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The Nitration of α- and β-Acylnaphthalenes

Steven D. Barker,[A] *Karen Wilson*[A] *and Robert K. Norris*[A,B]

[A] Division of Organic Chemistry, The School of Chemistry,
The University of Sydney, N.S.W. 2006.
[B] Author to whom correspondence should be addressed.

Abstract

The nitration of α- and β-acylnaphthalenes with copper(II) nitrate in acetic anhydride or nitric acid/acetic acid mixtures gives high yields of the corresponding mononitro compounds. The assignment of constitution to these products is made on the basis of extensive ^{1}H n.m.r. chemicl shift and coupling constant data. In the case of α-acylnaphthalenes, with the notable exception of α-pivalonaphthone, nitration occurs in the α-positions of the unsubstituted ring to give mixtures of 5- and 8-nitro compounds. α-Pivalonaphthone gives appreciable amounts of the 4-nitro compound and also of the 8-nitro compound. This result indicates that the pivaloyl group does not shield the 8-position sterically to any significant extent and is effectively electronically neutral, unlike the other acyl substituents, in allowing attack at the α-position (position 4) of the acylated ring. This result is ascribable to the lack of coplanarity of the pivaloyl group with the naphthalene system. All of the β-acylnaphthalenes gave mixtures of 4-, 5- and 8-nitro derivatives in proportions that did not vary significantly with the nature of the acyl group.

Introduction

As part of a study on the dehalogenation of anion radicals,[1] and a study of the $S_{RN}1$ reaction in some naphthalene derivatives[2] we nitrated 1-pivalonaphthone (1c)[1,2] and 2-pivalonaphthone (2c).[2] A mixture of mononitro compounds resulted. Since we required only the 5-nitro compound (3c) in the dehalogenation study, the proportions of the other isomers was not reported.[1] In another study, we found that nitration of pivalophenone gave a quite anomalous product distribution (ratio of *o*-, *m*- and *p*-nitro compounds was 30 : 44 : 26) when compared with that obtained from nitration of other acylbenzenes.[3] It was of interest to see if this anomalous directing effect was in evidence when the pivaloyl group was attached to the naphthalene nucleus. It quickly became apparent, however, that, unlike studies on the benzene system, the nitration of acylnaphthalenes in general had been studied to only a very limited extent.[4–7] The nitration of

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[2] Barker, S. D., Ph.D. Thesis, The University of Sydney, December 1982.
[3] Barker, S. D., Norris, R. K., and Randles, D., *Aust. J. Chem.*, 1981, **34**, 1875.
[4] Bamberger, E., and Lodter, W., *Ber. Dtsch. Chem. Ges.*, 1888, **21**, 256.
[5] Ruggli, P., and Burckhardt, E., *Helv. Chim. Acta*, 1940, **23**, 441.
[6] Sergievskaya, S. I., and Levshina, K. V., *J. Gen. Chem. (Engl. Transl.)*, 1950, **20**, 1071.
[7] Spiteller, G., and Derkosch, J., *Monatsh. Chem.*, 1959, **90**, 634.

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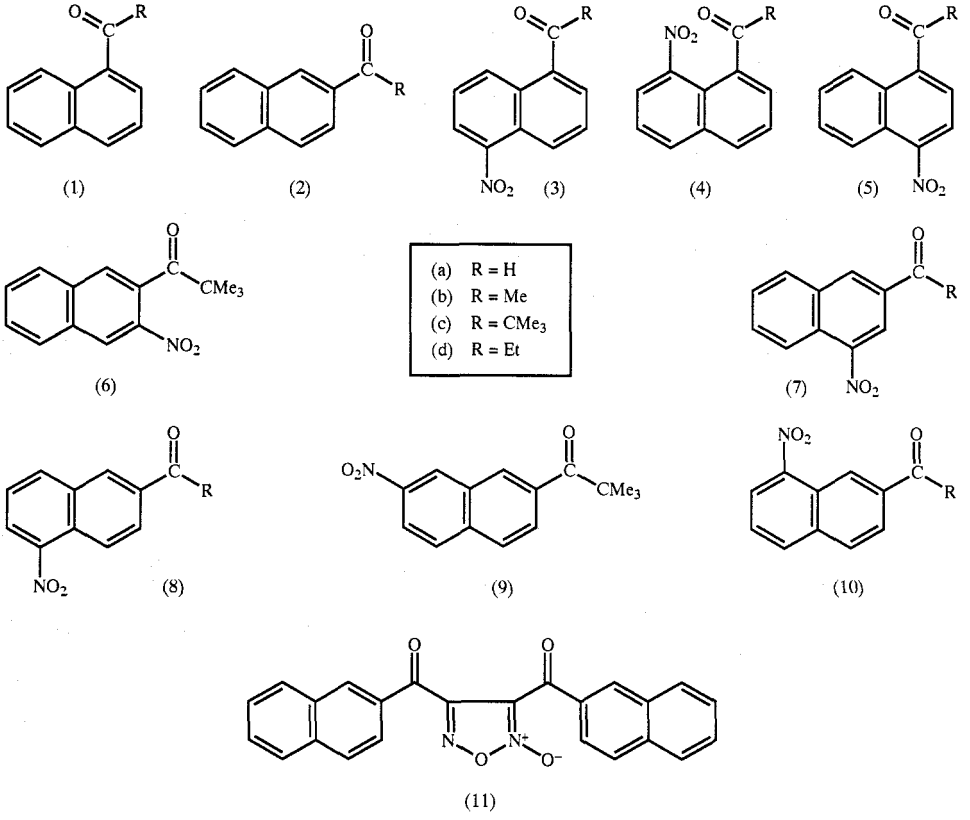
α-naphthaldehyde (1a) with nitric acid has been reported to give mixtures of the 5- and 8-nitro derivatives (3a) and (4a) respectively. The highest isolated yields and consequently the best estimate of proportions of these products gave (3a) 45%, and (4a) 34%. Spiteller and Derkosch also reported the nitration of the α-acetyl derivative (1b), which gave mixtures of the 5- and 8-nitro compounds (3b) and (4b), and the similar nitration of the corresponding α-benzoyl derivative.[7] To the best of our knowledge, the nitration of β-acylnaphthalenes has not been reported. The nitration of 2-(methoxymethyl)naphthalene that gave 8-nitronaphthalene-2-carbaldehyde (isolated in low yield) was presumed to proceed through the free aldehyde (2a), but this reaction was not studied in any detail.[8]

