colourless prismatic needles (2·0 g) m.p. 151–52°. The product agreed in all its properties and colour reaction with sakuranetin. Its acetate prepared by the procedure of Narasimhachari *et al.*[7] gave small colourless prisms, m.p. 98–99°.

The benzene insoluble portion gave on crystallisation from alcohol pale yellow needles (1 g) m.p. 236–38°, undepressed by prunetin and acetylation yielded colourless needles, m.p. 222–24° undepressed by prunetinacetate.

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The preparation of nitroanthraquinones by the peracetic acid oxidation of aminoanthraquinones

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SOME time ago, in connection with other work, the need arose for quantities of 1-chloro-2-nitroanthraquinone. This compound had been prepared previously in 36 per cent crude yield[1] from 2-amino-1-chloroanthraquinone via the diazonium sulfate, and in unspecified yield[2] by persulfuric acid oxidation of the amine. However, we were induced to consider the use of peracetic acid for this oxidation by a report[3] of the simple conversion, in this manner, of 1:2-diaminoanthraquinone into 1-amino-2-nitroanthraquinone.

The reaction proved to be so convenient and efficient that the preparation of other nitroanthraquinones was examined. Nine amino-anthraquinones were thus converted into their nitro homologs in yields ranging from 35–82 per cent. The best yields (61–82 per cent) were encountered in the oxidation of simple aminohaloanthraquinones. The presence of negative groups adjacent to the amino group appears beneficial, since 2:6-diamino-1:5-dichloroanthraquinone and 1:4-diamino-2:3-dichloroanthraquinone were successfully oxidized, while the corresponding unchlorinated diamines gave only mixtures of unidentified products.

Kopetschni reported[2] 1-amino-4-chloroanthraquinone to be oxidized only to the nitroso homolog by the action of persulfuric acid. Peracetic acid oxidation, however, readily produced 1-chloro-4-nitro-anthraquinone. Oxidation of 1:2-diaminoanthraquinone produced, as reported,[3] some 1-amino-2-nitroanthraquinone provided the reaction mixture was heated only briefly. Continued heating, however, gave mixtures of unidentified products, in which, to judge from the yellow color, the 1-amino group was no longer present.

The reaction of 1:4-diamino-2:3-dichloroanthraquinone was unique in that only one of the amino groups suffered oxidation. Heating the product with fresh peracetic acid produced no further oxidation. On the other hand, the introduction of two nitro groups into the same ring appears to be no obstacle, since 2:3-dinitroanthraquinone was obtained from 2-amino-3-nitroanthraquinone.

Recently, Emmons described[4] his careful work upon the peracetic acid oxidation of simple amines to nitro homologs, and indicated that inferior results were obtained in the case of weakly basic or negatively substituted amines. Our results appear to contradict this generalization (as amines of the anthraquinone series are very weakly basic), and are more in agreement with the results obtained[4] by using peroxytrifluoro-acetic acid as the oxidant. It is possible that the use of the latter reagent would give superior yields in the oxidation of aminoanthraquinones, but this was not investigated.

EXPERIMENTAL

General procedure. Commercial 40% peracetic acid and a product of similar strength prepared[5] by admixture of 30% hydrogen peroxide, acetic anhydride and acetic acid, were used interchangeably.

[1] W. Bradley and E. Leete, *J. Chem. Soc.* 2129 (1951).
[2] E. Kopetschni, *Ger. Pat.* 363,930; *Frdl.* **14**, 850 (1926).
[3] I. G. Farbenindustrie, A. G., *P.B. Report No.* 70341, frames 14040-2.
[4] W. D. Emmons, *J. Amer. Chem. Soc.* **79**, 5528 (1957).
[5] W. D. Emmons, *J. Amer. Chem. Soc.* **76**, 3470 (1954).

All melting points were taken in Pyrex capillaries using a Hershberg melting point apparatus and Anschütz thermometers.

TABLE 1. NITROANTHRAQUINONES FROM THE OXIDATION OF AMINOANTHRAQUINONES

Aminoanthraquinones	Nitroanthraquinones	Yield (%)	m.p. (°C)		Analyses C	H	Cl	N	O
2-Amino-1-chloro-	1-Chloro-2-nitro-	82	264·4–266·3[a]	Calc.:	58·42	2·11	12·33	4·87	22·27
				Found:	—	—	—	—	—
1-Amino-2-chloro-	2-Chloro-1-nitro-[b]	75	282–284[c]	Found:	58·42	2·10	12·60	5·22	—
1-Amino-4-chloro-	1-Chloro-4-nitro-[d]	73	257·0–258·5[e]	Found:	58·91	2·10	12·28	4·43	22·18
2-Amino-3-bromo-	2-Bromo-3-nitro-	61	281·5–283·1[f]	Calc.:	50·60	1·81	24·10[g]	4·21	19·28
				Found:	50·80	1·88	24·20	4·27	19·10
2:6-Diamino-1:5-dichloro-	1:5-Dichloro-2:6-dinitro-	52	346·0–347·5[h]	Calc.:	45·78	1·10	19·34	7·63	26·15
				Found:	45·75	1·37	18·97	8·04	25·65
1-Amino-5-nitro-	1:5-Dinitro-	62	·360[i]	Calc.:	56·40	2·02	—	9·39	32·20
				Found:	56·43	1·84	—	9·47	—
1-Amino-8-nitro-	1:8-Dinitro-	38	315–322d[j]	Found:	56·30	1·93	—	9·61	32·23
2-Amino-3-nitro-[k]	2:3-Dinitro-	36	276–277[l]	Found:	56·42	2·08	—	9·36	—
1:4-Diamino-2:3-dichloro-	1-Amino-2:3-dichloro-4-nitro-	35	328·4–330·5[m]	Calc.:	49·85	1·78	21·05	8·32	19·00
				Found:	50·42	1·86	21·01	8·23	18·74

