Substituent-Dependent Nitration of 9-Substituted 9,10-Dihydro-9,10-ethanoanthracenes*

Michael C. Harsanyi,^A Robert K. Norris,^{A,B} Gary Sze^A and Paul K. Witting^A

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

Abstract

Mononitration of 9-substituted ethanoanthracenes, bearing Me, Bu^t, F, Br, I, OMe, NO₂, CN, CHO or CO₂Me substituents at the bridgehead carbon, was found to occur exclusively at the β -positions of the aromatic ring. The mononitro products were isolated, identified by ¹H n.m.r. spectroscopy, and their relative proportions were estimated by quantitative g.l.c. and/or by ¹H n.m.r. spectroscopy. For all the above substrates the proportion of nitration at the β -position meta to the bridgehead carbon bearing the substituent to give compounds of the general form (4)] was greater than the proportion of nitration at the corresponding β -position para to the bridgehead substituent [to give compounds of the general form (3)]. Whilst the preferential nitration at the β -positions of the aromatic rings is consistent with the previously reported nitration of 9,10-dihydro-9,10-ethanoanthracene (2a) itself, no observations of this preferential meta attack have been made previously. No correlation could be made of this behaviour with available substituent parameters for the widely sterically and electronically disparate set of substituents used in this study, and the origin of this preferential attack remains unclear. Dinitration in this system was studied only superficially. The influence of the bridgehead substituent together with that of the nitro group already present on one aromatic ring appear to combine with quite unpredictable results in orienting the position of attack of the incoming nitro group onto the other (non-nitrated) aromatic ring.

Introduction

Nitration (i.e. electrophilic substitution) of 9,10-dihydro-9,10-ethanoanthracene[†] is known to occur almost exclusively at the β -positions (2, 3, 6 and 7) of the aromatic ring system.¹⁻³

Streitwieser proposed that electrophilic substitution occurred predominantly in the β -position of benzocycloalkenes due to the rehybridization of the carbon

² Terabe, S., and Konaka, R., J. Am. Chem. Soc., 1973, 95, 4976.

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^{*} Taken in most part from the M.Sc. thesis of G. Sze, University of Sydney, 1993.

 $[\]dagger$ For simplicity, this compound and its derivatives will be referred to as ethanoanthracene(s) from this point onwards.

¹ Hiroshi, T., and Ishitobi, H., Tetrahedron Lett., 1964, 15, 807.

³ Baldwin, J. E., Swanson, A. G., Cha, J. K., and Murphy, J. A., *Tetrahedron*, 1986, 42, 3943.



9,10-dihydro-9,10-ethanoanthracene



Fig. 1. Effect of ring strain in benzocycloalkenes on hybridization. Shaded orbitals show increased p character; unshaded orbital shows increased s character.

atoms at the ring junctions to accommodate the strained ring as shown in Fig. 1.⁴ These hybridization changes result in an increase in the electronegativity of the carbons α to the ring junction and this increase was then used to explain the reduced reactivity at the α -carbons toward electrophilic substitution. Baldwin³ used this model to explain the orientation of nitration in ethanoanthracene itself.

In the case of 9-substituted ethanoanthracenes, nitration can take place at one of two alternative β -positions. This paper reports on observations made of the systematic study of the orientation of nitration of a range of ethanoanthracenes with a wide range of bridgehead substituents, and our (unsuccessful) attempt to relate this orientation effect with available substituent parameters.

Results and Discussion

Preparation of 9-Substituted Ethanoanthracenes

The Diels-Alder reactions of the 9-substituted anthracenes (1b-j) with ethene under pressure, by the method of Meek and coworkers,⁵ gave the corresponding ethanoanthracenes (2b-j). These conversions were convenient to carry out and gave satisfactory yields. The methyl ester (2k) was prepared by esterification of the corresponding acid (2l).⁶

The 9-substituted anthracenes (1b,c,e-j,l) were all conveniently prepared by known literature methods; however, the 9-fluoro compound (1d) was prepared by a new procedure, since the two different literature procedures used previously^{7,8} were unsatisfactory in terms of convenience and gave very low overall yields after multistep processes. The possibility of direct substitution of the nitro group in 9-nitroanthracene (1h) was investigated. This reaction was carried out as shown in Scheme 1, and gave 9-(methylthio)anthracene (8) in 17% yield, and 9-fluoroanthracene (1d) in 5% yield. These products can be separated readily from one another and the very polar by-products by chromatography. The low yield of (1d), still higher than that reported previously,^{7,8} was balanced by the relative ease of the reaction and low cost of the materials involved. Attempts to optimize the yield of (1d) by purifying (carefully drying) the solvent, altering the temperature or using freeze-dried potassium fluoride were not successful. The formation of (8) as the major product is presumably the result of the presence in the dimethyl sulfoxide of either methanethiol or dimethyl sulfide. These two

⁴ Streitwieser, A., Jr, Ziegler, G. R., Mowery, P. C., Lewis, A., and Lawler, R. G., *J. Am. Chem. Soc.*, 1968, **90**, 1357.

⁵ Meek, J. S., Brice, W. E., Godefroi, V., Benson, W. R., Wilcox, M. F., Clark, W. G., and Tiedeman, T., *J. Org. Chem.*, 1960, **26**, 4281.

⁶ Wilhelm, M., and Schmidt, P., Helv. Chim. Acta, 1969, **52**, 1385.

⁷ Anderson, G. L., and Stock, L. M., J. Org. Chem., 1971, 36, 1140.

⁸ Dewar, M. J. S., and Michl, J., Tetrahedron, 1970, 26, 375.



latter compounds have been shown to arise from the thermal decomposition of dimethyl sulfoxide,⁹ although the decomposition process is normally catalysed by acids and is inhibited by bases.¹⁰ The effect of fluoride ion on the decomposition of dimethyl sulfoxide appears to be unknown. The reaction of methanethiol with the nitro compound (1h) will lead directly to the thioether (8), whereas reaction of dimethyl sulfide would give anthracen-9-yldimethylsulfonium ion whose nucleophilic cleavage with either nitrite or fluoride ion would also lead to the thioether (8).



Nitration of 9-Substituted Ethanoanthracenes

The nitrations were carried out principally with copper(II) nitrate and for convenience these products will be referred to as the *p*-nitro (3), *m*-nitro (4), m,p'-dinitro (5), m,m'-dinitro (6) and p,p'-dinitro (7) compounds. Copper(II) nitrate, a mild nitrating reagent, was chosen in most cases rather than more vigorous nitrating reagents such as nitric acid, thereby making the reactions easier to control (minimization of dinitration). In the early stages, the reactions

 ⁹ Head, D. L., and McCarty, C. G., *Tetrahedron Lett.*, 1973, 1405.
 ¹⁰ Santosusso, T. M., and Swern, D., *Tetrahedron Lett.*, 1974, 4255.

of the ethanoanthracene derivatives with copper(II) nitrate gave mononitrated isomers, but eventually dinitrated isomers, with nitro groups at the β -positions on each of the separate rings, were also obtained. The reaction mixtures were stirred vigorously as the samples of copper(II) nitrate, finely powdered and dried before use, were only sparingly soluble in acetic anhydride. The reactions were quenched and the reaction mixtures were worked up by addition of water and extraction with dichloromethane as soon as dinitro products became significant by t.l.c. Even with this precaution the preparative-scale reaction invariably contained some dinitrated compounds, and, for all the 9-substituted derivatives except the 9-bromo (2e) and 9-methoxycarbonyl (2k) compounds, analytical reactions (see Experimental) were performed under more dilute conditions with lower quantities of nitrating reagents. The bromo compound (2e) and the methyl ester (2k) were nitrated with fuming nitric acid in a mixture of acetic acid and acetic anhydride, and preparative reactions of the latter compound (2k) were also performed with copper(II) nitrate in acetic anhydride. Yields of the dinitro isomers were improved in separate reactions by allowing reactions to go further to completion (estimated by t.l.c.).

The nitration products obtained were separated by flash chromatography and, in the case of previously unreported compounds, the new compounds were fully characterized and the positions of the nitro groups were assigned by ¹H n.m.r. spectroscopy. Mononitration of derivatives (2b-k) gave the isomers (3b-k) and (4b-k), respectively, while dinitration of these compounds afforded the corresponding dinitro isomers (5) and (6), except for the compounds (2d,f,j) where dinitration was not pursued. In addition, the dinitro compound (7b) was isolated in low yield (8%) from dinitration of the 9-methyl compound (2b).

The *p*-isomer (3) invariably was found to be the less polar (by t.l.c.) of the two possible mononitro isomers and, in general, was distinguished from the *m*-nitro isomer (4) in each series by ¹H n.m.r. spectroscopy. This assignment was based on the chemical shifts (δH_{α}) of the α -protons *peri* to the 9-substituent in the *para*-isomers (3), $\delta H_{\alpha}(p)$, and the corresponding shift value in the *meta*-isomers (4), $\delta H_{\alpha}(m)$ (see Fig. 2). The absorptions for the protons $H_{\alpha}(m)$ (split only by J_m) and $H_{\alpha}(p)$ (split only by J_o) were readily identified in the signals arising from the aromatic protons on the mononitrated aromatic ring in each of the isomers. The internal consistency of the ¹H n.m.r. spectral data set is shown in Table 1. For comparison purposes, and for the calculation of two of the three parameters (*b* and *c*) used in Table 1, the chemical shifts of 2-nitro-9,10-ethanoanthracene (3a) [\equiv (4a)] are given in Fig. 2.



Fig. 2. Definition of $H_{\alpha}(p)$ and $H_{\alpha}(m)$ for isomeric series (3) and (4), and chemical shift values (δ) for the aromatic protons in 2-nitro-9,10-dihydro-9,10-ethanoanthracene (3a).

Substituent (X)	Isomer		$\delta H_{\alpha}(p)^{A}$	$\delta H_{\alpha}(m)^{A}$	a ^B	bC	c^{D}
	para	meta					
Н	$(3a)^{E}$	$(4a)^{E}$	7.41	8.14	0.73	0	0
Me	(3b)	(4b)	$7 \cdot 40$	$8 \cdot 13$	0.73	-0.01	-0.01
$\operatorname{Bu}^{\operatorname{t}}$	(3c)	(4c)	$7 \cdot 81$	8.57	0.76	0.43	$0 \cdot 40$
F	(3d)	(4d)	7.67	8.37	0.70	$0 \cdot 23$	0.26
Br	(3e)	(4e)	7.88	$8 \cdot 62$	$0\cdot 74$	$0 \cdot 48$	$0\cdot 47$
Ι	(3f)	(4f)	7.87	$8 \cdot 62$	0.75	0.47	0.49
OMe	(3g)	(4g)	7.65	8.35	0.70	$0 \cdot 22$	$0\cdot 24$
NO_2	(3h)	(4h)	$7 \cdot 43$	$8 \cdot 17$	0.74	0.03	$0 \cdot 02$
CN	(3i)	(4i)	7.80	8.50	0.70	0.36	0.39
CHO	(3j)	(4j)	$7 \cdot 62$	$8 \cdot 36$	0.74	$0 \cdot 22$	$0 \cdot 21$
$\rm CO_2Me$	(3k)	(4k)	7.53	$8 \cdot 21$	0.68	$0 \cdot 12$	0.07

Table 1. ¹H n.m.r. data for mononitro ethanoanthracenes

^A For the definition of these shift values see text and Fig. 2.

