginning absorption of the solvent and its maximum cannot be determined exactly.

previously described cases. The characterization of bands assigned to vibrations of the C—H bands was more difficult, because these bands were weak and uncharacteristically developed in the range above 3000 cm^{-1}, while in the range of bending vibrations they could not be unambiguously identified. It is known from the literature, however [16], that the grouping RR'=CR"H is reflected in the spectrum in such an unpronounced manner. As expected, lithiodiisopropyl ketone, which has no remaining hydrogen atom on the metalated carbon atom, did not exhibit any defined absorption in the range 3200—3000 cm^{-1}. Changes in the spectra of these lithioketones or change of solvent from THF to heptane were much less pronounced than for Li-Pin. It is thus not possible at present to extend the conclusions for Li-Pin to the other lithioketones.

Interaction of metalloketones alkaline t-butoxides

The interaction of Li-Pin with an equimolar amount of lithium t-butoxide in heptane was strongly reflected in the IR spectra, in particular in changes of the frequency and intensities of bands in the range near 1600 cm^{-1}, as can be seen from Table 2 and Fig. 2. Addition of a further molar equivalent of the alkoxide to the mixture did not lead to any further significant changes of the spectrum. In contrast complete dissolution of Na-Pin in heptane was achieved only by adding two molar equivalents of sodium t-butoxide. Compared with the sum of the spectra of components, the IR spectrum of a solution thus obtained exhibited differences similar to those of the lithium derivatives; moreover, after interaction with sodium t-butoxide the pair of bands of Na-Pin at approx. 3100 cm^{-1} appeared only as a single maximum. An intense band at 958 cm^{-1}, sensitive to such interactions, disappeared from the sodium t-butoxide bands [21]. The equimolar mixture of K-Pin and potassium t-butoxide did not dissolve in heptane, but in benzene a viscous solution was formed, the IR spectrum of

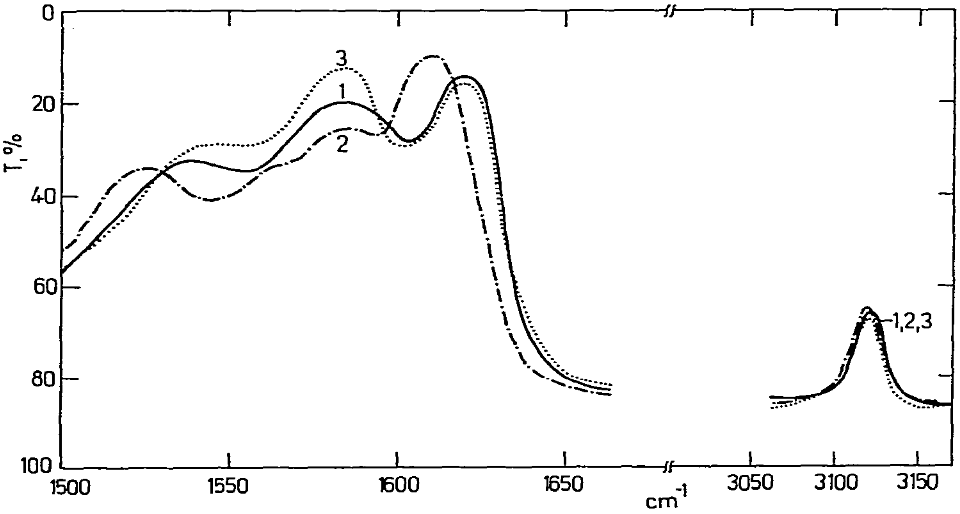
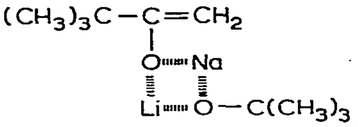


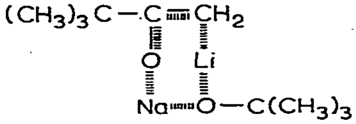
Fig. 2. IR spectrum of lithio-2,2-dimethyl-3-butanone before and after interaction with lithium t-butoxide or butyllithium in heptane. (1) Lithio-2,2-dimethyl-3-butanone (Li-Pin) 0.78 mol/l, (2) Li-Pin 0.76 mol/l and 0.80 mol/l lithium t-butoxide in heptane, (3) Li-Pin 0.83 mol/l and butyllithium 0.82 mol/l in heptane.

