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THE C-ALKYLATION OF NITROALKANE ANIONS BY 1-SUBSTITUTED-2-t-BUTYL-4-PHENYL- AND -2,4-DIPHENYL-5,6-DIHYDROBENZO[h]QUINOLINIUM CATIONS.

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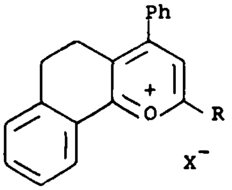
Abstract - The N-substituents are transferred from the title cations to the C-atom of nitroalkane anions in high yield at 25-80°C in DMSO solution. The title cations are readily available from the appropriate pyrylium cations and primary amines of types RCH_2NH_2 and $RR'CHNH_2$, allowing a general 2-step method for the preparation of higher nitroalkanes. Spectral properties of a variety of nitroalkanes are discussed.

We recently disclosed[1] the first general method for the C-alkylation of nitroalkane anions: this utilised N-substituent transfer from N-primary-alkyl-, N-secondary-alkyl- and N-benzyl-2,4,6-triphenylpyridinium cations. Extensive investigations[2,3] of the mechanism of this non-chain radicaloid process have led to the development of 2-t-butyl-5,6-dihydro-4-phenylbenzo[h]-quinoline as a superior leaving group for C-alkylation by primary alkyl groups. We now report preparative reactions under milder conditions than used previously, which proceed selectively and in high yield, even for the transfer of primary alkyl groups to the nitromethane and nitroethane anions which gave poor results by the earlier technique. For the transfer of secondary alkyl groups, 5,6-dihydro-2,4-diphenylbenzo[h]quinoline is a good leaving group.

Preparation of Salts. The appropriate pyrylium salt (see Experimental) and amine reacted smoothly to give the pyridinium compounds **2a-f** (Table 1) and **3a-d**, which were characterised spectrally. The ^1H NMR spectra (Table 2) show all the peaks expected for these compounds[4]; the C (3)-H proton appears as a singlet at 7.8-7.9 ppm, the other aromatic protons give a complex multiplet in the range of 6.9-8.4 ppm . The four protons at C (5) and C (6) resonate at 2.70-2.85, the t-butyl group shows a sharp singlet at 1.75-1.80 ppm , whereas the C_α-protons of the N-substituent appear at 6.45 ppm (N-benzyl) and 5.2-5.3 ppm (N-alkyl). The assignments of the ^{13}C NMR spectra (Table 3) were according to those made in a previous study[5], where a discussion of the chemical shifts of **2a** compared with **2c**, representing the N-alkyl substituted series, is given.



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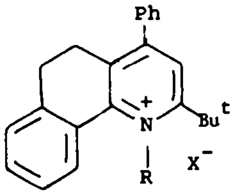

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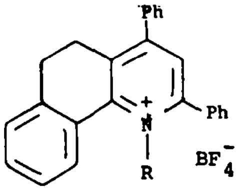

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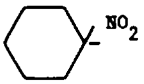
	R	X
a	Bu^t	BF_4
b	Bu^t	CF_3SO_3
c	Ph	BF_4

	R	X
a	CH_2Ph	BF_4
b	Pr^n	CF_3SO_3
c	Bu^n	BF_4
d	$CH_3(CH_2)_4$	BF_4
e	$CH_3(CH_2)_5$	BF_4
f	$CH_3(CH_2)_6$	BF_4

	R
a	$CH_3(CH_2)_5$
b	Pr^i
c	cyclo-C_6H_{11}
d	neo-C_5H_{11}

4 a $^-C(CH_3)_2NO_2$, b $^-CH(CH_3)NO_2$, c $^-CH_2NO_2$, d



Preparation of Nitroalkanes. Reactions were carried out in DMSO solution at 25-60°C, using pyridinium salt and nitroalkane anion in the ratio of 1:3. We found that nitromethane, nitroethane, and 2-nitropropane could all be C-alkylated with primary alkyl groups from compounds 2a-f in this manner in 65-98% yield (Table 4). The good yields obtained from nitromethane and nitroethane contrast with the difficulty formerly encountered[1] in the alkylation of the anions using N-alkyl-2,4,6-triphenylpyridinium salts.

Compounds of type 2 carrying a N-secondary alkyl substituent are not accessible[4], but we found that the compounds 3b, c transferred their secondary alkyl groups readily at 60-80°C to the anions of 2-nitropropane, nitroethane and nitrocyclohexane (Table 4).