^B $a = \Delta[\delta H_{\alpha}(m) - \delta H_{\alpha}(p)]$

 $\sum_{m=0}^{C} b = \Delta \left[\delta H_{\alpha}(m)(X) - \delta H_{\alpha}(m) (X = H) \right]$

 $\overset{\mathrm{D}}{=} c = \Delta [\delta \mathrm{H}_{\alpha}(p)(\mathrm{X}) - \delta \mathrm{H}_{\alpha}(p)(\mathrm{X} = \mathrm{H})]$

 E (3a) and (4a) are equivalent.

Parameter a (see Table 1) is the difference in chemical shift for an α -proton *peri* to the bridgehead group owing to the presence of the nitro group in different positions (*para* and *meta*). It was found to have the same value (0.72 ± 0.04) regardless of the bridgehead group. Parameter b reflects the influence of the bridgehead group on the chemical shift of the proton *peri* to the group in the *meta*-isomer while the parameter c is the corresponding value for the *para*-isomer. As mentioned above the values for b and c have been referenced to the case where the bridgehead group is hydrogen, i.e. compound (3a) [\equiv (4a)], for which both b and c are zero. Therefore b and c should have values that depend on the nature of the bridgehead group but b should equal c for the same group. The largest value determined for |b - c| was 0.05 ppm (X = CO₂Me) and for the remaining groups |b - c| was less than or equal to 0.03 ppm (see Table 1).

Surprisingly, a nitro group at the bridgehead has a very small effect on the chemical shift of the *peri* ring proton. This small effect is probably due to the fact that the nitro group is twisted out of the plane containing either of the adjacent benzene rings. Another surprising observation was that the t-butyl group had a large deshielding effect on the ring protons, whereas the methyl group has a slight shielding effect.

The t-butyl derivative (1c) and its nitration products (3c), (4c), (5c) and (6c) exhibit restricted rotation about the carbon-carbon bond at the bridgehead and consequently display non-equivalences in their constituent methyl groups. In the ¹H n.m.r. spectra for each of (1c) and the nitro derivatives (3c), (4c) and (6c) the resonance for the t-butyl group is split into two separate signals, a six-proton singlet and a three-proton singlet. A similar effect has been noted in a study carried out by Oki and Suda for an analogous t-butyl compound in the ethenoanthracene series.¹¹ In the ¹H n.m.r. spectrum for (5c), however, the t-butyl resonance is split into three separate three-proton singlets. This observation is consistent with the product (5c) having the unsymmetrical m,p'-dinitro structure.

¹¹ Oki, M., and Suda, M., Bull. Chem. Soc. Jpn, 1971, 44, 1876.

If the assignment of the position of the nitro group on the aromatic rings were reversed, that is all structures (3) were interchanged with (4), the values of b and c would become very close to zero regardless of the bridgehead group, a result which is inconsistent with the expectation that a variety of bridgehead substituents should produce a variety of shielding and deshielding effects.

Although the assignment of the positions of the nitro groups and hence the assignment of structures to (3) and (4) are supported by the self-consistent nature of the ¹H n.m.r. spectral data (see Table 1), in two cases unambiguous structural assignment for each mononitro isomer was not possible based on chemical shift data alone, since the parameters b and c were close to zero. Such was the case for the mononitro isomers obtained from the nitration of (2b) and (2h). In these cases, structural assignment was based on n.O.e. experiments performed on one of the mononitro isomers. For example mononitration of (2b) gave the isomers (3b) and (4b), as shown in Fig. 3. Assignment of the positions of the nitro groups was difficult solely on chemical shift grounds, owing to the nearly identical ¹H n.m.r. spectra of the products. N.O.e. experiments performed on the less polar isomer showed that it had constitution (3b), since irradiation of the bridgehead proton (H9) at δ 4.44 enhanced the signal for the most downfield narrow resonance (meta-coupled doublet) at $\delta 8.12$ (H1), and irradiation of the methyl group enhanced the signals for H4 (ortho-coupled doublet at δ 7.40) and H 5 (δ 7.30).



Fig. 3. ¹H n.m.r. chemical shift data (δ) for the nitro compounds obtained on nitration of 9-methyl-9,10-dihydro-9,10-ethanoanthracene (2b).

Additional independent confirmation of structures was given by the observation of long-range coupling to fluorine in the ¹H n.m.r. spectra of the two previously unknown mononitro isomers (3d) and (4d). In each compound, the fluorine atom at the bridgehead couples with the proton *peri* to the bridgehead proton. In the less polar compound, the signal for H1 appeared as a narrow doublet of doublets (J_m and $J_{\rm F,H}$) at δ 8.15 and therefore this compound was assigned the constitution (3d). The more polar compound was assigned the constitution (4d) since the signal for H4 appeared as a doublet of doublets (J_o and $J_{\rm F,H}$) at δ 7.55. Except for the case of nitration of the 9-methyl derivative (2b) (see below), nitration of the compounds (2c,e,g-i,k) afforded only two dinitro compounds. The constitution of these compounds was assigned on symmetry grounds after consideration of their ¹H n.m.r. spectra. The more symmetrical isomer, that was invariably the more polar by t.l.c., was assigned the m,m'-dinitro structure (6) (i.e. the 2,7-dinitro 9-substituted compound), while the less symmetrical isomer was assigned the m,p'-dinitro structure (5) (i.e. the 2,6-dinitro 9-substituted compound). The assignment of structure to the symmetrical dinitro compound as a m,m'-dinitro compound (6) rather than a p,p'-dinitro compound (7) also produced a self-consistent set of data, which closely parallel the data presented in Table 1. The ¹H n.m.r. data for the dinitro and trinitro derivatives (3h), (4h), (5h) and (6h), shown in Fig. 4, clearly illustrate this point.



Fig. 4. ¹H n.m.r. chemical shift data (δ) for the nitro compounds obtained on nitration of 9-nitro-9,10-dihydro-9,10-ethanoanthracene (2h).

In addition to the m,p'- and m,m'-products, (5b) and (6b) respectively, dinitration of (2b) also gave the p,p'-product (7b) whose analogue was not observed in other nitration reactions. Assignment of constitution to (5b), (6b) and (7b) was based on n.O.e. experiments performed on each of the three isomers (refer to Fig. 3). Irradiation of the methyl protons in (5b) enhanced the doublet for H 8 (J 8.2 Hz) at δ 7.47 and the doublet for H 1 (J 2.2 Hz) at δ 8.17 and this confirmed the unsymmetrical structure of compound (5b). Irradiation of the methyl group protons in (6b) enhanced the signal (doublet, J 2.2 Hz) for H 1 and H 8 at δ 8.18, whilst for (7b) irradiation of the methyl group protons resulted in enhancement of H 4 and H 5 (a two-proton doublet, J 8.4 Hz, at δ 7.45).

Proportions of Mononitration Products (3) and (4)

In most of the preparative reactions describing the production and isolation of compounds (3) and (4), there was some formation of dinitro compounds. Accordingly, for all nitrations except those of (2e,k), quantitative analyses of the mononitration reactions were performed by using significantly lower concentrations of both the appropriate ethanoanthracene (2) and of copper(II) nitrate. The percentage proportions of the *meta-* and *para-*nitro compounds [(4) and (3) respectively] as a function of the progress of the reactions were determined. The ratios of (4) to (3) were then plotted as a function of reaction time and extrapolated to zero time. In most cases a linear or near-linear plot of the ratio of (4) to (3) against time was obtained, indicating that dinitration was either not occurring or was not significantly distorting the ratio of mononitro compounds, (4) to (3). Only in the case of the nitro compound (2h) was a plot which deviated from excellent linearity obtained. Even in this case, the ratio from the line of best fit $(5 \cdot 0 : 1)$ and the extrapolated value $(4 \cdot 6 : 1)$ gave percentage proportions for the ratio of (4h) to (3h) of 17:83 and 18:82 respectively. This error was less than the reproducibility errors $(\pm 3\%)$ encountered in these experiments and even the largest (4h)-to-(3h) ratio obtained $(5 \cdot 8)$ in these experiments still only corresponds to 85% of (4h). For compounds (2e,k) the ratio of isomers was determined by ¹H n.m.r. spectroscopy on the mixture of mononitro isomers isolated from preparative reactions. The values for the ratio of para to meta nitration [(3) to (4)] obtained for the nitration of compounds (2b-k) are collected in Table 2, including the recently reported nitration of (2e).¹²

From the data in Table 2 it can be seen that the *meta* position is the preferred site in all of the nitration reactions. It is also apparent that the meta-to-para ratio varies substantially with changes in the bridgehead substituent. This ratio ranges from 1 (by symmetry), with hydrogen as the bridgehead substituent, to 5 with the nitro group at the bridgehead. Considering the distance of the bridgehead group to the reaction site, this is a surprising result. In the following discussion, the assumption has been made that acetyl nitrate (or a similar electrophile) is the reactive species in reactions involving fuming nitric acid¹³ or copper(II) nitrate¹⁴ in acetic anhydride. Although the more strongly electron-withdrawing groups lead to higher meta to para ratios, the slightly (inductively) electron-donating groups methyl and t-butyl still have meta-to-para ratios greater than unity, i.e. they will be on the 'wrong side' of hydrogen in any plot against parameters based on inductive effects. Similarly, iodine and bromine are anomalously placed with respect to fluorine and the methoxy group, and the latter two groups also do not seem to fit into a pattern based on inductive effects. Thus it is not surprising that plots of the meta-to-para ratio against a variety of the standard substituent parameters¹⁵ give no correlation. For example, a simple plot of the meta-to-para ratio against σ_I gives an extremely poor correlation (see Fig. 5a). Further, given the anomalous position of electron-donating (by resonance) groups in Table 2, attempts to correlate the *meta*-to-*para* ratio with parameters such as σ_R gave poorer correlations (see Fig. 5b). Thus, it would appear that there is no possibility of a correlation of the *meta*-to-*para* ratio with the electronic (inductive or resonance) nature of the bridgehead groups.

Examination of the results shows a significant difference between the *meta*-to-*para* ratio with fluorine and iodine, but the similarity of this ratio for the methyl

¹² Harsanyi, M. C., Lay, P. A., Norris, R. K., and Witting, P. K., *J. Org. Chem.*, 1995, **60**, 5487.

¹³ Bordwell, F. G., and Garbisch, E. W., J. Am. Chem. Soc., 1960, 82, 3588.

¹⁴ Crivello, J. V., J. Org. Chem., 1981, 46, 3056, and references cited therein.

¹⁵ March, J., 'Advanced Organic Chemistry: Reactions, Mechanism and Structure' 3rd Edn, pp. 242–250 (John Wiley: Brisbane 1985); Lowry, T. H., and Richardson, K. S., 'Mechanism and Theory in Organic Chemistry' 2nd Edn, pp. 130–145 (Harper & Row: Sydney 1981).

