compounds (Tables VI–X) and Figures 5, 7, and 10 (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. The author has deposited atomic coordinates for the structures of Table III with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Directed Ortho-Lithiation of Phenylcarbamic Acid 1,1-Dimethylethyl Ester (*N*-Boc-aniline). Revision and Improvements

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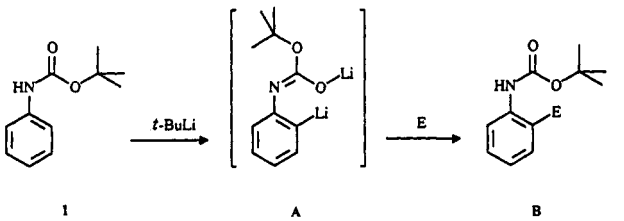
Evaluation of the results of a study, undertaken to examine the influence of the main reaction parameters (lithiation temperature, concentration, lithiating agent, and solvent) on the course of the title reaction, subsequently led to the development of an improved and more generally-applicable lithiation procedure. Hitherto unpublished stability data for solutions of *t*-BuLi and *n*-BuLi/TMEDA in diethyl ether and THF are reported for various temperatures.

The methodology of directed or heteroatom-facilitated lithiation has evoled—especially during the past decade—to an extremely powerful tool in the field of organic synthesis.[1] In particular, the development of new strategies for the buildup of polysubstituted aromatics and heteroaromatics was strongly influenced by this technique,[2] as substitution patterns difficult to obtain by standard substitution tactics became easily accessible starting with educts bearing suitable directed metalation groups (DMG's). In the meantime, an ever-increasing number of various functional groups, known to be applicable as ortho-directors,[2] became available to the synthetic chemist. Particularly among the known N-related DMG's, the *t*-BuOCONH[3] and the *t*-BuCONH functionalities[4] are of special value as they offer the advantage of an easy regeneration of the free amino function somewhere in the course of a multistep synthesis. Due to the fact that deprotection can be achieved under milder conditions, the carbamate structure seems favorable.

The first paper, where the *t*-BuOCONH group was applied as an ortho-director, was published by Muchowski and Venuti[3] in 1980. Dilithiation of 1 and subsequent reaction of the intermediate A with various electrophiles yielded a series of 2-substituted products B demonstrating the ortho-directing potential of this attractive functionality (Scheme I). The lithiation conditions recommended in this paper (addition of 2.4 equiv of *t*-BuLi to a 8% solution of 1 in THF at −78 °C and then stirring for 2–2.5 h at −20 °C) were referred unchanged in most cases where this DMG later was used in directed ortho-lithiations.[5] On the other hand, it is noteworthy that the yields reported in all these papers vary inexplicably over a wide range, reaching those of the initial paper (59–91%) only in two cases.[5j,k]

Scheme I



1 A B

Table I. Directed Ortho-Lithiation of 1 with *t*-BuLi/THF, 2.5 h at −20 °C, Me_2S_2 as Electrophile

entry	equiv of *t*-BuLi/concn[a] of 1	yield[b] of 2 (%)
1[c]	2.4/80	60–90
2	2.4/50	<10
3	2.4/100	52
4	2.4/200	65
5	5.0/100	66

[a] Concentration of 1 in mg/mL of THF. [b] Isolated yields of pure material. [c] Conditions in ref 3, reported yields obtained by using various electrophiles.

In the course of our own research work, we intended to exploit the ortho-directing power of the *t*-BuOCONH-group for the synthesis of some benzoannelated heterocyclic systems. Due to disappointing results obtained in our first attempts to lithiate 1 according to the cited standard conditions we became motivated to study this reaction in more detail. In particular, the influence of changes of the lithiation temperature, the applied concentration of 1, the kind and amount of the lithiating agent, and the solvent on the course of the title reaction had to be considered. To follow the progress of the lithiation reaction, samples of the reaction mixture were taken periodically and quenched with Me_2S_2. The conversion was then easily determined by comparing the integrals of the *t*-Bu groups of the educt 1 and the resulting 2-SMe product 2 in the ^{1}H-NMR.

Concerning the reaction temperature, it was observed that, below −40 °C, the rate of the ortho-lithiation of 1 is very low. Consequently, the lithiation must proceed mainly in the temperature range between −40 and −20 °C. Since no details are given in the literature about the time

