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147. Generation and Reactions of Tetrasubstituted *N*-Lithiomethyl-succinimides

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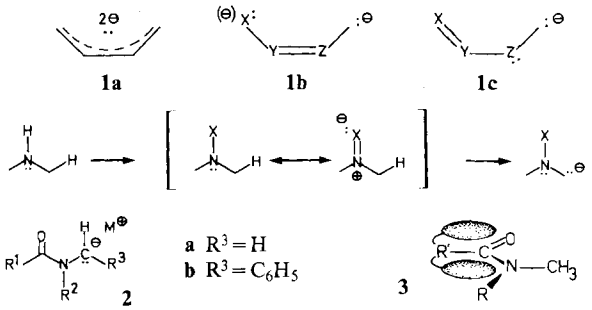
Summary

Of the isoelectronic 6-electron systems **1a**, **1b**, **1c** *(Table 1)* the deprotonated amides **2** might be useful derivatives for amine acidification (eq. (1)) if the carbonyl group is *sterically protected* as shown in **3**. The tetrasubstituted succinimides **4**, **5**, **7**, **8** and **9** (diacylamines) undergo the reactions (b), (c) and (d) of *Scheme 1* with various bases. Besides deprotonation, the 'self addition' to give dimers **4b**, **5b**, **8b** and **9b** is the most prominent transformation *(Table 2)*. Only in **9** is the steric hindrance to carbonyl addition large enough to get the lithiomethyl-succinimide **9c** in 80% yield (sec.BuLi/THF/HMPT/-100°) as evidenced by derivatization with alkyl halides, aldehyde, ketones, methyl benzoate, and chloro trimethylsilane (→**9d**-**9j**, *Table 3*). The possible structures and bonding descriptions for **9c** which 'decomposes' above −40° are discussed; the acidity of the precursor **9** is shown by equilibration studies to be comparable with that of diphenylmethane.

Introduction. - There is a whole series of mono- and dianions of type **1** which are of synthetic as well as of theoretical interest to organic chemists. They are isoelectronic with the butadiene dianion **1a** from which they can be derived by successive replacement of carbon by hetero atoms. Although the role of the



(1)

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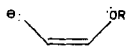
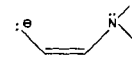
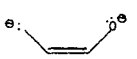
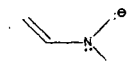
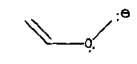
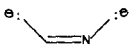
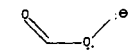
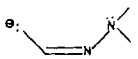
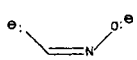
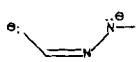
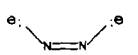
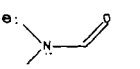
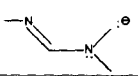
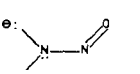
counterion cannot be neglected (see discussion below), they appear to prefer a cisoid configuration [1]. Some oxygen and nitrogen containing[3]) representatives are shown in *Table 1* which also gives pertinent references.

Table 1. *Some 6-electron systems of synthetic interest*

System		Ref.	System		Ref.
1a		[5]	**1c**		[10]
1c		[6]	**1c**		[11][a])
1b			**1b**		
1c			**1b**		
1c		[7]	**1c**		[13]
1c		[8]			
1c		[9]	**1b**		see text
1b			**1b**		[14]

[a]) Only the unsubstituted thia-analogue is known [12].

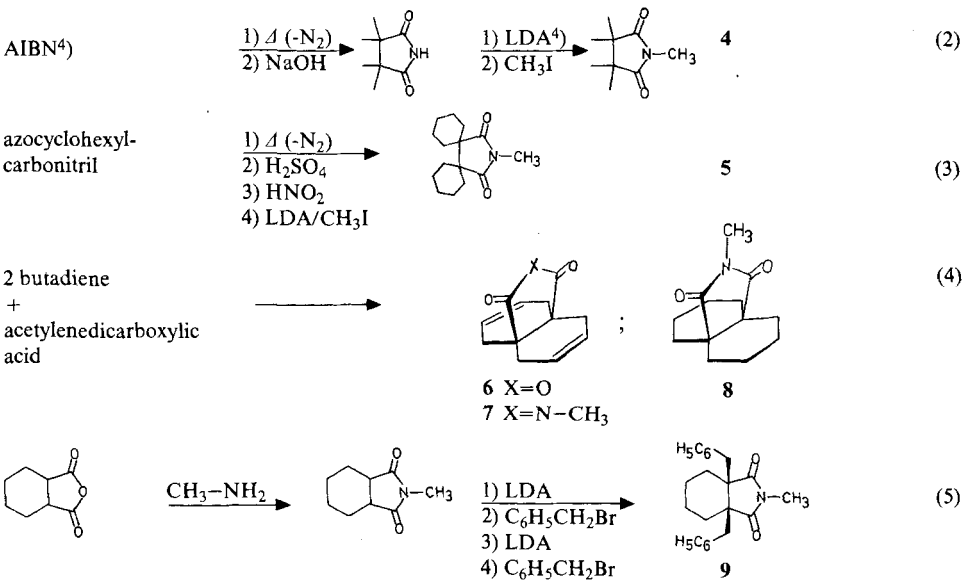
In context with our work on the acidification of *α-N*–CH-groups according to equation (1) [14] [15] we were especially intrigued by the fact that N–CH_3- and N–CH_2–C_6H_5-hydrogen atomes of carboxylic-acid amides are removable by strong bases such as lithium diisopropylamide (LDA) and 2,2,6,6-tetramethylpiperidide (LTMP) to give **1b** (X=O, Y=CR, Z=NR). This was demonstrated by the isolation of products derived from rearrangement [16], self condensations [17], and intramolecular interception [18] of the anionoids **2a, b**. Only in the presence of additional benzylic anion stabilization (**2b**) could these be trapped by external electrophiles [19].

Generally, there are three prerequisites for the verification of equation (1) [14] [15]: X must (i) have a strong enough acidifying effect, (ii) be free of hydrogen atoms which might compete with the *α*-N–CH-protons for the base, (iii) be a poor leaving group to prevent *α*-elimination from the desired anion, (iv) not contain groups which are electrophilic towards the deprotonating reagent or (v) towards the anion formed. The first three conditions are fulfilled or easily met in the case of amides, while the electrophilicity of the carbonyl group has so far prevented

[3]) Derivatives of sulfur and other elements are excluded from this discussion. See the reviews [2–4].

external trapping of simple methyl derivatives **2a**. It should be possible to 'wrap-up' the carbonyl group of the amide by attaching bulky groups to the substituent R^1 as shown in formula **3**. This must block attack at the carbonyl group but should not destroy the amide resonance by forcing the $R^2(CH_3)N$-group out of plane. As a first result of our efforts in this direction we report here the metallation of per-substituted *N*-methyl succinimides at the methyl group to form stable organolithium compounds.