We here report the nitration of the α- and β-acylnaphthalenes (1a–c) and (2a–d) respectively.



Results and Discussion

Nitration Reactions of α- and β-Acylnaphthalenes

The results from these nitration reactions are summarized in Table 1. The mononitro products isolated in the α-acyl series were the 4-nitro (5), 5-nitro (3) and 8-nitro (4) compounds, and in the β-acyl series were the 3-nitro (6), 4-nitro (7), 5-nitro (8), 7-nitro (9) and 8-nitro (10) derivatives. The best reagent for nitration of the aldehydes (1a) and (2a) was found to be fuming nitric acid

[8] Markees, D. G., *Helv. Chim. Acta.*, 1973, **56**, 1382.

in glacial acetic acid containing catalytic amounts of sulfuric acid (see entries 1 and 5 in Table 1). In the nitration of the ketones (1b), (2b) and (2d), the use of fuming or concentrated nitric acid alone or in mixtures with sulfuric or acetic acids or with acetic anhydride as cosolvent often gave reactions which were difficult to control, gave dinitrated products, or gave other products. For example, the reaction of the ketone (2b) with concentrated (*c.* 16 M) nitric acid in acetic acid (or acetic anhydride), gave the furazan oxide (11) in moderate yield. The formation of bis(arylcarbonyl)furazan 2-oxides from the reaction of aryl methyl ketones with nitric acid is well documented.[9] The conclusion of (11) was deduced from its mass spectrum (*m/z* 394), elemental analysis (consistent with formula $C_{24}H_{14}N_2O_4$) and its 400-MHz ^1H n.m.r. spectrum (see Experimental). The reagent of choice for nitration of all the naphthalenyl alkyl ketones was found to be copper(II) nitrate in acetic anhydride (Table 1, entries 2,3, 6-8). The yields of mononitrated products generally were high and the proportion of dinitration and other unwanted side-products (≤6%) was very low. The t-butyl ketones (1c) and (2c), which did not undergo oxidation reactions in the alkyl side chain, could also be nitrated with nitric acid in acetic acid. The results of these nitrations have been given in entries 4 and 9 (Table 1) for (1c) and (2c) respectively, for comparison with the results obtained with the copper(II) nitrate method. The $Cu(NO_3)_2/Ac_2O$ procedure could not be used with the aldehydes (1a) and (2a) since they were converted into the corresponding geminal diacetoxy derivatives by this reagent.

The products from the nitration reactions were separated by chromatography and were identified by ^1H n.m.r. spectroscopy (see below) and fully characterized in the usual way (see Experimental).

The results from nitration of the 1-acyl derivatives (1a) and (1b) (Table 1, entries 1 and 2) are in line with the general expectation that electrophilic attack

Table 1. Distribution of products from nitration of α- and β-acylnaphthalenes

The proportions of products were estimated by ^1H n.m.r. spectroscopy with 2,4,6-trinitrotoluene as internal standard. All estimations were performed at least in triplicate

Entry	Substrate	Conditions[A]	Proportions (%) of products			Overall yield (%)
			4-NO_2	5-NO_2	8-NO_2	
1	(1a)	*A*	<2	42±2	58±2	91–97
2	(1b)	*B*	<2	29±3	71±4	81–88
3	(1c)	*B*	26±3	36±3	38±3	86–93
4	(1c)	*C*	25±3	46±4	29±3	85–95
5	(2a)	*A*	9±1	46±4	45±4	89–93
6	(2b)	*B*	22±3	40±4	38±4	90–95
7	(2d)	*B*	21±3	41±4	38±4	90–95
8	(2c)[B]	*B*	12±3	44±4	36±4	>95
9	(2c)	*D*	7±3	51±4	42±4	60–65

[A] The following reagents were used (see Experimental for details): *A*, fuming nitric acid/sulfuric acid (18 M)/acetic acid (17 M); *B*, copper(II) nitrate in acetic anhydride; *C*, fuming nitric acid/acetic acid (17 M); *D*, nitric acid (15 M)/sulfuric acid (18 M)/acetic acid (17 M).
[B] 4±1% of the 3-nitro compound (6) and 4±1% of the 7-nitro compound (9) were detected.

[9] Tezuka, H., Kato, M., and Sonehara, Y., *J. Chem. Soc., Perkin Trans. 2*, 1985, 1643, and references cited therein.

on naphthalenes with deactivating *meta*-directing groups would be expected to take place in the 5- and 8-positions, as found, for example, in 1-nitronaphthalene and 1-naphthoic acid.[10a] The change in the ratio of 5- to 8-nitration from 42:58 to 29:71 on replacement of the hydrogen in the aldehyde (1a) by a methyl group on the ketone (1b) is in the opposite direction to that expected for a steric effect and is presumably the result of some subtle stereoelectronic effect.