Table 2. Ratio of mononitrated compounds (4) to (3) (meta-to-para ratio) for mononitration of 9-substituted ethanoanthracenes

Unless otherwise specified nitrations were carried out with copper(II) nitrate in acetic anhydride at 20°

9-Substituent (X)	Percentages meta para		meta-to- $para$ ratio ^A	9-Substituent (X)	Percentages meta para		<i>meta-</i> to- <i>para</i> ratio ^A	
Н	50	50	1 ^B	OMe ^D	53	47	$1 \cdot 15 \pm 0 \cdot 05$	
Me	58	42	$1 \cdot 40 \pm 0 \cdot 05$	NO_2^E	83	17	$5 \cdot 0 \pm 0 \cdot 5$	
$\operatorname{Bu}^{\operatorname{t}}$	60	40	$1 \cdot 50 \pm 0 \cdot 05$	CN	81	19	$4 \cdot 3 \pm 0 \cdot 4$	
F	63	37	$1 \cdot 7 \pm 0 \cdot 1$	CHO	73	27	$2 \cdot 7 \pm 0 \cdot 3$	
$\operatorname{Br}^{\mathbf{C}}$	77	23	$3 \cdot 3 \pm 0 \cdot 3$	$\rm CO_2Me^{F}$	70	30	$2 \cdot 3 \pm 0 \cdot 5$	
Ι	77	23	$3 \cdot 3 \pm 0 \cdot 3$					

^A Determined by h.p.l.c. unless otherwise stated (see Experimental).

^B By symmetry.

^C Nitration was carried out using fuming nitric acid in a mixture of acetic acid and acetic anhydride and the product ratios were determined by ¹H n.m.r. spectroscopy.¹²

^D Ratio of (4g) to (3g) was 1.15 with nitric acid in acetic acid.

^E Ratio of (4h) to (3h) was $6 \cdot 0 \pm 0 \cdot 5$ or $5 \cdot 5 \pm 0 \cdot 5$, respectively, when nitration was carried out with nitric acid in acetic anhydride or a mixture of nitric and sulfuric acids in acetic acid, respectively.

^F Estimated by ¹H n.m.r. spectroscopy; nitrations were carried out additionally with fuming nitric acid in a mixture of acetic acid and acetic anhydride and the ratio of mononitrated products was determined by h.p.l.c. (see Experimental).



Fig. 5. Plot of meta-to-para ratio against: (a) σ_I ; (b) σ_R .

and t-butyl groups rules out the last remaining substituent parameter, namely a specific steric effect. Also, it would appear that a steric interaction between the bridgehead group and the nitrating agent would favour nitration at the *para* position since it is farther away from the bridgehead group, and consideration of the pairs iodine/fluorine and t-butyl/methyl appear to militate against this. The use of σ_m and σ_p values for the groups is not applicable to this system and the σ_m and σ_p values of CH₂X groups do not appear to be readily available. To determine whether preferential nitration at the *meta* position was related solely to the nitrating system the nitrations of 9-nitro-9,10-dihydro-9,10-ethanoanthracene (2h) and 9-methoxy-9,10-dihydro-9,10-ethanoanthracene (2g) were repeated with two different nitrating reagents, namely nitric acid in acetic anhydride, and nitric acid in sulfuric and acetic acids. The relative ratios of the two nitration products were obtained by g.l.c. in the usual fashion. Nitration of the 9-nitro compound (2h) under these latter conditions gave *meta*-to-*para* ratios that were within experimental error of the ratio obtained with the copper nitrate system (see Table 2, footnote ^E). Nitration of (2g) with nitric acid and acetic anhydride gave an identical *meta*-to-*para* ratio (see Table 2, footnote ^D), but attempts to mononitrate (2g) with a mixture of nitric acid in sulfuric acid/acetic acid proved difficult, and led mainly to dinitro compounds (5g) and (6g). These results confirm that preferential nitration at the position *meta* to the bridgehead bearing the 9-substituent is not caused by a specific nitrating system but is a general, although at present inexplicable, substituent effect.

Given the lack of success in explaining the proportions of mononitration, the proportions of dinitrated products were not studied in any significant detail. In the case of dinitration of the parent compound (2a), with hydrogen at the bridgehead, formation of the isomers (5a) and (6a) was found to take place in approximately equal amounts. In most cases, in molecules with bridgehead substituents, isolated yields of the dinitro isomer (6) (m,m'-dinitrated) exceeded the isolated amounts of the corresponding isomer (5) (m,p'-dinitrated), but there appeared to be a levelling of the proportions of (5) and (6) relative to the proportions of isomers (3) and (4). For example, dinitration of the methyl ester (2k) gave approximately equal proportions of the nitro compounds (5k) and (6k). It is noteworthy, however, that in only the case of dinitration of the 9-methyl derivative (2b) was there any significant formation of the dinitro isomer (7) (p,p'-dinitrated).

Experimental

Melting points were determined on a Reichert hot stage melting point apparatus and are uncorrected. ¹H n.m.r. spectra were determined on a Bruker WM 400 spectrometer with $SiMe_4$ as internal standard in 10% w/v solutions in CDCl₃ unless otherwise stated. Chemical shifts (δ) are quoted in ppm downfield from SiMe₄ with multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants (J) are in Hz. Ultraviolet and infrared spectra were recorded on a Hitachi 150-20 spectrophotometer, and a BIO-RAD 20-80 Fourier transform i.r. or a Perkin Elmer 1600 Fourier transform i.r. spectrophotometer, respectively, and were for solutions in CHCl₃ unless otherwise stated. Mass spectra were recorded on an AEI MS-902 spectrometer at 70 eV, and are quoted in the form x(y), where x is the mass to charge ratio, and y is the percentage abundance relative to the base peak (abundance values less than 10%are not quoted unless significant). Elemental analyses were carried out by Chemical and Micro Analytical Services Pty Ltd, Melbourne and by the Microanalytical Unit, University of New South Wales. Gas-liquid chromatography (g.l.c.) was performed on a Hewlett-Packard 5890A chromatograph with a flame ionization detector with a temperature program. High-pressure liquid chromatography (h.p.l.c.) was carried out on a Waters and Associates System 500 analytical and preparative liquid chromatograph. Thin-layer chromatography (t.l.c.) was performed on Merck Kieselgel HF_{254} (type 60). Chromatography was performed by the method of Still¹⁶ with Merck silica gel 60 (230-240 mesh); solvents were redistilled prior to use. Light petroleum refers to the fraction with b.p. 65-70°. Benzene was dried over sodium

¹⁶ Still, W. C., Kahn, M., and Mitra, A., J. Org. Chem., 1978, 43, 2923.

wire and distilled prior to use. Copper(II) nitrate was powdered and dried under high vacuum to the trihydrated form. 'Workup in the usual manner' refers to the following procedure: the reaction mixture was quenched with water, followed by extraction with dichloromethane; the combined extracts were washed with water, sodium hydrogencarbonate (where necessary), brine, dried (MgSO₄) and the solvent removed under reduced pressure to give the crude product.

9-Fluoroanthracene (1d)

Potassium fluoride (60 g, 1 mol) was added to a stirred solution of 9-nitroanthracene $(1h)^{17}$ (10 g, 45 mmol) in dimethyl sulfoxide (200 ml). The mixture was heated at 140° for 2 days, quenched with water and worked up in the usual manner by extraction with ether. The products were separated by chromatography with light petroleum as eluent. The less polar fractions gave 9-(methylthio)anthracene (8) (1.7 g, 17%), as yellow crystals from ethanol, m.p. 64–65 (lit.¹⁸ 65–66). The more polar fractions gave 9-fluoroanthracene (1d) (441 mg, 5%), as light yellow needles from ethanol, m.p. 102–103° (lit.⁷ 103–104°).

9-Substituted 9,10-Dihydro-9,10-ethanoanthracenes

Compounds $(2a, {}^{1}d, {}^{7}f-j, {}^{5}l^{6})$, $(3e), {}^{12}$ and $(4e)^{12}$ were prepared by the indicated literature procedures.

9-Methyl-9,10-dihydro-9,10-ethanoanthracene (2b)

9-Methylanthracene (1b)¹⁹ (7.0 g, 0.037 mol) was dissolved in toluene (20 ml) and treated with ethene in an autoclave (315 ml) at 400 p.s.i. and 160° for 48 h as described by Meek and coworkers.⁵ The reaction mixture was diluted with dichloromethane and the solvents were evaporated under reduced pressure. The crude product on recrystallization from ethanol gave 9-methyl-9,10-dihydro-9,10-ethanoanthracene (2b) (3.03 g, 38%), as pale yellow crystals, m.p. 91–92° (Found: C, 93.2; H, 7.2. C₁₇H₁₆ requires C, 92.7; H, 7.3%). ν_{max} 2955, 1458, 589 cm⁻¹. λ_{max} 272 (ϵ 1780), 265 (1520), 238 nm (880). ¹H n.m.r. δ 1.53, m, CH₂CH₂; 1.79, m, CH₂CH₂; 1.95, s, CH₃; 4.30, t, J 2.5 Hz, H10; 7.12, m, H2,3,6,7; 7.28, m, H1,4,5,8. m/z 221 (M+1, 17%), 220 (M, 66), 202 (13), 193 (69), 192 (100), 191 (86), 189 (47), 178 (10), 165 (28), 96 (46), 83 (24), 45 (40), 31 (83).

9-t-Butyl-9,10-dihydro-9,10-ethanoanthracene (2c)

9-t-Butylanthracene $(1c)^{20}$ (5·1 g, 0·02 mol) was treated with ethene in an autoclave (315 ml) as described above for (1b). Purification of the crude product by chromatography with 3% ethyl acetate/light petroleum gave on recrystallization from methanol 9-t-butyl-9,10-dihydro-9,10-ethanoanthracene (2c) (2·14 g, 38%), as colourless crystals, m.p. 177° (Found: C, 91·6; H, 8·7. C₂₀H₂₂ requires C, 91·6; H, 8·5%). ν_{max} 2951, 1455, 574 cm⁻¹. λ_{max} 274 (ϵ 1440), 267 (1280), 240 nm (1360). ¹H n.m.r. δ 1·58, s, 6H, CMe₂Me; 1·81, m, CH₂CH₂; 1·91, s, 3H, CMe₂Me; 4·18, t, J 2·5 Hz, H10; 7·05, m, H2,3,6,7; 7·26, m, H4,5; 7·67, m, H1,8. N.O.e. results: irradiation of Bu^t (δ 1·58 and 1·91) gave 0·4 and 1·4% enhancements respectively of the signal for H1/H8 (δ 7·67). m/z 263 (M+1, 14%), 262 (M, 60), 234 (100), 219 (80), 203 (17), 202 (16), 191 (7), 178 (21), 28 (36).

Methyl 9,10-Dihydro-9,10-ethanoanthracene-9-carboxylate (2k)

Anthracene-9-carboxylic acid $(11)^{21}$ $(10 \cdot 5 \text{ g})$ was dissolved in dimethylformamide (60 ml) and treated with ethene in an autoclave (315 ml) at 400 p.s.i. and 170° for 48 h to give the acid (21). The crude acid was not purified but was heated under reflux with methanol (200 ml) and sulfuric acid (98%, 3 ml) for 16 h. Evaporation of the methanol, followed by

- ¹⁹ Krollpfeiffer, F., and Branscheid, F., Ber. Dtsch. Chem. Ges., 1923, 56, 1617.
- ²⁰ Parish, R. C., and Stock, L. M., J. Org. Chem., 1966, **31**, 4265.
- ²¹ Bachmann, W. E., and Kloetzel, M. C., J. Org. Chem., 1938, 3, 55.

