Preparation of 1,1-Disubstituted Hydrazines and their 2-Acyl Derivatives†

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1-(1-Hydroxymethyl)benzotriazole converts 1-acyl- and 1-acyl-2-aryl-hydrazines into their 2-mono-*N*- or 2,2-bis-*N*-[(benzotriazol-1-yl)methyl] derivatives, respectively, in high yields. These adducts react readily with $NaBH_4$, Grignard reagents, and lithium acetylides to give the corresponding 2-substituted, or 2,2-disubstituted, 1-acylhydrazines in high yields. The *N*-(t-butoxycarbonyl)hydrazines are readily hydrolysed offering a convenient synthetic route to 1,1-dialkyl- and 1-alkyl-1-aryl-hydrazines.

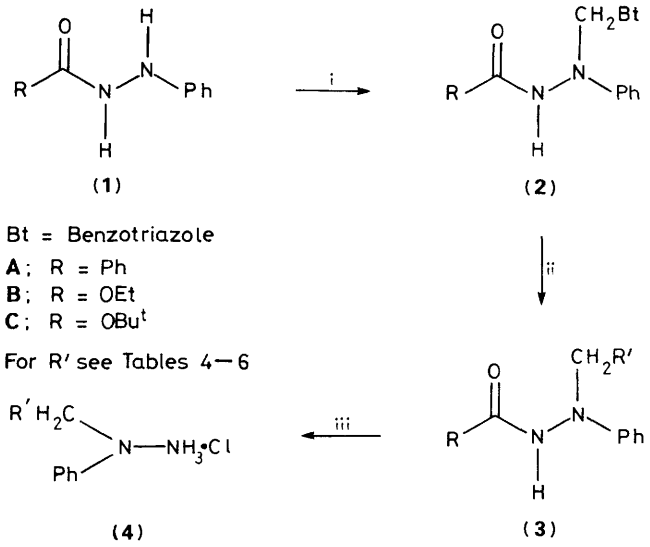
Considerable effort has been devoted to the preparation of 1,2-disubstituted hydrazines[1-7] and of their 2-acyl derivatives.[3,8] The classical method, *N*-nitrosation of secondary amines followed by reduction,[1] is no longer recommended because of the carcinogenicity of the intermediates. Hofmann rearrangement of 1,1-disubstituted ureas[2] or the thermolysis of diarylcarbamoyl azides[3] are preferable routes, but in both cases the availability of the secondary amine precursor limits the generality of the preparation. 1-Substituted hydrazines have been transformed into 1,1-disubstituted hydrazines by alkylation of their hydrazones,[4] or by direct alkylation of their sodium salts.[5]

1,1-Dialkylhydrazines have also been prepared from secondary amines by amination with hydroxylamine-*O*-sulphonic acid;[6] however, yields were only 32—34% for the three examples given. 1-Alkyl-1-arylhydrazines have been obtained from diazotized primary aromatic amines by Japp–Klingemann condensation with 3-methylpentane-2,4-dione followed by alkylation and hydrazinolysis.[7] Yields of 80—90% are quoted, although these are based on the isolated *N*-arylhydrazones.

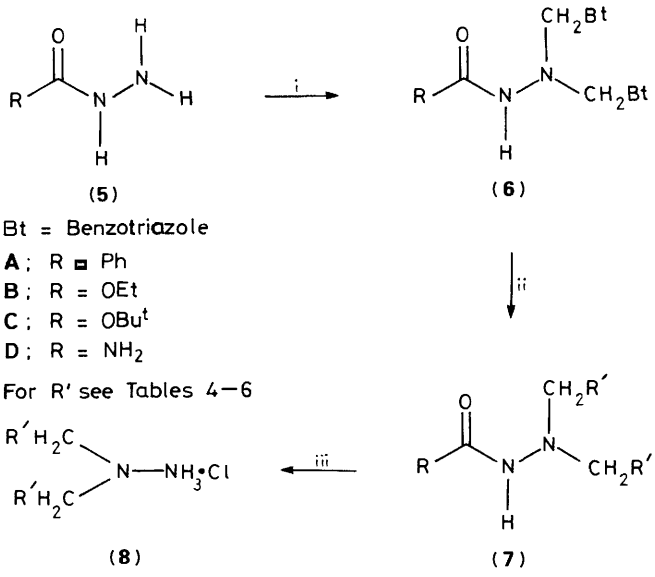
1,1-Dialkylhydrazines are important for the preparation of compounds containing N–N bonds,[9,10] of tetrazines,[11,12] of dibenzazepines[13] and of substituted indoles.[14,15] 1,1-Dialkyl-2-acylhydrazines are used as intermediates for amine imides[8] and for polysubstituted hydrazines.[16]

We now present novel methods for the preparation of 1,1-disubstituted hydrazines of types $ArN(CH_2R)NH_2$ (Scheme 1) and $(RCH_2)_2NNH_2$ (Scheme 2), and of their acyl derivatives, based on our benzotriazole methodology. Previous work from our group showed that a wide variety of NH groups could be converted into NCH_2Bt (where Bt is benzotriazole) by the action of *N*-hydroxymethylbenzotriazole, and that the Bt residue in the adducts could be replaced by H, by reaction with BH_4^-, or by R, by reaction with RMgBr (see refs. quoted for amines,[17] hydroxylamine,[18] amides,[19] thioamides,[20] sulphonamides[21]). We have now extended this methodology to acylhydrazines.

1-Benzoyl-2-phenylhydrazine[22] (**1A**) with hydroxymethylbenzotriazole gave 1-(benzotriazol-1-ylmethyl)-2-benzoyl-1-phenylhydrazine (**2A**). 1-Ethoxycarbonyl-2-phenylhydrazine (**1B**)[23] and 1-phenyl-2-(t-butoxycarbonyl)hydrazine[24] (**1C**) gave the analogous adducts (**2B**) and (**2C**), respectively (*cf* Table 1). Simple acylhydrazines reacted with hydroxymethylbenzotriazole to give bis-adducts by replacement of both the hydrogen atoms of the NH_2 group: thus, benzoylhydrazine (**5A**), ethyl carbazate (**5B**), and t-butyl carbazate (**5C**) produced the bis-adducts (**6A**), (**6B**) and (**6C**), whereas semicarbazide[25] (**5D**) gave (**6D**). However, reaction of *N*-aminophthalimide[26] (**9**) even with a three-fold excess of hydroxymethylbenzotriazole in benzene under reflux afforded only the mono adduct (**10**),



Scheme 1. *Reagents:* i, HMBT; ii, $NaBH_4$ (R′ = H), R′MgBr or R′Li; iii, MeOH/HCl or 5M HCl



Scheme 2. *Reagents:* i, HMBT; ii, $NaBH_4$ (R′ = H), R^1MgBr or R′Li; iii, MeOH/HCl

† This is a paper in our series 'Chemistry of Benzotriazole'.