IR Spectra of Nitroalkanes. The symmetrical and asymmetrical NO_2 stretching modes are characteristic[6], and are shown in Table 5. If the NO_2-group is attached to a carbon atom also carrying a methyl group, now mixing occurs between the methyl C-H s-bend and the NO_2 asymmetric stretch. As reported by previous workers[7], for $MeC-NO_2$ this results in two bands at 1400 and

Table 1. Preparation of 1-Substituted-2-(*t*-butyl)-5,6-dihydro-4-phenylbenzo[*h*]quinolinium Salts

Quinolinium Salt	1-Substituent	Anion	Time (h)	Yield (%)	M.p. (°C)	Recryst. Solvent[a]	Required (%) C	H	N	Molecular Formula	Found (%) C	H	N
2a	CH_2Ph	BF_4	4	72	149-151[b]	EtOH	73.3	6.1	2.8	$C_{30}H_{30}BF_4N$	73.2	6.2	2.8
2b	Pr^n	CF_3SO_3	6	71	181-182	EtOH	64.1	6.0	2.8	$C_{27}H_{30}F_3NO_3S$	64.1	6.0	2.8
2c	Bu^n	BF_4	6	72	141-142[c]	EtOH	70.9	7.1	3.1	$C_{27}H_{32}BF_4N$	70.9	7.1	3.1
2d	$CH_3(CH_2)_4$	BF_4	8	73	109-110	Me_2CO/Et_2O	71.3	7.3	3.0	$C_{28}H_{34}BF_4N$	71.3	7.3	3.0
2e	$CH_3(CH_2)_5$	BF_4	10	72	103-104	"	71.8	7.5	2.9	$C_{29}H_{36}BF_4N$	71.8	7.5	2.9
2f	$CH_3(CH_2)_6$	BF_4	12	70	93-94	"	72.2	7.7	2.8	$C_{30}H_{38}BF_4N$	72.2	7.7	2.8

[a] All compounds crystallised as needles. [b] Lit.[17] m.p. 149-152°C. [c] Lit.[17] m.p. 136-137°C.

Table 2 ^1H NMR[a] Spectra of 1-Substituted-2-(*t*-butyl)-5,6-dihydro-4-phenylbenzo[*h*]quinolinium Salts.

Quinolinium Salt	1-Substituent	Anion	Aromatic (m) δ	H	3-H (s,1H)	N-Substituent α δ	H	M	β,γ,... (m) δ	H	CH_3 (t,3H,J=6Hz)	Bu^t (s,9H)	CH_2CH_2[b] (m,4H)
2a	CH_2Ph	BF_4	6.9-8.4	14	7.32	6.45	2	s	-	-	-	1.80	2.7
2b	Pr^n	CF_3SO_3	7.5-8.3	9	7.83	5.2-5.3	2	m	0.7-1.5	2	0.71	1.76	2.85
2c	Bu^n	BF_4	7.6-8.4	9	7.82	5.2-5.3	2	m	0.7-1.5	4	0.70	1.76	2.85
2d	$CH_3(CH_2)_4$	BF_4	7.6-8.3	9	7.82	5.2-5.3	2	m	0.7-1.6	6	0.69	1.76	2.85
2e	$CH_3(CH_2)_5$	BF_4	7.5-8.4	9	7.81	5.2-5.3	2	m	0.7-1.6	8	0.68	1.76	2.85
2f	$CH_3(CH_2)_6$	BF_4	7.6-8.3	9	7.81	5.2-5.3	2	m	0.7-1.5	10	0.68	1.76	2.85

[a] In $CDCl_3$ solution; chemical shift (δ) in ppm; H = number of protons; M = multiplicity: s = singlet, t = triplet, m = multiplet. [b] α,β-Dihydronaphtho.

1370 cm^{-1}. For Me_2C-NO_2 a highly characteristic pattern of four bands at 1400, 1370, 1350 and 850 cm^{-1} is observed, little affected by the nature of the fourth substituent, whereas compounds of the type cyclo-$C_6H_{10}(R)NO_2$ show three absorptions at 1370, 1345, and 840 cm^{-1}.

Table 3. ^{13}C NMR Spectra[a] of 1-Substituted-2-(*t*-butyl)-5,6-dihydro-4-phenylbenzo[*h*]quinolinium Salts.