¹⁷ Braun, C. E., Cook, C. D., Merritt, C, Jr, and Rousseau, J. E., Org. Synth., Collect. Vol. 4, 1956, 711.

¹⁸ Conway, W., and Tarbell, D. S., J. Am. Chem. Soc., 1956, 78, 2228.

dissolution of the residue in ether and washing with dilute sodium hydroxide solution followed by workup in the usual fashion gave methyl 9,10-dihydro-9,10-ethanoanthracene-9-carboxylate (2k) (8.02 g, 64%), as colourless needles from methanol, m.p. 135–136° (Found: C, 81.8; H 6.0. C₁₈H₁₆O₂ requires C, 81.8; H, 6.1%). ν_{max} 2950, 1730, 1445, 1250, 1195 cm⁻¹. λ_{max} (ethanol) 271 nm (ϵ 470). ¹H n.m.r. δ 1.74, m, CH₂CH₂; 1.95, CH₂CH₂; 4.02, s, CO₂CH₃; 4.26, t, J 2.5 Hz, H10; 7.14, m, ArH. m/z 265 (M+1, 4%), 264 (M, 14), 237 (19), 236 (100), 205 (42), 177 (21), 88 (25).

Mono- and Di-nitration of Compounds (2a-k)

2-Nitro-9, 10-dihydro-9, 10-ethanoanthracene (3a) $[\equiv (4a)]$

A solution of 9,10-dihydro-9,10-ethanoanthracene $(2a)^5$ (0.5 g, 2.4 mmol) in acetic anhydride (14 ml) was chilled to -10° and rapidly added to a finely ground suspension of copper(II) nitrate (2.52 g, 12 mmol, 5 equiv.) in acetic anhydride (18 ml) at -10° . The reaction mixture was allowed to warm to room temperature over a period of 30 min. The reaction mixture was quenched with water and worked up in the usual fashion to give the crude product as an orange oil which was chromatographed on silica gel with 10% ethyl acetate/light petroleum as eluent. The less polar component on recrystallization from ethyl acetate gave starting material (2a) (0.18 g). The more polar component (0.26 g) on recrystallization from methanol gave pure 2-nitro-9,10-dihydro-9,10-ethanoanthracene (3a) [\equiv (4a)] (0.20 g, 33%), m.p. 165–168° (lit.¹ 165–166°).

2,6-Dinitro-9,10-dihydro-9,10-ethanoanthracene (5a) and 2,7-Dinitro-9,10-dihydro-9,10-ethanoanthracene (6a)

Fuming nitric acid (1.5 g) was added slowly to a mixture of glacial acetic acid (0.38 g)and acetic anhydride (0.38 g) at 20° and the mixture chilled below 0°. This mixture was added dropwise, over 2 min, to a stirred solution of 9,10-dihydro-9,10-ethanoanthracene (1a) (0.5 g, 2.4 mmol) in acetic anhydride (0.38 g) at 20°. After stirring at 20° for a further 2 h the reaction mixture was quenched with water (100 ml) and extracted with dichloromethane. The extracts were carefully washed with sodium hydrogencarbonate, followed by workup in the usual fashion, to give the crude product as a yellow oil which was chromatographed on silica gel with 30% dichloromethane/light petroleum as eluent to give a mixture of the dinitro isomers (5a) and (6a) in the ratio 44:56 as estimated by analytical h.p.l.c. The mixture of isomers was separated by h.p.l.c. with 7% ethyl acetate/light petroleum as eluent. The less polar component on recrystallization from methanol gave 2,6-dinitro-9,10-dihydro-9,10ethanoanthracene (5a) (0.26 g, 37%), m.p. $190-191^{\circ}$ (lit.¹ 190°). The more polar component on recrystallization from methanol gave 2,7-dinitro-9,10-ethanoanthracene (6a) (0.20 g, 28%), m.p. $198-200^{\circ}$ (lit.¹ 197-198°).

10-Methyl-2-nitro-9,10-dihydro-9,10-ethanoanthracene (3b) and 9-Methyl-2-nitro-9,10-dihydro-9,10-ethanoanthracene (4b)

The ethanoanthracene (2b) (613 mg, 2.8 mmol) was dissolved in acetic anhydride (10 ml) and the solution was added to a suspension of finely powdered copper(II) nitrate $(1 \cdot 0 \text{ g})$ in acetic anhydride (5 ml) at 25°. The reaction mixture was quenched after 10 min and worked up by dilution with a 10-fold volume of water, followed by stirring at room temperature for 15-20 min (to ensure hydrolysis of the acetic anhydride). The reaction mixture was then worked up in the usual fashion followed by chromatography with 5% ethyl acetate as eluent to give starting material (2b) (190 mg) and a mixture of products which were further separated by h.p.l.c. with 1.5% ethyl acetate/light petroleum as eluent.

The less polar component gave 10-methyl-2-nitro-9,10-dihydro-9,10-ethanoanthracene (3b) (141 mg, 19%), as colourless crystals from light petroleum, m.p. 95–96° (Found: C, 77·0; H, 5·7; N, 5·2. C₁₇H₁₅NO₂ requires C, 77·0; H, 5·7; N, 5·3%). ν_{max} 1523, 1457 cm⁻¹. λ_{max} 285 nm (ϵ 9310). ¹H n.m.r. δ 1·57, m, CH₂CH₂; 1·83, m, CH₂CH₂; 2·00, s, CH₃; 4·44, t, J 2·7 Hz, H9; 7·16, ddd, J_{5,6} 6·8, J_{6,7} 7·2, J_{6,8} 1·7 Hz, H6; 7·19, ddd, J_{6,7} 7·2, J_{7,8} 6·8, J_{5,7} 1·7 Hz, H7; 7·30, m, H5,8; 7·40, d, J_{3,4} 8·3 Hz, H4; 8·04, dd, J_{1,3} 2·4, J_{3,4} 8·3 Hz, H3; 8·12, d, J_{1,3} 2·4 Hz, H1. N.O.e. results: irradiation of CH₃ (δ 2·00) gave 1·5% enhancements for each of the signals for H4 (δ 7·40) and H5 (δ 7·30). Irradiation of H9

 $(\delta 4.44)$ gave 5.5% enhancements for each of the signals for H1 ($\delta 8.12$) and H8 ($\delta 7.30$). m/z 265 (M, 13%), 237 (100), 220 (5), 207 (10), 192 (33), 191 (30), 46 (58), 45 (100), 43 (33), 31 (62).

The more polar component gave 9-methyl-2-nitro-9,10-dihydro-9,10-ethanoanthracene (4b) (183.3 mg, 24.7%), as colourless crystals from light petroleum, m.p. 167–168° (Found: C, 77.0; H, 5.7; N, 5.3. C₁₇H₁₅NO₂ requires C, 77.0; H, 5.7; N, 5.3%). ν_{max} 1524, 1348 cm⁻¹. λ_{max} 285 nm (ϵ 9370). ¹H n.m.r. δ 1.58, m, CH₂CH₂; 1.83, m, CH₂CH₂; 2.03, s, CH₃; 4.44, t, J 2.7 Hz, H 10; 7.15, ddd, J_{6,7} 7.2, J_{5,6} 7.4, J_{6,8} 1.3 Hz, H 6; 7.19, ddd, J_{6,7} 7.2, J_{7,8} 7.4, J_{5,7} 1.6 Hz, H 7; 7.30, m, H 5,8; 7.40, d, J_{3,4} 8.1 Hz, H 4; 8.02, dd, J_{1,3} 2.3, J_{3,4} 8.1 Hz, H 3; 8.13, d, J_{1,3} 2.3 Hz, H 1. m/z 266 (M+1, 4%), 265 (M, 18), 238 (20), 237 (100), 191 (28), 188 (22), 45 (18), 31 (34).

9-Methyl-2,6-dinitro-9,10-dihydro-9,10-ethanoanthracene (5b), 9-Methyl-2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene (6b) and 10-Methyl-2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene (7b)

Dinitration of (2b) (784 mg) was achieved with copper(II) nitrate $(2 \cdot 0 \text{ g})$ and acetic anhydride (10 ml). The reaction was quenched after 8 h and the reaction mixture worked up to give a mixture of products which were separated by chromatography with 25% ethyl acetate/light petroleum as eluent.

The least polar component was 9-methyl-2,6-dinitro-9,10-dihydro-9,10-ethanoanthracene (5b) (237 mg, 22%), as white crystals from ethyl acetate/light petroleum, m.p. 191–192° (Found: C, 65 ·9; H, 4 ·6; N, 9 ·0. C₁₇H₁₄N₂O₄ requires C, 65 ·8; H, 4 ·6; N, 9 ·0%). ν_{max} 1526, 1347 cm⁻¹. λ_{max} 281 nm (ϵ 18000). ¹H n.m.r. δ 1 ·64, m, CH₂CH₂; 1 ·88, m, CH₂CH₂; 2 ·09, s, CH₃; 4 ·59, t, J 2 ·8 Hz, H 10; 7 ·47, d, J_{3,4} (= J_{7,8}) 8 ·2 Hz, H 4,8; 8 ·08, dd, J_{1,3} 2 ·2, J_{3,4} 8 ·2 Hz, H 3 (or H 7); 8 ·10, dd, J_{5,7} 2 ·2, J_{7,8} 8 ·2 Hz, H 7 (or H 3); 8 ·17, d, J_{1,3} (= J_{5,7}) 2 ·2 Hz, H 1,5. N.O.e. results: irradiation of CH₃ (δ 2 ·09) gave a 1 ·5% enhancement for each of the signals for H 8 (δ 7 ·47) and H 1 (δ 8 ·17). m/z 310 (M, 1%), 283 (30), 282 (100), 236 (14), 224 (13), 190 (42), 189 (75), 178 (25), 163 (9).

The next component was recrystallized from ethyl acetate/light petroleum to yield 10methyl-2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene (7b) (92 mg, 8%) as white crystals, m.p. 215-216° (Found: C, 66·3; H, 4·5; N, 9·0. C₁₇H₁₄N₂O₄ requires C, 65·8; H, 4·6; N, 9·0%). $\nu_{\rm max}$ 1526, 1346 cm⁻¹. $\lambda_{\rm max}$ 281 nm (ϵ 21200). ¹H n.m.r. δ 1·63, m, CH₂CH₂; 1·89, m, CH₂CH₂; 2·06, s, CH₃; 4·60, t, J 2·8 Hz, H9; 7·45, d, J_{3,4} (= J_{5,6}) 8·4 Hz, H4,5; 8·10, dd, J_{3,4} (= J_{5,6}) 8·4, J_{1,3} (= J_{6,8}) 2·4 Hz, H3,6; 8·17, d, J_{1,3} (= J_{6,8}) 2·4 Hz, H1,8. N.O.e. results: irradiation of CH₃ (δ 2·06) gave a 3·3% enhancement of the signal for H4 and H5 (δ 7·45). m/z 310 (M, 6%), 283 (16), 282 (100), 190 (16), 189 (25), 43 (14).