Table 1. Preparation of *N*-(benzotriazol-1-ylmethyl)- and *N*,*N*-bis(benzotriazol-1-ylmethyl)-hydrazines

Product	Starting material	Method A: equiv. of HMBT	Method A: Solvent	Method A: reflux time (h)	Product yield (%)	Recrystallisation solvent	Crystalline form[a]	M.p. (°C)	Formula	Found (%) C	Found (%) H	Found (%) N
										(Required) C	(Required) H	(Required) N
(2A)	**(1A)**	1	EtOH	30	95	EtOH[b]	Ne	199—200	$C_{20}H_{17}N_5O$	69.75 (69.96)	4.85 (4.99)	20.4 (20.39)
(2B)	**(1B)**	1	C_6H_6	20	92	Et_2O[c]	Ne	144—145	$C_{16}H_{17}N_5O_2$	61.9 (61.72)	5.5 (5.50)	22.75 (22.49)
(2C)	**(1C)**	1	C_6H_6	5	80	Et_2O[c,d]	Ne	148—149	$C_{18}H_{21}N_5O_2$	63.4 (63.70)	6.25 (6.24)	20.5 (20.63)
(6A)	**(5A)**	2	EtOH	30	96	EtOH[b]	Mi	218	$C_{21}H_{18}N_8O$	63.1 (63.31)	4.25 (4.55)	28.4 (28.12)
(6B)	**(5B)**	2	C_6H_6	20	92	EtOH[b]	Ne	188—189	$C_{17}H_{18}N_8O_2$	55.55 (55.73)	5.0 (4.95)	30.85 (30.58)
(6C)	**(5C)**	2	C_6H_6	5	90	Et_2O[c,d]	Mi	189—190	$C_{19}H_{22}N_8O_2$	58.05 (57.86)	5.65 (5.62)	28.65 (28.41)
(6D)	**(5D)**	2	C_6H_6	20	60	EtOH[b]	Mi	152—153[e]	$C_{15}H_{15}N_9O$	53.1 (53.41)	4.35 (4.48)	36.95 (37.37)
(10)	**(9)**	1	C_6H_6	20	98	EtOH[b]	Ne	184	$C_{15}H_{11}N_5O_2$	61.55 (61.43)	3.45 (3.78)	23.95 (23.88)
(12)	**(11)**	2	EtOH	30	90	EtOH[b]	Mi	217—218	$C_{30}H_{28}N_{10}O_4$	60.65 (60.80)	4.75 (4.76)	23.5 (23.64)

[a] Ne = needles, Mi = microcrystals. [b] Triturated with hot EtOH. [c] Triturated with diethyl ether. [d] Recrystallised from $CHCl_3$–light petroleum. [e] With decomposition.

Table 2. ^1H N.m.r.[a] spectral data of *N*-(benzotriazol-1-ylmethyl)- and *N*,*N*-bis(benzotriazol-1-ylmethyl)-hydrazines

Compound	Aromatic-H	NH	NCH_2 (s)	NCH_2 H	Other H
(2A)[b]	6.89—8.1 (14 H, m)	10.84	6.58	2	
(2B)[b]	6.86—8.05 (9 H, m)	9.22	6.36	2	1.09 (3 H, t, *J* 7), 3.99 (2 H, q, *J* 7)
(2C)[c]	6.88—7.97 (9 H, m)	7.45	6.21	2	1.0—1.51 (9 H, m)
(6A)[b]	7.38—7.6 (9 H, m), 7.93 (2 H, d, *J* 8), 8.07 (2 H, d, *J* 8)	9.97	6.24	4	
(6B)[b,d]	7.37—7.57 (4 H, m), 7.86 (2 H, d, *J* 8), 8.05 (2 H, d, *J* 8)	8.58	6.03	4	0.83—0.86 (3 H, m), 3.67—3.73 (2 H, m)
(6C)[c]	7.37—7.42 (2 H, m), 7.49—7.53 (2 H, m), 7.64 (2 H, d, *J* 8.4), 8.06 (2 H, d, *J* 8.4)	6.71	5.82	4	1.37 (9 H, br, s)
(6D)[b]	7.27—8.09 (11 H, m)[e]	[e]	5.91	4	
(10)[b]	7.39 (1 H, t, *J* 8), 7.55 (1 H, t, *J* 8)	7.23[e]	5.76[g]	2	
(12)[b]	6.71 (2 H, m), 7.22—7.57 (12 H, m), 8.06 (4 H, t, *J* 9)	10.39[f]	6.4	4	4.55 (2 H, d, *J* 6), 6.15 (2 H, d, *J* 6)

[a] Chemical shift (δ) in p.p.m. and coupling constants (*J*) in Hz. [b] Solutions in $[^2H_6]Me_2SO$. [c] Solutions in $CDCl_3$. [d] Recorded at 80 °C. [e] t, *J* 5. [f] 2 H, s. [g] Doublet, 2 H, *J* 5. [f] Signal overlap with other signals.