Quinolinium Salt	1-Substituent	Anion	Pyridinium Ring[b] C-2	C-3	C-4	C-4a	C-10b
2a	CH_2Ph	BF_4	165.4	124.7	156.6	127.4	156.6
2b	Pr^n	CF_3SO_3	164.4	125.6	155.5	127.9	156.4
2c	Bu^n	BF_4	164.2	125.6	156.2	127.9	155.2
2d	$CH_3(CH_2)_4$	BF_4	164.3	125.8	155.7	128.0	155.9
2e	$CH_3(CH_2)_5$	BF_4	164.2	125.6	155.2	127.8	156.3
2f	$CH_3(CH_2)_6$	BF_4	164.2	125.6	155.2	127.9	156.3

Quinolinium Salt	α,β-Dihydronaptho C-5	C-6	1-Substituent C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C-7'
2a	29.7	27.8	60.6[c]	-	-	-	-	-	-
2b	28.2	26.9	58.7	24.9	10.4	-	-	-	-
2c	28.3	26.6	57.1	33.3	19.2	12.9	-	-	-
2d	28.4	26.5	57.4	38.8	31.1	21.5	13.4	-	-
2e	28.3	26.7	57.2	38.7	31.3	25.6	21.8	13.5	-
2f	28.4	26.8	57.3	38.7	31.2	26.7	25.9	22.1	13.7

[a] In $CDCl_3$ solution; chemical shift in ppm; all the compounds showed also $C(CH_3)_3$: 38.9 (s), 31.4 (q). [b] Phenyl carbons appear in the range of 125.7 - 141.5. [c] Benzylic carbon.

^{1}H NMR Spectra of Nitroalkanes. The proton NMR spectra (Table 6) show the expected signals[1]. Chemical shifts depend on the position relative to the nitro group: α-protons absorb at 4.2-4.6 ppm, the β-CH_2 and -CH groups at 1.8-3.3 ppm, and the β-CH_3 group at 1.5-1.7 ppm.

^{13}C NMR Spectra of Nitroalkanes. The nitroalkanes were further characterised by ^{13}C NMR (Table 7). α-Carbons in the nitroalkanes resonate at 95.4-79.3 ppm, with β-methyl-carbons appearing at 28.7-22.7 ppm and 29.9-19.1 ppm for tertiary and secondary α-carbons respectively. The chemical shifts of β-methylene carbons appear at 52.6-36.5 ppm when attached to tertiary α-carbons and at 41.9-32.8 ppm when linked to a secondary α-carbon. An increasing upfield shift is observed for the carbons of the increasing *n*-alkyl chain of the nitroalkanes. Previous work[8], has shown that α-carbons of nitrocyclohexane, 2-nitrobutane, 2-nitropropane and 1-nitro-

Table 4 Preparation of Nitroalkanes by the Reactions of 1-Substituted-2-(*t*-butyl-4-phenyl-and-2,4-diphenyl)-5,6-dihydro-4-phenylbenzo[*h*]quinolinium Salts with Simple Nitronate Anions in DMSO