The most polar component gave 9-methyl-2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene (6b) (361 mg, 33%), as white flakes from ethyl acetate/light petroleum, double m.p. 213 and 221-222° (Found: C, 65·8; H, 4·6; N, 9·0. C₁₇H₁₄N₂O₄ requires C, 65·8; H, 4·6; N, 9·0%). $\nu_{\rm max}$ 1529, 1346 cm⁻¹. $\lambda_{\rm max}$ 283 nm (ϵ 16600). ¹H n.m.r. δ 1·64, m, CH₂CH₂; 1·88, m, CH₂CH₂; 2·12, s, CH₃; 4·58, t, J 2·7 Hz, H10; 7·45, d, J_{3,4} (= J_{5,6}) 8·1 Hz, H4,5; 8·08, dd, J_{3,4} (= J_{5,6}) 8·1, J_{1,3} (= J_{6,8}) 2·2 Hz, H3,6; 8·18, d, J_{1,3} (= J_{6,8}) 2·2 Hz, H1,8. N.O.e. results: irradiation of CH₃ (δ 2·12) gave a 2·9% enhancement of the signal for H 1 and H8 (δ 8·18). m/z 310 (M, 2%), 283 (18), 282 (100), 190 (24), 189 (42), 178 (16), 28 (17).

10-t-Butyl-2-nitro-9,10-dihydro-9,10-ethanoanthracene (3c) and 9-t-Butyl-2-nitro-9,10-dihydro-9,10-ethanoanthracene (4c)

The t-butyl derivative (2c) (1 g, 3.8 mmol) was treated with copper(II) nitrate (2.7 g, 11 mmol) in acetic anhydride (46 ml) for 3 min, followed by the usual workup procedure to give the crude product. The crude products were separated by chromatography with 5% ethyl acetate/light petroleum as eluent. The mononitrated products were further separated by h.p.l.c. with 1% ethyl acetate/light petroleum as eluent.

The less polar component gave 10-t-butyl-2-nitro-9,10-dihydro-9,10-ethanoanthracene (3c) (141 mg, 12%), as white crystals from light petroleum, m.p. 209–210° (Found: C, 78.0; H, 7.1; N, 4.5. C₂₀H₂₁NO₂ requires C, 78.2; H, 6.9; N, 4.6%). $\nu_{\rm max}$ 1520, 1346 cm⁻¹. $\lambda_{\rm max}$ 289 (ϵ 9460), 239 nm (6770). ¹H n.m.r. δ 1.57, s, 6H, Bu^t; 1.84, m, CH₂CH₂; 1.91, s, 3H,

Bu^t; 4·33, t, J 2·7 Hz, H9; 7·12, m, H6,7; 7·30, m, H8; 7·69, m, H5; 7·81, d, $J_{3,4}$ 9·0 Hz, H4; 7·96, dd, $J_{3,4}$ 9·0, $J_{1,3}$ 2·8 Hz, H3; 8·09, d, $J_{1,3}$ 2·8 Hz, H1. m/z 307 (M, 9%), 279 (100), 264 (48), 250 (5), 217 (10), 218 (10), 202 (19), 28 (39).

The more polar component gave 9-t-butyl-2-nitro-9,10-dihydro-9,10-ethanoanthracene (4c) (210 mg, 18%), as white crystals from light petroleum, m.p. 199-201° (Found: C, 78.0; H, 7.1; N, 4.6. C₂₀H₂₁NO₂ requires C, 78.2; H, 6.9; N, 4.6%). ν_{max} 1521, 1347 cm⁻¹. λ_{max} 290 (ϵ 11000), 239 nm (10400). ¹H n.m.r. δ 1.60, s, 6H, Bu^t; 1.84, m, CH₂CH₂; 1.96, s, 3H, Bu^t; 4.32, t, J 2.7 Hz, H10; 7.12, m, H6,7; 7.28, m, H5; 7.38, d, J_{3,4} 8.1 Hz, H4; 7.71, dd, J_{7,8} 6.7, J_{6,8} 2.0 Hz, H8; 7.97, dd, J_{3,4} 8.1, J_{1,3} 2.0 Hz, H3; 8.57, d, J_{1,3} 2.0 Hz, H1. m/z 307 (M, 6%), 279 (100), 264 (51), 203 (19).

9-t-Butyl-2,6-dinitro-9,10-dihydro-9,10-ethanoanthracene (5c) and 9-t-Butyl-2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene (6c)

Dinitration of (2c) (680 mg) was achieved with copper(II) nitrate $(1 \cdot 9 \text{ g})$ in acetic anhydride (10 ml) for 1 h followed by workup in the usual manner. The products were separated by chromatography with 10% ethyl acetate/light petroleum as eluent.

The less polar component gave 9-t-butyl-2,6-dinitro-9,10-dihydro-9,10-ethanoanthracene (5c) (392 mg, 43%), as white crystals from light petroleum/ethyl acetate, m.p. 223-224° (Found: C, 68.5; H, 5.9; N, 7.8. C₂₀H₂₀N₂O₄ requires C, 68.2; H, 5.7; N, 8.0%). $\nu_{\rm max}$ 1523, 1347 cm⁻¹. $\lambda_{\rm max}$ 284 nm (ϵ 20300). ¹H n.m.r. δ 1.60, s, 3H, Bu^t; 1.63, s, 3H, Bu^t; 1.90, m, CH₂CH₂; 1.97, s, 3H, Bu^t; 4.50, t, J 2.7 Hz, H10; 7.44, d, J_{3,4} 8.1 Hz, H4; 7.86, d, J_{7,8} 8.1 Hz, H8; 8.02, dd, J_{3,4} 8.1, J_{1,3} 2.3 Hz, H3; 8.04, dd, J_{7,8} 8.1, J_{5,7} 2.3 Hz, H5; 8.59, d, J_{1,3} 2.3 Hz, H1. m/z 352 (M, 5%), 325 (20), 324 (100), 309 (44), 215 (14), 202 (14), 57 (18), 41 (15).

The more polar component gave 9-t-butyl-2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene (6c) (224 mg, 25%), as white crystals from light petroleum/ethyl acetate, m.p. 299-301° (Found: C, 68·4; H, 5·9; N, 7·9. C₂₀H₂₀N₂O₄ requires C, 68·2; H, 5·7; N, 8·0%). ν_{max} 1524, 1344 cm⁻¹. λ_{max} 285 (ϵ 19200), 239 nm (11900). ¹H n.m.r. δ 1·63, s, 6H, Bu^t; 1·88, m, CH₂CH₂; 2·00, s, 3H, Bu^t; 4·45, t, J 2·7 Hz, H 10; 7·42, d, J_{3,4} (= J_{5,6}) 8·1 Hz, H4,5; 8·02, dd, J_{3,4} (= J_{5,6}) 8·1, J_{1,3} (= J_{6,8}) 2·1 Hz, H3,6; 8·60, d, J_{1,3} (= J_{6,8}) 2·1 Hz, H 1,8. m/z 352 (M, 5%), 325 (21), 324 (100), 309 (38), 215 (12), 202 (17), 57 (22).

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Copper(II) nitrate (320 mg, 1.3 mmol) was added to a solution of the fluoro compound (2d) (180 mg, 0.8 mmol) in acetic anhydride (10 ml); the reaction was quenched after 2 h and the reaction mixture was worked up in the usual manner. The crude products were separated by chromatography with 5% ethyl acetate/light petroleum as eluent.

The less polar component gave 10-fluoro-2-nitro-9,10-dihydro-9,10-ethanoanthracene (3d) (38 mg, 18%), as white crystals from light petroleum, m.p. 128–130° (Found: C, 71·8; H, 4·5; N, 5·3. C₁₆H₁₂FNO₂ requires C, 71·4; H, 4·5; N, 5·2%). ν_{max} 1526, 1349, 1307 cm⁻¹. λ_{max} 279 nm (ϵ 20300). ¹H n.m.r. δ 1·88, m, CH₂CH₂; 2·00, m, CH₂CH₂; 4·43, t, J 2·7 Hz, H9; 7·20, ddd, J_{6,7} 8·8, J_{7,8} 7·2, J_{5,7} 1·4 Hz, H7; 7·25, ddd, J_{6,7} 8·8, J_{5,6} 7·5, J_{6,8} 1·5 Hz, H6; 7·32, ddd, J_{7,8} 7·2, J_{7,F} 2·2, J_{6,8} 1·5 Hz, H8; 7·54, dd, J_{5,6} 7·5, J_{5,7} 1·4 Hz, H5; 7·67, d, J_{3,4} 8·2 Hz, H4; 8·12, dd, J_{3,4} 8·2, J_{1,3} 2·2 Hz, H3; 8·15, dd, J_{1,F} 2·0, J_{1,3} 2·2 Hz, H1. m/z 269 (M, 6%), 241 (100), 195 (89), 194 (47), 183 (50), 175 (17), 30 (37).

The more polar component gave 9-fluoro-2-nitro-9,10-dihydro-9,10-ethanoanthracene (4d) (110 mg, 51%), as white crystals from light petroleum, m.p. 173–174° (Found: C, 71·7; H, 4·4; N, 5·3. C₁₆H₁₂FNO₂ requires C, 71·4; H, 4·5; N, 5·2%). ν_{max} 1526, 1349 cm⁻¹. λ_{max} 277 nm (ϵ 22200). ¹H n.m.r. δ 1·87, m, CH₂CH₂; 2·02, m, CH₂CH₂; 4·42, t, J 2·6 Hz, H 10; 7·20, ddd, J_{6,7} 8·8, J_{5,6} 7·3, J_{6,8} 1·5 Hz, H 6; 7·25, ddd, J_{6,7} 8·8, J_{7,8} 7·6, J_{5,7} 1·5 Hz, H 7; 7·31, ddd, J_{5,6} 7·3, J_{5,F} 2·0, J_{5,7} 1·5 Hz, H 5; 7·43, dd, J_{3,4} 8·2, J_{4,F} 1·9 Hz, H 4; 7·55, dd, J_{7,8} 7·6, J_{6,8} 1·5 Hz, H 8; 8·07, dd, J_{3,4} 8·2, J_{1,3} 2·2 Hz, H 3; 8·37, d, J_{1,3} 2·2 Hz, H 1. m/z 269 (M, 2·5%), 257 (1), 241 (100), 195 (66), 194 (38), 183 (42), 175 (13).