Table 3. ^{13}C N.m.r.[a] chemical shifts (δ) of *N*-(benzotriazol-1-ylmethyl)- and *N*,*N*-bis(benzotriazol-1-ylmethyl)-hydrazines

Compound	Benzotriazole ring signals: N–C=O	C-3a	C-4	C-5	C-6	C-7	C-7a	N–C=	=C–C–O	NCH_2	Phenyl resonances	Others
(2A)	166.0	145.4	119.9	124.1	127.4	111.1	132.1[b]	146.8	133.0	63.8	112.9, 119.1, 127.5, 128.5, 129.2, 132.4[b]	
(2B)	156.1	145.7	119.8	124.0	127.7	109.6	132.9	146.1		65.0	113.9, 121.5, 129.3	14.3, 62.0
(2C)[c]	154.8	145.7	113.7	124.0	127.7	109.6	127.7	146.3	133.0	65.0	119.7, 121.3, 129.3	28.1, 81.6
(6A)	166.0	145.4	120.0	124.0	127.3	111.0	132.9		133.2	65.0	127.3, 128.2, 131.3	
(6B)[d]	155.0	145.2	118.6	123.4	126.8	110.5	132.9			65.5		13.5, 59.7
(6C)[c]	154.6	145.7	119.6	124.2	127.9	109.9	133.1			65.4		27.9, 81.3
(6D)	156.5	145.1	118.9	123.5	127.3	110.7	133.3			66.0		
(10)	165.8	145.4	119.0	123.2	127.2	111.1	132.7[b]		124.0	61.6	129.5, 134.7[b]	
(12)	171.2	145.3	119.7[b]	124.1	127.5	111.5	133.0	146.6		65.0	113.1, 118.9[b], 128.9	73.0

[a] In $[^2H_6]Me_2SO$ with 39.5 p.p.m. as reference. [b] Assignments could be reversed. [c] Solutions in $CDCl_3$. [d] Recorded at 80 °C

probably because of steric hindrance. Tartaric phenylhydrazide[27] (**11**), with hydroxymethylbenzotriazole in ethanol under reflux, afforded adduct (**12**). Compounds (**1A**), (**5A**), (**5D**), and (**11**) gave the expected mono- or bis-adducts in refluxing ethanol, but not in benzene or toluene, probably because of poor solubility.

I.r. spectra of the adducts showed the presence of the amide carbonyl absorption $\nu_{C=O}$ in the range 1 645—1 720 cm^{-1}. In most instances the structures were demonstrated by ^1H n.m.r. spectroscopy (Table 2). ^1H N.m.r. spectra of all the adducts showed the presence of NCH_2 protons as singlets in the range δ 5.76—6.58 and NH protons at δ 6.17—10.84. ^{13}C N.m.r.

Table 4. Preparation of *N,N*-disubstituted *N'*-acylhydrazines

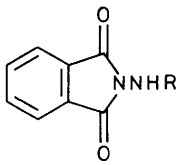
Product	R'	Starting material	Reagent	Preparative details: Type	Reagent moles	Chromatography (silica gel)	Product yield (%)	Recryst. solvent	Cryst. form[a]	M.p. (°C)	Formula	Found (%) (Required): C	H	N
(3Aa)	H	**(2A)**	$NaBH_4$	B	1.5	—	98	$CHCl_3$–hexane	Pr	154—155[b]	$C_{14}H_{14}N_2O$	—	—	—
(3Ab)	Ph	**(2A)**	PhMgBr	C	2.0	—	96	$CHCl_3$–hexane	Ne	138—139[c]	$C_{20}H_{18}N_2O$	—	—	—
(3Ac)	CH_2Ph	**(2A)**	$PhCH_2MgBr$	C	2.0	EtOAc–hexane (1:4)	80	EtOAc–hexane	Ne	162—163	$C_{21}H_{20}N_2O$	79.82 (79.72)	6.38 (6.37)	8.82 (8.85)
(3Ad)	C≡CPh	**(2A)**	PhC≡CLi	E	1.0	—	92	EtOAc–hexane	Pr	143—144	$C_{22}H_{18}N_2O$	80.77 (80.96)	5.65 (5.56)	8.60 (8.58)
(3Ba)	H	**(2B)**	$NaBH_4$	B	1.5	EtOAc–hexane (1:4)	98	$CHCl_3$–petroleum ether	Ne	49[d]	$C_{10}H_{14}N_2O_2$	—	—	—
(3Bb)	Ph	**(2B)**	PhMgBr	C	3.0	EtOAc–hexane (1:4)	90	$CHCl_3$–hexane	Ne	67—68	$C_{16}H_{18}N_2O_2$	71.52 (71.09)	6.78 (6.71)	10.37 (10.36)
(3Bc)	CH_2Ph	**(2B)**	$PhCH_2MgBr$	C	3.0	EtOAc–hexane (1:5)	90	$CHCl_3$–hexane	Pl	116—117	$C_{17}H_{20}N_2O_2$	72.01 (71.81)	7.09 (7.09)	9.39 (9.85)
(3Bd)	C≡CPh	**(2B)**	PhC≡CLi	E	2.0	EtOAc–hexane (1:3)	95	$CHCl_3$–hexane	Ne	101	$C_{18}H_{18}N_2O_2$	73.30 (73.45)	6.18 (6.16)	9.49 (9.52)
(3Cb)	Ph	**(2C)**	PhMgBr	D	2.0	EtOAc–hexane (1:4)	95	$CHCl_3$–light petroleum	Ne	95—96	$C_{18}H_{22}N_2O_2$	72.13 (72.46)	7.50 (7.43)	9.24 (9.39)
(3Cc)	CH_2Ph	**(2C)**	$PhCH_2MgBr$	D	2.0	EtOAc–hexane (1:4)	96	$CHCl_3$–light petroleum	Mi	110—111	$C_{19}H_{24}N_2O_2$	72.74 (73.05)	7.85 (7.74)	9.04 (8.92)
(3Ce)	$CH=CH_2$	**(2C)**	$CH_2=CHMgBr$	D	2.0	EtOAc–hexane (1:4)	98	—	Oil[e]					
(7Aa)	H	**(6A)**	$NaBH_4$	B	3.0	—	95	$CHCl_3$–hexane	Pl	105[f]	$C_9H_{12}N_2O$	—	—	—
(7Ab)	Ph	**(6A)**	PhMgBr	C	3.0	—	97	$CHCl_3$–hexane	Ne	169[g]	$C_{21}H_{20}N_2O$	—	—	—
(7Ac)	CH_2Ph	**(6A)**	$PhCH_2MgBr$	C	3.0	EtOAc–hexane (1:5)	83	$CHCl_3$–hexane	Ne	142—143	$C_{23}H_{24}N_2O$	79.97 (80.20)	7.05 (7.02)	7.85 (8.13)
(7Ad)	C≡CPh	**(6A)**	PhC≡CLi	E	2.0	—	94	$CHCl_3$–hexane	Pr	118	$C_{25}H_{20}N_2O$	82.66 (82.39)	5.53 (5.53)	7.68 (7.69)
(7Ba)	H	**(6B)**	$NaBH_4$	B	3.0	$CHCl_3$[h]	90	—	Oil[9]	—	$C_6H_{12}N_2O_2$	—	—	—
(7Bb)	Ph	**(6B)**	PhMgBr	C[i]	3.0	EtOAc–hexane (1:3)	95	$CHCl_3$–hexane	Ne	54—55[j]	$C_{17}H_{20}N_2O_2$	71.56 (71.81)	7.15 (7.09)	9.77 (9.85)
(7Bc)	CH_2Ph	**(6B)**	$PhCH_2MgBr$	D[i]	3.0	EtOAc–hexane (1:3)	94	EtOAc–light petroleum	Pl	93—94	$C_{19}H_{24}N_2O_2$	72.80 (73.05)	7.73 (7.74)	8.93 (8.97)
(7Bd)	C≡CPh	**(6B)**	PhC≡CLi	E[i]	2.0	EtOAc–hexane (1:3)	92	$CHCl_3$–light petroleum	Ne	81—82	$C_{21}H_{20}N_2O_2$	76.16 (75.88)	6.10 (6.06)	8.40 (8.43)
(7Cb)	Ph	**(6C)**	PhMgBr	D[i]	3.0	EtOAc–hexane (1:3)	94	$CHCl_3$–light petroleum	Pl	117	$C_{19}H_{24}N_2O_2$	72.61 (73.05)	7.78 (7.74)	8.80 (8.97)
(7Cc)	CH_2Ph	**(6C)**	$PhCH_2MgBr$	D	3.0	—	92	$CHCl_3$–light petroleum	Ne	112—113	$C_{21}H_{28}N_2O_2$	74.44 (74.08)	8.41 (8.29)	8.19 (8.23)
(7Cf)	Et	**(6C)**	CH_3CH_2MgBr	D	3.0	EtOAc–hexane (1:4)	80	—	Oil[k]	—		—	—	—