Metallations of *N*-methyl succinimides. – In succinimides, there are two acidifying acyl groups bonded to the nitrogen atom, and the coplanarity of the system is secured; on the other hand, more reactive carbonyl groups are present as compared to simple amides. We prepared tetrasubstituted *N*-methyl succinimides with increasingly bulky substitution at the *a*-carbonyl positions. These syntheses are outlined in equations (2)–(5). The tetramethyl derivative **4** was obtained from the



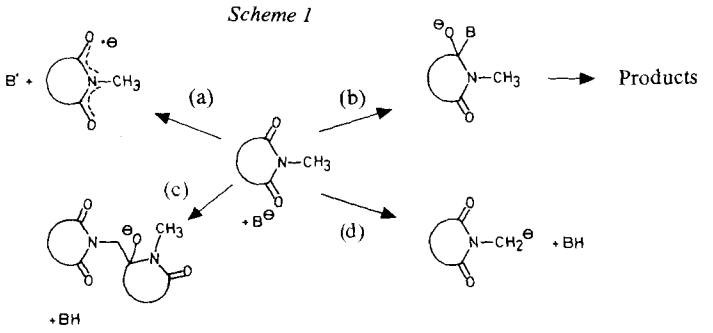
known [20] precursor by methylation of the lithium salt, the bispentamethylenimide **5** was prepared likewise[5]). The anhydride **6** [22] was converted to the olefinic *N*-methylimide **7** by reaction with methylamine, catalytic reduction furnished the saturated compound **8**. Finally, the commercially available *cis*-hexahydrophthalic anhydride and methylamine gave the imide which was benzylated twice (→**9**) as shown in eq. (5); the *cis*- or *meso*-configuration of **9** follows from the results described below.

During our search for a suitable *N*-methyl-imide we encountered the following general problems (see *Scheme 1*): Route (a) can lead to a ketyl-type-radical anion by

[4]) AIBN = Azo-bis-isobutyronitrile, LDA = Lithiumdiisopropylamide.

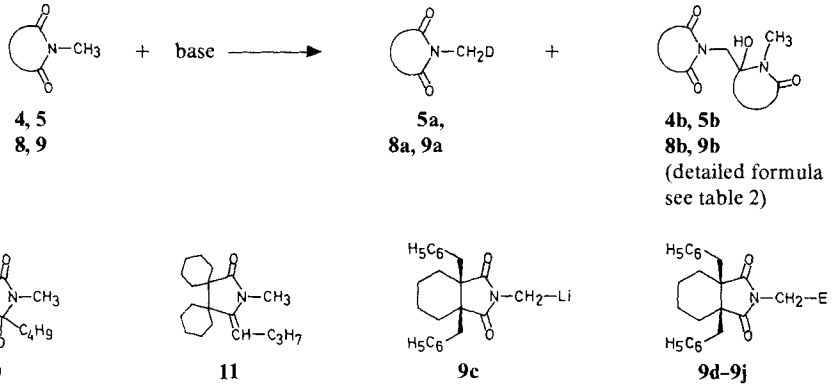
[5]) The *N*-desmethyl compound has been described in [21], but given the wrong structure (see spectroscopic data in experimental part).

Scheme 1



one electron transfer (observed with *N*-methyl-phthalimide [23]); according to (b) and (c) either the base used or the desired anion formed in step (d) can add to the imide-carbonyl-carbon atom if it is not sterically hindered enough.

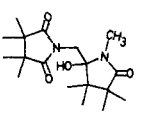
In order to find out whether the *N*-methyl groups of the above imides are lithiated we added a variety of bases to their solutions in THF/HMPT at temperatures between $-78°$ and $-100°$ and quenched the resulting bright yellow solutions with D_2O. Work-up gave mixtures of the deuterio derivatives **5a**, **8a**, **9a** [(d) in *Scheme 1*] and the dimers **4b**, **5b**, **8b**, **9b** [(c) in *Scheme 1*] in ratios which are given in *Table 2*. The unsaturated bicyclic imide **7** did not yield any of these two



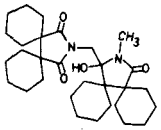
products. The presence of HMPT was necessary to keep the reactions stirrable but not essential for the metallations. Under most of the conditions the deuteriated species and the dimer were the only detectable products. From the reaction of **5** with butyl lithium we isolated the adduct **10** and its dehydration product **11** [24] [(b) of *Scheme 1*]. The results in *Table 2* show clearly that **9** gives the highest yield of the lithium derivative **9c**. This was therefore chosen to do reactions with electrophiles other than $D^{\oplus}$. As shown in *Table 3*, we obtained the imides **9d-9i** derived from higher amines by alkylation with iodoalkanes, hydroxyalkylation with an aldehyde and ketones, and acylation with methyl benzoate in yields ranging from 55 to 95%; silylation furnished the *N*-(trimethylsilyl-methyl)-imide **9j**. In the ^{1}H-NMR. spectra of **9f**, **9h**, **9i** and **9j** the methylene-hydrogen atoms of the E–CH_2–N-groups appear

Table 2. *Metallation experiments with the succinimides* **4**, **5**, **8** *and* **9**. *Optimization by deuteriolysis*

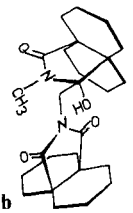
N-methyl-imide	base	time/temp.	DH_2C–N-imide No.	yield [%] after chromatography (spectrosc.[a]))	dimer No.	yield [%] after chromatography (spectrosc.[a]))
4	LTMP[c])	10 h/-60°-25°	**4a**	–	**4b**	48 (88)
5	*t*-BuLi	30 min/-78°	**5a**	18 (30)	**5b**	26 (30)
8	*t*-BuLi	9 min/-60°	**8a**	(50)	**8b**	(50)
8	*t*-BuLi	25 min/-78°	**8a**	38 (53)	**8b**	(43)
8	*t*-BuLi	25 min/-100°	**8a**	(59)	**8b**	30 (39)
9	*s*-BuLi	20 min/-78°	**9a**	44 (~50)	**9b**	41 (~50)
9	*s*-BuLi	25 min/-100°	**9a**	(~80)	**9b**	(~20)



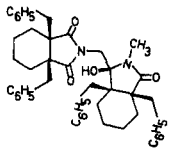
4b



5b



8b



9b

[a]) From the weight of the crude product and careful NMR. analysis.

[b]) One diastereomer only was isolated; we assume that it has been formed by attack of **9c** from the face of **9** which is *trans* to the benzyl groups.

[c]) = Lithium 2,2,6,6-tetramethylpiperidide.

as singlets which supports our assignment of the meso configuration of the bicyclic skeleton of all compounds **9** [25a][6]). The spectroscopic data and the elemental analyses are in agreement with the structures shown.