9-Bromo-2,6-dinitro-9,10-dihydro-9,10-ethanoanthracene (5e) and 9-Bromo-2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene (6e)

A chilled mixture of fuming nitric acid $(1 \cdot 6 \text{ g})$ in glacial acetic acid $(0 \cdot 20 \text{ g})$ and acetic anhydride $(0 \cdot 2 \text{ g})$ was added dropwise to a stirred solution of the bromide $(2e)^5$ $(1 \cdot 0 \text{ g}, 2 \cdot 5 \text{ mmol})$ in acetic anhydride (3 ml) at 0°. The reaction mixture was allowed to warm to room temperature and then stirred for a further 3 h. The reaction mixture was then worked up by quenching with water and extraction with chloroform to give the crude product as a viscous oil. Extraction of the crude product with ethanol gave an ethanol-insoluble fraction which on recrystallization from ethyl acetate gave *9-bromo-2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene* (6e) (580 mg, 44%), as colourless microneedles, m.p. 248–250°. (Found: C, 51 \cdot 2; H, 2 \cdot 9; N, 7 \cdot 7. C₁₆H₁₁N₂O₄ requires C, 51 \cdot 2; H, 3 \cdot 0; N, 7 \cdot 5%). ν_{max} 1595, 1525, 1345 cm⁻¹. λ_{max} (ethanol) 277 nm (ϵ 19600). ¹H n.m.r. δ 1 · 97, m, CH₂CH₂; 2 · 33, m, CH₂CH₂; 4 · 63, t, J 2 · 6 Hz, H 10; 7 · 49, d, J_{3,4} (= J_{5,6}) 7 · 8 Hz, H 4,5; 8 · 14, dd, J_{3,4} (= J_{5,6}) 7 · 8, J_{1,3} (= J_{6,8}) 2 · 1 Hz; H 3,6; 8 · 62, d, J_{1,3} (= J_{6,8}) 2 · 1 Hz, H 1,8.

The ethanol-soluble fraction on removal of the ethanol under reduced pressure gave an orange oil that was chromatographed on silica gel with 24% ethyl acetate/light petroleum as eluent. The less polar component on recrystallization from ethyl acetate gave a further crop of dinitro bromo compound (6e) (65 mg; combined yield of 65%) and recrystallization of the more polar fraction from ethyl acetate gave 9-bromo-2,6-dinitro-9,10-dihydro-9,10-ethanoanthracene (5e) (240 mg, 18%), as pale yellow crystals, m.p. 179.5–180.5° (Found: C, 50.9; H, 3.2; N, 7.2. C₁₆H₁₁BrN₂O₄ requires C, 51.2; H, 3.0; N, 7.5%). ν_{max} 1585, 1515, 1450, 1340 cm⁻¹. λ_{max} (ethanol) 272 nm (ϵ 19800). ¹H n.m.r. δ 1.99, m, CH₂CH₂; 2.34, m, CH₂CH₂; 4.65, t, J 2.5 Hz, H10; 7.51, d, J_{3,4} 8.2 Hz, H4; 7.95, d, J_{7,8} 8.4 Hz, H8; 8.14, dd, J_{7,8} 8.4, J_{5,7} 2.2 Hz, H7; 8.15, dd, J_{3,4} 8.2, J_{1,3} 2.2 Hz, H3; 8.18, d, J_{5,7} 2.2 Hz; H5; 8.63, d, J_{1,3} 2.2 Hz, H1. m/z 376 (M+2, 1%), 374 (M, 0.7), 349 (18), 348 (88), 347 (13), 346 (100), 302 (17), 300 (21), 256 (12), 254 (10), 221 (15), 202 (13), 175 (21), 163 (11).

10-Methoxy-2-nitro-9,10-dihydro-9,10-ethanoanthracene (3g) and 9-Methoxy-2-nitro-9,10-dihydro-9,10-ethanoanthracene (4g)

The ethanoanthracene $(2g)^5$ (500 mg, 2·1 mmol) was treated with copper(II) nitrate $(1 \cdot 5 \text{ g})$ in acetic anhydride (26 ml) and the reaction mixture was quenched and worked up after 1 min. The mononitrated products were separated by chromatography with 10% ethyl acetate/light petroleum as eluent.

The less polar compound gave 10-methoxy-2-nitro-9,10-dihydro-9,10-ethanoanthracene (3g) (176 mg, 30%), as white crystals from light petroleum, m.p. 134–135° (Found: C, 73·0; H, 5·0; N, 4·8. C₁₇H₁₅NO₃ requires C, 72·6; H, 5·4; N, 5·0%). ν_{max} 1524, 1347 cm⁻¹. λ_{max} 286 (ϵ 8420), 238 nm (4800). ¹H n.m.r. δ 1·94, m, CH₂CH₂; 2·05, m, CH₂CH₂; 3·89, s, OCH₃; 4·37, t, J 2·3 Hz, H9; 7·15, ddd, J_{6,7} 8·0, J_{7,8} 7·2, J_{5,7} 1·4 Hz, H7; 7·21, ddd, J_{6,7} 8·0, J_{5,6} 7·2, J_{6,8} 1·2 Hz, H6; 7·30, dd, J_{7,8} 7·6, J_{6,8} 1·2 Hz, H8; 7·50, d, J_{5,6} 7·1 Hz, H5; 7·65, d, J_{3,4} 8·3 Hz, H4; 8·06, dd, J_{3,4} 8·3, J_{1,3} 2·4 Hz, H3; 8·11, d, J_{1,3} 2·4 Hz, H1. N.O.e. results: irradiation of H9 (δ 4·37) gave a 4·6% enhancement of the signal for H8 (δ 7·30) and a 3·2% enhancement for H1 (δ 8·11). Irradiation of OCH₃ (δ 3·89) gave 0·3% enhancement of the signals for each of H4 (δ 7·65) and H5 (δ 7·50). m/z 282 (M+1, 0·5%), 281 (M, 1), 267 (1), 254 (69), 253 (100), 238 (80), 192 (61), 164 (60), 163 (64).

The more polar compound gave 9-methoxy-2-nitro-9,10-dihydro-9,10-ethanoanthracene (4g) (185 mg, 31%), as white crystals from light petroleum, m.p. 137–138° (Found: C, 72·4; H, 5·5; N, 5·0. C₁₇H₁₅NO₃ requires C, 72·6; H, 5·4; N, 5·0%). ν_{max} 1524, 1348 cm⁻¹. λ_{max} 284 (ϵ 8550), 239 nm (6050). ¹H n.m.r. δ 1·94, m, CH₂CH₂; 3·90, s, OCH₃; 4·37, t, J 2·3 Hz, H10; 7·15, ddd, J_{6,7} 8·0, J_{7,8} 7·3, J_{5,7} 1·4 Hz, H6; 7·21, ddd, J_{6,7} 8·0, J_{7,8} 7·3, J_{5,7} 1·4 Hz, H7; 7·28, dd, J_{5,6} 7·3, J_{5,7} 1·4 Hz, H5; 7·38, d, J_{3,4} 8·1 Hz, H4; 7·51, dd, J_{7,8} 7·4, J_{6,8} 1·4 Hz, H8; 8·01, dd, J_{3,4} 8·1, J_{1,3} 2·4 Hz, H3; 8·35, d, J_{1,3} 2·4 Hz, H1. m/z 281 (M, 0·3%), 253 (100), 238 (33), 164 (14).

9-Methoxy-2,6-dinitro-9,10-dihydro-9,10-ethanoanthracene (5g) and 9-Methoxy-2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene (6g)

The reaction was repeated on $(2g)^5$ (400 mg) with copper(II) nitrate (1 2 g) in acetic anhydride (30 ml). After 3 h the reaction mixture was quenched and worked up to give

the crude products that were separated by chromatography with 30% ethyl acetate/light petroleum as eluent.

The less polar component gave 9-methoxy-2,6-dinitro-9,10-dihydro-9,10-ethanoanthracene (5g) (203 mg, 37%), as white crystals from light petroleum/ethyl acetate, m.p. 162-164° (Found: C, 62.6; H, 4.2; N, 8.4. C₁₇H₁₄N₂O₅ requires C, 62.6; H, 4.3; N, 8.6%). $\nu_{\rm max}$ 1526, 1347 cm⁻¹. $\lambda_{\rm max}$ 280 nm (ϵ 19300). ¹H n.m.r. δ 1.98, m, CH₂CH₂; 3.92, s, OCH₃; 4.51, t, J 2.3 Hz, H10; 7.46, d, J_{3,4} 8.2 Hz, H4; 7.69, d, J_{7,8} 8.3 Hz, H8; 8.07, dd, J_{3,4} 8.2, J_{1,3} 2.3 Hz, H3; 8.12, dd, J_{7,8} 8.3, J_{5,7} 2.2 Hz, H7; 8.15, d, J_{5,7} 2.2 Hz, H5; 8.37, d, J_{1,3} 2.3 Hz, H1. m/z 327 (M+1, 0.2%), 326 (M, 0.1), 312 (0.7), 299 (53), 298 (100), 283 (53), 269 (20), 252 (18), 237 (21), 176 (33), 163 (55), 30 (36).

The more polar component gave 9-methoxy-2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene (6g) (194 mg, 35%), as white crystals from light petroleum/ethyl acetate, m.p. 223-225° (Found: C, 62.8; H, 4.2; N, 8.3. C₁₇H₁₄N₂O₅ requires C, 62.6; H, 4.3; N, 8.6%). $\nu_{\rm max}$ 1527, 1345 cm⁻¹. $\lambda_{\rm max}$ 281 nm (ϵ 17300). ¹H n.m.r. δ 1.98, m, CH₂CH₂; 3.93, s, OCH₃; 4.51, t, J 2.3 Hz, H 10; 7.44, d, J_{3.4} (= J_{5.6}) 8.2 Hz, H 4.5; 8.06, dd, J_{3.4} (= J_{5.6}) 8.2, J_{1.3} (= J_{6.8}) 2.4 Hz, H 3.6; 8.37, d, J_{1.3} (= J_{6.8}) 2.4 Hz, H 1.8. m/z 326 (M, 0.02%), 312 (0.4), 298 (100), 283 (34), 176 (17), 163 (22).

2,10-Dinitro-9,10-dihydro-9,10-ethanoanthracene (3h) and 2,9-Dinitro-9,10-dihydro-9,10-ethanoanthracene (4h)

The ethanoanthracene $(2h)^5$ (420 mg, 1.67 mmol) dissolved in acetic anhydride (11 ml) was treated with a stirred suspension of copper(II) nitrate (1.2 g, 5 mmol) in acetic anhydride (10 ml). The reaction mixture was quenched after 4.5 h and worked up in the usual manner to give a mixture of products which were separated by chromatography with 20% ethyl acetate/light petroleum as eluent.

The less polar component gave 2,10-dinitro-9,10-dihydro-9,10-ethanoanthracene (3h) (51 mg, 10%), as colourless crystals from ethyl acetate/light petroleum, m.p. 176° (Found: C, 64.8; H, 3.9; N, 9.4. C₁₆H₁₂N₂O₄ requires C, 64.9; H, 4.1; N, 9.5%). ν_{max} 1549, 1528, 1350 cm⁻¹. λ_{max} 269 nm (ϵ 9870). ¹H n.m.r. δ 1.93, m, 2H, CH₂CH₂; 2.32, m, 1H, CH₂CH₂; 2.37, m, 1H, CH₂CH₂; 4.55, t, J 2.8 Hz, H9; 7.21, m, H5; 7.28, m, H6,7; 7.40, m, H8; 7.43, d, J_{3,4} 8.6 Hz, H4; 8.13, dd, J_{3,4} 8.6, J_{1,3} 2.3 Hz, H3; 8.23, d, J_{1,3} 2.3 Hz, H1. m/z 297 (M+1, 7%), 296 (M, 38), 268 (100), 250 (86), 203 (94), 189 (23), 176 (50), 164 (35), 152 (20), 150 (20), 101 (30).