[a] Pr = Prisms, Ne = Needles, Pl = plates, Mi = microcrystals. [b] M.p. 153 °C, J. Tafel, *Ber. Dtsch. Chem. Ges.*, 1885, **18**, 1739. [c] M.p. 140 °C, H. Franzen, *Ber.*, 1909, **42**, 2465. [d] 49—50 °C, K. Hafner, D. Zinser, and K. L. Moritz, *Tetrahedron Lett.*, 1964, 1733. [e] *m/e*, Theoretical/measured molecular weight, 248.152 48/248.153 18. [f] M.p. 105—106 °C, R. F. Meyer and B. L. Cummings, *J. Heterocycl. Chem.*, 1964, **1**, 186. [g] M.p. 171—172 °C, R. O. C. Norman, R. Purchase, C. B. Thomas, and J. B. Aylward, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1692. [h] Neutral alumina. [i] Reagent added to the cooled compound (0—5 °C). [j] M.p. 54—55 °C, M. A. Iorio, *Gazz. Chim. Ital.*, 1964, **94**, 1391 (*Chem. Abstr.*, 1966, **65**, 3 861 h). [k] *m/e*, Theoretical/measured molecular weight, 216.183 78/216.182 24.

Table 5. ^{1}H N.m.r.[a] spectral data of *N,N*-disubstituted *N*-acylhydrazines

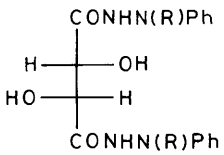
Compound	R′	Aromatic	NH	NCH$_2$ δ	NCH$_2$ H	NCH$_2$ M	NCH$_2$ *J*	Other-H
(**3Aa**)[b]	H	6.77—6.85 (3 H, m), 7.15—7.47 (5 H, m), 7.74 (2 H, d, *J* 8)	8.54	3.1	3	s		—
(**3Ab**)[b]	Ph	6.84—6.92 (3 H, m), 7.17—7.46 (10 H, m), 7.61 (2 H, d, *J* 8)	8.18	4.75	2	s		—
(**3Ac**)[b]	CH_2Ph	6.82 (2 H, d, *J* 8), 6.80—6.88 (1 H, m), 7.16—7.60 (12 H, m)	7.75	3.87	2	t	7	2.99 (2 H, t, *J* 7)
(**3Ad**)[c]	C≡CPh	6.8—7.05 (3 H, m), 7.22—7.65 (10 H, m), 7.92—8.05 (2 H, m)	10.86	4.69	2	s		—
(**3Ba**)[c]	H	6.71—6.78 (3 H, m), 7.16—7.24 (2 H, m)	9.38	3.07	3	s		1.17—1.23 (3 H, m), 4.06 (2 H, q, *J* 7)
(**3Bb**)[c]	Ph	6.72—6.81 (3 H, m), 7.15—7.45 (7 H, m)	9.54	4.66	4	s		1.18 (3 H, t, *J* 7), 4.06 (2 H, q, *J* 7)
(**3Bc**)[c]	CH_2Ph	6.71—6.81 (3 H, m), 7.17—7.32 (7 H, m)	9.45	3.64	2	t	8	1.24 (3 H, t, *J* 7), 2.89 (2 H, t, *J* 8), 4.11 (2 H, q, *J* 7)
(**3Bd**)[b]	C≡CPh	6.92—7.01 (3 H, m), 7.23—7.38 (7 H, m)	6.74	4.46				1.26 (3 H, t, *J* 7), 4.22 (2 H, q, *J* 7)
(**3Cb**)[b]	Ph	6.81—6.89 (2 H, m), 7.2—7.32 (8 H, m)	6.43	4.70	2	s		1.44 (9 H, s)
(**3Cc**)[c,e]	CH_2Ph	6.68—6.77 (3 H, m), 7.13—7.33 (7 H, m)	8.78	3.58—3.63	2	m		1.41 (9 H, s), 2.89 (2 H, t, *J* 7.8)
(**3Ce**)[b]	$CH=CH_2$	6.79—6.84 (3 H, m), 7.19—7.25 (2 H, m)	6.49	4.08	2	s		1.47 (9 H, s), 5.19—5.29 (2 H, m), 5.87—5.95 (1 H, m)
(**7Aa**)[b]	H	7.27—7.48 (4 H, m),[d] 7.95 (2 H, d, *J* 8)	7.46[d]	2.87	6	s		—
(**7Ab**)[b]	Ph	7.23—7.44 (15 H, m)	7.02	4.3	4	s		—
(**7Ac**)[b]	CH_2Ph	7.17—7.62 (15 H, m)	6.87	3.22	4	t	7	2.90 (4 H, t, *J* 7)
(**7Ad**)[b]	C≡CPh	7.22—7.43 (13 H, m),[d] 7.77—7.81 (3 H, m)	7.35[d]	4.11	4	s		—
(**7Ba**)[b]	H	—	5.59	2.59	6	s		1.24—1.29 (3 H, m), 4.16—4.18 (2 H, m)
(**7Bb**)[c]	Ph	7.19—7.41 (10 H, m)	8.30	3.94	4	s		1.03 (3 H, t, *J* 7), 3.81—3.95 (2 H, q, *J* 7)
(**7Bc**)[c,e]	CH_2Ph	7.13—8.25 (10 H, m)	8.25	2.82—2.95	4	m		1.2 (3 H, t, *J* 7), 2.68—2.75 (4 H, m), 3.81 (2 H, q, *J* 7)
(**7Bd**)[b]	C≡CPh	7.22—7.29 (6 H, m), 7.41—7.44 (4 H, m)	6.36	3.96	4	s		1.22 (3 H, t, *J* 7), 4.17 (2 H, q, *J* 7)
(**7Cb**)[b]	Ph	7.22—7.39 (10 H, m)	5.66	3.95—4.05	4	m		1.35 (9 H, m)
(**7Cc**)[b]	CH_2Ph	7.16—7.29 (10 H, m)	5.48	2.96—2.98	4	m		1.48 (9 H, s), 2.83 (4 H, t, *J* 7.5)
(**7Cf**)[b]	Et	—	5.22	2.61	4	s		0.92 (6 H, d, *J* 7), 1.45 (9 H, s), 1.51 (4 H, q, *J* 7)

