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3-DIMETHYLAMINOPROPYL-LITHIUM—AN ANALYTICAL AND KINETIC INVESTIGATION OF A NEW INITIATOR SYSTEM FOR POLYMER SYNTHESIS

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Abstract—The formation of 3-dimethylaminopropyl-lithium from the reaction of 3-chloro-1-(dimethylamino)-propane with powdered lithium in tetrahydrofuran (THF) at −25° and in cyclopentane (CP) at +49·5°, respectively, has been investigated. The kinetic and analytical determinations of this reaction were made by gas chromatography. The lithium compound was obtained in a > 90% yield in THF, although in this solvent its stability was limited even at low temperatures. In contrast in CP a more stable solution of the organometallic compound was formed, but lower yields (50% at most) were realized; this solution, unlike the THF solution, was contaminated with by-products.

1. INTRODUCTION

Uniform polymers with defined end-groups are usually prepared anionically, i.e. the end-groups are formed by reactions of the living chain end (carbanionic centre) with a terminating agent (electrophile), cf. [1]. With bifunctional initiators, the same end-groups can be placed on both ends of the polymer chain. Alternatively, a functional group can be introduced from the initiator (e.g. in zwitter-ion polymerization [2]) but this approach has been used infrequently in anionic systems. Using a bifunctional initiator and a suitable terminating agent, it should be possible to obtain polymers with different end-groups.

We now report our analytical and kinetic findings pertaining to the formation of such a lithium organic initiator, 3-dimethylaminopropyl-lithium, DMAP-Li (for the analogous Grignard reagent, cf. [3]). The application of this compound to prepare macromolecules with two different end-groups is described elsewhere [4,5].

2. CHOICE OF SYSTEM

An organo-lithium compound was chosen because of its high initiator efficiency [6,7] and the subsequent fast propagation rate of the growing polymer chain [8,9]. The functional *tert.* amino group of the organometallic initiator was selected primarily since it would enable one to effect a desired chain-analogue conversion [10] of the end-group of the polymer so obtained, cf. [4,5]. In accordance to the usual method for the preparation of alkyl lithium compounds, the halide, 3-chloro-1-(dimethylamino)-propane (DMAP-Cl), was reacted with finely dispersed lithium [11,12], Eqn. (1):

$$(CH_3)_2N{-}(CH_2)_3Cl + 2Li \rightarrow (CH_3)_2N{-}(CH_2)_3Li + LiCl. \qquad (1)$$

DMAP-Cl DMAP-Li

In DMAP-Li, the distance between N and Li should be enough to guarantee a high initiator efficiency (similar to butyl-Li); in addition, the use of a γ-chloroamine should minimize side-reactions known for halogeno amines [13–15] because of its small tendency for intramolecular cyclization [16,17].

An ether, THF (tetrahydrofuran, a common solvent in anionic polymerizations), and a hydrocarbon, CP, (cyclopentane) were employed as solvents in order to examine the differences between polar and nonpolar solvents for this reaction [1,18]. The boiling point of CP (49·5°) limits the reaction temperature; at higher temperatures (attainable, e.g. with hexane) more side-reactions [cf. Eqns. (2) and (3)] might occur. Its high volatility assures non-interference in analysis by gas chromatography (GC); the retention time of CP has been short enough on all columns employed to permit quantitative evaluation of the other compounds.

In conjunction with the standard double Gilman titration [19,20], GC was used to determine the concentration of DMAP-Li (cf. experimental). GC affords proof and quantitative detection of unreacted as well as of starting material, DMAP-Cl. In addition, this method can be used to examine selectively the formation of side products [21].

3. PREPARATION OF 3-DIMETHYLAMINOPROPYL-LITHIUM IN TETRAHYDROFURAN

With lithium powder, high yields of DMAP-Li were obtained, cf. Table 1; doubling of excess Li did not have much influence on yields provided that reaction times were sufficiently long.

The reaction of DMAP-Cl with Li was much more violent than the similar reaction of butyl chloride.