Quinolinium Salt	1-Substituent	Nitronate Anion	Nitroalkane[a]	Yield (%)	Reaction Conditions Time (h)	Temp (°C)	B.p. (°C/mmHg)	Lit. b.p. (°C/mmHg)	Lit. ref.
2a	CH_2Ph	4a	$PhCH_2C(CH_3)_2NO_2$	93	0.5	25	98-101/2	99-102/2	1
2b	Pr^n	4a	$Pr^nC(CH_3)_2NO_2$	83	3	50	69-72/6	-	-
		4b	$Pr^nCH(CH_3)NO_2$	75	5	50	58-60/20	148-149/760	9
		4d	cyclo-$C_6H_{10}(Pr^n)NO_2$	95	2	50	80-85/0.5	-	-
2c	Bu^n	4a	$Bu^nC(CH_3)_2NO_2$	82	5	50	56-62/2	55-60/2	1
		4b	$Bu^nCH(CH_3)NO_2$	75	6	50	62-64/20	64-66/20	10
		4c	$Bu^nCH_2NO_2$	62	8	60	50-52/20	90/100	11
		4d	cyclo-$C_6H_{10}(Bu^n)NO_2$	97	2	50	110-115/0.5	-	-
2d	$CH_3(CH_2)_4$	4a	$CH_3(CH_2)_4C(CH_3)_2NO_2$	85	3	50	72-75/1	-	-
		4b	$CH_3(CH_2)_4CH(CH_3)NO_2$	78	5	50	85-90/1	95/25	11
		4c	$CH_3(CH_2)_4CH_2NO_2$	63	8	60	60-61/1	91/50	11
		4d	cyclo-$C_6H_{10}[(CH_2)_4CH_3]NO_2$	98	2	50	120-121/0.6	-	-
2e	$CH_3(CH_2)_5$	4a	$CH_3(CH_2)_5C(CH_3)_2NO_2$	85	3	50	93-95/0.5	95-98/0.5	1
		4b	$CH_3(CH_2)_5CH(CH_3)NO_2$	78	5	50	81-83/4	102-105/23	10
		4c	$CH_3(CH_2)_5CH_2NO_2$	64	8	60	69-71/1	91/25	11
2f	$CH_3(CH_2)_6$	4a	$CH_3(CH_2)_6C(CH_3)_2NO_2$	86	3	50	100-140/0.5	-	-
		4b	$CH_3(CH_2)_6CH(CH_3)NO_2$	75	5	50	87-89/1	-	-
		4c	$CH_3(CH_2)_6CH_2NO_2$	64	9	60	76-78/1	106/20	11
3a	$CH_3(CH_2)_5$	4a	$CH_3(CH_2)_5C(CH_3)_2NO_2$	60	3	80	138-140/5	95-98/0.5	1
3b	Pr^i	4a	$Pr^iC(CH_3)_2NO_2$	50	24	65	70/15	42-43/5	1
		4b	$Pr^i CH(CH_3)NO_2$	36	15	75	50-52/20	88/100	11
		4d	cyclo-$C_6H_{10}(Pr^i)NO_2$	69	2.5	75	105-107/6	-	12
3c	cyclo-C_6H_{11}	4a	(cyclo-$C_6H_{11})C(CH_3)_2NO_2$	53	24	60	110-112/5	82-84/1	1
3d	neo-C_5H_{11}	4a	(neo-$C_5H_{11})C(CH_3)_2NO_2$	25	48	75	92-93/20	54/3	13

[a] All new compounds gave satisfactory elemental analysis: C (±0.3%), H (±0.25%) and N (±0.15%).

pentane appear at 84.7, 85.0, 78.7 and 76.1 ppm respectively in SO_2ClF at -60°C. As expected these chemical shifts are quite close to those found in the present work in $CDCl_3$.

Mass Spectra of Nitroalkanes. The mass spectra of aliphatic nitro compounds usually lack any discernible molecular ions, with the notable exception of nitromethane[14]. Loss of NO_2 with subsequent decomposition of the alkyl cation constitutes the most important fragmentation mode[15]. However, a moderate peak at m/e =30 and a weaker peak at m/e =46 corresponding to NO^+ and NO_2^+ are also characteristic of nitroalkanes[6].

Table 5. IR[a] Spectra of Nitroalkanes

Nitroalkane	ν_{NO_2} $\nu_{asym.}$	$\nu_{sym.}$	Other Absorptions
$(CH_3)_3CNO_2$	1535s	1377m	1355m, 855m
$4\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2$	1550s	1367m	1380s, 1350w, 860m
$PhCH_2C(CH_3)_2NO_2$	1540s	1370m	1380s, 1350w, 857m
$Pr^nC(CH_3)_2NO_2$	1532s	1372m	1401w, 1351m, 853m
$Pr^nCH(CH_3)NO_2$	1542s	1362m	1380m
$cyclo\text{-}C_6H_{10}(Pr^n)NO_2$	1530s	1370sh	1342m, 835w
$Bu^nC(CH_3)_2NO_2$	1539s	1375m	1400m, 1350s, 860w
$Bu^nCH(CH_3)NO_2$	1545s	1363m	1400m
$Bu^nCH_2NO_2$	1549s	1377m	1440w
$cyclo\text{-}C_6H_{10}(Bu^n)NO_2$	1532s	1375m	1345m, 840m
$CH_3(CH_2)_4C(CH_3)_2NO_2$	1532s	1378m	1405m, 1355s, 865w
$CH_3(CH_2)_4CH(CH_3)NO_2$	1541s	1368m	1340w
$CH_3(CH_2)_4CH_2NO_2$	1550s	1377m	1438w
$cyclo\text{-}C_6H_{10}[(CH_2)_4CH_3]NO_2$	1535s	1376m	1346m, 840w
$CH_3(CH_2)_5C(CH_3)_2NO_2$	1535s	1375m	1400m, 1350m, 855w
$CH_3(CH_2)_5CH(CH_3)NO_2$	1550s	1360m	1390s
$CH_3(CH_2)_5CH_2NO_2$	1549s	1378m	1435w
$CH_3(CH_2)_6C(CH_3)_2NO_2$	1535s	1370m	1395m, 1345m, 855m
$CH_3(CH_2)_6CH(CH_3)NO_2$	1547s	1365m	1322w
$CH_3(CH_2)_6CH_2NO_2$	1550s	1378m	1435w
$Pr^iC(CH_3)_2NO_2$	1540s	1373m	1400m, 1348m, 850m
$Pr^iCH(CH_3)NO_2$[b]	1535s	1380m	1358m
$cyclo\text{-}C_6H_{10}(Pr^i)NO_2$	1525s	1370m	1343m, 840m
$(cyclo\text{-}C_6H_{11})C(CH_3)_2NO_2$	1530s	1372m	1395m, 1340m, 848m
$(neo\text{-}C_5H_{11})C(CH_3)_2NO_2$[b]	1545s	1365m	1455m, 1340m, 845w