[a] Chemical shift (δ) in p.p.m. and coupling constants (*J*) in Hz. [b] Solutions in $CDCl_3$. [c] Solutions in [$^2H_6$]Me_2SO. [d] Signal overlap with other signals. [e] Recorded at 80 °C.



(**9**) R = H

(**10**) R = CH_2Bt



(**11**) R = H

(**12**) R = CH_2Bt

spectroscopy (Table 3) disclosed the NCH_2 carbon resonances at δ 61.6—66.0 and the N–C=O carbons at δ 154.6—171.2.

Reductions of Adducts with Sodium Borohydride.—The adducts were smoothly reduced to the corresponding methylhydrazines in high yield. Thus, compounds (**2A**), (**2B**), (**6A**), and (**6B**), with $NaBH_4$ in dry THF, gave 1-benzoyl- (**3Aa**) and 1-ethoxycarbonyl-2-methyl-2-phenylhydrazine (**3Ba**), 1-benzoyl- (**7Aa**) and 1-ethoxycarbonyl-2,2-dimethylhydrazine (**7Ba**), respectively, in 94—98% yields (Table 4). The crude products were purified by column chromatography or by crystallization (see Experimental Section) and characterized by melting point, elemental analysis and ^{1}H and ^{13}C n.m.r. spectroscopy (Tables 5 and 6).

The ^{1}H n.m.r. spectra of methylhydrazines (**3Aa**), (**3Ba**), (**7Aa**) and (**7Ba**) showed the NCH_3 protons as singlets at δ 2.59—3.10 and the disappearance of the signal for the NCH_2 group. ^{13}C N.m.r. spectra showed the NCH_3 resonances (δ 39.8 to 59.3) and N–C=O carbon resonances at 155.1—169.3.

Reactions of Adducts with Grignard Reagents.—Treatment of adducts (**2A**), (**2B**) and (**2C**) with phenylmagnesium bromide in dry THF afforded 1-benzoyl-2-benzyl-2-phenylhydrazine (**3Ab**), 1-benzyl-2-ethoxycarbonyl-1-phenylhydrazine (**3Bb**), and 1-benzyl-1-phenyl-2-(t-butoxycarbonyl)hydrazine (**3Cb**). Adducts (**6A**), (**6B**) and (**6C**) similarly yielded 1-benzoyl-2,2-dibenzylhydrazine (**7Ab**), 1,1-dibenzyl-2-ethoxycarbonylhydrazine (**7Bb**) and 1,1-dibenzyl-2-(t-butoxycarbonyl)hydrazine (**7Cb**), respectively. Yields were 90—97% (Table 4). Similar treatment of adducts (**2A**), (**2B**) and (**2C**) with benzylmagnesium bromide gave 1-benzoyl- (**3Ac**), 1-ethoxycarbonyl-2-(2-phenethyl)-2-phenylhydrazine (**3Bc**) and 1-(2-phenethyl)-1-phenyl-2-(t-butoxycarbonyl)hydrazine (**3Cc**), while (**6A**), (**6B**) and (**6C**) formed 1-benzoyl- (**7Ac**), 1-ethoxycarbonyl-2,2-bis(2-phenethyl)hydrazine (**7Bc**) and 1,1-bis(2-phenethyl)-2-(t-butoxycarbonyl)hydrazine (**7Cc**) respectively, in 80—96% yield. Grignard reactions of adducts (**2C**) and (**6C**) with vinylmagnesium bromide and ethylmagnesium bromide gave 1-allyl-1-phenyl-2-(t-butoxycarbonyl)hydrazine (**3Ce**) and 1,1-dipropyl-2-(t-butoxycarbonyl)hydrazine (**7Cf**) respectively, in 80—98% yield (Table 4).