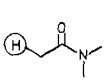
Discussion. – With **9c** we have generated for the first time solutions of an acylaminomethyllithium reagent without additional stabilization at the carbanionoid center. **9c** is stable at temperatures below $-40°$ above which it appears to go to

Table 3. *Reactions of the lithiated imide* **9c** *with electrophiles.* The yields given are calculated from the electrophiles used (see experimental section)

Electrophile	Product **9** No.	E	Yield [%] spectroscopic[a])	after chromatography
D_2O	**9a**	D	80	–
iodo-methane	**9d**	CH_3	–	71
1-iodo-hexane	**9e**	C_6H_{13}	–	59
cyclohexanone	**9f**	$C_6H_{10}(OH)$	95	91
benzaldehyde	**9g**	$C_6H_5CH(OH)$	–	68
benzophenone	**9h**	$(C_6H_5)_2C(OH)$	66	54
methyl benzoate	**9i**	C_6H_5CO	59	53
chloro-trimethylsilane	**9j**	$(CH_3)_3Si$	80	38

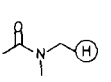
[a]) From the weight of the crude product and careful NMR. analysis.

[6]) It is well known that anhydrides and imides with annelated five- and sixmembered ring as in **9** are more stable in the *cis* configuration [25b].

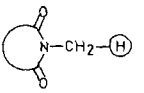


12
($pK_a \lesssim 30$ [26][7])

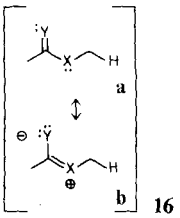
13
(pK_a 17–20 [27] 21–25 [28])



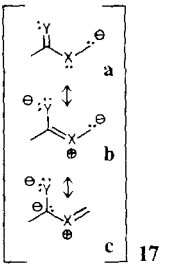
14
($pK_a \lesssim 38$)[8]



15
(pK_a 31–35)[9]



16



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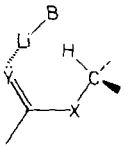

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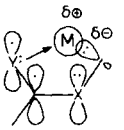
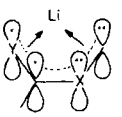
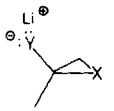


19a



19b



20

oligomeric material (see experimental section). The acidity of **9** is surprisingly high: equilibrating experiments with diphenylmethane show that the two compounds are of comparable CH-acidity. Still, the 'enolate-type' acidities of amides **12** and **13** are about 10 pK_a units larger than the 'homoenolate-type' acidities of **14** and **15**. According to the conclusions of Beak et al. [17], the following two effects are important in the homoenolate generation from systems **16**, X, Y = NR, O, S [15] [29][10]: (a) a polarization which makes X in **16** positive (see **16b**) and which 'dipole-stabilizes' an anion **17** (see **17b**), and (b) a chelation (*cf.* the other systems in *Table 1*) which kinetically helps in the deprotonation step (see **18**) and which may also thermodynamically stabilize the resulting species **19**. The full positive charge of a $(CH_3)_3N^{\oplus}$-group acidifies an adjacent CH-hydrogen by *ca.* 10 pK_a units [33]. This inductive or polar stabilization should be operative even if the carbon lithium bond is perpendicular to the π-system as shown in **19a**, *i.e.* in the absence of resonance. At the present state of information it is not possible to distinguish between this type of structure and the one drawn in **19b** or even a cyclic arrangement such as **20**[11]).

Generous support by the *Deutsche Forschungsgemeinschaft* (Project No Se 158/12) and by the *Fonds der Chemischen Industrie* is gratefully acknowledged.

[7]) We have shown that lithio triphenylmethane in THF converts *N,N*-dimethyl acetamide quantitatively into its enolate.

[8]) Deprotonated with lithio dialkylamides [17] [18], the conjugate acids of which have this estimated pK_a.

[9]) Value depends upon the pK_a 'chosen' for diphenyl methane.

[10]) Compare also the 'vinylic homoenolates' generated from β-amino-α,β-unsaturated carboxylic acid esters [30] and amides [31] and the metallated phosphoric acid amides [32].

[11]) A ^{13}C-NMR. spectrum of the **9c**-solution measured at $-73°$ shows broad absorptions in the aromatic and carbonyl regions.

Experimental Part

General remarks. – The techniques and instruments used are described in detail in earlier papers [34]. – NMR.-shifts are given in δ (ppm) relative to TMS as internal standard. Mass spectra were obtained with a *Varian*-MAT-111 at 80 eV. – *n*-, *s*- and *t*-butyllithium solutions were purchased from the *Metallgesellschaft Frankfurt*. – HMPT was distilled from calcium hydride and stored under argon.

Preparation of the *N*-Methylsuccinimides 4, 5, 7, 8 and 9. – N-*Methyl-2,2,3,3-tetramethyl-succinimide* (**4**). A solution of 96 mmol of LDA[4]), prepared from 13.5 ml of diisopropylamine and butyl lithium, in THF/hexane/HMPT 20:6:3 is combined with stirring at −78° with a solution of 14.1 g (91 mmol) of 2,2,3,3-tetramethyl-succinimide [20]. The cooling bath is removed for 30 min, the solution is cooled to −40°, and 13.5 ml (220 mmol) of iodomethane are added dropwise. After stirring overnight at RT. the slightly yellow suspension is poured into 100 ml of H_2O. After two extractions with each 100 ml of ether, washing the organic phase once each with 7% KOH-solution and water, drying over Na_2SO_4, evaporating the solvent, and distilling in vacuo 11.8 g (77%) of **4** are obtained. B.p. 77°/3 Torr. – ^{1}H-NMR. (CCl_4): 1.17 (*s*, 12H, $4CH_3$): 2.98 (*s*, 3H, NCH_3). – IR. (neat): 2980, 2940, 2870, 1775, 1700, 1510, 1475, 1430, 1375, 1300, 1260, 1150, 1035, 1000, 935, 855, 760, 665, 555 cm^{-1}. – MS. *(m/e)*: 169 (M^+), 154 ($M^+ - CH_3$), 141, 127, 97, 84, 69, 43.

$C_9H_{15}NO_2$ (169.2) Calc. C 63.88 H 8.93 N 8.27% Found C 63.42 H 8.93 N 8.23%

*2,3-Di(pentamethylene)-succinimide (**5**, H instead of CH_3).* A mixture of 10 g (52 mmol) of 2,3-bis-(pentamethylene)succinonitril [35] and 200 ml of conc. H_2SO_4 is heated at 100° for 30 min. A brown solution results which is stirred and cooled in an ice bath and combined with a solution of 10.5 g (150 mmol) of $NaNO_2$ in 35 ml of water. The addition is carried out with a pipette immersed just slightly below the surface of the solution, the addition rate is adjusted so that the temperature of the solution does not exceed 20°. After 1 h at RT. heating slowly to 100° causes vigorous N_2-evolution above 70°. After 1 h the mixture is poured on 600 g of ice, the precipitate is filtered off, washed until free of acid, dried, and recrystallized from 80% aq. CH_3OH. Yield 9.2 g (85%); m.p. 189–190° ([21], ligroin/$CHCl_3$). – ^{1}H-NMR. (CCl_4): 2.1–0.8 (*m*, 20H, $10CH_2$); 8.0 (br. *s*, 1H, NH). – IR. (KI): 3200, 3060, 2960, 2930, 2870, 1765, 1700, 1460, 1450, 1380, 1355, 1345, 1315, 1280, 1255, 1095, 1060, 1020, 960, 935, 880, 805, 750, 660, 630, 555 cm^{-1}. These data show that the imide has been isolated, and not the previously proposed [22], isomeric cyano acid.