[a] Neat; s = strong, m = medium, w = weak, sh = shoulder. [b] In $CHBr_3$

In line with this previous work, we observed no molecular ion peaks, but did see weak peaks at m/e =30 and 46. As expected, major fragment ions were derived by loss of NO_2 (Table 8), but an interesting feature of the mass spectra of the nitroalkanes was the fission of the C_α-C_β bond in compounds $RCH_2CH_2CMe_2NO_2$, with simultaneous migration of a proton to yield $C_3H_7NO_2^+$, probably as $(CH_3)_2C{=}NOOH^+$ with elimination of an olefin. This type of fragmentation was previously observed in the mass spectrum of nitrobutane[15]. Accurate masses of the main fragments were determined (Table 8).

Table 6. ^1H NMR Spectra[a] of Nitroalkanes

	α			β(CH_3)			β(CH_2)			γ			ω(CH_3)		
Nitroalkane	δ[b]	H[c]	M[d,e]	δ	H[b]	M[c]	δ[b]	H[c]	M[d]	δ[b]	H[c]	M[d]	δ[b]	H[c]	M[d]
$(CH_3)_3CNO_2$	-	-	-	1.58	9	s	-	-	-	-	-	-	-	-	-
$4\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2$	-	-	-	1.62	6	s	3.28	2	s	7.50	4	m	-	-	-
$PhCH_2C(CH_3)_2NO_2$	-	-	-	1.60	6	s	3.25	2	s	7.30	5	s	-	-	-
$Pr^nC(CH_3)_2NO_2$	-	-	-	1.52	6	s	1.90	2	m	1.26	2	m	0.97	3	t
$Pr^nCH(CH_3)NO_2$	4.50	1	m	1.54	3	d	2.25	2	m	1.25	2	m	0.85	3	t
cyclo-$C_6H_{10}(Pr^n)NO_2$	-	-	-	-	-	-	2.32	2	m	0.90-2.0[f]	12	m	0.85	3	t
$Bu^nC(CH_3)_2NO_2$	-	-	-	1.51	6	s	1.98	2	m	1.18-2.0	6	m	0.83	3	t
$Bu^nCH(CH_3)NO_2$	4.45	1	m	1.50	3	d	2.2	2	m	1.19-2.0	6	m	0.79	3	t
$Bu^nCH_2NO_2$	4.63	2	t	-	-	-	2.02	2	m	1.10-1.94	4	m	0.92	3	t
cyclo-$C_6H_{10}(Bu^n)NO_2$	-	-	-	-	-	-	2.32	2	m	0.98-2.0[f]	14	m	0.91	3	t
$CH_3(CH_2)_4C(CH_3)_2NO_2$	-	-	-	1.55	6	s	2.0	2	m	1.19-1.85	6	m	0.85	3	t
$CH_3(CH_2)_4CH(CH_3)NO_2$	4.45	1	m	1.56	3	d	2.29	2	m	1.18-2.08	6	m	0.84	3	t
$CH_3(CH_2)_4CH_2NO_2$	4.62	2	t	-	-	-	2.01	2	m	1.69-2.0	6	m	0.93	3	t
cyclo-$C_6H_{10}[(CH_2)_4CH_3]NO_2$	-	-	-	-	-	-	2.35	2	m	0.97-2.0[f]	16	m	0.89	3	t
$CH_3(CH_2)_5C(CH_3)_2NO_2$	-	-	-	1.61	6	s	2.0	2	m	1.18-1.95	8	m	0.79	3	t
$CH_3(CH_2)_5CH(CH_3)NO_2$	4.46	1	m	1.59	3	d	2.29	2	m	1.13-2.0	8	m	0.78	3	t
$CH_3(CH_2)_5CH_2NO_2$	4.49	2	t	-	-	-	2.09	2	m	1.10-2.0	8	m	0.79	3	t
$CH_3(CH_2)_6C(CH_3)_2NO_2$	-	-	-	1.59	6	s	2.0	2	m	1.12-1.89	10	m	0.77	3	t
$CH_3(CH_2)_6CH(CH_3)NO_2$	4.45	1	m	1.57	3	d	2.29	2	m	1.17-2.09	10	m	0.76	3	t
$CH_3(CH_2)_6CH_2NO_2$	4.43	2	t	-	-	-	2.13	2	m	1.05-2.0	10	m	0.79	3	t
$Pr^iC(CH_3)_2NO_2$[g]	-	-	-	1.5	6	s	-	-	-	0.95	6	d	-	-	-
$Pr^iCH(CH_3)NO_2$[g]	4.15-4.60			1.5	3	d	-	-	-	1.00	6	d	-	-	-
cyclo-$C_6H_{10}(Pr^i)NO_2$[h]	-	-	-	-	-	-	-	-	-	1.05-2.65	10	m	-	-	-
										0.95	6	d			
(cyclo-$C_6H_{11})C(CH_3)_2NO_2$	-	-	-	1.5	6	s	-	-	-	0.65-2.3	11	m	-	-	-
(neo-$C_5H_{11})C(CH_3)_2NO_2$	-	-	-	1.65	6	s	2.0	2	s	-	-	-	0.95	9	s