The crude products were purified by column chromatography or by crystallization (see Experimental section). They were characterized by ^{1}H and ^{13}C n.m.r. spectroscopy (Tables 5 and 6) and either by comparison with their literature melting points, or by elemental analysis. Compounds (**3Ce**) and (**7Cf**) were characterized by ^{1}H and ^{13}C n.m.r. spectroscopy (Tables 5 and 6) and by high resolution mass spectral analysis (Table 4). The Grignard reactions were carried out at 20 °C for adducts (**2A**), (**2B**) and (**6A**). For adduct (**6B**) cooling at 0—5 °C was needed

Table 6. ^{13}C N.m.r. spectral data of *N,N*-disubstituted *N'*-acylhydrazines

Compound	R'	N–C=O	N–C=	C–C=	O=C–C=	NCH_2	Phenyl resonances	Others
(**3Aa**)[a]	H	166.6	149.3		132.6	40.5	112.6, 119.5, 127.2, 128.5, 129.0, 131.9	
(**3Ab**)[a]	Ph	166.8	148.7	137.0	132.7	56.5	113.1, 119.7, 127.1, 127.4, 128.0, 128.6, 129.2, 131.9	
(**3Ac**)[a]	CH_2PH	166.3	147.8	139.7	132.5	53.9	112.7, 119.4, 126.4, 127.1, 128.6, 128.8, 129.3, 132.0	33.1
(**3Ad**)[b]	C≡CPh	165.9	148.4	122.4	132.8	42.7	113.2, 119.2, 127.6, 128.5, 128.6, 129.0, 131.4, 131.9	84.2, 85.6
(**3Ba**)[b,c]	H	155.6	149.8			39.8	112.0, 117.8, 128.3	14.1, 59.9
(**3Bb**)[b]	Ph	155.9	149.3	138.1		56.9	112.4, 118.4, 127.0, 127.6, 128.2, 128.8, 138.1	14.6, 60.4
(**3Bc**)[b]	CH_2Ph	166.0	149.0	139.3		53.6	112.3, 118.2, 126.1, 128.3, 128.7, 128.9	14.6, 32.5, 60.4
(**3Bd**)[b,c]	C≡CPh	155.6	148.2	122.2		43.0	113.1, 118.9, 127.9, 128.0, 128.3, 130.9	14.0, 60.0, 83.9, 84.9
(**3Cb**)[a]	Ph	154.7	149.2	137.1		56.5	112.9, 119.4, 127.3, 127.9, 128.5, 129.1	28.2, 80.8
(**3Cc**)[a]	CH_2Ph	154.9	148.6	139.3		54.0	112.5, 119.1, 126.3, 128.6, 128.9, 129.1	28.2, 33.0, 80.8
(**3Ce**)[a]	$CH=CH_2$	154.9	148.8			55.4	112.9, 129.0, 132.7	28.2, 80.7, 118.2, 119.3
(**7Aa**)[a]	H	169.3			127.8	52.9	128.1, 128.2, 131.7	
(**7Ab**)[a]	Ph	167.3		137.4	133.9	59.3	126.7, 127.4, 128.3, 128.4, 129.2, 131.3	
(**7Ac**)[a]	CH_2Ph	166.8		139.7	133.6	59.3	126.1, 126.9, 128.4, 128.5, 128.6, 131.6	33.7
(**7Ad**)[a]	C≡CPh	165.7		122.0	133.1	46.1	126.9, 127.9, 128.1, 128.2, 131.4	82.3, 86.2
(**7Ba**)[a]	H	155.5				47.9		14.5, 61.1
(**7Bb**)[b]	Ph	155.1		138.1		59.3	126.9, 128.0, 128.6	14.5, 59.9
(**7Bc**)[b,c]	CH_2Ph	155.7		139.8		58.2	125.2, 127.6, 128.1	14.1, 32.8, 59.2
(**7Bd**)[a]	C≡CPh	155.2		122.1		46.5	127.9, 128.1, 131.4	14.2, 61.0, 82.1, 86.0
(**7Cb**)[a]	Ph	154.5		137.5		59.6	127.2, 128.2, 129.2	28.2, 80.8
(**7Cc**)[a]	CH_2Ph	155.3		139.8		59.6	126.0, 128.3, 128.7	28.3, 33.7, 79.8
(**7Cf**)[a]	Et	155.1				60.2		11.6, 20.2, 28.3, 79.4

[a] In $CDCl_3$ with 77.0 p.p.m. as reference. [b] In $[^2H_6]Me_2SO$ with 39.5 p.p.m. as reference. [c] Recorded at 80 °C.

to avoid formation of a black polymer. For adducts (**3C**) and (**6C**), the reactions were also carried out at low temperature (−78 °C), both to avoid the decomposition of the adduct, and to increase the yield.

^1H N.m.r. spectra for the compounds (**3Ab**), (**3Bb**), (**3Cb**), (**7Ab**) and (**7Bb**) showed in each case the NCH_2 protons as a singlet, at δ 3.94—4.75. For compounds (**3Ac**), (**3Bc**), and (**7Ac**) the NCH_2 protons were observed as triplets (due to the presence of the adjacent CH_2 group) at δ 3.22—3.87. In the spectrum of compound (**7Bc**) the NCH_2 protons appeared as a multiplet or a pair of merged triplets. This is a result of the nonequivalence of two NCH_2 groups, which is due to hindered rotation about the N–CO bond.[28] ^1H N.m.r. of compound (**3Cc**) at 20 °C in deuteriated dimethyl sulphoxide showed two peaks at δ 1.27 and 1.45 of unequal intensity (1:5) for the t-butyl group. At 80 °C, these had coalesced into a single peak at δ 1.41. This is again due to restricted rotation around the N–CO bond.[28]

Reaction of Adducts with Lithium Acetylides.—Acetylide nucleophiles react with *N*-substituted benzotriazoles to form the expected products by replacement of the benzotriazole group. Treatment of adducts (**2A**), (**2B**), (**6A**), and (**6B**) with lithium phenylacetylide (prepared from phenylacetylene and BuLi in THF at −78 °C) in THF afforded 1-benzoyl- (**3Ad**) and 1-ethoxycarbonyl-2-[3-(1-phenylpropynyl)]-2-phenylhydrazine (**3Bd**), and 1-benzoyl- (**7Ad**) and 1-ethoxycarbonyl-2,2-bis[3-(1-phenylpropynyl)]hydrazine (**7Bd**) respectively, in 92—95% yield. The crude compounds were purified by column chromatography or by crystallization (see Experimental Section), and characterized by ^1H and ^{13}C n.m.r. spectroscopy and by elemental analysis (Tables 2, 5 and 6).