(1) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1.
(2) (a) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. (b) Narasimhan, N. S.; Mali, R. S. *Synthesis* **1983**, 957. (c) Narasimhan, N. S.; Mali, R. S. *Top. Curr. Chem.* **1987**, *38*, 63. (d) Snieckus, V. *Bull. Soc. Chim. Fr.* **1988**, 67. (e) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879.
(3) Muchowski, J. M.; Venuti, M. C. *J. Org. Chem.* **1980**, *45*, 4798.
(4) Fuhrer, W.; Gschwend, H. W. *J. Org. Chem.* **1979**, *44*, 1133.
(5) (a) Fishwick, C. W. G.; Storr, R. C.; Manley, P. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1304. (b) Clark, R. D.; Caroon, J. M.; Kluge, A. F.; Repke, D. B.; Roszkowski, A. P.; Strosberg, A. M.; Baker, S.; Bitter, S. M.; Okada, M. D. *J. Med. Chem.* **1983**, *26*, 657. (c) Reed, J. N.; Rotchford, J.; Strickland, D. *Tetrahedron Lett.* **1988**, *29*, 5725. (d) Salituro, F. G.; McDonald, I. A. *J. Org. Chem.* **1988**, *53*, 6138. (e) Clark, R. D.; Caroon, J. M. *J. Org. Chem.* **1982**, *47*, 2804. (f) Thornton, T. J.; Jarman, M. *Synthesis* **1990**, 295. (g) Fisher, L. E.; Caroon, J. M. *Synth. Commun.* **1989**, *19*, 233. (h) Reavill, D. R.; Richardson, S. K. *Synth. Commun.* **1990**, *20*, 1423. (i) Saa, C.; Guitian, E.; Castedo, L.; Suau, R.; Saa, J. M. *J. Org. Chem.* **1986**, *51*, 2781. (j) Gomez-Bengoa, E.; Echavarren, A. M. *J. Org. Chem.* **1991**, *56*, 3497. (k) Iwao, M., private communication.

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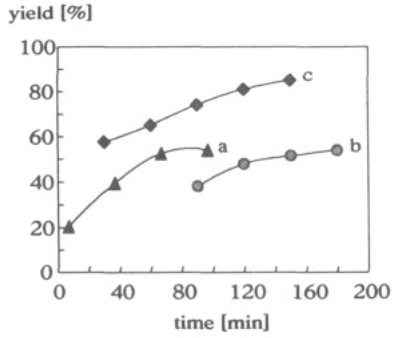


Figure 1. Key: (a) 2.4 equiv of *t*-BuLi/THF, −78 to −20 °C in 7 min; (b) 2.4 equiv of *t*-BuLi/THF, −78 to −20 °C in 1.5 h; (c) 2.2 equiv of *t*-BuLi/diethyl ether, −10 °C.

period in which the reaction mixture was allowed to warm from −78 to −20 °C, we enclosed this parameter into our study, too. Thus, two experiments were carried out applying the lithiation conditions of ref 3 but significantly varying the warming up procedure:

(1) The cooling bath was removed immediately after the addition of the *t*-BuLi solution at −80 °C, leading to the desired internal temperature of −20 °C within only 7 min. As illustrated in Figure 1 (curve a) about 20% of **1** was lithiated within this short period, reaching the maximum of about 54% after 1.5 h at −20 °C.

(2) Upon addition of the *t*-BuLi solution, the reaction mixture was allowed to warm immersed in the cooling bath reaching −20 °C and 37% conversion after 1.5 h. Further lithiation proceeded slowly at −20 °C, again reaching about 55% conversion 1.5 h later (Figure 1, curve b).

These experiments indicate that the achievable yields are not dependent on the warming procedure but they also show clearly that under these reaction conditions the conversion does not exceed 60%. This observation is in good agreement with entry 3 in Table I (**2**, isolated in 52% yield) as well as with the moderate yields published in most papers using the *t*-BuOCONH group as DMG in the last 10 years,[5] a surprising exception being those reported by Muchowski and Venuti.[3] Considering the limited stability of ethereal solutions of organolithium compounds, during the lithiation a substantial part of the applied *t*-BuLi obviously must be destroyed by the solvent in the well-known fragmentation reaction.[6] As expected and illustrated in Table I, the desired lithiation reaction can be somewhat favored by increasing the concentration of **1** (entry 4, 65%) or the amount of *t*-BuLi (entry 5, 66%), respectively. On the other hand, not considering this very significant concentration dependence, already noticed by Reed,[7] in our first attempts (entry 2) we obtained only very low yields as we applied **1** only in 5% solution. One can assume that not paying attention to these connections could also be the reason for the low and varying yields reported in the literature.[5]