[a] In $CDCl_3$ solution. [b] δ = chemical shift in ppm. [c] H = number of protons. [d] M = multiplicity: s = singlet, d = doublet, t = triplet, and m = multiplet. [e] The coupling constants of all doublets and triplets was 7 Hz. [f] This multiplet also contains protons of the cyclohexane ring which overlap with the protons of *n*-alkyl chain. [g] β(CH) at 1.95-2.65 (m). [h] β(CH) at 1.8-2.3 (m).

Table 7. ^{13}C NMR Spectra[a] of Nitroalkanes

Nitroalkane	C-1	C-2 (CH_3)	C-2 (CH_2, CH)	C-3	C-4	C-5	C-6	C-7	C-8	C-a[b]	C-b[b]	C-c[b]
$PhCH_2C(CH_3)_2NO_2$[c]	88.4	25.2	46.4	-	-	-	-	-	-	-	-	-
$Pr^nC(CH_3)_2NO_2$	88.3	25.7	43.1	17.5	13.9	-	-	-	-	-	-	-
$Pr^nCH(CH_3)NO_2$	83.3	25.7	41.9	17.2	14.0	-	-	-	-	-	-	-
cyclo-$C_6H_{10}(Pr^n)NO_2$	91.4	-	42.7	16.4	13.8	-	-	-	-	34.0	22.3	24.8
$Bu^nC(CH_3)_2NO_2$	88.2	25.5	41.9	23.2	19.8	13.7	-	-	-	-	-	-
$Bu^nCH(CH_3)NO_2$	83.4	27.6	34.7	22.0	19.0	13.6	-	-	-	-	-	-
$Bu^nCH_2NO_2$	79.3	-	30.5	22.3	19.3	13.9	-	-	-	-	-	-
cyclo-$C_6H_{10}(Bu^n)NO_2$	91.5	-	40.3	22.4	22.3	13.6	-	-	-	34.0	22.0	24.8
$CH_3(CH_2)_4C(CH_3)_2NO_2$	88.0	25.4	40.7	31.4	23.5	22.1	13.6	-	-	-	-	-
$CH_3(CH_2)_4CH(CH_3)NO_2$	83.5	29.5	33.5	22.9	22.3	16.8	13.2	-	-	-	-	-
$CH_3(CH_2)_4CH_2NO_2$	79.7	-	29.7	23.2	21.9	17.1	14.1	-	-	-	-	-
cyclo-$C_6H_{10}[(CH_2)_4CH_3]NO_2$	91.1	-	40.3	23.7	22.4	22.0	13.4			33.7	22.0	24.6
$CH_3(CH_2)_5C(CH_3)_2NO_2$	88.2	25.6	40.9	31.3	29.0	23.9	22.3	13.8	-	-	-	-
$CH_3(CH_2)_5CH(CH_3)NO_2$	83.4	29.7	33.0	23.5	22.9	21.9	15.9	12.9	-	-	-	-
$CH_3(CH_2)_5CH_2NO_2$	79.6	-	29.6	23.8	22.5	21.8	16.2	14.2	-	-	-	-
$CH_3(CH_2)_6C(CH_3)_2NO_2$	88.1	25.6	40.8	31.5	29.3	28.8	23.9	22.4	13.8	-	-	-
$CH_3(CH_2)_6CH(CH_3)NO_2$	83.7	29.9	32.9	27.9	26.0	22.7	20.6	14.8	12.6	-	-	-
$CH_3(CH_2)_6CH_2NO_2$	79.8	-	29.9	26.6	25.9	22.3	19.6	15.1	14.1	-	-	-
$Pr^i\,C(CH_3)_2NO_2$	92.0	22.7	36.5	17.1	-	-	-	-	-	-	-	-
$Pr^i\,CH(CH_3)NO_2$	89.0	19.1	32.8	16.0 17.8	-	-	-	-	-	-	-	-