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* C. D. Eisenbach, Part of Ph.D. Thesis. Universität Mainz (1974).

Table 1. Preparation of DMAP-Li in THF by dropwise addition of DMAP-Cl solution (20 ml) to Li (20 ml suspension); molar ratio Li/DMAP-Cl ~4

				Double titration		Gas chromatography			
Exp. no.	[DMAP-Cl]$_0$ (mol/l)	Temp.	Reaction time (min)*	[DMAP-Li] (mol/l)	DMAP-Cl conversion (%)†	[DMAP-Li] (mol/l)	[DMAP-Cl] (mol/l)	DMAP-Cl conv., % on DMAP-Li‡	Total§
7	0·89	− 20	150	0·67	75	0·70	0·10	78·5	88·8
			480	0·72	81	0·78	0·03	87·5	96·9
8	1·04	+ 10	270	0·57	55	0·68	0·04	65	96
9	0·96	− 25	870	0·85	89	0·94	0	98	100
10	1·01	− 25	1230	0·88	87	0·98	0·04	97	96
11	0·80	− 25	630	—	—	0·80	0·03	100	96

* Inclusive 30 min addition time.

† Calculated from column 5.

‡ Calculated from column 7.

§ Calculated from column 8.

probably because of the complexing ability of the *tert.* amino group with lithium compounds [22]. Due to the low stability of organo-lithium compounds in THF, even a small temperature increase above −20° resulted in side-reactions and reduced yield.

The experiments of Table 1 demonstrate that almost no side-reactions occur if low temperatures and long reaction times are maintained: >10 hr at −25° affords nearly quantitative conversion of DMAP-Cl to DMAP-Li according to GC analysis (experiments 9–11, Table 1).* The presence of some starting halide (in spite of the excess Li) is surprising and has not been reported to our knowledge; it would indicate limitations in the active surface of finely dispersed Li and/or incomplete Wurtz coupling.

The freshly prepared initiator solution should be used within a few days, since there was slow decomposition even during storage in a refrigerator at −20°.

4. PREPARATION OF 3-DIMETHYLAMINOPROPYL-LITHIUM IN CYCLOPENTANE

In view of the prolonged reaction times necessary for quantitative yields of DMAP-Li in THF and in view of the known increased stability of Li-organic compounds in aliphatic solvents, some additional reactions were conducted in CP. It was demonstrated that the reaction of DMAP-Cl with Li at room temperature was extremely slow in CP, but heating to 30–35° was sufficient to effect a rapid initiation of the reaction. The preliminary experiments of Table 2 show that complete conversion of the halide (no detectable DMAP-Cl by GC) gives only 45–50% of the desired product. Obviously, the reaction is finished after 30 min (cf. experiment 13, Table 2). It was shown by GC that longer reaction times did not cause changes in yield.

Thus, it was concluded that THF is the preferred solvent with respect to yield of the organo-Li compound and purity of the initiator solution; this is proved in the following section.

5. DETERMINATION OF BY-PRODUCTS DURING INITIATOR PREPARATION

GC analysis permitted identification of by-products which account to > 50% with respect to DMAP-Cl conversion in CP.

Using THF as solvent at −25°, the initiator solution was contaminated only by traces of 6-dimethylamino-1-hexene, DMAH in Eqn. (2b) [for the origin of allylic chloride cf. Eqn. (3b)]. At higher temperatures (e.g. experiment 8, Table 1) ether cleavage [Eqn. (2d)] was the predominant side-reaction and besides DMAH only a small amount of the Wurtz product, 1,6-bis(dimethylamino)-hexane (BDMAH) could be identified. In the GC analysis, no evidence was observed for metallation of THF, a reaction that should

Table 2. Attempts to prepare DMAP-Li from DMAP-Cl in CP at +49·5° (b.p. of CP); molar ratio Li/DMAP-Cl ~4–5