To get further support for our assumption, we were looking for some data concerning the stability of *t*-BuLi solutions in THF under comparable conditions. Although there is a host of papers dealing with synthetic applications of lithiation reactions,[1,2] only few of them reported stabilities of solutions of the widely used lithiation reagents (*n*-, *s*-, or *t*-BuLi) under typical reaction conditions (temperature range between −80 °C and room temperature) in diethyl ether or THF.[6] Some data concerning the cleavage of diethyl ether by *n*-BuLi at 25 °C ($t_{1/2}$ = 153 h) and 35 °C ($t_{1/2}$ = 31 h) are available from an early study by Gilman et al.[8] Owing to experimental problems no similar rate studies were undertaken at that time for the system *t*-BuLi/diethyl ether but some comments indicate a very fast decomposition rate ($t_{1/2}$ < 30 min at rt). For solutions of *n*-BuLi in THF, some semiquantitative data are reported by Gilman and Gaj[9] followed by a kinetic study published by Honeycutt[10] and a paper of Bates et al.[11] ($t_{1/2}$ = 10 min at 35 °C). In a more recent work, Fitt and Gschwend[12] reported very short half-lives for *n*-, *s*-, and *t*-BuLi in dimethoxyethane at −20 and −70 °C. Stability studies of the system *t*-BuLi/THF at typically applied low temperatures to the best of knowledge are not published until now. Once we started to fill this gap we determined not only the required half-life of the reaction of *t*-BuLi with THF at −20 °C, but we extended the study also to the system *t*-BuLi/diethyl ether as well as to the commonly used lithiation reagent *n*-BuLi/TMEDA in both solvents. We would like to emphasize that our aim in this context was not to make an exact kinetic study for these decomposition reactions but to supply some guiding principles for the efficient application of these reagent/solvent combinations in the area of lithiation chemistry.

For practical reasons, we preferred the very convenient titration technique reported by Watson and Eastham.[13] This method has the great advantage that the determi-

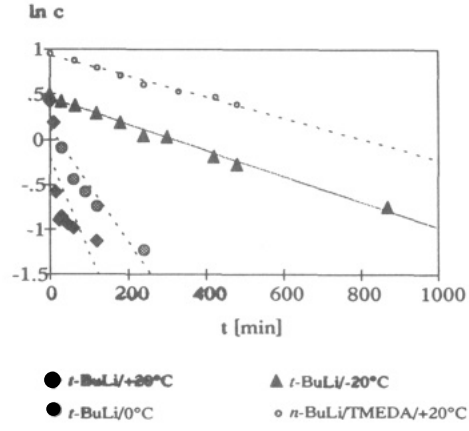


Figure 2. Decomposition of BuLi solutions in diethyl ether.

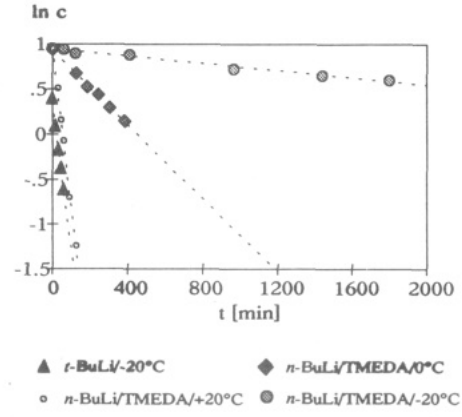


Figure 3. Decomposition of BuLi solutions in THF.

(6) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: Oxford, 1974; pp 198–199.
(7) Reed, N. PhD Thesis, University of Waterloo, 1984.
(8) Gilman, H.; Haubein, A. H.; Hartzfeld, H. *J. Org. Chem.* **1954**, *19*, 1034.
(9) Gilman, H.; Gaj, B. J. *J. Org. Chem.* **1957**, *22*, 1165.
(10) Honeycutt, S. C. *J. Organomet. Chem.* **1971**, *29*, 1.
(11) Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560.
(12) Fitt, J. J.; Gschwend, H. W. *J. Org. Chem.* **1984**, *49*, 209.
(13) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

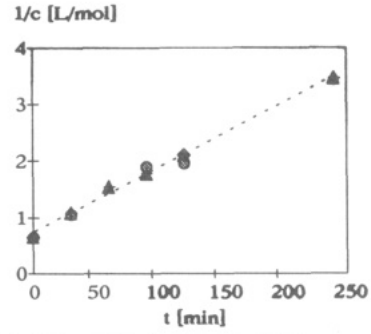


Figure 4. *t*-BuLi in diethyl ether at 0 °C.

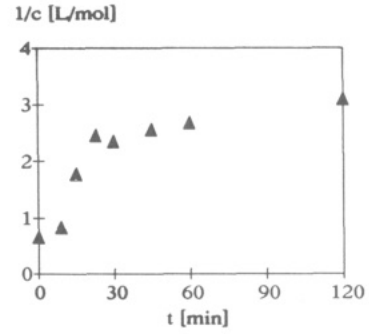


Figure 5. *t*-BuLi in diethyl ether at 20 °C.

nation of the actual concentration of the lithiating agent can be carried out directly in the reaction flask, maintained at observation temperature, whereas in all more recently developed methods[14] it is necessary to remove aliquots periodically from the cooled mixture and use these samples as titrating solutions at room temperature. Each point in the following kinetic plots (Figures 2–5) represents a different experiment. As no aliquots had to be taken, the reproducibilities of the titrations were high, and control experiments (Gilman double-titration) gave good agreement (error limits below 5%).