cyclo-$C_6H_{10}(Pr^i)NO_2$	95.4	-	37.4	17.2	-	-	-	-	-	31.0	22.3	24.9
(cyclo-C_6H_{11})$C(CH_3)_2NO_2$	92.1	22.9	46.8	-	-	-	-	-	-	27.4	26.1	25.9
(neo-C_5H_{11})$C(CH_3)_2NO_2$	87.3	28.1	52.6	31.4	30.2	-	-	-	-	-	-	-

[a] In $CDCl_3$; chemical shift in ppm [b] Carbons of cyclohexane ring.

[c] Aromatic carbons appear at 134.8, 129.8, 128.2 and 127.1 ppm

EXPERIMENTAL

M.ps. were determined with a "Hot Stage" apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 283B spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM 360L spectrometer, ^{13}C NMR on a Jeol FX-100 spectrometer, and mass spectra (MS) on a AEI MS30 mass spectrometer.

The following compounds were prepared by the literature method quoted: 2-(*t*-butyl)-5,6-dihydro-4-phenylbenzo[*h*]chromenylium tetrafluoroborate (1a), m.p. 178-180°C (lit.[16], m.p. 175-176°C) ; 2-(*t*-butyl)-5,6-dihydro-4-phenylbenzo[*h*]chromenylium trifluoromethanesulphonate (1b), m.p. 205-207°C (lit.[17], m.p. 203°C); 5,6-dihydro-2,4-diphenylbenzo[*h*]chromenylium tetrafluoroborate (1c), m.p. 268-270°C (lit.[17], m.p. 270°C); 1-benzyl-2-(*t*-butyl)-5,6-dihydro-4-phenyl-

Table 8 Mass Spectra of Nitroalkanes[a]

Nitroalkane	Molecular Formula	Molecular Weight	Fragment Ion (Intensity %)		Accurate Mass Calculated m/e	Accurate Mass Found m/e
$Pr^{n}C(CH_3)_2NO_2$	$C_6H_{13}NO_2$	131.17	$C_3H_7NO_2^+$	(73)	89.048	89.048
			$C_6H_{13}^+$	(65)	85.102	85.102
$Bu^{n}C(CH_3)_2NO_2$	$C_7H_{15}NO_2$	145.20	$C_3H_7NO_2^+$	(72)	89.048	89.048
			$C_7H_{15}^+$	(68)	99.197	99.196
$CH_3(CH_2)_4C(CH_3)_2NO_2$	$C_8H_{17}NO_2$	159.23	$C_3H_7NO_2^+$	(76)	89.048	89.048
			$C_8H_{17}^+$	(64)	113.133	113.133
$CH_3(CH_2)_5C(CH_3)_2NO_2$	$C_{10}H_{21}NO_2$	187.28	$C_3H_7NO_2^+$	(75)	89.048	89.048
			$C_{10}H_{21}^+$	(69)	141.164	141.164
$PhCH_2C(CH_3)_2NO_2$[b]	$C_{10}H_{13}NO_2$	179.21	$C_{10}H_{13}^+$	(80)	133.102	133.101
cyclo-$C_6H_{10}(Pr^{i})NO_2$	$C_9H_{17}NO_2$	171.24	$C_9H_{17}^+$	(87)	125.133	125.133