			Double titration		Gas chromatography			
Exp. nr.	[DMAP-Cl]$_0$ (mol/l)	Reaction time (min)	[DMAP-Li] (mol/l)	DMAP-Cl conversion (%)*	[DAMP-Li] (mol/l)	[DMAP-Cl] (mol/l)	[BDMAH] (mol/l)†	DMAP-Cl conversion (%)‡
12	1·47	420	0·56	38	0·69	0	0·32	47
13	1·86	30	—	—	0·94	0	0·40	50
		75	—	—	0·90	0	0·40	49
		125	—	—	0·90	0	0·42	48
14	1·99	60	0·87	44	—	—	—	—
15	1·53	120	0·58	38	—	—	—	—

* Calculated from column 4.

† Wurtz-product, Eqn. (2c).

‡ Calculated from column 6.

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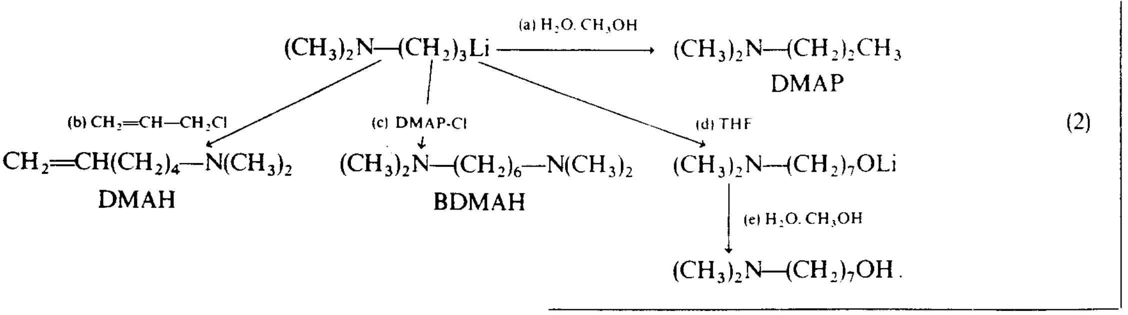
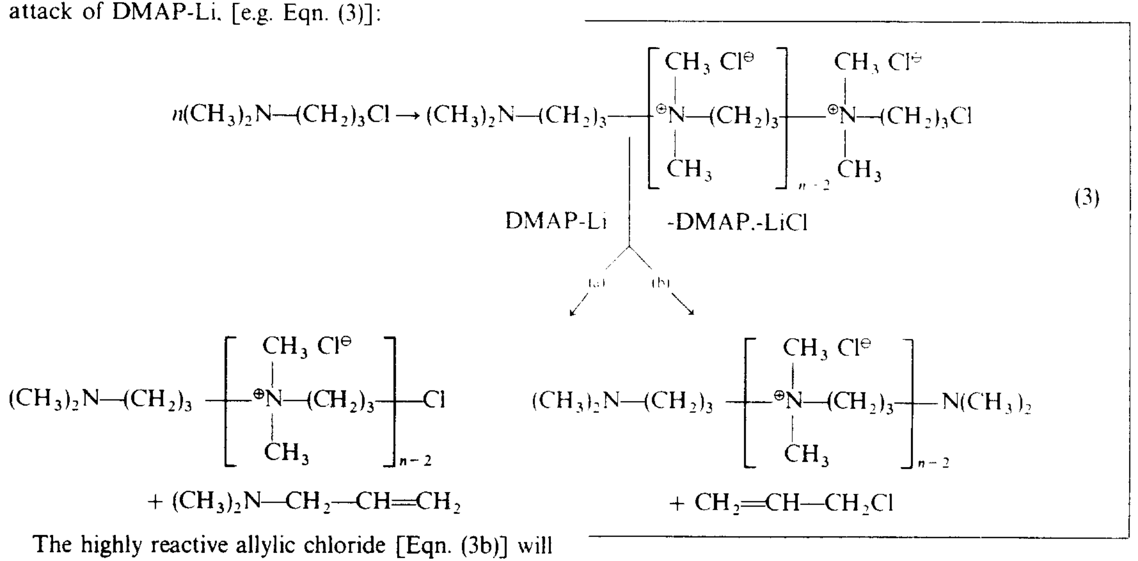
* In several cases, the somewhat lower figures by Gilman titration (column 6 vs 9, Table 1) are due to traces of humidity present during preparation of the catalyst (cf. experiments 9 and 10); these form DMAP [Eqn. (2a)], identical to the methanolysis product (cf. section 7.4). In these cases, the Gilman titration proves to be advantageous, unless specific reagents are employed. This is demonstrated in a paper devoted to a novel quantitative GC analysis method for organo-lithium compounds [21].