Due to the fact that the solvent was always used in a 10–15-fold molar excess and according to results in similar studies,[8,9] we expected pseudo-first-order kinetics, but the graphically presented data in Figure 2 for diethyl ether and in Figure 3 for THF show that this is definitely not the case for the system *t*-BuLi/diethyl ether at 0 °C and 20 °C. For the cleavage of diethyl ether by *t*-BuLi at 0 °C, a second-order kinetic behavior appears to give a better fit to the data (Figure 4), whereas at 20 °C rather complex kinetics with a decreasing decomposition rate was observed (Figure 5). This behavior perhaps can be correlated to the results of a recent kinetic study published by Thomas et al.[15] where the occurance of a complex $(t\text{-BuLi}\cdot 2Et_2O)_2$, stable even at room temperature, was established.

The half-lives $t_{1/2}$ were calculated using the equations $t_{1/2} = \ln 2/k$ (first order) or $t_{1/2} = 1/(k[\text{BuLi}]_0)$ (second order), respectively, and are listed together with the rate constants in Table II. If only the first four data points are taken into account, a half-life of approximately 10 min can be estimated for *t*-BuLi in diethyl ether at 20 °C, assuming that second-order kinetic behavior is followed.

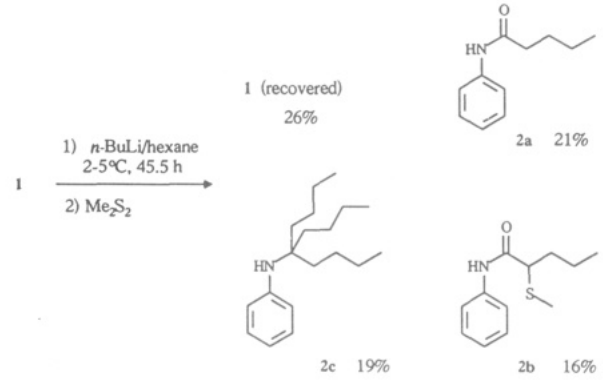
(14) (a) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879. (b) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87. (c) Juaristi, E.; Martinez-Richa, A.; Garcia-Rivera, A.; Cruz-Sanchez, J. S. *J. Org. Chem.* **1983**, *48*, 2603. (d) Suffert, J. *J. Org. Chem.* **1989**, *54*, 509. (e) Aso, Y.; Yamashita, H.; Otsubo, T.; Ogura, F. *J. Org. Chem.* **1989**, *54*, 5627. (f) Kiljunen, H.; Hase, T. A. *J. Org. Chem.* **1991**, *56*, 6950.

(15) Bates, T. F.; Clarke, M. T.; Thomas, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5109.

Table II. Rate Constants and Half-Lives of *t*-BuLi and *n*-BuLi/TMEDA in Diethyl Ether and THF

condns	k (min^{-1})	$t_{1/2}$ (min)	r
t-BuLi/THF/−20 °C	1.61×10^{-2}	42 ± 3	0.995
t-BuLi/ether/−20 °C	1.43×10^{-3}	483 ± 25	0.996
t-BuLi/ether/0 °C	1.16×10^{-2} (L mol^{-1} min^{-1}) second order	61 ± 8	0.995
n-BuLi/TMEDA/THF/−20 °C	2.09×10^{-4}	3317 ± 98	0.994
n-BuLi/TMEDA/THF/0 °C	2.05×10^{-3}	338 ± 7	0.999
n-BuLi/TMEDA/THF/20 °C	1.81×10^{-2}	38 ± 3	0.998
n-BuLi/TMEDA/ether/20 °C	1.15×10^{-3}	603 ± 22	0.992

Scheme II



Returning to the problem of the directed lithiation of **1**, now the short half-life (42 ± 3 min) determined for a solution of *t*-BuLi in THF at −20 °C can explain the significant concentration dependence, noticed without any comment the first time by Reed.[7] As a logical consequence of this result, two ways for improvements were envisioned: (1) changing of the lithiating agent, e.g., trying *n*-BuLi or *s*-BuLi instead of *t*-BuLi, or (2) changing of the solvent, e.g., using diethyl ether instead of THF.

Muchowski and Venuti[3] reported that even under forced conditions ("several hours at room temperature, with or without TMEDA") dilithiation of **1** occurred neither with *n*-BuLi nor with *s*-BuLi in THF. On the other hand, more recently Conley and Barton[16] as well as Bengtsson and Högberg[17] described the lithiation of the 3,4-dimethoxy derivative of **1** with *n*-BuLi/TMEDA in THF showing that lithiation takes place mainly at the 2-position. In this case the additional directing effect of the 3-methoxy group may be responsible for the observed regioselectivity, but probably for the successful lithiation with the less reactive reagent as well. Nevertheless, we tried the lithiation of **1** with *n*-BuLi/TMEDA instead of *t*-BuLi. Taking into account the short half-life of 38 min at 20 °C (Table II), we started at lower temperatures. Although lithiation proceeded very slowly at −25 °C, after 102 h **2** was isolated as the single product in 37% yield after separation from the remaining educt. Lithiating **1** for 30 h at −10 °C and even for 164.5 h at 2–5 °C, in agreement with Muchowski and Venuti,[3] only small amounts of **2** were detectable, but some new products of higher polarity as well as an increasing amount of decomposition products occured in the reaction mixture. These results give clear evidence for the significant acceleration of the THF decomposition at higher temperatures ($t_{1/2}$ = 3317 min at −20 °C but 338 min at 0 °C) superseeding completely the desired lithiation reaction.