[a] Other characteristic peaks of nitroalkanes were observed for $\overset{+}{NO}$ (m/e = 30) (7%) , $\overset{+}{NO}_2$ (m/e = 46) (2%) and $C_3\overset{+}{H}_7$ (m/e = 43) (100%, last example 19.8%).

[b] Additional peak for $PhCH_2$ (m/e=91) (100%) was also observed.

benzo[*h*]quinolinium tetrafluoroborate (2a), m.p. 149-151°C (lit.[4], m.p. 145-147°C); 1-(*n*-butyl)-2-(*t*-butyl)-5,6-dihydro-4-phenylbenzo[*h*]quinolinium tetrafluoroborate (2c), m.p. 141-142°C (lit.[4], m.p. 142-144°C); 1-cyclohexyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborate (3c), m.p. 133-135°C (lit.[18], m.p. 136-139°C); 1-neopentyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborate (3d), m.p. 225-227°C (lit.[19], m.p. 228-230°C).

General procedure for the preparation of **2b**, **2d-f**. To a suspension of the chromenylium salt (10 mmol) in CH_2Cl_2 (20 ml) the appropriate amine (20 mmol) was added dropwise at 25°C. The reaction mixture was stirred for the time given (Table 1), then EtOH (10 ml) was added and the product precipitated with cold Et_2O. Recrystallisation from EtOH (2b) or Me_2CO/Et_2O (2d-f) afforded the quinolinium salts as needles.

1-n-Hexyl- and -1-isopropyl-5,6-dihydro-2,4-diphenylbenzo[h]quinolinium tetrafluoroborate 3a,b. To a suspension of the chromenylium salt (10 mmol) in CH_2Cl_2 (20 ml) the appropriate amine (10 mmol) was added at 25°C, followed by NEt_3 (10 mmol). After 3 h, HOAc (10 mmol) was added, and the reaction mixture stirred for another 5 h. The product was precipitated with Et_2O/EtOH (30:1) and recrystallised from EtOH/Et_2O to give the title salts. [Compound 3a as light yellow prisms (74%); m.p. 129-131 °C; Found: C, 73.6; H, 6.4; N, 2.7; $C_{31}H_{32}BF_4N$ requires C, 73.7; H, 6.4; N, 2.8]: $\nu_{max.}$ ($CHBr_3$) 1610, 1595, 1040 cm^{-1} (BF_4^-); ^1H NMR δ ($CDCl_3$) 0.5-1.6 (11 H,m), 2.95 (4 H,s), 5.20 (2 H,t), 7.5-8.6 (15 H,m). Compound 3b as light yellow plates (62%); m.p. 140°C (dec.); Found: C, 72.7; H, 5.7; N, 3.0; $C_{28}H_{26}BF_4N$ requires: C, 72.6; H, 5.7;

N, 3.0%; ν_{max} ($CHBr_3$) 1605, 1595, 1040 cm^{-1} (BF_4^-): ^1H NMR δ ($CDCl_3$) 1.45 (6 H, d, J=7Hz, 2.90 (4 H,s), 5.55 (1 H, h, J=7Hz), 7.2-8.1 (15 H,m)].

General procedure for the preparation of nitroalkanes. Sodium hydride (0.72 g, 30 mmol) was dissolved in MeOH (10 ml), and the appropriate nitroalkane (30 mmol) was added with stirring. After removal of the solvent *in vacuo*, the resulting white solid was mixed with the quinolinium salt (10 mmol) and suspended in DMSO (25 ml). The mixture was flushed with nitrogen and stirred for the time and at the temperature given (Table 4). On cooling down, the quinoline separated partially and was filtered off. The filtrate was added to H_2O (50 ml), extracted with Et_2O (3 x 25 ml) and the extract dried over anhydrous $MgSO_4$. Dry HCl gas was passed to remove residual quinoline from the solution, the salt was filtered off, Et_2O was removed and the crude prodouct distilled *in vacuo*, yielding the pure nitroalkanes.

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