have produced ethylene and acetaldehyde [23]. The following reaction scheme explains the origin of the identified compounds:



In CP, Wurtz coupling [Eqn. (2c)] is the predominant side-reaction consuming 30–40% of the starting material. The preponderance of this reaction in hydrocarbon solvents is confirmed by examination of butyl-Li solutions in hexane, where octane was the largest impurity in the GC traces. Besides, some reactions specific to N-containing organo-halogen compounds will occur with partial scission of the formed dimeric [14] or polymeric ("ionene") [15] salts by attack of DMAP-Li, [e.g. Eqn. (3)]:



The highly reactive allylic chloride [Eqn. (3b)] will immediately react with DMAP-Li to form DMAH [Eqn. (2b)], a reaction occurring to a much smaller extent in THF, too. The absence of 3-dimethylamino-1-propene in the GC traces confirms that no N-terminal Hoffmann degradation [e.g. Eqn. (3a)] occurs.

6. KINETIC INVESTIGATION

Whereas numerous papers have been published on the formation of organo-lithium compounds by reaction of organic halides with lithium (cf. [24]), there are only a few results on the kinetics of this reaction [25,26]. Therefore we conducted two runs in each solvent, THF (at −25°) and CP (at +49·5°) for information on the time–conversion dependence of the initiator formation.

Two main reactions were taken in consideration; viz. formation of DMAP-Li [Eqn. (1)], almost 100% of the product in THF, and Wurtz coupling (*ca.* 35–40% in CP), Eqns. (2c) and (4), respectively.

$$\underset{\text{DMAP-Cl}}{2(CH_3)_2N(CH_2)_3Cl} + 2Li \rightarrow \underset{\text{BDMAH}}{(CH_3)_2N(CH_2)_6-N(CH_3)_2} + 2LiCl. \tag{4}$$

Figure 1 (THF solution) and Fig. 2 (CP solution) show the corresponding time–conversion curves for DMAP-Cl. In both cases a short induction period is followed by a fast reaction to *ca.* 90% conversion of the starting material after *ca.* 20 min (curve 1); then in CP at 49·5°, conversion is nearly complete after 60 min, whereas in THF at −25° even after 720 min *ca.* 5% of unconverted DMAP-Cl remains. The deficit in the mass balance of Fig. 2 between the starting compound DMAP-Cl (curve 1) and the conversion to DMAP-Li (curve 2) and BDMAH (curve 3) is caused by formation of the dimeric [14] and polymeric [15] salts.

The order of the reaction, n, and the rate constant k_n were determined with the formal equation

$$v = k_n \times c_A^n \tag{i}$$

$$\log v = n \times \log c_A + \log k_n \tag{ii}$$

(with v = reaction rate $\Delta c_A/\Delta t$, and c_A = concentration of DMAP-Cl) by plotting log v vs log c_A (both based on the time–conversion curves, Figs. 1 and 2). The various constants are summarized in Table 3.