$C_{14}H_{21}NO_2$ (235.3) Calc. C 71.45 H 8.99 N 5.95% Found C 71.69 H 9.12 N 5.90%

2,3-Di(pentamethylene)-N-*methyl-succinimide* (**5**). By using exactly the same procedure as described for the preparation of **4** above, 7.27 g (31 mmol) of the NH-compound were methylated to give 5.8 g (75%) of **5** which was recrystallized from petroleum ether (50–70), m.p. 92.0–92.4°. – ^{1}H-NMR. (CCl_4): 2.4–0.8 (*m*, 20H, $10CH_2$); 2.82 (*s*, 3H, NCH_3). – IR. (KI): 2960, 2940, 2860, 1765, 1695, 1455, 1430, 1380, 1345, 1320, 1280, 1170, 1080, 1050, 1030, 1020, 965, 860, 825, 765, 565 cm^{-1}. – MS. *(m/e)*: 249 (M^+, 29), 221 (4), 206 (6), 195 (100), 182 (67), 166 (13), 138 (15), 82 (25), 77 (26).

$C_{15}H_{23}NO_2$ (249.3) Calc. C 72.25 H 9.30 N 5.61% Found C 72.49 H 9.32 N 5.57%

cis-N-*Methyl-bicyclo[4.4.0]deca-3,7-dien-1,6-dicarboximide* (**7**). A mixture of 2.0 g (10 mmol) of *cis*-bicyclo[4.4.0]deca-3,7-dien-1,6-dicarboxylic anhydride (**6**) [22] and 100 ml of 40% aqueous CH_3NH_2 is heated under reflux for 4 h. The colorless precipitate is filtered off, washed with water, dried, and recrystallized from petroleum ether (50–70°)/$CHCl_3$ 20:1. Yield 1.35 g (64%); m.p. 160–161°; ^{1}H-NMR. ($CDCl_3$): 2.33 (*AB*-part of *ABX*-system, 8H, allylic); 2.87 (*s*, 3H, NCH_3); 5.80 (*X* part of *ABX*-system, 4H, vinylic). – IR. (KI): 3080, 3040, 2960, 2940, 2880, 2840, 1765, 1700, 1450, 1380, 1330, 1280, 1200, 1150, 1010, 960, 730, 700, 550 cm^{-1}. – MS. *(m/e)*: 217 (M^+, 50), 163 ($M^+ - CH_2{-}CH{=}CH{-}CH_2$, 100), 162 (58), 134 (17), 117 (13), 105 (27), 91 (29), 77 (28).

$C_{13}H_{15}NO_2$ (217.3) Calc. C 71.86 H 6.96 N 6.44% Found C 71.48 H 6.96 N 6.44%

cis-N-*Methyl-bicyclo[4.4.0] decane-1,6-dicarboximide* (**8**). In a low pressure hydrogenating apparatus a solution of 2.1 g (9.7 mmol) of **7** in 70 ml of glacial acetic acid containing 18 mg of PtO_2 is stirred at RT.

until the calculated amount of H_2 has been consumed. The filtered solution is diluted with 100 ml of H_2O and extracted twice with 50 ml each of pentane. After washing with 7% KOH-solution and water evaporation of the solvent yields 1.96 g (89%) of **8**. M.p. 74–75° (Ligroin/$CHCl_3$ 10:1). – ^{1}H-NMR. (CCl_4): 1.9–1.2 (*m*, 16H, $8CH_2$); 2.87 (*s*, 3H, NCH_3). – IR. (KI): 2940, 2860, 1765, 1700, 1450, 1430, 1380, 1310, 1285, 1210, 1170, 1145, 1105, 1090, 1080, 1050, 1020, 955, 895, 840, 740, 690, 555 cm^{-1}. – MS. *(m/e)*: 221 (M^+, 100), 192 ($M^+ - NCH_3$, 28), 174 (28), 167 (78), 166 (76), 136 ($M^+ - 2CO - NCH_3$, 83), 135 (50), 121 (17), 107 (207), 95 (31), 94 (44), 93 (30), 72 (19).

$C_{13}H_{19}NO_2$ (221.3) Calc. C 70.56 H 8.65 N 6.33% Found C 70.45 H 8.66 N 6.26%

cis-*1,2-Dibenzyl*-N-*methyl-cyclohexane-1,2-dicarboximide* (**9**). – (a) N-*Methyl-cyclohexane-1,2-dicarboximide.* 50 g (0.32 mol) of the commercial cyclohexane-1,2-dicarboxylic anhydride are dissolved in 100 ml of 40% aqueous CH_3NH_2-solution (ice bath). After stirring at RT. for 24 h, evaporation at atmospheric pressure gives a residue which was extracted with 200 ml of CCl_4. The resulting pale solution is filtered, washed with water, dried over Na_2SO_4 and concentrated, the residue recrystallized from pentane/$CHCl_3$. Yield 37 g (68%); m.p. 43–44°. – ^{1}H-NMR. ($CDCl_3$): 2.1–1.1 (*m*, 8H, $4CH_2$); 2.87 (*m*, 2H, 2CH); 2.95 (*s*, 3H, NCH_3). – IR. (neat): 2950, 2930, 1775, 1700, 1430, 1380, 1270, 1130, 1070, 1050, 1030, 995, 940, 890, 775, 750, 675, 600 cm^{-1}. – MS. *(m/e)*: 167 (M^+, 3), 152 ($M^+ - CH_3$, 2), 139 ($M^+ - CO$, 10), 138 ($M^+ - NCH_3$, 13), 126 (2), 125 (4), 113 (24), 112 (15), 82 ($C_6H_{10}^+$, 80), 67 (100), 54 (46).

$C_9H_{13}NO_2$ (167.2) Calc. C 64.65 H 7.84 N 8.37% Found C 64.69 H 7.81 N 8.37%

(b) *1-Benzyl*-N-*methyl-cyclohexane-1,2-dicarboximide.* A solution of 6.7 g (40 mmol) of the *N*-methylimide (described under (a)) in 20 ml of THF is added to an LDA solution (42 mmol, from 5.9 ml of diisopropylamin, 40 ml THF/10 ml HMPT) stirred at −78°. After 45 min the redbrown solution is combined with 5.0 ml (42 mmol) of benzyl bromide. The mixture is allowed to warm up to RT. overnight to furnish a colorless suspension which is poured into 100 ml of water. The organic phase obtained from two extractions with ether (100 ml each) is washed four times with water, dried over Na_2SO_4 and concentrated evaporatively. Chromatography over 100 g of SiO_2 gives excess bromide (eluted with pentane) and 8.3 g (80%) of the monobenzylated imide (ether elution). M.p. 61.2–61.8° (ligroin 50–70). – ^{1}H-NMR. (CCl_4): 1.9–0.9 (*m*, 8H, $4CH_2$); 2.43 (*m*, 1H, CH); 2.78 (*s*, 3H, NCH_3); 2.97 (*AB*-system, $J = 13$, 2H, benzylic). – IR. (neat): 3460, 3080, 3060, 3020, 2930, 2860, 1775, 1700, 1600, 1580, 1460, 1450, 1430, 1380, 1270, 1180, 1130, 1065, 1030, 990, 925, 850, 820, 775, 760, 700, 680, 625, 600 cm^{-1}. – MS. *(m/e)*: 257 (M^+, 42), 214 (11), 165 (37), 118 (15), 109 (9), 91 ($C_6H_5CH_2^+$, 100), 81 (25).