(16) Conley, R. A.; Barton, D. L. US Pat. 4,617,417, Oct 14, 1986; *Chem. Abstr.* **1987**, *106*, P 49801h.

(17) Bengtsson, S.; Högberg, T. *J. Org. Chem.* **1989**, *54*, 4549.

Table III. Directed Ortho-Lithiation of 1 with t-BuLi/Diethyl Ether, 3 h, Me_2S_2 as Electrophile

entry	equiv of t-BuLi/ concn[a] of 1	temp (°C)	yield[b] (%)
1	2.4/100	−40	30
2	2.4/100	0	81
3	2.2/100	0	74
4	2.2/100	−10	89
5	2.2/50	−10	87
6	2.1/100	−10	81

[a] Concentration of 1 in mg/mL of diethyl ether. [b] Isolated yields, after flash column chromatography.

Table IV. Directed Ortho-Lithiation of 1 with t-BuLi/Diethyl Ether

compd	electrophile	yield (%)
2	Me_2S_2	89
3	$ClCONEt_2$	81
4	t-BuN=C=O	78
5	$ClCON(Me)CH_2Ph(4\text{-}t\text{-}Bu)$	77

It is well-known that addition of TMEDA leads to an increased basicity of organolithium compounds but has a rather decreasing effect on their nucleophilicity. To confirm our assumption that the products observed in the reaction with n-BuLi/TMEDA are derived from an attack at the carbonyl group, we tried the reaction now with n-BuLi alone at 2–5 °C in THF. After 45 h the obtained product mixture was separated by flash chromatography and the products **2a**, **2b**, and **2c** were isolated and identified (Scheme II). Under even more vigorous conditions (n-BuLi/hexane, 2 h reflux) **2b** and **2c** were the only products detected.

As can be seen in Table III, a substantial improvement of the situation was finally achieved by changing the solvent. In diethyl ether, where the stability of t-BuLi is significantly increased ($t_{1/2}$ = 489±25 min at −20°C, 61±8 min at 0°C) the decomposition of the lithiating agent is strongly suppressed and now about 90% dilithiation of 1 was achieved within 3 h (Figure 1, curve c). Although the lithiating conditions of entry 4 (Table III) gave the best results, carrying out the reaction in diethyl ether instead of THF has the advantage that the concentration of 1 can be lowered now without affecting the yields (entry 5, Table III). This can be very important in cases where one is forced to carry out the reaction in diluted solutions due to solubility problems. Although the optimal temperature seems to be −10 °C, variations between −20 and 0 °C show again no significant effect on the yields (entries 2 and 4, Table III). The results listed in Table IV with selected C-electrophiles being of interest in our synthetic project show that the high yields are achievable also with more complex electrophiles.

Experimental Section

General. The melting points were determined on a Reichert micro hot stage apparatus and are uncorrected. The NMR spectra were recorded for solutions in $CDCl_3$ with a JEOL FX 90Q (90-MHz) or a Bruker AC 200 (200-MHz) spectrometer; chemical shifts are reported in ppm using Me_4Si as internal standard. Thin-layer chromatography was performed on Merck precoated silica gel plates (5554) and flash-chromatography on silica gel 60 from E. Merck (40–63 μm, 9385). Elemental analyses were obtained from Microanalytical Laboratory, University of Vienna. All lithiation reactions were carried out under nitrogen, in glassware dried at 110 °C in an oven prior to assembly. THF and diethyl ether were distilled from sodium–benzophenone and N,N,N′,N′-tetramethylethylenediamine (TMEDA) from calcium hydride immediately before use. n-BuLi (2.5 M in hexane) and t-BuLi (1.7 M in pentane) were purchased from Aldrich, and the concentration was determined by the method of Watson and Eastham.[13] The applied indicator 1,10-phenanthroline (Aldrich) was dried and stored in an desiccator; 1 was prepared according to the procedure in ref.[3]

Titration Procedure for the Determination of RLi Contents. A few crystals (approx. 1 mg) of 1,10-phenanthroline and a magnetic stirring bar were placed in a 50-mL round-bottom flask with a white-painted bottom. This flask was flushed with nitrogen, fitted with a septum, and equipped with a nitrogen balloon. By syringe 2 mL of dry solvent (diethyl ether or THF) were charged into the flask, which then was cooled 20–30 °C below the observation temperature to avoid warming during the addition of the BuLi solution. Then 1 mL of the BuLi solution was added by syringe (eventually followed by 1 equiv of TMEDA). The nitrogen balloon was then removed, the septum tightened, and the flask placed in a cooling bath maintained at the observation temperature and stirred. The titration in each case was carried out with a solution of 2-butanol in dry toluene by syringe, the flask being immersed in the cooling bath again held 20–30 °C below the observation temperature to avoid warming through the exothermic reaction.