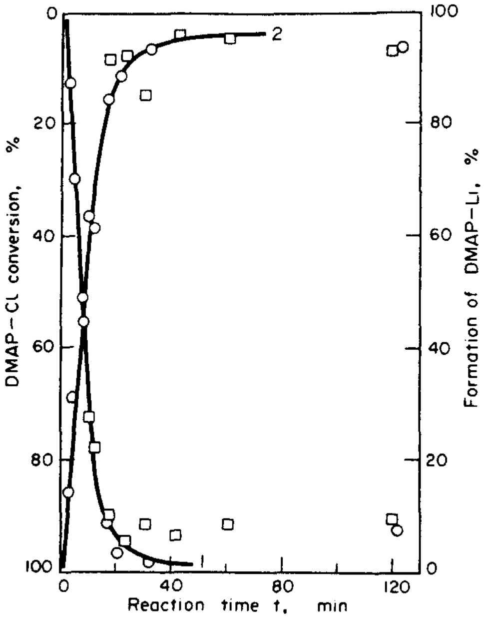
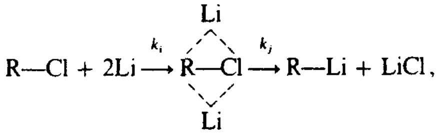


Fig. 1. Conversion–time curves for DMAP-Cl (curve 1) and formation–time curve for DMAP-Li (curve 2) in the reaction of DMAP-Cl with Li in THF at −25°. GC-analysis of 1 ml samples from the reaction mixture. ○: 50 ml total solution volume; $[\text{DMAP-Cl}]_0$ = 0·970 mol/l; molar ratio Li/DMAP-Cl = 4·5. □: 48 ml total solution volume; $[\text{DMAP-Cl}]_0$ = 0·987 mol/l; molar ratio Li/DMAP-Cl = 5·8.

In both solvents the order with respect to DMAP-Cl consumption and DMAP-Li formation, Eqn. (1), is the same within the range of error (5–10%), indicating a negligible influence of the solvent on *n*.

Obviously a higher k_n and $n > 1$ is valid for the total conversion of DMAP-Cl in CP since side-reactions (salt formation and mainly Wurtz coupling) are included. The conversion of DMAP-Cl to the Wurtz product BDMAH is slower than the formation of DMAP-Li; this is already detectable from Fig. 2. For the formation of BDMAH, Eqn. (4), one would expect a second order reaction; the smaller figure of n = 1·6 indicates that the formation of DMAP-Li [Eqn. (1)] is rate determining.

Without consideration of the solvent influence, the reaction in CP at +49·5° should be approximately 130 times faster than that in THF at −25°, assuming a doubling of the rate for each 10° temperature increase. The measured k_n-value in CP, however, is only 2·5 of that in THF, i.e. only 1/50 of the expected figure. This discrepancy is explicable by the nature of the solvent because reactions in which neutral partners (R-Cl and Li) form compounds of ionic character (R-Li, *ca.* 30% ionicity [27]) are accelerated by ionizing solvents. In the reaction scheme



$$\mathrm{R{-}Cl} + 2\mathrm{Li} \xrightarrow{k_i} \overset{\mathrm{Li}}{\underset{\mathrm{Li}}{\mathrm{R{-}Cl}}} \xrightarrow{k_j} \mathrm{R{-}Li} + \mathrm{LiCl}, \qquad (5)$$