Since none of the 4-nitro isomer (5a) could be isolated from the nitration of α-naphthaldehyde, an authentic sample was prepared.[11] The crude product from nitration of 1-naphthaldehyde was examined by h.p.l.c. and none (<0·5%) of the 4-nitro compound (5a) could be detected and so the significant result in the series of nitration of 1-acylnaphthalenes is the considerable amount of nitration in the 4-position in the t-butyl ketone (1c) under both acidic and relatively non-acidic conditions (entries 3 and 4). The pivaloyl group clearly does not deactivate the 4-position electronically and, consistent with the result noted above, does not appear to shield the *peri*-position from attack to any significant extent, since the proportion of nitration in the 8-position relative to that in the 5-position is similar for the aldehyde (1a) and the t-butyl ketone (1c) (see entries 1 and 3, Table 1). The absence of deactivation of the 4-position is consistent with the pivaloyl group being out of the plane of the naphthyl ring and, as a consequence, being unable significantly to deactivate the ring to which it is attached. The high proportion of *m*-nitration in pivalophenone has been rationalized similarly.[2,3] Further, physical measurements on α-pivalonaphthone (1c), and also β-pivalonaphthone (2c) confirm that the pivaloyl groups are out of the plane of the naphthalene ring by 90±10 and 53±8° respectively.[12]

The nitration of the 2-acyl derivatives would be expected to take place in the 5- and/or 8-positions in accord with the generalization based on fairly limited data that *m*-directing substituents on the 2-position of naphthalene rings appear to direct substitution into these positions. This orientation behaviour is demonstrated in the bromination (5-position) and nitration (5- and 8-positions) of 2-nitronaphthalene and naphthalene-2-carboxylic acid.[10b] In fact, the 2-acyl derivatives, (2a–d) used in this study gave mixtures of 4-, 5- and 8-nitro compounds, with the 5- and 8-substituted products predominating and being formed in near equal amounts (in proportion in the range 36–51%) regardless of the nature of the acyl group. Furthermore the ratio of substitution in the 5- and 8-positions did not vary in any systematic or significant fashion down the series. The proportion of substitution in the 4-position did vary with changes in the acyl group, but in a somewhat inexplicable and fairly minor fashion. The 2-formyl and 2-pivaloyl derivatives, presumably with the largest difference in electronic and steric properties, are nitrated to the extent of 7–12% in the 4-position, whereas the 2-acetyl and 2-propionyl analogues give rise to about 20% nitration at the 4-position. Clearly, in contrast with the α-acylnaphthalenes, the variation in nature of the acyl substituent does not significantly affect the proportion of 4-, 5- and 8-nitration in the β-acylnaphthalenes.

[10] de la Mare, P. B. D., and Ridd, J. H., 'Aromatic Substitution, Nitration and Halogenation' (*a*) p. 178; (*b*) p. 179 (Butterworths: London 1959).
[11] Sergievskaya, S. I., and Elina, A. S., *J. Gen. Chem. USSR*, 1943, **13**, 868 (*Chem. Abstr.*, 1945, **39**, 1158).
[12] Mirarchi, D., and Ritchie, G. L. D., *Aust. J. Chem.*, 1982, **35**, 2341.

^1H N.M.R. Spectra of Nitrated α- and β-Acylnaphthalenes

The constitution of the various nitrated acylnaphthalenes isolated in this study, together with that of an independently prepared sample of 4-nitro-1-naphthaldenhyde,[11] were assigned by ^1H n.m.r. spectroscopy, and the data are presented in Table 2 (chemical shifts) and Table 3 (coupling constants). These data form a very self-consistent set, and in most cases assignment of structure and of individual resonances was straightforward and was based on the multiplicity of signals and magnitude of coupling constants, together with the expected downfield shift of resonances for protons *ortho* or *peri* to the nitro and acyl groups, although in some cases downfield shifts were not observed (see below). In the case of coupling constants, the values for $J_{2,3}$ and $J_{6,7}$ ($J_{\beta,\beta'}$) were in the range 6·9–7·8 Hz, whilst $J_{3,4}$ and $J_{7,8}$ ($J_{\alpha,\beta}$) were in the different range 8·1–9·2 Hz,

Table 2. ^1H n.m.r. chemical shift data for mononitro α- and β-acylnaphthalenes

Chemical shifts were obtained on approximately 5% solutions (w/v) and are measured in ppm downfield from internal tetramethylsilane

Compound	Chemical shift (ppm)[A] for position 1	2	3	4	5	6	7	8
(3a)	10·40[B]	8·13	7·89	8·76	[C]	8·26	7·77	9·63
(4a)	10·14[B]	8·12	7·76	8·16	8·16	7·65	8·13	[C]
(5a)	10·50[B]	8·06	8·14	[C]	8·33	7·76	7·80	9·26
(7a)	8·61	10·21[B]	8·62	[C]	8·56	7·89	7·76	8·15
(8a)	8·47	10·23[B]	8·18	8·70	[C]	8·39	7·70	8·32
(10a)	9·13	10·12[B]	8·13	8·08	8·22	7·75	8·38	[C]
(3b)	2·78[D]	8·05	7·73	8·62	[C]	8·18	7·65	8·99
(4b)	2·73[D]	7·90	7·62	8·09	8·01	7·56	8·06	[C]
(7b)	8·67	2·77[D]	8·69	[C]	8·52	7·82	7·71	8·09
(8b)	8·55	7·76[D]	8·23	8·64	[C]	8·35	7·65	8·26
(10b)	9·19	2·77[D]	8·18	8·03	8·17	7·69	8·31	[C]
(3c)	1·32[E]	7·50	7·71	8·53	[C]	8·20	7·58	7·90
(4c)	1·52[E]	7·93	7·58	7·97	8·07	7·54	8·00	[C]
(5c)	1·32[E]	7·39	8·17	[C]	8·54	7·74	7·64	7·68
(6)	7·70	1·32[E]	[C]	8·79	8·05	7·69	7·75	7·94
(7c)	8·55	1·45[E]	8·61	[C]	8·57	7·82	7·70	8·06
(8c)	8·28	1·42[E]	8·00	8·62	[C]	8·32	7·62	8·20
(9)	8·75	1·33[E]	7·85	7·88	7·88	8·19	[C]	8·75
(10c)	9·03	1·44[E]	7·88	8·01	8·16	7·65	8·33	[C]
(7d)	8·70	[F]	8·73	[C]	8·54	7·83	7·71	8·09
(8d)	8·56	[G]	8·23	8·63	[C]	8·34	7·64	8·25
(10d)	9·20	[H]	8·19	8·03	8·17	7·68	8·31	[C]