General Procedure for the Lithiation of 1 and the Preparation of the Products 2–5. A solution of 0.50 g (2.59 mmol) of 1 in 5 mL of anhydrous diethyl ether was cooled to −20 °C, treated with 2.2 equiv of t-BuLi (1.7 M in pentane), and then stirred for 3 h at −10 °C. After the mixture was cooled to −100 °C an ethereal solution of 1.1 equiv of the electrophile was added and the resulting mixture allowed to warm to room temperature, stirred overnight, and quenched with brine. The separated organic layer was dried over Na_2SO_4 and filtered, the solvent evaporated, and the residue purified by flash chromatography using petroleum ether (bp 40–60 °C)/ethyl acetate as eluent. Further purification was done by distillation or recrystallization.

[2-(Methylthio)phenyl]carbamic Acid 1,1-Dimethylethyl Ester (2). Electrophile: Me_2S_2. Yield: 0.55 g (89%), colorless oil. Bp: 85–90 °C/0.005 mmHg (Kugelrohr). ^1H NMR: δ 1.53 (s, 9 H, $C(CH_3)_3$), 2.36 (s, 3 H, SCH_3), 6.84–7.52 (m, 3 H, arom), 7.58 (br s, 1 H, NH), 8.09 (dd, $J_{5,6}$ = 8 Hz, $J_{4,6}$ = 1 Hz, 1 H, H-6). ^{13}C NMR: δ 18.5 (q, SCH_3), 28.0 (q, $C(CH_3)_3$), 80.0 (s, $C(CH_3)_3$), 118.5 (d, C-6), 122.7 (d, C-4), 124.0 (s, C-2), 128.4 (d, C-5), 132.6 (d, C-3), 138.6 (s, C-1), 152.2 (s, CO). Anal. Calcd for $C_{12}H_{17}NO_2S$ (239.34): C, 60.22; H, 7.16; N, 5.85. Found: C, 60.49; H, 7.32; N, 6.07.

[2-[(N,N-Diethylamino)carbonyl]phenyl]carbamic Acid 1,1-Dimethylethyl Ester (3). Electrophile: N,N-diethylcarbamoyl chloride. Yield: 0.61 g (81%), colorless crystals. Mp: 67–70 °C (diisopropyl ether). ^1H NMR: δ 1.19 (t, J = 7 Hz, 6 H, 2 × CH_3), 1.52 (s, 9 H, $C(CH_3)_3$), 3.43 (q, J = 7 Hz, 4 H, 2 × CH_2), 7.02 (dt, 1 H, H-4), 7.17 (dd, 1 H, H-5), 7.35 (dt, 1 H, H-3), 7.63 (br s, 1 H, NH), 8.07 (dd, $J_{5,6}$ = 8 Hz, $J_{4,6}$ = 1 Hz, 1 H, H-6). ^{13}C NMR: δ 13.1 (q, CH_3), 27.8 (q, $C(CH_3)_3$), 41.1 (t, CH_2), 79.8 (s, $C(CH_3)_3$), 120.8, 121.8 (2d, C-4 and C-6), 125.3 (s, C-2), 125.9 (d, C-5), 129.5 (d, C-3), 136.0 (s, C-1), 152.4 (s, NCOO), 169.3 (s, CON). Anal. Calcd for $C_{16}H_{24}N_2O_3$ (292.38): C, 65.73; H, 8.27; N, 9.58. Found: C, 65.68; H, 8.13; N, 9.46.

[2-[[(1,1-Dimethylethyl)amino]carbonyl]phenyl]carbamic Acid 1,1-Dimethylethyl Ester (4). Electrophile: *tert*-butyl isocyanate. Yield: 0.59 g (78%) colorless crystals. Mp: 145–148 °C (petroleum ether, bp 40–60 °C). ^1H NMR: δ 1.46 (s, 9 H, $NC(CH_3)_3$), 1.52 (s, 9 H, $OC(CH_3)_3$), 5.97 (br s, 1 H, NHCOO), 6.94 (dt, 1 H, H-4), 7.31–7.45 (m, 2 H, H-3 and H-5), 8.31 (dd, $J_{5,6}$ = 8 Hz, $J_{4,6}$ = 1 Hz, 1 H, H-6), 9.97 (br s, 1 H, CONH). ^{13}C NMR: δ 28.2, 28.6 (2q, $NC(CH_3)_3$ and $OC(CH_3)_3$), 51.7 (s, $NC(CH_3)_3$), 79.9 (s, $OC(CH_3)_3$), 119.5, 121.1 (2d, C-4 and C-6), 121.3 (s, C-2), 126.6 (d, C-5), 131.6 (d, C-3), 139.6 (s, C-1), 153.0 (s, NCOO), 168.6 (s, CON). Anal. Calcd for $C_{16}H_{24}N_2O_3$ (292.38): C, 65.73; H, 8.27; N, 9.58. Found: C, 65.49; H, 8.40; N, 9.80.