$C_{16}H_{19}NO_2$ (257.3) Calc. C 74.68 H 7.33 N 5.44% Found C 74.95 H 7.39 N 5.45%

(c) *Second Benzylation to give* **9**. The dark red enolate solution obtained from 8.3 g (32 mmol) of the monobenzyl derivative and 34 mmol of LDA is reacted with 35 mmol of benzyl bromide (*cf.* (b)). Work-up with water/ether/CH_2Cl_2 gives a solid crude product **9** which is recrystallized from ligroin/$CHCl_3$ 4:1. Yield 7.6 g (68%); m.p. 167–168°. – ^{1}H-NMR. ($CDCl_3$): 1.9–1.0 (*m*, 8H, $4CH_2$); 2.80 (*s*, 3H, NCH_3); 3.03 (*AB*-system, $J = 13$, 4H, benzylic); 7.23 (*s*, 10H, aromatic). – IR. (KI): 3060, 3020, 2930, 2860, 1765, 1690, 1600, 1490, 1450, 1430, 1380, 1270, 1060, 1030, 980, 825, 750, 695 cm^{-1}. – MS. *(m/e)*: 348 ($M^+ + 1$,9), 347 (M^+, 6), 256 ($M^+ - C_6H_5CH_2$, 8), 91 ($C_6H_5CH_2^+$, 100).

$C_{23}H_{25}NO_2$ (347.5) Calc. C 79.51 H 7.25 N 4.03% Found C 79.71 H 7.22 N 4.01%

N−CH_2D *Imides* **5a**, **8a**, **9a** *and dimeric products* **4b**, **5b**, **8b**, **9b** *of 'self condensation' (see* Table 2*).* The CH_2D-derivatives described in the following procedures showed melting points identical with those of the unlabelled compounds. IR. bands which are different from or not present in the spectra of the CH_3-imides are given below. The NMR. spectra showed 1:1:1 triplets ($J = 2$Hz) at the same δ-value at which the CH_3-groups appear. The mass spectra exhibit the expected molecular ion peaks. The elemental analyses gave lower carbon and somewhat higher hydrogen contents, as expected.

5-Hydroxy-1,3,3,4,4-pentamethyl-5-(2',2',3',3'-tetramethyl-succinimidomethyl)-2-pyrrolidone (**4b**). A solution of 15.1 mmol of LTMP, prepared from 2.55 ml of 2,2,6,6-tetramethyl-piperidine and butyllithium in 25 ml of THF is combined with stirring at −78° with a solution of 2.54 g (15.0 mmol) of **4** in 5 ml of THF. The mixture is allowed to warm up to RT. overnight, poured into 50 ml of water and

extracted twice with 50 ml each of pentane. The organic phase is dried over Na_2SO_4 and concentrated, the residue recrystallized from ligroin. Yield of **4b**: 0.4 g. Chromatography of the oil, obtained by evaporation of the mother liquor over 9 g of SiO_2 with pentane/ether 9:1 gave additional 0.8 g of **4b**, total yield 1.2 g (48%). M.p. 112–114° (ligroin). – ^{1}H-NMR. ($CDCl_3$): 1.27 (*mc*, 24H, $8CH_3$); 2.77 (*s*, 3H, NCH_3); 3.87 (*s*, 2H, NCH_2); 4.5 (*s*, 1H, OH). – IR. (KI): 3380, 2980, 1770, 1690, 1460, 1450, 1400, 1380, 1330, 1280, 1240, 1165, 1100, 1050, 990, 975, 905, 860. 775. 760, 605 cm^{-1}. – MS. *(m/e)*: 338 (M^+, 1), 320 (M^+-H_2O, 18), 305 (12), 227 (6), 208 (6), 169 ($M^+/2$, 100), 149 (30), 97 (32), 84 (33), 69 (31).

$C_{18}H_{30}N_2O_4$ (338.4) Calc. C 63.88 H 8.93 N 8.27% Found C 63.65 H 8.96 N 8.12%

*2,3-Di(pentamethylene)-*N*-deuteriomethyl-succinimide* (**5a**). 3.5 mmol of *t*-butyl lithium in hexane and 1 ml of HMPT are added dropwise to a solution of 0.84 g (3.37 mmol) of **5** in 10 ml THF stirred at −78°. After 30 min the yellow solution is combined with 0.5 ml (25 mmol) of D_2O. The colourless mixture is allowed to warm-up to RT. and poured into 20 ml of water. The organic phase obtained from two extractions with 30 ml each of ether is washed 4× with water and dried over Na_2SO_4. Evaporation of the solvent gave a residue which was chromatographed by prep. TLC. over SiO_2 with pentane/ether 9:1: 0.15 g (18%) **5a**. – IR. (KI): 1405, 1230, 1195, 940, 920 cm^{-1}.

5-Butylidene-1-methyl-2,3-di(pentamethylene)-2-pyrrolidone (**11**). 5.5 mmol of butyl lithium are added to a solution of 1.25 g (5.02 mmol) of **5** in 15 ml of THF/2 ml of HMPT stirred at −78°. After 1 h the yellow mixture is combined with 0.5 ml (25 mmol) of D_2O, allowed to warm-up to RT., poured into 50 ml of water and extracted twice with 50 ml each of CH_2Cl_2. The organic phase is washed with water, dried over Na_2SO_4, and concentrated by evaporation of the solvent. Chromatography of the residue over 100 g of SiO_2 with ether yields 1.26 g (87%) of **11**. M.p. 38–39° (pentane). – ^{1}H-NMR. (CCl_4): 2.43–0.73 (*m*, 28H, $11CH_2$, $2CH_3$); 3.03 (*s*, 3H, NCH_3); 4.63 (*t*, $J=7$, 1H, vinylic). – IR. (KI): 2930, 2860, 1710, 1665, 1450, 1415, 1370, 1345, 1330, 1310, 1290, 1260, 1160, 1105, 1070, 1030, 1010, 955, 900, 870, 820, 745 cm^{-1}. – MS. *(m/e)*: 289 (M^+, 100), 260 ($M^+-C_2H_5$, 61), 246 ($M^+-C_3H_7$, 22), 236 (68), 235 (49), 220 (61), 206 (15), 192 (17), 179 (57), 150 (16), 122 (21), 121 (21), 109 (24), 91 (22), 81 (39), 79 (25).