[A] The chemical shifts are those of the proton on the stated position or of the alkyl group on the carbonyl group attached to the stated position.
[B] CHO group.
[C] NO_2 group.
[D] COMe group.
[E] $COMe_3$ group.
[F] δ 1·31 (Me, t, *J* 7·2 Hz); 3·17 (CH_2, q, *J* 7·2 Hz).
[G] δ 1·30 (Me, t, *J* 7·2 Hz); 3·16 (CH_2, q, *J* 7.2).
[H] δ 1·30 (Me, t, *J* 7·2 Hz); 3·18 (CH_2, q, *J* 7·2 Hz).

Table 3. Proton–proton coupling constants in mononitro α- and β-acylnaphthalenes

Compound	Proton–proton coupling constants (Hz)														
	$J_{1,3}$	$J_{1,4}$	$J_{1,5}$	$J_{1,8}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{4,5}$	$J_{4,8}$	$J_{5,6}$	$J_{5,7}$	$J_{5,8}$	$J_{6,7}$	$J_{6,8}$	$J_{7,8}$
(3a)	—	—	—	—	7·2	1·1	8·9	—	0·8	—	—	—	7·7	1·2	8·7
(4a)	—	—	—	—	7·2	1·2	8·3	[A]	—	8·5	1·2	—	7·5	—	—
(5a)[B]	—	—	—	—	7·7	—	—	—	—	8·6	1·5	[A]	7·2	1·5	8·3
(7a)	1·5	—	0·6	0·6	—	—	—	—	—	8·7	1·1	0·5	7·1	1·4	8·3
(8a)[C]	1·8	0·6	—	0·6	—	—	9·1	—	0·7	—	—	—	7·7	1·2	8·2
(10a)[C]	1·5	0·7	0·8	—	—	—	8·6	0·7	—	8·3	1·2	—	7·7	—	—
(3b)	—	—	—	—	7·3	1·1	8·8	—	0·8	—	—	—	7·7	1·1	8·8
(4b)	—	—	—	—	7·2	1·2	8·3	0·5	—	8·3	1·1	—	7·6	—	—
(7b)	1·5	—	0·6	0·6	—	—	—	—	—	8·5	1·1	0·5	6·9	1·3	8·1
(8b)	1·8	0·5	—	0·5	—	—	9·2	—	0·6	—	—	—	7·7	1·2	8·3
(10b)	1·6	0·6	0·7	—	—	—	8·6	0·5	—	8·3	1·1	—	7·7	—	—
(3c)	—	—	—	—	7·1	1·2	8·8	—	0·9	—	—	—	7·6	1·2	8·5
(4c)	—	—	—	—	7·3	1·1	8·2	[A]	—	8·3	1·3	—	7·6	—	—
(5c)[B]	—	—	—	—	7·8	—	—	—	—	8·6	1·2	0·7	7·4	1·6	8·7
(6)	—	0·7	0·7	0·6	—	—	—	0·7	0·7	8·2	1·3	0·7	6·9	1·3	8·2
(7c)[D]	1·7	—	0·8	0·7	—	—	—	—	—	8·7	1·1	0·5	6·9	1·3	8·2
(8c)	1·8	0·6	—	0·5	—	—	8·9	—	0·6	—	—	—	7·6	1·2	8·2
(9)	1·5	0·6	0·7	0·6	—	—	8·7	0·6	0·7	9·0	—	0·6	—	2·2	—
(10c)	1·6	0·7	0·7	—	—	—	8·6	0·5	—	8·3	1·2	—	7·7	—	—
(7d)	1·7	—	0·7	0·7	—	—	—	—	—	8·8	1·1	0·6	7·1	1·3	8·3
(8d)	1·8	0·6	—	0·5	—	—	9·1	—	0·7	—	—	—	7·7	1·2	8·3
(10d)	1·6	0·6	0·8	—	—	—	8·7	0·7	—	8·3	1·1	—	7·7	—	—

[A] This coupling could not be resolved.
[B] H6 and H7 are tightly coupled and first-order analysis may lead to errors of ±0·3 Hz.
[C] $J_{4,CHO}$ 0·7 Hz.
[D] $J_{1,7} = J_{3,7} = 0·15$ Hz.

consistent with the general rule that in naphthalene systems $J_{\beta,\beta'} < J_{\alpha,\beta}$.[13] The J_{meta} coupling constants, $J_{1,3}$ (1·5–1·8 Hz), $J_{2,4}$ (1·1–1·2 Hz), $J_{5,7}$ (1·1–1·5 Hz) and $J_{6,8}$ (1·1–1·6 Hz and one value of 2·2 Hz), fall into relatively narrow ranges. The significantly larger value for $J_{6,8}$ (2·2 Hz) in compound (9) is consistent with the fact that in this compound only is there a nitro group between the *meta*-coupled protons. The remaining coupling constants, J_{para} and cross-ring coupling constants, were small (≤0·8 Hz), were determined by double-irradiation experiments and in all cases confirmed the assigned structures.