The more polar component gave 2,9-dinitro-9,10-dihydro-9,10-ethanoanthracene (4h) (370 mg, 75%), as colourless crystals from ethyl acetate/light petroleum, m.p. 204° (Found: C, 65·1; H, 4·0; N, 9·5. C₁₆H₁₂N₂O₄ requires C, 64·9; H, 4·1; N, 9·5%). ν_{max} 1549, 1529, 1349 cm⁻¹. λ_{max} 275 nm (ϵ 9290). ¹H n.m.r. δ 1·93, m, 2H, CH₂CH₂; 2·32, m, 1H, CH₂CH₂; 2·41, m, 1H, CH₂CH₂; 4·54, t, J 2·7 Hz, H10; 7·22, m, H8; 7·28, m, H6,7; 7·39, m, H5; 7·53, d, J_{3,4} 8·8 Hz, H4; 8·16, dd, J_{3,4} 8·8, J_{1,3} 2·2 Hz, H3; 8·17, d, J_{1,3} 2·2 Hz, H1. N.O.e. results: irradiation of H10 (δ 4·54) gave an 8·2% enhancement for each of the signals for H4 (δ 7·53) and H5 (δ 7·39). m/z 297 (M+1, 10%), 296 (M, 42), 268 (90), 250 (85), 203 (100), 202 (98), 189 (26), 176 (55), 163 (44), 152 (23), 150 (20), 101 (27).

2,6,9-Trinitro-9,10-dihydro-9,10-ethanoanthracene (5h) and 2,7,9-Trinitro-9,10-dihydro-9,10-ethanoanthracene (6h)

Dinitration of $(2h)^5$ (510 mg) was achieved with copper(II) nitrate $(1 \cdot 5 \text{ g})$ in acetic anhydride (25 ml). The reaction was quenched after 47 h and the reaction mixture was worked up to give a mixture of the mononitro products (3h) and (4h) and two more polar products. The polar components were separated by chromatography with 30% ethyl acetate/light petroleum as eluent, and the least polar component gave 2,6,9-trinitro-9,10-dihydro-9,10-ethanoanthracene (5h) (184 mg, 27%), as white crystals from ethyl acetate, double m.p. 250-251 and 265° (Found: C, 56 · 3; H, 3 · 2; N, 12 · 5. C₁₆H₁₁N₃O₆ requires C, 56 · 3; H, 3 · 3; N, 12 · 3%). ν_{max} 1553, 1530, 1351 cm⁻¹. λ_{max} 269 nm (ϵ 22100). ¹H n.m.r. δ 2 · 00, m, CH₂CH₂; 2 · 44, m, CH₂CH₂; 4 · 70, t, J 2 · 8 Hz, H 10; 7 · 45, d, J_{7,8} 8 · 4 Hz, H 8; 7 · 60, d, J_{3,4} 8 · 2 Hz, H 4; 8 · 18, d, J_{1,3} 2 · 2 Hz, H 1; 8 · 19, dd, J_{7,8} 8 · 4, J_{5,7} 2 · 3 Hz, H 7; 8 · 23, dd, J_{3,4} 8 · 2, J_{1,3} 2 · 2 Hz, H 3; 8 · 28, d, J_{5,7} 2 · 3 Hz, H 5. m/z 342 (M+1, 4%), 341 (M, 22), 325 (10), 313 (100), 295 (81), 249 (26), 202 (93), 189 (28), 175 (23), 163 (44), 30 (30).

The more polar component gave 2,7,9-trinitro-9,10-dihydro-9,10-ethanoanthracene (6h) (236 mg, 34%), as white crystals from ethyl acetate, m.p. 248-249° (Found: C, 56·4; H, 3·2; N, 12·5. C₁₆H₁₁N₃O₆ requires C, 56·3; H, 3·3; N, 12·3%). ν_{max} 1553, 1531, 1351 cm⁻¹. λ_{max} 274 nm (ϵ 20400). ¹H n.m.r. 2·00, m, CH₂CH₂; 2·45, m, CH₂CH₂; 4·69, t, J 2·8 Hz, H 10; 7·59, d, J_{3,4} (= J_{5,6}) 8·2 Hz, H 4,5; 8·18, d, J_{1,3} (= J_{6,8}) 2·2 Hz, H 1,8; 8·23, dd, J_{3,4} (= J_{5,6}) 8·2, J_{1,3} (= J_{6,8}) 2·2 Hz, H 3,6. m/z 342 (M+1, 4%), 341 (M, 24), 325 (13), 313 (100), 295 (86), 249 (24), 202 (60), 189 (20), 163 (24), 44 (33).

3-Nitro-9,10-dihydro-9,10-ethanoanthracene-9-carbonitrile (3i) and 2-Nitro-9,10-dihydro-9,10-ethanoanthracene-9-carbonitrile (4i)

The ethanoanthracene $(2i)^5$ (911 mg) was dissolved in acetic anhydride (10 ml) and the solution was added to a suspension of copper(II) nitrate $(5 \cdot 0 \text{ g})$ in acetic anhydride (10 ml). The reaction mixture was quenched after $3 \cdot 5$ h and worked up in the usual manner to give a mixture of products which were separated by chromatography with 20% ethyl acetate/light petroleum as eluent.

The less polar component gave 3-nitro-9,10-dihydro-9,10-ethanoanthracene-9-carbonitrile (3i) (73 mg, 7%), as pale yellow crystals from ethyl acetate/light petroleum, m.p. 123–124° (Found: C, 74·2; H, 4·4; N, 10·2. C₁₇H₁₂N₂O₂ requires C, 73·9; H, 4·4; N, 10·1%). ν_{max} 2250, 1527, 1351 cm⁻¹. λ_{max} 271 nm (ϵ 9190). ¹H n.m.r. δ 1·90, m, CH₂CH₂; 2·15, m, CH₂CH₂; 4·55, t, J 2·7 Hz, H10; 7·29, m, H6,7; 7·37, m, H5; 7·66, m, H8; 7·80, d, J_{1,2} 8·3 Hz, H1; 8·15, dd, J_{1,2} 8·3, J_{2,4} 2·3 Hz, H2; 8·20, d, J_{2,4} 2·3 Hz, H4. m/z 276 (M, 13%), 249 (20), 248 (100), 202 (46), 201 (19), 190 (15), 175 (10).

The more polar component gave 2-nitro-9,10-dihydro-9,10-ethanoanthracene-9-carbonitrile (4i) (355 mg, 33%), from ethyl acetate, m.p. 227° (lit.²² 215°). ¹H n.m.r. δ 1.89, m, CH₂CH₂; 2.15, m, CH₂CH₂; 4.54, t, J 2.7 Hz, H10; 7.28, m, H6, 7; 7.35, m, H5; 7.50, d, J_{3,4} 8.0 Hz, H4; 7.68, m, H8; 8.15, dd, J_{1,3} 2.2, J_{3,4} 8.0 Hz, H3; 8.50, d, J_{1,3} 2.2 Hz, H1.

2,6-Dinitro-9,10-dihydro-9,10-ethanoanthracene-9-carbonitrile (5i) and 2,7-Dinitro-9,10-dihydro-9,10-ethanoanthracene-9-carbonitrile (6i)

Dinitration of $(2i)^5$ (516 mg) was performed with copper(II) nitrate $(3 \cdot 0 \text{ g})$ and acetic anhydride (10 ml). The reaction was quenched after 24 h and the mixture was worked up in the usual manner to give a mixture of the mononitro and dinitro products. The dinitrated products were isolated by chromatography with 50% ethyl acetate/light petroleum as eluent.

The less polar component gave 2,6-dinitro-9,10-dihydro-9,10-ethanoanthracene-9-carbonitrile (5i) (73 mg, 10%), as white crystals from ethyl acetate, m.p. 229–230° (Found: C, 63·7; H, 3·4; N, 13·0. C₁₇H₁₁N₃O₄ requires C, 63·6; H, 3·5; N, 13·1%). ν_{max} 2250, 1528, 1350 cm⁻¹. λ_{max} (ethanol) 269 nm (ϵ 18400). ¹H n.m.r. δ 1·96, m, CH₂CH₂; 2·23, m, CH₂CH₂; 4·71, t, J 2·8 Hz, H10; 7·57, d, J_{3,4} 8·4 Hz, H4; 7·87, d, J_{7,8} 8·3 Hz, H8; 8·21, dd, J_{3,4} 8·3, J_{1,3} 2·2 Hz, H3; 8·21, dd, J_{7,8} 8·3, J_{5,7} 2·2 Hz, H7; 8·25, d, J_{5,7} 2·2 Hz, H5; 8·54, d, J_{1,3} 2·2 Hz, H1. m/z 321 (M, 5%), 294 (18), 293 (100), 247 (22), 235 (16), 201 (52), 189 (18), 149 (16), 43 (15).

The more polar component gave 2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene-9-carbonitrile (6i) (258 mg, 36%), as white crystals from ethyl acetate, m.p. 259-260° (Found: C, 63·4; H, 3·4; N, 13·4. C₁₇H₁₁N₃O₄ requires C, 63·6; H, 3·5; N, 13·1%). ν_{max} 2250, 1529, 1350 cm⁻¹. λ_{max} 274 nm (ϵ 21500). ¹H n.m.r. δ 1·96, m, CH₂CH₂; 2·24, m, CH₂CH₂; 4·70, t, J 2·8 Hz, H 10; 7·56, d, J_{3,4} (= J_{5,6}) 8·2 Hz, H 4,5; 8·21, dd, J_{3,4} (= J_{5,6}) 8·20, J_{1,3} (= J_{6,8}) 2·2 Hz, H 3,6; 8·54, d, J_{1,3} (= J_{6,8}) 2·2 Hz, H 1,8. m/z 321 (M, 5%), 294 (18), 293 (100), 247 (20), 235 (18), 201 (51), 189 (18), 174 (10), 149 (10), 43 (12).

3-Nitro-9,10-dihydro-9,10-ethanoanthracen-9-carbaldehyde (3j) and 2-Nitro-9,10-dihydro-9,10-ethanoanthracen-9-carbaldehyde (4j)

The ethanoanthracene $(2j)^5$ (111 mg, 0.47 mmol) was treated with copper(II) nitrate (0.5 g) in acetic anhydride (10 ml) in the usual fashion. The reaction was quenched after 5 h and the mixture worked up to give a crude mixture of products that was separated by h.l.p.c. with 30% dichloromethane/light petroleum as eluent to yield, as the less polar component,

²² Wilhelm, M., Ger. Pat., DE 1964797 (1970) (Chem. Abstr., 1970, 73, 66342).

3-nitro-9,10-dihydro-9,10-ethanoanthracene-9-carbaldehyde (3j) (17 mg, 13%), as white crystals from light petroleum, m.p. 109–110° (Found: C, 73·1; H, 4·7; N, 5·2. C₁₇H₁₃NO₃ requires C, 73·1; H, 4·7; N, 5·0%). ν_{max} 1729, 1524, 1348 cm⁻¹. λ_{max} 278 nm (ϵ 44600). ¹H n.m.r. δ 1·83–2·03, m, CH₂CH₂; 4·50, t, J 2·0 Hz, H10; 7·20, ddd, J_{6,7} 8·0, J_{5,6} 6·8, J_{6,8} 1·5 Hz, H6; 7·23, ddd, J_{6,7} 8·0, J_{7,8} 7·0, J_{5,7} 1·5 Hz, H7; 7·34, m, H5; 7·38, m, H8; 7·62, d, J_{1,2} 8·4 Hz, H1; 8·06, dd, J_{1,2} 8·4, J_{2,4} 2·3 Hz, H2; 8·19, d, J_{2,4} 2·3 Hz, H4; 10·83, s, CHO. m/z 279 (M, 16%), 251 (100), 250 (25), 204 (14), 176 (31).