[2-[[N-[[4-(1,1-Dimethylethyl)phenyl]methyl]-N-methylamino]carbonyl]phenyl]carbamic Acid 1,1-Dimethylethyl Ester (5). Electrophile: N-[[4-(1,1-dimethylethyl)phenyl]methyl]-N-methylcarbamoyl chloride. Yield: 0.79 g (77%) colorless crystals. Mp: 114–117 °C (diisopropyl ether). ^1H NMR: δ 1.32 (s, 9 H, $C(CH_3)_3$), 1.53 (s, 9 H, $OC(CH_3)_3$), 2.94 (br s, 3 H, NCH_3), 4.53, 4.71 (2 br s, 2 H, NCH_2, E/Z), 6.92–7.44 (m, 7 H, arom), 7.95 (br s, 1 H, NH), 8.12 (dd, $J_{5,6}$ = 8 Hz, $J_{4,6}$ = 1 Hz, 1 H, H-6). ^{13}C NMR: δ 28.1 (q, $OC(CH_3)_3$), 31.0 (q, $C(CH_3)_3$), 34.1 (s, $C(CH_3)_3$), 35.1 (q, NCH_3), 52.2 (t, NCH_2), 80.0

(s, $OC(CH_3)_3$), 120.9, 121.7 (2d, C-4 and C-6), 124.2 (s, C-2), 125.3 (d, C-3′), 126.7, 127.1 (2d, C-2′ and C-5), 130.1 (d, C-3), 133.2 (s, C-1′), 136.8 (s, C-1), 150.2 (s, C-4′), 152.2 (s, NCOO), 170.1 (s, CON). Anal. Calcd for $C_{24}H_{32}N_2O_3$ (396.53): C, 72.70; H, 8.13; N, 7.06. Found: C, 72.73; H, 8.42; N, 6.96.

Lithiation of 1 with *n*-BuLi in Hexane Leading to Products 2a, 2b, and 2c. A solution of 1.00 g of 1 in 10 mL of hexane was cooled to 0 °C. After addition of 3.3 equiv of *n*-BuLi (2.5 M) at 0 °C the mixture was stirred at 2–5 °C for 45.5 h. Me_2S_2, 1.1 equiv, was added and the mixture allowed to warm to rt (1 h). After the mixture was quenched with brine the layers were separated, the organic layer was dried over Na_2SO_4 and filtered, and the solvent was evaporated. The crude mixture (0.96 g) was separated by column chromatography (petroleum ether (bp 40–60 °C)/ethyl acetate = 15/1). Besides recovered 1 (26%), products **2a**, **2b**, and **2c** were isolated.

***N*-Phenylpentanamide (2a).** Yield: 0.19 g (21%), colorless crystals. Mp: 60–61.5 °C (lit.[18] mp 60.5–61.5 °C). ^1H NMR: δ 0.95 (t, J = 7 Hz, 3 H, CH_3), 1.44 (sext, J = 7 Hz, 2 H, CH_2CH_3), 1.71 (sext, J = 7 Hz, 2 H, CH_2), 2.36 (t, J = 7 Hz, 2 H, $COCH_2$), 7.03–7.16 (m, 1 H, H-4), 7.18–7.42 (m, 3 H, H-3, H-5 and NH), 7.44–7.60 (m, 2 H, H-2 and H-6). ^{13}C NMR: δ 13.6 (q, CH_3), 22.2 (t, CH_2CH_3), 27.5 (t, CH_2), 37.4 (t, $COCH_2$), 119.7 (d, C-2), 124.0 (d, C-4), 128.8 (d, C-3), 137.8 (s, C-1), 171.4 (s, CO).

2-(Methylthio)-*N*-phenylpentanamide (2b). Yield 0.19 g (16%), colorless crystals. Mp: 80–82 °C. ^1H NMR: δ 0.95 (t, J = 7 Hz, 3 H, CH_3), 1.54 (sext, J = 7 Hz, 2 H, CH_2CH_3), 1.65–2.05 (m, 2 H, CH_2), 2.14 (s, 3 H, SCH_3), 3.35 (t, J = 7 Hz, 1 H, SCH), 7.03–7.19 (m, 1 H, H-4), 7.23–7.43 (m, 2 H, H-3 and H-5), 7.47–7.65 (m, 2 H, H-2 and H-6), 8.57 (br s, 1 H, NH). ^{13}C NMR: δ 13.7, 14.4 (2q, SCH_3 and CH_3), 20.7 (t, CH_2CH_3), 34.2 (t, CH_2), 52.4 (d, SCH), 119.7 (d, C-2), 124.4 (d, C-4), 129.0 (d, C-3), 137.7 (s, C-1), 170.1 (s, CO). Anal. Calcd for $C_{12}H_{17}NOS$ (223.34): C, 64.54; H, 7.67; N, 6.27. Found: C, 64.25; H, 7.45; N, 6.11.