The assignment of chemical shifts, based on splitting patterns and expected deshielding by nitro and (normally by) acyl groups, generally led to unambiguous results, but in several cases additional double-irradiation and n.O.e. experiments were required. The need for these additional experiments particularly applied to compounds containing the pivaloyl group, which, as mentioned earlier, is significantly out of plane and thus might produce unexpected shielding effects. For example, in compound (3c) (see Table 2), the aromatic pattern consisted of two three-spin sets, each arising from a benzene ring which is 1,2,3-trisubstituted. Irradiation of the methyl resonance of the pivaloyl group (on C 1) gave enhancement of the most *upfield* signal at δ 7·50 and a signal at 8·20. These were assigned respectively to the resonances from the protons *ortho* (H 2) and *peri* (H 8) to the t-butylcarbonyl group. Irradiation of the most downfield proton (δ 8·53), which could be assigned to the proton *peri* to the nitro group (i.e. H 4) on chemical shift grounds, caused loss of an *ortho* coupling ($J_{\alpha,\beta}$ 8·8 Hz) from the resonance at δ 7·71, removed a *meta* coupling from the most upfield resonance at 7·50 and sharpened the resonance at 7·90 by removal of the cross-ring coupling (*J* 0·9 Hz). The three protons affected by irradiation of H 4 then are H 3, H 2 and H 8 respectively. The two remaining resonances at δ 8·20 (second most downfield and *ortho* to the nitro group) and 7·58 (second most upfield) are then assignable on multiplicity grounds to H 6 and H 7 respectively. These assignments are in contrast with those for the corresponding aldehyde (3a) (see Table 2) with particular regard to the protons *peri* (H 8) and *ortho* (H 2) to the formyl group which resonate at δ 9·63 and 8·13, i.e. 1·73 and 0·63 ppm downfield of the corresponding protons in (3c). This large difference in chemical shift is presumably the result of differing degrees of coplanarity of the formyl and pivaloyl groups with the naphthalene ring.

Experimental

General Procedures

Melting points were determined thermoelectrically on a Reichert hot-stage melting point apparatus and are uncorrected. ^{1}H n.m.r. spectra were determined on a Varian Associates XL-100, or a Bruker WM-400 spectrometer, with $SiMe_4$ as internal standard on *c.* 3-5% w/v solutions in $CDCl_3$. Chemical shifts are quoted in ppm downfield of $SiMe_4$. Infrared spectra were recorded in $CHCl_3$ or as liquid films on a Perkin–Elmer 221 or a Biorad 20-80 Fourier-transform infrared spectrophotometer, and ultraviolet spectra were recorded on a Perkin–Elmer 402 or a Hitachi 150-20 spectrophotometer. Mass spectra were recorded on an A.E.I. MS-902 spectrometer at 70 eV. Analyses were carried out by the Australia Microanalytical Service, Melbourne, or the Chemical and Micro Analytical Services Pty Ltd, Melbourne.

[13] Jackman, L. M., and Sternhell, S., 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry' pp. 306–310 (Pergamon: Oxford 1969).

Preparative layer chromatography (p.l.c.) was performed on Merck Kieselgel 60 $PF_{254+366}$. Thin-layer chromatography (t.l.c.) was performed on Merck Kieselgel $HF_{254+366}$ (type 60). Column chromatography was performed on Merck silica gel (70–230 mesh). Flash chromatography[14] was performed on Merck silica gel 60 (230–240 mesh). Light petroleum refers to the fraction of b.p. 65–70°. Reaction mixtures were routinely worked up by dilution with water and threefold extraction with ether (or another solvent when specified), followed by washing the combined extracts with water, 5% sodium hydrogencarbonate, water and brine. The extracts were then dried ($MgSO_4$) and the solvent was removed under reduced pressure.

'Anhydrous' nitric acid, b.p. 80°, was prepared by distilling 'fuming' nitric acid from an equivolume mixture with concentrated sulfuric acid, and was stored at 0°.

Preparation of Acylnaphthalenes

α- and β-Naphthaldehydes were commercial products (Aldrich). Addition of methylmagnesium iodide or ethylmagnesium iodide to α- or β-naphthaldehyde as appropriate followed by oxidation of the resulting alcohol with Jones reagent in acetone[15] gave α-acetonaphthone (1b) (b.p. 170–173°/15 mmHg; lit.[16] 166–167°/12 mmHg), β-acetonaphthone (2b) (m.p. 55–56°; lit.[17] 53°) and β-propionaphthone (2d) (56–57°; lit.[17] 60°), each of which had the expected 400-MHz ^1H n.m.r. spectrum. An authentic sample of 4-nitro-1-naphthaldehyde (5a), prepared by nitration of (1-naphthyl)acrylic acid and oxidation of the resulting (4-nitro-1-naphthyl)acrylic acid,[11] had m.p. 106° (lit.[11] 106–107°).

1-Pivalonaphthone (1c)

1-Bromonaphthalene (103·5 g), magnesium (12·2 g), ether (350 ml) and pivalonitrile (64 g) were allowed to react according to the method of Pearson.[18] The hydrolysis of the intermediate imine, however, required 5 days for completion. The crude product was distilled, and the fraction of boiling point 181–188°/16 mmHg was recrystallized from light petroleum to give 1-pivalonaphthone (1c) (27·2 g, 26%), white crystals, m.p. 77–78° (lit.[19] 76–77°).