The ^1H n.m.r. spectra of these compounds showed the presence of NCH_2 protons as singlets in the range δ 3.96—4.69 and the ^{13}C n.m.r. spectra showed the presence of NCH_2 carbon resonances in the range δ 42.7—46.5, as well as the characteristic acetylene carbons (C≡C) in the range δ 83.9—84.2 and δ 84.9—86.2.

^{13}C N.m.r. spectra of these compounds (**3Ba—d**) and (**7Ba—d**) at room temperature showed a broad signal of low intensity for the amide carbon, probably due to the restricted rotation of the N–CO bond. A similar line broadening of resonances for the OCH_2 and NCH_2 carbons was observed in the spectra of compounds (**3Bc**) and (**7Bb** and **c**). When these were recorded at 80 °C in $[^2H_6]DMSO$, sharp signals were observed. Solvent effects ($CDCl_3$ and $[^2H_6]DMSO$) on ^{13}C n.m.r. spectra at room temperature for compounds (**3Bc**) and (**7Bb**) were also observed. When recorded in $CDCl_3$ at room temperature, broad peaks of low intensity for NCH_2 and OCH_2, and almost insignificant peaks for the amide carbons, were observed. When recorded in $[^2H_6]DMSO$ sharper signals for these carbons were observed, signifying free rotation of the N–CO bond in polar solvents.

Conversion of Acylhydrazines to the Corresponding Hydrazine Hydrochloride Salts.—The ethyl esters (**3Ba—d** and **7Ba—d**) did not easily hydrolyse to the alkyl- or arylhydrazines[3] (**4Ba—d** and **8Ba—d**). Debenzoylation of (**3Ab**) in 6M HCl[29] gave 1-benzyl-1-phenylhydrazine hydrochloride in only 20% yield. In contrast the t-butyl esters (**3Cb**), (**7Cb**) and (**7Cc**) smoothly underwent quantitative hydrolysis with concentrated hydrogen chloride in methanol[3] to afford 1-benzyl-1-phenyl- (**4b**), 1,1-dibenzyl- (**8b**), and 1,1-bis-(2-phenylethyl)-hydrazine (**8c**) hydrochlorides, respectively.

^1H N.m.r. spectra for the compounds (**4b**), (**4e**), (**8b**), and (**8c**) showed in each case the presence of the NH_2 protons as a singlet in the range δ 7.73—10.77 and the disappearance of the signal for the t-butyl group at δ 1.35—1.48. Similarly, the absence of signals for carbonyl and t-butyl carbons in the ^{13}C n.m.r. spectra was observed.

General conclusions.—The work described in this paper provides the basis of convenient general routes to *N,N*-dialkylhydrazines (3 stages from t-butoxycarbonylhydrazines) and to *N*-alkyl-*N*-arylhydrazines (4 stages from the arylhydrazines). Corresponding *N'*-acyl derivatives are obtained even more readily, and this route should be that of choice for these classes of derivatives.

Experimental

M.p.s were determined with a hot-stage microscope and are uncorrected; i.r. spectra were recorded on a Perkin-Elmer Model 283B grating spectrophotometer. ^1H and ^{13}C N.m.r. spectra were recorded on a Varian XL-200 or VXR-300 spectrometer, and the chemical shifts are measured in δ from Me_4Si or a specified internal standard. High resolution mass spectra were recorded on AEI-MS30 Mass spectrometer.

The following compounds were prepared by literature methods: 1-benzoyl-2-phenylhydrazine[22] (**1A**), m.p. 172—173 °C (lit.,[30] m.p. 171—172 °C), 1-ethoxycarbonyl-2-phenylhydrazine (**1B**), m.p. 76 °C (lit.,[23] m.p. 71—75 °C), 1-phenyl-1-(t-butoxycarbonyl)hydrazine (**1C**) m.p. 92—93 °C (lit.,[24] m.p. 92—93.5 °C), semicarbazide (**5C**), m.p. 96 °C (lit.,[25] m.p. 96 °C), *N*-aminophthalimide (**9**), m.p. 203—204 °C (lit.,[26] m.p. 200—205 °C), 2',2''-diphenyltartarohydrazide (**11**), m.p. 231—232 °C (lit.,[27] m.p. 231 °C), and 1-hydroxymethylbenzotriazole m.p. 147—149 °C (lit.,[31] m.p. 148—151 °C).

Reaction of 1-*Hydroxymethylbenzotriazole with Substituted Hydrazines.—General procedure A.* 1-Hydroxymethylbenzotriazole (0.7 g, 4.7 mmol or 1.4 g, 9.4 mmol), the hydrazine (4.7 mmol) and absolute ethanol or benzene (100 ml) (see Table 1) were heated under reflux with stirring for 5—30 h. The reaction mixture was cooled, and the solvent evaporated under reduced pressure, triturated with ethanol or ether, filtered, and dried. The crude samples were of >95% purity by ^1H and ^{13}C n.m.r. spectroscopy. In some cases, the traces of starting materials were removed by washing the crude solid with 5% aqueous NaOH followed by water and ether. For details of preparation, physical characteristics, spectral data and elemental analysis, see Tables 1—3.

Reduction of N-(*Benzotriazol*-1-*ylmethyl*)- *and* N,N-*bis*-(*Benzotriazol*-1-*ylmethyl*)*hydrazines* (**2A**), (**2B**), (**6A**), *and* (**6B**) *with Sodium Borohydride.—General procedure B.* The adduct (10 mmol) and sodium borohydride (0.57 g, 15 mmol or 1.14 g, 30 mmol) were stirred and heated under reflux for 8 h, with tetrahydrofuran (THF) (30 ml, distilled over sodium–benzophenone). The mixture was poured into ice–water (100 ml) and extracted with ether or ethyl acetate (**3Aa**) (2 × 50 ml). The combined organic phase was washed with 5% aqueous sodium carbonate (2 × 40 ml) and with water (40 ml), dried (Na_2SO_4), and evaporated to afford the crude product. The purity was usually >95% by ^1H and ^{13}C n.m.r. spectroscopy. The crude products were purified by column chromatography or by crystallization. For details of preparation, physical characteristics, spectral data and elemental analysis, see Tables 4—6.