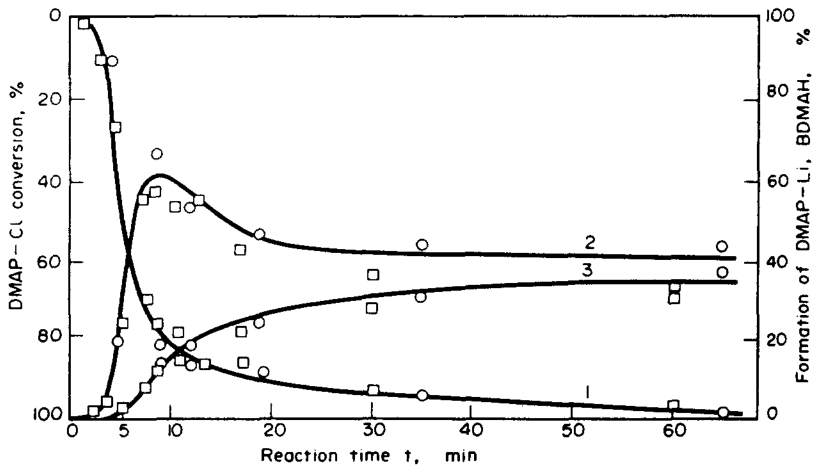


Fig. 2. Conversion–time curve for DMAP-Cl (curve 1) and formation–time curve for DMAP-Li (curve 2) and BDMAH (curve 3) in the reaction of DMAP-Cl with Li in CP at 49·5°. GC-analysis of 1 ml samples from the reaction solution. ○: 48 ml total solution volume; $[\text{DMAP-Cl}]_0$ = 1·18 mol/l; molar ratio Li/DMAP-Cl = 5·1. □: 46 ml total solution volume; $[\text{DMAP-Cl}]_0$ = 1·174 mol/l; molar ratio Li/DMAP-Cl = 4·8.

Table 3. Reaction order *n* and rate constant k_n [in $1/\mathrm{min(mol/l)}^{n-1}$] for the system DMAP-Cl/Li in THF and CP

Solvent (temp.)	DMAP-Cl decrease and DMAP-Li formation, Eqn. (1)		Total conversion of DMAP-Cl		DMAP-Cl decrease, Eqn. (4)	
	n	k_n	n	k_n	n	k_n
THF (−25)	0·88	0·11	0·88*	0·11*	—	—
CP (+49·5)	0·96†	0·26†	1·2	0·32	1·6	0·22

* Same figures as in columns 2 and 3 since in THF no side-reactions.

† DMAP-Li, consumed for Wurtz coupling, taken in consideration.

an activated complex is formed as an intermediate product. The rate constant k_j of the consecutive reaction to form the final product (DMAP-Li in our case) will be smaller in CP than in THF, but this is not the determining factor. The acceleration due to precipitation of LiCl in CP might be counterbalanced by better solvation of both reaction products in THF. Thus k_i can be considered as decisive, and the intermediate activated complex will have incomplete solvation in the unpolar CP and consequently a lower probability of formation as compared to THF. Our results are in agreement with this proposal. Kinetically, this is equivalent to a higher ΔG^* as a consequence of a more negative ΔS^*.

7. EXPERIMENTAL SECTION

7.1 *Starting reagents*

THF (p.a., Merck AG) was refluxed in the dark for 2 days with 1 wt % K in Ar atmosphere; after addition of benzophenone, it was refluxed for an additional 24 hr. The deep blue solution was always refluxed for 3 hr prior to use and distilled off over a column. CP (p.a., Merck AG) was refluxed for 24 hr with 2 wt % $LiAlH_4$ under Ar; it was again refluxed prior to distillation.

DMAP-Cl was isolated from its hydrochloride (Schuchardt) by addition of a double molar amount of 40% aqueous NaOH solution followed by extraction (3 ×) with ether: the ether extracts were dried at −15° over KOH and the amine was vacuum distilled on a column under N_2 (100 torr. 110–120° bath temp.); b.p. = 70° (b.p.$_{760}$ = 134°).

Analysis. Calcd: C 49·35; H 9·86; N 11·60. Obs: C 49·38; H 9·95; N 11·22. Li powder (Metallgesellschaft) was used as obtained; it contained 0·4–1% Na. For the importance of foreign metal content, cf. [28, 29].

7.2 *Model compounds*

BDMAH (purum, Fluka), GC > 98%.

DMAH was prepared in a modified version after Merling [30]: b.p.$_{760}$ = 142°; n_{23}^{D} = 1·4238. *Analysis.* Calcd. C 75·52; H 13·47; N 11·01. Obs. C 75·50; H 13·41; N 10·40.