2-Pivalonaphthone (2c)

2-Bromonaphthalene (103·5 g), magnesium (12·2 g), ether (350 ml) and pivalonitrile (64 g) were allowed to react by the general method of Pearson.[18] The crude product was distilled, and the fraction of boiling point 191–195°/16 mmHg was recrystallized from light petroleum to give 2-pivalonaphthone (2c) (60·3 g, 57%), white crystals, m.p. 59–60° (lit.[19] 59–60°).

Nitration of Acylnaphthalenes

Four sets of nitration conditions, methods *A–D* were used. Yields of products were estimated by taking a known fraction of the crude reaction products, adding a known mass of 2,4,6-trinitrotoluene and estimating the proportion of products from the integrals in the resulting ^1H n.m.r. spectra. The products were isolated from the reaction mixtures by chromatography on silica gel with 5–15% ethyl acetate/light petroleum as eluent (unless otherwise specified).

Method A

Concentrated sulfuric acid (0·35 ml) was added dropwise with stirring to a solution of the naphthaldehyde (0·5 g, 3·2 mmol) in glacial acetic acid (10 ml) and fuming nitric acid (7·0 ml) at room temperature. When all the starting aldehyde had reacted (15–20 h), the reaction mixture was poured onto ice and worked up by extraction with ether in the usual fashion.

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Method B

The ketone (6·0 mmol) in redistilled acetic anhydride (36 ml) was added at 5–12° over 30 min to a rapidly stirring suspension of an excess of copper(II) nitrate (5·4 g, 24 mmol) in acetic anhydride (45 ml). The reaction mixture was then allowed to warm to room temperature and was stirred thereat until t.l.c. examination of the reaction mixture indicated that all the starting material had been consumed (3–16 h). The reaction mixture was then poured into water and worked up by extraction with ether in the usual fashion.

Method C

Fuming nitric acid (50 ml, *d* 1·506) was added dropwise to a solution of α-pivalonaphthone (10·0 g) in glacial acetic acid (100 ml), and the solution was stirred at room temperature for 4 days. The reaction mixture was worked up by dilution with water followed by ether extraction in the usual fashion.

Method D

Concentrated sulfuric acid (5 ml) was added to a solution of β-pivalonaphthone (10·0 g) in glacial acetic acid (150 ml) and concentrated nitric acid (100 ml, 15 M), and the mixture was stirred at room temperature for 2 days. The reaction mixture was worked up by dilution with water followed by ether extraction in the usual fashion.

Isolation and Characterization of Nitration Products

The ^{1}H n.m.r. data for all of the nitrated acylnaphthalenes isolated in the this study are collected in Table 2 (chemical shift data) and Table 3 (coupling constants). Products from each nitration reaction are listed in order of increasing polarity.

Nitration of α-Naphthaldehyde (Table 1, Entry 1)

Separation of the products obtained from nitration of α-naphthaldehyde by method *A* by chromatography on silica gel with 15% ethyl acetate/light petroleum as eluent gave 5-nitro-1-naphthaldehyde (3a), m.p. 138–139° (chloroform) (lit.[5] 136–137°), and 8-nitro-1-naphthaldehyde (4a), m.p. 123–125° (ethyl acetate) (lit.[7] 122–124°).

Nitration of α-Acetonaphthone (1b) (Table 1, Entry 2)

Separation of the products obtained from α-acetonaphthone by method *B* by chromatography on silica gel with 10% ethyl acetate/light petroleum as eluent gave (5-nitro-1-naphthyl)ethanone (3b), m.p. 113° (ethanol) (lit.[7] 107–108°) (Found: C, 67·0; H, 4·1; N, 6·8. Calc. for $C_{12}H_9NO_3$: C, 67·0; H, 4·2; N, 6·5%), and (8-nitro-1-naphthyl)ethanone (4b), m.p. 129–130° (ethanol) (lit.[7] 130°).

Nitration of α-Pivalonaphthone (1c) (Table 1, Entry 4)

Separation of the products obtained from nitration of α-pivalonaphthone by method *C* by chromatography on silica gel with 2% ether/light petroleum as eluent gave two fractions, a 1:1 mixture of 4-nitro- and 5-nitro-1-pivalonaphtone (7·5 g) and 8-nitro-1-pivalonaphthone (3·4 g). Chromatography of the first fraction by h.p.l.c. with 2% ethyl acetate/light petroleum gave the following two compounds.

4-Nitro-1-pivalonaphthone (5c) (3·4 g, 28%), m.p. 66–68° (from methanol at −40°) (Found: C, 70·2; H, 6·0; N, 5·4. $C_{15}H_{15}NO_3$ requires C, 70·0; H, 5·9; N, 5·4%). ν_{max} 1685, 1507, 1347, 1377 cm^{-1}. λ_{max} (ethanol) 243 (ε 8700), 333 nm (4400). *m/z* 257 (M, 20%), 201 (87), 200 (74), 184 (54), 170 (13), 154 (54), 126 (48), 57 (100), 41 (36).

5-Nitro-1-pivalonaphthone (3c) (3·7 g, 31%), m.p. 81–82° (from light petroleum) (lit.[1] 81–82°).

Recrystallization of the second fraction from the original chromatographic separation gave *8-nitro-1-pivalonaphthone* (4c) (3·4 g, 28%), m.p. 136–142° (dec.) (from light petroleum) (Found: C, 69·9; H, 5·8; N, 5·5. $C_{15}H_{15}NO_3$ requires C, 70·0; H, 5·9; N, 5·4%). ν_{max} 1679, 1527, 1405 cm^{-1}. λ_{max} (methanol) 256 (ε 9400), 305 (6900), 318 (6100), 334 (4600), 355 nm (2900). *m/z* 202 (M − C_4H_7, 6%), 201 (49), 200 (12), 172 (18), 171 (100), 126 (12), 115 (35), 57 (39), 41 (19).