which, exhibited smaller shifts of frequencies compared with the sum of the spectra of components. It follows that 2,2-dimethyl-3-butanone substituted with lithium, sodium or potassium is able to interact with the t-butoxide of the respective metal, and that this interaction was reflected not only in changes in the IR spectrum but also in an increased solubility of metallo-2,2-dimethyl-3-butanones in hydrocarbons. In contrast the IR spectra of mixtures of lithium t-butoxide and lithio-di-n-propyl ketone or lithiodiisopropyl ketone were not significantly different from the sum of the spectra of components, and therefore their interaction could not be proved. In the case of n-butyllithium, the interaction with Li-Pin was reflected in the IR spectrum, as documented by Fig. 2. This spectrum remained unchanged at ambient temperature for 6 h, so that no other reaction between the two components seems to occur under the conditions used.

The IR spectrum of an equimolar mixture of Li-Pin and sodium t-butoxide in benzene was identical with that of a solution of Na-Pin and lithium t-butoxide in the same solvent. It did not coincide, however, with the superimposed spectra of components of the first and second system, especially in the range 600—250 cm^{-1}. Hence one may infer the existence of an adduct in benzene, probably having the structure I or II.



(I)



(II)

If, however, cyclohexane or heptane solutions of Li-Pin and sodium t-butoxide were mixed, a precipitate appeared within 5 min, and after isolation was identified by means of its analysis and IR spectrum as Na-Pin (cf. Table 4). Obviously, a metal—metal exchange reaction occurred:

$$RLi + R'OM \rightarrow RM + R'OLi$$

$$(M = Na, K; R = (CH_3)_3CCOCH_2)$$

The reaction has been observed earlier with other types of organolithium compounds and alkoxides of heavier alkali metals [15,25—28]. Similarly, K-Pin was prepared by treating Li-Pin with potassium (—)menthoxide in heptane (Table 4).

TABLE 4

METALATED 2,2-DIMETHYL-3-BUTANONES PREPARED BY AN EXCHANGE REACTION

Product	Yield (%)	Alkalinity[a] (%)	Na or K content[b] (%) Found (calcd.) (%)	Li content[b] (%)
$(CH_3)_3CCOCH_2Na$	29	18.80	19.80 (18.82)	0.8
$(CH_3)_3CCOCH_2K$	69	28.24	25.2 (28.28)	0.60

[a] Acidimetrically, expressed in % of the respective metal. [b] By means of atomic absorption spectroscopy.

Experimental

General remarks

All operations involving organic compounds of alkali metals were performed under purified argon. The acidolysis of metalloketones was performed in benzene with acetic acid; the content of ketones thus obtained was determined by GLC with a Perkin—Elmer 30 apparatus. After the hydrolysis, the content of alkali metals was determined by atomic absorption spectrometry, using a Perkin—Elmer 303 apparatus. The IR spectra were recorded in CsI cells, mostly 0.1 mm thick, using 5—10% solutions or suspensions, by means of a Perkin—Elmer 457. The UV spectra were recorded with a Cary 14 apparatus; a JEOL JNM FX 60 was used to record the NMR spectra.

Chemicals

The ketones were purified by distillation and dried over calcium hydride. The solvents were then redistilled immediately before use in the presence of anion radicals; heptane was distilled from lithium aluminium hydride. *N*-Lithium diisopropyl amide and sodium or potassium hexamethyldisilazane were prepared by a simple method based on a reaction of the particular alkali metal with amine in the presence of an activator (styrene) in toluene, and isolated by crystallization in a good yield [29]. t-Butoxides of alkali metals were prepared by a literature method [30].

Metalation of ketones (conditions suitable for a particular ketone are given in Table 1).

To a solution (suspension) of the relevant alkali amide in hydrocarbon (10 ml/1 g), the ketone was added dropwise with stirring at 20°C during a few minutes (molar ratio amide/ketone 1/0.95). The mixture was stirred for 2 h and the product was isolated and dried at room temperature for 10 h in vacuo.

Exchange reaction of lithio-2,2-dimethyl-3-butanone with alkoxides of heavier alkali metals

To a solution of sodium t-butoxide in cyclohexane (potassium (—)menthoxide in heptane), an equimolar amount of a solution of Li-Pin in heptane (7 ml/1 g) was added dropwise with stirring at 20°C. After stirring for 2 h, the precipitate was isolated, washed with heptane, and dried as above.

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