DMAP was prepared [31] from 59 g (1 mol) propylamine, 230 g (5 mol) formic acid (85%) and 77 g (2·5 mol) formaldehyde (40%); b.p. = 65°; n_{23}^{D} = 1·3830; picrate (m.p. = 106°). *Analysis.* Calcd: C 41·78; H 5·10; N 17·71. Obs: C 42·18; H 5·40; N 17·31.

7.3 *Preparation of the organo-*Li *initiator*

In THF: 1·5–2 g (0·2–0·3 mol) Li-powder under Ar were placed in a dry 100-ml 2-neck round-bottomed flask with magnetic stirrer and thermometer; 20 ml THF were then distilled in. DMAP-Cl [5–6 g (0·04–0·05 mol)] was added in a 50-ml dropping funnel filled with 15–20 ml dry THF under Ar. The Li-suspension was cooled to −25° where it was kept (±2°) by external cooling (−30 to −35°) for the addition of DMAP-Cl (25–30 min; intensive stirring). After exchange of the funnel for a 3-way stopcock with serum cap and Ar-balloon, the solution was stirred for a further 12 hr at −25°. The ~1 M initiator solution was kept in a freezer at −20° and the required volumes were removed by a syringe.

In CP: a similar apparatus was used. The flask with the Li-suspension was fitted under Ar with an intensive condenser (with drying tube) and a dropping funnel. After fast addition of DMAP-Cl to the vigorously stirred suspension at room temperature (no reaction) the dropping funnel was exchanged for a 3-way stopcock. The reaction was carried out in a constant temperature bath at 60° and the system was refluxed for 2 hr. This solution was then stored at room temperature.

In the kinetic studies, the general reaction conditions for the formation of DMAP-Cl described above were slightly modified for an exact starting point. In THF solvent, the DMAP-Cl solution was cooled to 0° and added at once into the precooled Li-suspension at −78° (thereafter exchange of the funnel for a 3-way stopcock); the reaction temperature could then be kept constant at −25 ± 2° by methanol–dry ice. In CP solvent, the Li-suspension was preheated at +30°, and immediately after DMAP-Cl addition (starting point t_0) it was heated to reflux within 1 min (heating bath +60°). With a syringe, 1-ml samples were removed from the reaction flask and the reaction products quantitatively determined by GC after quenching with methanol and centrifuging the LiOH (cf. Sections 7.4 and 7.5).

7.4 *Quantitative determination of organo-*Li *compounds*

The analysis were performed according to Gilman *et al.* [20]. As terminating agents, allylic bromide (puriss., stabilized with Ag, Fluka) and 1,2-dibromo ethane (Hoechst AG; dried over P_2O_5, freshly distilled) were employed. The solvent diethyl ether (p.a., Merck AG) was dried on Na-wire. Methyl orange served as indicator in the titrations with N/10 HCl; phenolphthaleine (colour change at pH 9·5) cannot be used due to the weakly acid character of the ammonium compound formed from the cotitrated *tert.* amino group; it already decolorized when only 80% of the amino groups were neutralized.

For the decomposition of the organometallic compound [cf. Eqn. (2a)] an aliquot (1 ml) of the clear reaction solution was treated with methanol (0·075 ml, molar excess with respect to $[\text{DMAP-Cl}]_0$). After centrifuging the Li-alcoholate, the concentration of DMAP was determined by GC.

7.5 *GC analysis*

Details of the procedure are published elsewhere [21]. Identification of unknown peaks was done by separate addition of model compounds to reaction solutions (peak enlargement). Calibration curves were prepared and shown to be linear in all cases.

For the quantitative investigations of the THF- and CP-initiator solutions, usually a 1 m Porapak Q column (120–150) mesh) was used (temp. programme: 120–240°; heating rate 10°/min). Further identification of the by-products were made by using Chromosorb G columns (100–120 mesh) covered with 5% Ucon 50LB 550 × (3 m; 120°), 15% Carbowax 20M (2 m; 120°) and 5% Silicon Dow 11 (60–80 mesh; 2·5 m; 50° isotherm for 3 min, then temperature programme to 110°, heating rate 20°/min).

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