Nitration of β-Naphthaldehyde (2a) (Table 1, Entry 5)

Separation of the products obtained from nitration of β-naphthaldehyde by method *A* by chromatography on silica gel with 18% ethyl acetate/light petroleum as eluent gave the following compounds (in increasing polarity).

8-Nitro-2-naphthaldehyde (10a), m.p. 167–168° (from dichloromethane/light petroleum) (lit.[8] 166–168°).

4-Nitro-2-naphthaldehyde (7a), m.p. 140–141° (from ethanol) (Found: C, 66·0; H, 3·4; N, 7·4. $C_{11}H_7NO_3$ requires C, 65·7; H, 3·5; N, 7·0%). ν_{max} 1700, 1520, 1335 cm^{-1}. λ_{max} (ethanol) 237 (ϵ 10000), 333 nm (1800). *m/z* 201 (M, 100%), 171 (11), 155 (24), 143 (20), 127 (77), 115 (52), 101 (14), 77 (23), 63 (12), 51 (13).

5-Nitro-2-naphthaldehyde (8a), m.p. 135–136° (from dichloromethane/pentane) (Found: C, 65·6; H, 3·4; N, 6·8. $C_{11}H_7NO_3$ requires C, 65·7; H, 3·5; N, 7·0%). ν_{max} 1705, 1520, 1340 cm^{-1}. λ_{max} (ethanol) 240 (ϵ 31600), 270 (14300), 332 nm (4200). *m/z* 201 (M, 100%), 185 (3), 171 (13), 155 (32), 143 (15), 127 (58), 115 (55), 99 (15), 77 (27).

Nitration of β-Acetonaphthone (2b) with Nitric Acid in Acetic Acid

β-Acetonaphthone (0·25 g) in glacial acetic acid (5 ml) and concentrated nitric acid (3 ml) were stirred at room temperature for 20 h. Workup in the usual fashion followed by chromatography with 10% ethyl acetate/light petroleum as eluent gave a 55% yield (0·16 g) of *3,4-bis(2-naphthylcarbonyl)furazan 2-oxide* (11), m.p. 154° (CH_2Cl_2/light petroleum) (Found: C, 73·3; H, 3·8; N, 7·6. $C_{24}H_{14}N_2O_4$ requires C, 73·1; H, 3·6; N, 7·1%). ν_{max} 1678, 1658, 1609, 1465, 1321 cm^{-1}. λ_{max} (ethanol) 261 (ϵ 43500), 305 (26700), 362 nm (6400). *m/z* 394 (M, 0·7%), 378 (1·7), 334 (0·4), 326 (0·8), 181 (10), 172 (11), 155 (100), 127 (56). High-resolution mass spectrum: M^+ 394·0970 ($C_{24}H_{14}N_2O_4$ requires 394·0954). ^1H n.m.r. (400 MHz, $CDCl_3$): δ 7·53, ddd, H6″ or H7″; 7·58, ddd, H7′; 7·63, ddd, H7″ or H6″; 7·66, ddd, H6′; 7·88, m, 3H, H5′, H5″, H8″; 7·90, m, 2H, H4′, H4″; 7·92, m, H3″; 8·00, dd, H8′; 8·09, br dd, H3′; 8·34, br d, H1″; 8·86, br d, H1′; $J_{1',3'}$ 1·8, $J_{1'',3''}$ 1·6, $J_{3',4'}$ 8·7, $J_{5',7'} = J_{5'',7''} = J_{6',8'} = J_{6'',8''} = 1·4$, $J_{6',7'} = J_{6'',7''} = 6·8$, $J_{5',6'} = J_{5'',6''} = J_{7',8'} = J_{7'',8''} = 8·4$ Hz.

Nitration of β-Acetonaphthone (2b) (Table 1, Entry 6)

Separation of the products obtained from β-acetonaphthone, on nitration by method *B*, by chromatography on silica gel with 15% ethyl acetate/light petroleum as eluent gave the following compounds.

(5-Nitro-2-naphthyl)ethanone (8b), m.p. 113° (ethanol) (Found: C, 67·3; H, 4·0; N, 6·7. $C_{12}H_9NO_3$ requires C, 67·0; H, 4·2; N, 6·5%). ν_{max} 1680, 1510, 1347, 1335 cm^{-1}. λ_{max} (ethanol) 237 (ϵ 38200), 271 (14800), 332 nm (4100). *m/z* 215 (M, 41%), 200 (100), 185 (1·5), 172 (5), 154 (47), 142 (6), 126 (39), 114 (15), 101 (5), 89 (5), 75 (7), 63 (11), 58 (9), 50 (5), 43 (68).

(8-Nitro-2-naphthyl)ethanone (10b), yellow prisms, m.p. 98–99° (dichloromethane/pentane) (Found: C, 67·1; H, 4·1; N, 6·9. $C_{12}H_9NO_3$ requires C, 67·0; H, 4·2; N, 6·5%). ν_{max} 1680, 1515, 1345 cm^{-1}. λ_{max} (ethanol) 230 (ϵ 33000), 327 nm (4600). *m/z* 215 (M, 35%), 200 (100), 185 (2), 173 (2), 154 (41), 142 (5), 126 (35), 114 (15), 101 (6), 89 (6), 63 (10), 43 (35).