The more polar component gave 2-nitro-9,10-dihydro-9,10-ethanoanthracene-9-carbaldehyde (4j) (45 mg, 34%), as white crystals from ethyl acetate/light petroleum, m.p. 176–177° (lit.²³ 170–175°). ¹H n.m.r. δ 1.87, m, 3H, CH₂CH₂; 2.01, m, 1H, CH₂CH₂; 4.50, t, *J* 2.1 Hz, H 10; 7.21, m, H 6,7; 7.36, m, H 5,8; 7.49, d, *J*_{3,4} 8.0 Hz, H 4; 8.10, dd, *J*_{1,3} 2.1, *J*_{3,4} 8.0 Hz, H 3; 8.36, d, *J*_{1,3} 2.1 Hz, H 1.

$Methyl \ 3-Nitro-9, 10-dihydro-9, 10-ethanoanthracene-9-carboxylate \ (3k) \ and \ Methyl \ 2-Nitro-9, 10-dihydro-9, 10-ethanoanthracene-9-carboxylate \ (4k)$

Furning nitric acid $(1 \cdot 5 \text{ g})$ was added slowly to a mixture of glacial acetic acid $(1 \cdot 5 \text{ g})$ and acetic anhydride $(1 \cdot 5 \text{ g})$ and cooled below 10° . The mixture was added dropwise to a solution of the ester (2k) ($1 \cdot 89 \text{ g}$, $7 \cdot 1 \text{ mmol}$), in acetic anhydride (30 ml), and stirred at 0° . After $1 \cdot 5$ h the reaction was quenched with water, basified with sodium hydroxide (3 M) and worked up in the usual fashion to give the crude product as a yellow oil which was chromatographed on silica gel with 15% ethyl acetate/light petroleum as eluent.

The least polar component was a mixture of the mononitro products (3k) and (4k), in the ratio 73:27 of (4k) to (3k) (estimated by analytical h.p.l.c.). The mixture of mononitro products was recrystallized from ethyl acetate followed by methanol to give pure *methyl* 2-nitro-9,10-dihydro-9,10-ethanoanthracene-9-carboxylate (4k) (0.86 g, 39%), as white needles, m.p. 130-132° (Found: C, 69.9; H, 4.9; N, 4.4. C₁₈H₁₅NO₄ requires C, 69.9; H, 4.9; N, 4.5%). ¹H n.m.r. (200 MHz) δ 1.80, m, CH₂CH₂; 1.97, m, CH₂CH₂; 4.09, s, CO₂CH₃; 4.42, t, J 2.6 Hz, H 10; 7.17, m, 4H, H 5,6,7,8; 7.36, d, J_{3,4} 7.90 Hz, H 4; 8.00, dd, J_{1,3} 2.2, J_{3,4} 7.90 Hz, H 3; 8.21, d, J_{1,3} 2.2 Hz, H 1. ν_{max} 2930, 1730, 1515, 1450, 1345, 1260, 1245, 1200 cm⁻¹. λ_{max} (ethanol) 280 nm (ϵ 8600). *m/z* 310 (M+1, 2%), 309 (M, 8), 293 (3), 282 (18), 281 (100), 265 (4), 250 (23), 235 (5), 220 (17), 203 (12), 176 (16). The combined mother liquors were further separated into components by h.p.l.c. with 72% methanol/water as eluent to give a further sample of (4k) (0.31 g; total yield 1.17 g, 53%).

The less polar component on recrystallization from methanol gave methyl 3-nitro-9,10dihydro-9,10-ethanoanthracene-9-carboxylate (3k) (0.43 g, 20%), as colourless crystals, m.p. 130–132° (Found: C, 70.1; H, 4.8; N, 4.3. C₁₈H₁₅NO₄ requires C, 69.9; H, 4.9; N, 4.5%). ¹H n.m.r. (200 MHz) δ 1.81, m, CH₂CH₂; 1.96, m, CH₂CH₂; 2.09, m, CH₂CH₂; 4.11, s, CO₂CH₃; 4.48, t, J 2.6 Hz, H10; 7.20, m, 2H, H6,7; 7.25, m, H5; 7.34, m, H8; 7.53, d, J_{1,2} 8.5 Hz, H1; 8.04, dd, J_{2,4} 2.2, J_{1,2} 8.5 Hz, H2; 8.16, d, J_{2,4} 2.2 Hz, H4. ν_{max} 1736, 1524, 1348, 1271, 1256 cm⁻¹. λ_{max} (ethanol) 275 nm (ϵ 6200). m/z 310 (M+1, 2%), 309 (M, 13), 282 (18), 281 (95), 265 (20), 250 (20), 237 (16), 236 (100), 220 (5), 205 (37), 177 (22), 176 (23), 88 (15).

Methyl 2,6-Dinitro-9,10-dihydro-9,10-ethanoanthracene-9-carboxylate (5k) and Methyl 2,7-Dinitro-9,10-dihydro-9,10-ethanoanthracene-9-carboxylate (6k)

Concentrated nitric acid (10 ml, 70% w/w) was slowly added dropwise to a suspension of the methyl ester (2k) (1.0 g, 3.8 mmol) in concentrated sulfuric acid (10 ml, 98% w/w) and gently stirred at 0°. The reaction mixture was allowed to warm to room temperature and after all the solid had dissolved the reaction was quenched with water (100 ml). The reaction mixture was carefully neutralized with sodium hydroxide (5 M) and worked up in the usual fashion to give the crude product (1.28 g) which was chromatographed on silica gel with 15% ethyl acetate/light petroleum as eluent.

The less polar component (0.65 g) on recrystallization from methanol gave pure *methyl* 2,6-dinitro-9,10-dihydro-9,10-ethanoanthracene-9-carboxylate (5k) (0.58 g, 43%), as fine white

²³ Meek, J. S., Monroe, P. A., and Bouboulis, C. J., J. Org. Chem., 1963, 28, 2527.

needles, m.p. 182–183° (Found: C, 61·0; H, 4·0; N, 7·9. C₁₄H₁₄N₂O₆ requires C, 61·0; H, 4·0; N, 7·9%). ¹H n.m.r. (400 MHz) δ 1·87, m, CH₂CH₂; 2·1, m, CH₂CH₂; 4·17, s, CO₂CH₃; 4·63, t, J 2·60 Hz, H10; 7·49, d, J_{7,8} 8·50 Hz, H 8; 7·52, d, J_{3,4} 8·1 Hz, H4; 8·08, dd, J _{5,7} 2·40, J_{7,8} 8·50 Hz, H7; 8·16, dd, J_{1,3} 2·20, J_{3,4} 8·10 Hz, H3; 8·20, d, J_{5,7} 2·40 Hz, H5; 8·24, d, J_{1,3} 2·20 Hz, H1. ν_{max} 3008, 2929, 1740, 1526, 1348, 1273, 1258, 1016, 900 cm⁻¹. λ_{max} 276 nm (ϵ 21750). m/z 355 (M+1, 3%), 354 (M, 6%), 326 (100), 295 (19), 280 (7), 202 (10), 163 (13), 69 (7).

The more polar component (0.54 g) on recrystallization from methanol gave methyl 2,7-dinitro-9,10-dihydro-9,10-ethanoanthracene-9-carboxylate (6k) (0.46 g, 34%), as colourless crystals, m.p. 207-209° (Found: C, 60.7; H, 4.0; N, 8.0. C₁₄H₁₄N₂O₆ requires C, 61.0; H, 4.0; N, 7.9%). ν_{max} 2957, 1740, 1529, 1346, 1277, 1251, 1013, 906 cm⁻¹. λ_{max} 280 nm (ϵ 20270). ¹H n.m.r. (400 MHz) δ 1.88, m, CH₂CH₂; 2.10, m, CH₂CH₂; 4.21, s, CO₂CH₃; 4.62, t, J 2.70 Hz, H10; 7.50, d, J_{3,4} (= J_{5,6}) 8.20 Hz, H4,5; 8.12, dd, 2H, J_{1,3} (= J_{6,8}) 2.20, J_{3,4} (= J_{5,6}) 8.20 Hz, H3,6; 8.23, d, 2H, J_{1,3} (= J_{6,8}) 2.20 Hz, H1,8. m/z 355 (M+1, 3%), 354 (M, 6%), 326 (100), 295 (19), 280 (5), 202 (12), 163 (13), 69 (10).

Alternative Nitration of Methyl 9,10-Dihydro-9,10-ethanoanthracene-9-carboxylate (2k)

A solution of methyl 9,10-dihydro-9,10-ethanoanthracene-9-carboxylate (2k) ($1 \cdot 0$ g, $3 \cdot 8$ mmol) in acetic anhydride (29 ml) was added rapidly to a stirred finely ground suspension of copper(II) nitrate ($4 \cdot 3$ g, 18 mmol, $4 \cdot 7$ equiv.) in acetic anhydride (23 ml) kept below -10° . The reaction mixture was allowed to warm to room temperature (20°) over a period of 30 min. The reaction mixture was quenched with water, basified with sodium hydroxide (3 M) and worked up in the usual fashion to give the crude product which was chromatographed on silica gel with 15% ethyl acetate/light petroleum as eluent to give the less polar component as a mixture of the mononitro isomers (4k) and (3k) in the ratio 66:34 of (4k) to (3k) (by ¹H n.m.r. spectroscopy). The next component was a mixture of the dinitrated isomers (5k) and (6k) in approximately equal amounts. The esters (3k), (4k), (5k) and (6k) were isolated in 14, 35, 22 and 19% yields respectively in the same fashion as, and had identical properties with, the corresponding compounds described above.

Quantitative Nitration Studies

General experimental procedure for nitration of compounds (2b-d,f-j) with copper(II) nitrate in acetic anhydride.—The particular ethanoanthracene (2) (0.3-0.45 mmol) together with the internal standard m-dinitrobenzene were dissolved in acetic anhydride (10 ml). Powdered and vacuum-dried copper(II) nitrate (0.4-1.8 mmol) was added to the stirred solution. Reactions were monitored for up to 6 h depending on the reactivity of the substrates, the concentration of the substrates and the amount of copper(II) nitrate used. At appropriate time intervals, aliquots (1 ml) were pipetted out of the reaction mixture into a mixture of ammonia (16 M, 10 ml), water (10 ml) and chloroform (10 ml), and the distribution of the nitration products was estimated by g.l.c. The combined recoveries of starting material and mononitrated products (the proportion of dinitrated products was not determined) for each of the 9-substituted ethanoanthracenes studied after the indicated times were near quantitative (>98%) except for: (2d), 86% after 2 h; (2h), 86% after 2 h; (2i), 83%