Preparation of N,N-*Disubstituted* N'-*Acylhydrazines* (**3Ab**), (**3Ac**), (**3Bb**), (**3Bc**), (**7Ab**), *and* (**7Ac**).—*General procedure C.* The Grignard reagents were either purchased or prepared from equimolar amounts of magnesium turnings and the alkyl or aryl halide, in dry THF (30 ml) under nitrogen. The Grignard reagent (2 or 3 mmol) was added dropwise to either a slurry or solution of the appropriate adduct (1 mmol), in dry THF (25 ml), over 15 min. The mixture was stirred at room temperature for 12 h and then poured into crushed ice (containing 5 g of NH_4Cl and water). The mixture was extracted with ethyl acetate [(**3Ab**), (**3Ac**), (**7Ab**), and (**7Ac**)] or ether (3 × 40 ml). The combined organic layer was washed with 5% aqueous Na_2CO_3 (2 × 40 ml) and with water, dried (Na_2SO_4) and evaporated to afford the crude product, which was purified by column chromatography or by crystallization. For details of preparation, physical characteristics, spectral data, and elemental analysis, see Tables 4—6.

Table 7. Preparation of *N,N*-dialkylhydrazine hydrochlorides

Product	Starting material	Product yield (%)	Cryst. form[a]	M.p. (°C)	Lit. m.p.
(**4b**)	(**3Cb**)	97	Ne.	171—172	170—172[6b]
(**4e**)	(**3Ce**)	100	Ne.	149—150	148—151[6b]
(**8b**)	(**7Cb**)	98	Pl.	200—201	191—201[b]
(**8c**)	(**7Cc**)	98	Pl.	162—163	163[c]

[a] Ne = needles, Pl = plates (all hydrazine hydrochlorides were recrystallized from EtOH–Ether). [b] H. H. Fox, J. T. Gibas and A. Motchane, *J. Org. Chem.*, 1956, **21**, 349. [c] M. A. Iorio and R. Landi-Vittory, *Farmaco* (*Pavia*), *Ed. Sci.*, 1963, **18**, 453 (*Chem. Abstr.*, 1963, **59**, 8642g)

Table 8. ^1H N.m.r.[a] spectral data of *N,N*-dialkylhydrazine hydrochlorides

Compound	Aromatic	NH_2	NCH_2 δ	NCH_2 H	NCH_2 M	NCH_2 *J*	Others
(**4b**)[b]	7.05—7.32 (10 H, m)	10.77	4.77	2	s		
(**4e**)[b]	7.05—7.38 (5 H, m)	10.76	4.26	2	d	6.3	5.23—5.27 (2 H, m), 5.81—5.9 (1 H, m)
(**8b**)[b]	7.17—7.27 (10 H, m)	9.77	3.97	4	s		
(**8c**)[b]	7.15—7.33 (10 H, m)	7.73	3.17—3.3	4	m		2.55—3.0 (4 H, m)

[a] Chemical shift (δ) in p.p.m. and coupling constants (*J*) in Hz. [b] Solutions in $[^2H_6]Me_2SO$

Table 9. ^{13}C N.m.r.[a] chemical shifts (δ) of *N,N*-dialkylhydrazine hydrochlorides

Compound	N–*C*=	*C*–*C*=	Phenyl resonances	Others
(**4b**)	146.5	135.2	118.9, 123.9, 127.9, 128.5, 128.8, 129.0	58.7
(**4e**)	146.3	—	118.1, 129.1, 131.0	57.1, 120.8, 123.3
(**8b**)	—	135.0	128.0, 128.6, 129.2	58.4
(**8c**)	—	138.5	126.3, 128.4, 128.8	30.9, 57.3

[a] In $[^2H_6]Me_2SO$ with 39.5 p.p.m. as reference

General Procedure D for the Preparation of N,N-*Disubstituted*-N′-*Acylhydrazines* (**3Cb**), (**3Cc**), (**3Ce**), (**7Bb**), (**7Bc**), (**7Cb**), (**7Cc**), *and* (**7Cf**).—Preparation of these compounds was according to procedure C except that the Grignard reagent was added to a stirred slurry or solution of the adduct in dry THF (30 ml) at −78 °C, under an argon atmosphere. The mixture was stirred for 1 h at −78 °C and then allowed to attain room temperature (30—60 min). For compounds (**7Bb**) and (**7Bc**) the Grignard reagent was added to a stirred slurry or solution of the adduct in dry THF (30 ml) at (0—5 °C). Further work-up as in procedure C. For details of preparation, physical characteristics, spectral data, and elemental analysis, see Tables 4—6.

Reaction of N-(*Benzotriazol*-1-*ylmethyl*)- *and* N,N-*Bis*(*benzotriazol*-1-*ylmethyl*)-*hydrazines* (**2A**), (**2B**), (**6A**), *and* (**6B**) *with Phenyl Acetylides.—General procedure E for preparation of compounds* (**3Ad**), (**3Bd**), (**7Ad**), *and* (**7Bd**). To a stirred solution of phenylacetylene (0.3 ml, 2.6 mmol or 0.6 ml, 5.2 mmol), in dry THF (25 ml), was added BuLi (2.5M in hexane; 1.4 ml, 3.5 mmol or 2.8 ml, 7 mmol) at −78 °C, by syringe, under argon. The mixture was stirred for 15 min at −78 °C, and then for 2 h at room temperature. After this period the solution was added dropwise by syringe to a stirred slurry or solution of the adduct (2.6 mmol) in dry THF (20 ml), under argon. The reaction mixture was stirred for 8 h and then the solvent was evaporated under reduced pressure. Aqueous Na_2CO_3 (20%; 50 ml), followed by ether (50 ml) was added and the aqueous layer was again extracted with ether (2 × 40 ml). Further work-up as in procedure C. For details of preparation, physical characteristics, spectral data and elemental analysis, see Tables 4—6.

N,N-*Dialkylhydrazine Hydrochlorides* (**4b**), (**8b**), *and* (**8c**).—*General procedure F.* The t-butyl ester (400 mg) in methanol (100 ml) and conc. HCl (5 ml) was stirred and heated under reflux for 4 h. The mixture was cooled and the solvent was removed under reduced pressure. The solid was washed with anhydrous ether, filtered and dried to give a crude yield of 97—98%. The crude salt was recrystallized by dissolution in hot ethanol followed by the addition of ether.

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