(4-Nitro-2-naphthyl)ethanone (7b), yellow needles, m.p. 127° (dichloromethane/pentane) (Found: C, 67·0; H, 4·3; N, 6·5. $C_{12}H_9NO_3$ requires C, 67·0; H, 4·2; N, 6·5%). ν_{max} 1695, 1525, 1360, 1345, 1265 cm^{-1}. λ_{max} (ethanol) 235 (ϵ 31700), 267 (12500), 330 nm (3900). *m/z* 215 (M, 65%), 200 (100), 169 (6), 154 (31), 143 (11), 126 (53), 115 (15), 75 (8), 63 (10), 43 (58).

Nitration of β-Propionaphthone (2d) (Table 1, Entry 7)

Separation of the products, obtained from β-propionaphthone by method *B*, by chromatography on silica gel with 15% ethyl acetate/light petroleum as eluent, followed by further separation of the 5- and 8-nitro compounds with 10% ethyl acetate/light petroleum and h.p.l.c. separation of the 8- and 4-nitro isomers (Whatman Partisil 10μ M20) with 6% ethyl acetate/light petroleum gave the following compounds.

1-(5-Nitro-2-naphthyl)propan-1-one (8d), yellow needles, m.p. 132–133° (ethanol) (Found: C, 68·1; H, 4·7; N, 6·2. $C_{13}H_{11}NO_3$ requires C, 68·1; H, 4·8; N, 6·1%). ν_{max} 1690, 1525, 1345 cm^{-1}. λ_{max} (ethanol) 236 (ε 39300), 271 (14800), 332 nm (4300). *m/z* 229 (M, 19%), 200 (100), 170 (3), 154 (25), 142 (3), 126 (29).

1-(8-Nitro-2-naphthyl)propan-1-one (10d), yellow needles, m.p. 91° (ethanol) (Found: C, 67·1; H, 4·8; N, 5·9. $C_{13}H_{11}NO_3$ requires C, 68·1; H, 4·8; N, 6·1%). ν_{max} 1680, 1510, 1345 cm^{-1}. λ_{max} (ethanol) 230 (ε 35000), 330 nm (4800). *m/z* 229 (M, 20%), 201 (13), 200 (100), 154 (23), 126 (22), 114 (12).

1-(4-Nitro-2-naphthyl)propan-1-one (7d), yellow prisms, m.p. 107° (ethanol) (Found: C, 68·3; H, 5·0; N, 6·2. $C_{13}H_{11}NO_3$ requires C, 68·1; H, 4·8; N, 6·1%). ν_{max} 1685, 1520, 1340 cm^{-1}. λ_{max} (ethanol) 235 (ε 32100), 267 (12300), 333 nm (4000). *m/z* 229 (M, 30%), 201 (12), 200 (100), 170 (3), 154 (22), 142 (5), 126 (37).

Nitration of β-Pivalonaphthone (2c) (Table 1, Entry 8)

Separation, by chromatography on silica gel with 15% ethyl acetate/light petroleum as eluent, of the products obtained on nitration of β-pivalonaphthone by method *B* gave the following compounds.

4-Nitro-2-pivalonaphthone (7c), m.p. 123–124° (methanol) (Found: C, 69·8; H, 5·8; N, 5·4. $C_{15}H_{15}NO_3$ requires C, 70·0; H, 5·9; N, 5·4%). ν_{max} 1680, 1522, 1382 cm^{-1}. λ_{max} (ethanol) 233 (ε 18000), 342 nm (2400). *m/z* 257 (M, 11%), 201 (22), 200 (100), 184 (14), 170 (10), 154 (22), 126 (46), 57 (92), 41 (21).

5-Nitro-2-pivalonaphthone (8c), m.p. 128–130° (methanol) (Found: C, 69·9; H, 5·8; N, 5·5. $C_{15}H_{15}NO_3$ requires C, 70·0; H, 5·9; N, 5·4%). ν_{max} 1680, 1522, 1390, 1200, 900 cm^{-1}. λ_{max} (ethanol) 235 (ε 27500), 269 (9600), 330 nm (4100). *m/z* 257 (M, 9%), 201 (16), 200 (100), 184 (7), 154 (17), 126 (18), 57 (38), 41 (12).

8-Nitro-2-pivalonaphthone (10c), m.p. 91–93° (light petroleum) (Found: C, 70·2; H, 5·9; N, 5·3. $C_{15}H_{15}NO_3$ requires C, 70·0; H, 5·9; N, 5·4%). ν_{max} 1676, 1525, 1392 cm^{-1}. λ_{max} (methanol) 228 (ε 29400), 335 nm (4400). *m/z* 257 (M, 6%), 201 (28), 200 (100), 184 (22), 154 (26), 126 (25), 57 (46).

In addition to the compounds (7c), (8c) and (10c) as described above, very small samples of two additional substances were identified as follows.

3-Nitro-2-pivalonaphthone (6), m.p. 148° (ethanol) (Found: $M^{+\bullet}$, 257·1036. $C_{15}H_{15}NO_3$ requires $M^{+\bullet}$, 257·1052). ν_{max} 1694, 1535, 1342 cm^{-1}. λ_{max} (ethanol) 260 (ε 20100), 309 (6400), 358 nm (2500). *m/z* 257 (M, 0·1%), 242 (1), 201 (100), 184 (1), 171 (65), 126 (33), 115 (43), 57 (46).

7-Nitro-2-pivalonaphthone (9), m.p. 88–89° (ethanol) (Found: $M^{+\bullet}$, 257·1054. $C_{15}H_{15}NO_3$ requires $M^{+\bullet}$, 257·1052). ν_{max} 1676, 1527, 1346 cm^{-1}. λ_{max} (ethanol) 266 (ε 31900), 348 nm (2400). *m/z* 257 (M, 10%), 227 (6), 207 (7), 200 (100), 184 (10), 170 (28), 161 (5), 154 (15), 142 (11), 126 (39), 115 (16), 57 (54), 41 (33).

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