***N*-(1,1-Dibutylpentyl)benzenamine (2c).** Yield: 0.27 g (19%), yellow oil. Bp: 78–84 °C (0.007–0.013 mmHg; Kugelrohr) (lit.[19] bp 186 °C (36 mmHg)). ^1H NMR: δ 0.89 (t, J = 7 Hz, 9 H, 3 × CH_3), 1.10–1.38 (m, 12 H, 3 × CH_2CH_2), 1.42–1.68 (m, 6 H, 3 × CCH_2), 3.30 (br s, 1 H, NH), 6.54–6.72 (m, 3 H, H-2, H-6, and H-4), 6.98–7.20 (m, 2 H, H-3 and H-5). ^{13}C NMR: δ 14.0 (q, CH_3), 23.0 (t, CH_2CH_3), 25.2 (t, CH_2), 36.2 (t, CCH_2), 66.5 (s, CCH_2), 115.6, 116.9 (2d, C-2 and C-4), 128.8 (d, C-3), 146.9 (s, C-1).

Registry No. 1, 3422-01-3; 2, 144303-96-8; **2a**, 10264-18-3; **2b**, 144304-01-8; **2c**, 35282-60-1; 3, 144303-97-9; 4, 144303-98-0; 5, 144303-99-1; Me_2S_2, 624-92-0; $ClCONEt_2$, 88-10-8; *t*-BuN=C=O, 1609-86-5; ClCON(Me)CH_2Ph(4-*t*-Bu), 144304-00-7; *n*-BuLi, 109-72-8; *t*-BuLi, 594-19-4.

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Spontaneous Homopolymerization Competes with Diels–Alder Cycloaddition of 1-Aryl-1,3-butadienes to Dienophiles Containing a Leaving Group

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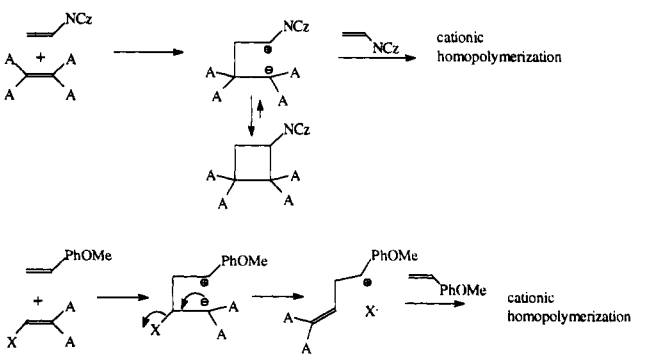
The competition between Diels–Alder cycloaddition and spontaneous concurrent polymerization was investigated in the reactions of 1-phenyl-1,3-butadiene (1) and 1-*p*-anisyl-1,3-butadiene (2) with electrophilic olefins. The reactions of 1 and 2 with electrophilic olefins trisubstituted with cyano and/or carbomethoxy groups gave only concerted [4 + 2] cycloaddition products. However, when olefins with a leaving group in the β-position were allowed to react with 1 and 2, cationic homopolymerization of the 1-arylbutadiene competed with the concerted cycloaddition. More polymer was formed with increased electrophilic character of the olefin and with better leaving groups. Formation of a 2-hexene-1,6-zwitterionic intermediate from the s-trans diene and the olefin, which can undergo elimination of the leaving group, is postulated. The resulting carbocation can then initiate cationic homopolymerization.

Introduction

The reactions of donor olefins with acceptor olefins are being extensively investigated in this laboratory.[1–4] Spontaneous chain polymerizations often compete with cycloadditions in these reactions. In the [2 + 2] cycloaddition of the very electron-rich *N*-vinylcarbazole with electrophilic olefins tetrasubstituted with cyano and/or carbomethoxy groups, the zwitterionic tetramethylene intermediate cyclizes or initiates the observed concurrent cationic homopolymerization of *N*-vinylcarbazole.[4] With less electron-rich donor olefins, such as *p*-methoxystyrene, cationic homopolymerization caused by electrophilic olefins only occurs if the latter has a leaving group in the β-position.[5–7] Again the proposed mechanism involves formation of a zwitterionic tetramethylene intermediate, here

Scheme I



NCz = N-carbazolyl, PhOMe = p-methoxyphenyl
A = CN or COOMe, X = leaving group

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