$C_{19}H_{31}NO$ (289.4) Calc. C 78.84 H 10.80 N 4.84% Found C 78.67 H 10.84 N 4.77%

5-Hydroxy-1-methyl-3,4-di(pentamethylene)-5-[2,3-di(pentamethylene)-succinimido-methyl]-2-pyrrolidone (**5b**). 2.4 mmol of *t*-butyl lithium and 1 ml of HMPT are added to a suspension of 0.61 g (2.44 mmol) of **5** in 10 ml of pentane/ether/THF stirred at −110°. After 30 min, the orange solution is combined with 0.5 ml (25 mmol) of D_2O, allowed to warm-up to RT., and poured into 20 ml of water. After two extractions with 30 ml each of ether, washing the organic phase 4× with 20 ml of water, drying over Na_2SO_4, evaporating the solvent, and recrystallizing the residue from ether 0.16 g (26%) of **5b** are obtained. M.p. 207–208°. – ^{1}H-NMR. ($CDCl_3$): 2.4–0.8 (*m*, 40H, CH_2); 2.67 (*s*, 3H, NCH_3); 3.88 (*AB*-system, $J=17$, 2H, NCH_2); 4.57 (*s*, 1H, OH). – IR. (KI): 3400, 2940, 2870, 1765, 1690, 1450, 1390, 1355, 1310, 1265, 1215, 1155, 1145, 1080, 1050, 1030, 1015, 940, 935, 875, 825, 820, 765, 735, 665, 605, 565 cm^{-1}.

$C_{30}H_{46}N_2O_4$ (498.6) Calc. C 72.25 H 9.30 N 5.61% Found C 72.48 H 9.24 N 5.62%

cis-N-*(Deuteriomethyl)-bicyclo[4.4.0]deca-1,6-dicarboximide* (**8a**). 0.94 mmol of *t*-butyl lithium in hexane are combined with stirring at −78° with a solution of 0.16 g (0.72 mmol) of **8** and 0.5 ml of HMPT in 5 ml of THF. After 30 min 0.5 ml (25 mmol) of D_2O are added. The colourless suspension is allowed to warm-up to RT., poured into 20 ml of water and extracted twice with 20 ml each of ether. The organic phase is washed 4× with water, dried over Na_2SO_4 and concentrated. Prep. TLC. of the residue over SiO_2 with pentane/ether 3:1 gives 60 mg (38%) of **8a**. – IR. (KI): 1400, 1235, 1165, 1000, 880 cm^{-1}.

cis-*Bicyclo[4.4.0]decane-1,6-dicarboximidomethyl]-(12-aza-11-hydroxy-12-methyl-13-oxo-tricyclo-[4.4.3.0]tridecan* (**8b**). 4.8 mmol of *t*-butyl lithium in hexane are added at −100° to a stirred solution of 1.0 g (4.5 mmol) of **8** and 2 ml of HMPT in 20 ml of THF. After 30 min the solution is combined with 0.5 ml (25 mmol) of D_2O, allowed to warm-up to RT., poured into water and extracted twice with ether. The solution is dried over Na_2SO_4 and concentrated to a 50 ml volume and then stored for 20 h

at −25°. The crystals are filtered off: 0.3 g (30%) of **8b**. M.p. 172–173°. – ^{1}H-NMR. ($CDCl_3$): 2.2–0.9 (*m*, 32H, $16CH_2$); 2.80 (*s*, 3H, NCH_3); 3.83 (*s*, 2H, NCH_2); 4.20 (*s*, 1H, OH). – IR. (KI): 3460, 2940, 2900, 2860, 1765, 1700, 1690, 1480, 1460, 1450, 1420, 1390, 1335, 1240, 1220, 1175, 1155, 1130, 1100, 1080, 1065, 1045, 1010, 975, 890, 850, 750, 645, 615, 565, 550 cm^{-1}. – MS. *(m/e)*: 424 ($M^+ - H_2O$, 37), 370 (31), 369 (30), 279 (10), 222 (66), 221 (15), 220 (10), 204 (24), 163 (100), 150 (12), 136 (18), 135 (17), 91 (30).

$C_{26}H_{38}N_2O_4$ (442.6) Calc. C 70.56 H 8.65 N 6.33% Found C 70.71 H 8.71 N 6.24%

cis-*1,2-Dibenzyl*-N-*deuteriomethyl-cyclohexane-1,2-dicarboximide* (**9a**) *and* cis-*3,4-Dibenzyl-5-hydroxy-1-methyl-3, 4-tetramethylene-5-(*cis-*1, 2-dibenzyl-cyclohexane-1, 2-dicarboximidomethyl)-2-pyrrolidone* (**9b**). A solution of 1.0 g (2.9 mmol) of **8** in 10 ml of THF is combined with 3.2 mmol of *s*-butyl lithium in isopentane with stirring at −78°. Addition of 0.5 ml (25 mmol) of D_2O after 30 min gives a colorless suspension which is allowed to warm-up to RT., poured into 50 ml of water and extracted twice with 50 ml each of ether. The organic phase is dried over Na_2SO_4 and the solvent is evaporated. Chromatography of the residue over 25 g of SiO_2 with $CHCl_3$ yields 0.44 g (44%) of **9a** [IR. (KI): 1400, 1335, 1200, 1180 cm^{-1}] and 0.41 g (41%) of **9b**: [M.p. 218–219; ^{1}H-NMR. ($CDCl_3$): 2.2–0.7 (*m*, 16H, $8CH_2$); 2.73 (*s*, 3H, NCH_3); 3.1 (*mc*, 8H, benzylic); 4.00 (*AB*-system, $J = 15$, 2H, NCH_2); 4.27 (*s*, 1H, OH); 7.3 (*m*, 20H, aromatic); IR. (KI): 3420, 3060, 3030, 2940, 2865, 1770, 1690, 1600, 1495, 1450, 1390, 1340, 1070, 1045, 980, 745, 700 cm^{-1}; MS. *(m/e)*: 679 ($M^+ - CH_3$, 3), 588 ($M^+ - CH_3 - C_6H_5CH_2$, 10), 495 (1), 404 (1), 348 (3), 252 (2), 91 ($C_6H_5CH_2^+$, 100)].

$C_{46}H_{50}N_2O_4$ (694.9) Calc. C 79.51 H 7.25 N 4.03% Found C 79.41 H 7.27 N 3.95%

Generation of solutions of 9c and reactions with electrophiles to give 9d-9i. – *Lithiation of* **9** *to* cis-*1,2-Dibenzyl*-N-*(lithiomethyl)-cyclohexane-1,2-dicarboximide* (**9c**). To a suspension of 3.58 g (10 mmol) of **9** and 4 ml of HMPT in 40 ml of THF stirred at −100° are added dropwise 10.5 mmol of *s*-butyl lithium. Further stirring at −100° for 25 min gives an orange solution containing ca. 80% of **9c** and 20% of **9b**. This procedure is used for the reactions with electrophiles described below; the amount of electrophile used is calculated for an 80% conversion of **9** to **9c**. The yields of products **9d-9j** are accordingly calculated from the amount of electrophile and not from that of **9** employed in the reaction. All reaction mixtures are worked up in the following manner: The solution is allowed to warm-up to RT., poured into 100 ml of water and extracted twice with 50 ml each of ether. The organic phase is washed 4× with 50 ml of water and dried over Na_2SO_4. The purification of the crude products obtained by evaporation of the solvent is described below.

cis-*1,2-Dibenzyl*-N-*ethyl-cyclohexane-1,2-dicarboximide* (**9d**). A solution of **9c** (from 10 mmol of **9**) and 4 ml of HMPT in 40 ml of THF stirred at −100° is combined with 0.55 ml (8.5 mmol) of iodomethane. The resulting pale yellow mixture is stirred at −100° for 1 h and worked up as described above. Chromatography of the crude product over 120 g of SiO_2 ($CHCl_3$/ether 10:1) gives 2.2 g (71%) of **9d**. M.p. 101–102° (ligroin). – ^{1}H-NMR. ($CDCl_3$): 1.8–0.7 (*m*, 11H, $4CH_2$, CH_3); 2.92 (*AB*-system, $J = 16$, 4H, benzylic); 3,29 (*q*, $J = 7$, CH, NCH_2); 7.17 (*s*, 10H, aromatic). – IR. (KI): 3060, 3030, 2980, 2940, 2860, 1765, 1700, 1600, 1495, 1450, 1395, 1375, 1345, 1220, 1070, 1050, 830, 760, 700, 655, 560 cm^{-1}. – MS. *(m/e)*: 361 (M^+, 1); 270 ($M^+ - C_6H_5CH_2$, 26), 167 (7), 149 (3), 91 ($C_6H_5CH_2^+$, 100), 77 ($C_6H_5^+$, 12).

$C_{27}H_{27}NO_2$ (361.5) Calc. C 79.44 H 7.53 N 3.88% Found C 79.59 H 7.46 N 3.74%

cis-*1,2-Dibenzyl*-N-*heptyl-cyclohexane-1,2-dicarboximide* (**9e**). – 1.1 ml (7.5 mmol) of 1-iodohexane are added at −100° to a solution of **9c** (from 9.36 mmol of **9**) in 40 ml of THF/4 ml of HMPT. After stirring for 1 h at −100° and for 3 h at −78° the solution is worked up in the usual way. Chromatography over 130 g of SiO_2 with pentane/ether 7:1 yields 1.9 g (59%) of **9e**. M.p. 57.5–58.0° (ligroin). – ^{1}H-NMR. (CCl_4): 1.8–0.5 (*m*, 21H, $9CH_2$, $1CH_3$); 2.90 (*AB*-system, $J = 16$, 4H, benzylic); 3.22 (br. *t*, 2H, NCH_2); 7.20 (*s*, 10H, aromatic). – IR. (KI): 3060, 3030, 2940, 2860, 1770, 1710, 1605, 1495, 1450, 1395, 1380, 1345, 1090, 1030, 755, 700, 550 cm^{-1}. – MS. *(m/e)*: 431 (M^+, 1), 340 ($M^+ - C_6H_5CH_2$, 43), 248 (7), 199 (6), 164 (11), 121 (7), 91 ($C_6H_5CH_2^+$, 100).

$C_{29}H_{37}NO_2$ (431.6) Calc. C 80.70 H 8.64 N 3.24% Found C 80.94 H 8.60 N 3.14%

cis-*1,2-Dibenzyl*-N-*[(1-hydroxy-1-cyclohexyl)-methyl]-cyclohexane-1,2-dicarboximide* (**9f**). The addition of 0.78 ml (7.46 mmol) of cyclohexanone to a solution of **9c** (from 9.33 mmol of **9**) in 44 ml of THF/HMPT 10:1 at −100° gives a yellow mixture which is combined with 0.46 ml (8 mmol) of glacial

acetic acid after stirring for 30 min at – 100° and for 2 h at – 78°. The crude product of the general work-up procedure is chromatographed over 120 g of SiO_2 ($CHCl_3$/ether 20:1) to yield 3.1 g (92%) of **9f**. M.p. 140–141° (ligroin/$CHCl_3$). – ^{1}H-NMR. ($CDCl_3$): 1.9–0.8 (*m*, 18H, CH_2); 2.90 (*s*, 1H, OH); 3.03 (*AB*-system, J = 14, 4H, benzylic); 3.37 (*s*, 2H, NCH_2); 7.27 (*s*, 10H, aromatic). – IR. (KI): 3560, 3505, 3060, 3020, 2930, 2855, 1770, 1700, 1600, 1495, 1450, 1390, 1330, 1130, 1090, 1035, 985, 760, 700, 630 cm^{-1}. – MS. *(m/e)*: 445 (M^+, 1), 427 ($M^+ - H_2O$, 10), 347 ($M^+ - C_6H_{10}O$, 74), 334 (22), 256 ($M^+ - C_6H_{10}O - C_6H_5CH_2$, 68), 227 (29), 199 (13), 164 (39), 91 ($C_6H_5CH_2^+$, 100).

$C_{29}H_{35}NO_3$ (445.6) Calc. C 78.17 H 7.92 N 3.14% Found C 78.23 H 7.90 N 3.05%

cis-*1,2-Dibenzyl*-N-*[(2-hydroxy-2-phenyl)-ethyl]-cyclohexane-1,2-dicarboximide* (**9g**). A solution of **9c** (from 9.48 mmol of **9**) in 44 ml of THF/HMPT 10:1 stirred at – 100° is combined with 0.8 ml (8.0 mmol) of benzaldehyde. The mixture is allowed to warm-up to – 60° within 1 h and is worked up as described above after addition of 0.56 ml (10 mmol) of glacial acetic acid. Chromatography over 120 g of SiO_2 with $CHCl_3$ gives 2.50 g (68%) of **9g**. M.p. 173.0–173.8° (ligroin/$CHCl_3$). – ^{1}H-NMR. (CCl_4): 1.6–0.3 (*m*, 8H, CH_2); 2.80 (*AB*-system, J = 15, 4H, benzylic); 3.50 (*m*, 2H, NCH_2); 5.61 (*s*, 1H, OH); 7.10 (*m*, 15H, aromatic). – IR. (KI): 3395, 3060, 3030, 2960, 2940, 2860, 1775, 1710, 1690, 1600, 1500, 1455, 1385, 1335, 1150, 1085, 1060, 970, 755, 705 cm^{-1}. – MS. *(m/e)*: 435 (M^+, 1), 360 (5), 347 (17), 334 (10), 256 (31); 228 (15), 199 (7), 164 (21), 105 (33), 91 ($C_6H_5CH_2^+$, 100), 77 ($C_6H_5^+$, 18).

$C_{30}H_{31}NO_3$ (453.5) Calc. C 79.43 H 6.89 N 3.09% Found C 79.35 H 6.80 N 3.09%

cis-*1,2-Dibenzyl*-N-*[(2-hydroxy-2,2-diphenyl)-ethyl]-cyclohexane-1,2-dicarboximide* (**9h**). 1.44 g (7.9 mmol) of benzophenone are added to a solution of **9c** (from 9.9 mmol of **9**) in 44 ml of THF/HMPT 10:1 stirred at – 100°. The resulting mixture is stirred for 1 h at – 78°, combined at – 30° with 0.5 ml (10 mmol) of glacial acetic acid, and worked-up as described above. Chromatography over 170 g of SiO_2 (pentane/ether 5:1) yields 1.25 g (54%) of **9h**. M.p. 204–205° (ligroin/$CHCl_3$). – ^{1}H-NMR. (CCl_4): 1.6–0.9 (*m*, 8H, CH_2); 2.87 (*AB*-system, J = 13, 4H, benzylic); 4,03 (*s*, 2H, NCH_2); 5.60 (*s*, 1H, OH); 7.07 (*m*, 20H, aromatic). – IR. (KI): 3340, 3080, 3060, 3030, 2950, 2930, 2870, 1770, 1695, 1600, 1495, 1450, 1390, 1325, 1140, 1065, 1050, 920, 765, 700, 600 cm^{-1}. – MS. *(m/e)*: 347 ($M^+ - (C_6H_5)_2CO$, 50), 256 ($M^+ - (C_6H_5)_2CO - C_6H_5CH_2$, 45), 228 (21), 139 (100), 105 (57), 91 (81), 77 (26), 69 (19).

$C_{35}H_{35}NO_3$ (529.6) Calc. C 81.63 H 6.66 N 2.64% Found C 81.20 H 6.46 N 2.64%

cis-*1,2-Dibenzyl*-N-*phenacyl-cyclohexane-1,2-dicarboximide* (**9i**). A solution of **9c** (from 9.22 mmol of **9**) in 44 ml of THF/HMPT 10:1 is combined at – 100° with 0.92 ml (7.37 mmol) of methyl benzoate, stirred for 5 h at – 78° and worked up as described above. The crude product is chromatographed over 110 g of SiO_2 with $CHCl_3$ to give 1.76 g (53%) of **9i**. M.p. 163.6–164.0° (ligroin/$CHCl_3$). – ^{1}H-NMR. ($CDCl_3$): 2.1–1.1 (*m*, 8H, $4CH_2$); 3.15 (*AB*-system, 4H, benzylic); 4.80 (*s*, 2H, NCH_2); 7.30 (*m*, 15H, arom.). – IR. (KI): 3060, 3020, 2930, 2860, 1770, 1700, 1595, 1495, 1450, 1410, 1225, 1115, 1075, 960, 760, 750, 685, 555 cm^{-1}. – MS. *(m/e)*: 309 (4), 231 (28), 153 (28), 121 (33), 110 (19), 109 (23), 105 (34), 91 ($C_6H_5CH_2^+$, 43), 77 (47), 51 (37), 44 (100).

$C_{30}H_{29}NO_3$ (451.5) Calc. C 79.79 H 6.47 N 3.10% Found C 79.57 H 6.36 N 3.08%

cis-*1,2-Dibenzyl*-N-*(trimethylsilylmethyl)-cyclohexane-1,2-dicarboximide* (**9j**). 0.9 ml (7.0 mmol) chloro trimethylsilane are added at – 100° to a solution of **9c** (from 8.2 mmol **9**) in 33 ml of THF/HMPT 10:1. The yellow mixture is stirred at – 100° for 30 min and worked-up as described above. Chromatography of the crude product over 100 g of SiO_2 with pentane/ether 2:1 yields 1.3 g (38%) of **9j**. M.p. 94–95° (pentane). – ^{1}H-NMR. (CCl_4): 0.0 (*s*, 9H, $Si(CH_3)_3$); 1.0–1.7 (*m*, 8H, $4CH_2$); 2.67 (*s*, 2H, NCH_2); 2.90 (*AB*-system, J = 16, 4H, benzylic); 7.13 (*s*, 10H, aromatic). – IR. (KI): 3080, 3030, 2950, 2900, 2870, 1765, 1695, 1600, 1495, 1455, 1400, 1375, 1330, 1250, 1140, 1095, 1065, 1030, 975, 960, 905, 865, 845, 755, 700 cm^{-1}. – MS. *(m/e)*: 404 ($M^+ - CH_3$, 35), 328 ($M^+ - C_6H_5CH_2$, 100), 222 (17), 91 (86).

$C_{16}H_{33}NO_2Si$ (419.6) Calc. C 74.77 H 7.96 N 3.35% Found C 74.77 H 7.96 N 3.29%

'Decomposition' of **9c**. A solution of **9c** obtained from 7.0 mmol of **9** as described above (33 ml THF/HMPT 10:1) is slowly warmed above – 100°. Samples are withdrawn with a syringe, worked-up and analysed by TLC. Above – 40° an increasing number of new spots appeared. After keeping the mixture at – 10° for

3 h no **9** was recovered; it was quenched with 50 ml of water. Two extractions with $CHCl_3$ which was subsequently dried over Na_2SO_4 and removal of the solvent led to the isolation of 2.4 g of a colourless resin which according to TLC. analysis consisted of at least 8 substances. Column chromatography of 1.2 g of this crude product over 100 g of SiO_2 with ether gave 0.47 g of the main component as a white solid. Mol. weight (osmom. in $CHCl_3$): 1000 ± 50. – ^{1}H-NMR. ($CDCl_3$): uncharacteristic broad multiplets at 2.20–0.35 (*m*, 8H, $4CH_2$); 2.5–5.0 (*m*, 7H); 7.1 (*m*, 10H, arom.). – IR. (KI): 3440, 3080, 3060, 3030, 2940, 2860, 1770, 1695, 1600, 1495, 1450, 1390, 1260, 1110, 1075, 1050, 1030, 975, 910, 750, 700 cm^{-1}. – MS. *(m/e)*: 676 (3), 665 (15), 592 (7), 482 (10), 389 (6), 352 (14), 296 (61), 91 (100).

Reaction of lithio diphenyl methane with **9**. To a solution of 0.47 g (2.79 mmol) of diphenyl methane in 9 ml of THF was added at – 40° a hexane solution of butyl lithium (3.0 mmol). After stirring for 15 min at RT., 0.97 g (2.79 mmol) of **9** in 10 ml of THF was added dropwise with cooling in an ice bath. After 3 h at 0° 0.5 ml of D_2O caused decolouration of the redbrown solution. The usual work-up with pentane gave a product mixture which was analysed for diphenylmethane by GC./MS. The ratio of the peaks 168/169/170 was 0.755: 0.223:0.022. A comparison with the molecular ions of $(C_6H_5)_2CH_2$ and $(C_6H_5)_2CHD$ with the aid of a nomogram showed that this corresponded to a $(C_6H_5)_2CH_2/(C_6H_5)_2CHD$ ratio of 0.75:0.25.

Addition of diphenyl methane to a solution of **9c**. After adding neat diphenyl methane (0.38 g, 2.26 mmol) to a **9c** solution (from 2.26 mmol of **9** in 20 ml of THF/HMPT 1:1) at – 100° bath temperature the mixture was warmed up to – 30° and quenched with 0.5 ml of D_2O. Work-up as above and GC./MS. analysis showed a 27% monodeuteriation of diphenylmethane.

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