[a] Yellow irregular platelets, crystallized once from acetic acid. Lit.,[1,8] m.p. 262–263°; 257 258°.

[b] Previously prepared[1] in 11·8 per cent yield by nitration of 2-chloroanthraquinone.

[c] Ochre needles, crystallized three times from acetic acid. Lit.,[1] m.p. 280 281°.

[d] Previously prepared[6] in 30 per cent yield by nitration of 1-chloroanthraquinone.

[e] Orange needles, twice crystallized from acetic acid. Lit.,[6] m.p. 259°.

[f] Yellow platelets, twice crystallized from benzene and once from chlorobenzene.

[g] Bromine analysis.

[h] Yellow platelets, crystallized three times from acetic acid.

[i] Tan microcrystals from glycol diacetate. Lit.,[7] m.p. 385°.

[j] Golden prisms, three times crystallized from chlorobenzene. Lit.,[7] m.p. 312°.

[k] Prepared by tosylamidation of 2-bromo-3-nitroanthraquinone, followed by hydrolysis.

[l] Golden-tan platelets, twice crystallized from chlorobenzene and twice from glycol diacetate.

[m] Brown microneedles, crystallized three times from chlorobenzene and once from glycol diacetate.

[1] A. Eckert and K. Steiner, *Monatsh.* **35**, 1129 (1914).

[7] E. Hefti, *Helv. Chim. Acta* **14**, 1404 (1931).

The amines employed were purified samples of commerically available vat dye intermediates. The aminoanthraquinone was mixed with the peracetic acid (20 ml/g amine) and the mixture was heated to the boiling point for ½–¾ hr. When larger (>10 g) quantities of amine were used, the peracetic acid was diluted with an equal volume of glacial acetic acid to moderate the reaction. The cooled solution was drowned, and the nitroanthraquinone was filtered and crystallized. The products are listed in Table 1, and the yields are those of the purified products.

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2-Benziminazolylmethyl*iso*thiouronium salts

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The recent publication[1] of a preparation of 2-benziminazolylmethyl*iso*thiouronium hydrochloride prompts us to report an examination of this compound which we carried out some time ago as an alternative to benzyl*iso*thiouronium hydrochloride for the characterisation of carboxylic acids. It was thought that the associating properties of the benziminazole ring system might lead to carboxylic acid salts with higher melting points than those of the benzyl analogs, and that the difference in melting point between neighbouring members of homologous series might be increased. A few salts of the more volatile carboxylic acids were prepared by metathesis from the hydrochloride; they showed similar solubility characteristics and melting points which are compared in Table 1. Basification of solutions of 2-benziminazolylmethyl*iso*thiouronium hydrochloride in air produced a colourless, odourless solid, m.p. 184–186°C; which is probably the corresponding disulphoxide (Found: N, 15·9, calc. for $C_{16}H_{14}O_2N_4S_2$: N, 15·65%). Hughes and Lions[2] reported its melting point as 182°; the corresponding mercaptan melted at 158°. Thus, the only advantage that might be claimed over the use of the well established benzyl*iso*thiouronium hydrochloride was the freedom from the nauseating smell of benzyl mercaptan frequently associated with its use, and so the investigation was not continued. The fact that the melting points of benzyl- and 2-benziminazolylmethyl*iso*thiouronium salts are in the main so close together supports the view[3] that the nature of the radicals attached to the thiourea and to the carboxyl group make little or no contribution to the stability of the crystal. Walker based this conclusion on a comparison of the melting points of benzyl and substituted benzyl*iso*thiouronium salts and some additional support is now available from a system containing a markedly different heterocyclic structure attached to the thiourea group.

TABLE 1. 2-BENZIMINAZOLYLMETHYL*ISO*THIOURONIUM SALTS

Acid	M.p.	Formula	Nitrogen Calc.	Nitrogen Found
Trifluoroacetic	167°	$C_{11}H_{11}O_2N_4F_3S$	17·5	18·0
Formic	154° (152°)	$C_{10}H_{12}O_2N_4S$	22·2	21·9
Acetic	150° (136°)	$C_{11}H_{14}O_2N_4S$	21·1	21·3
n-Butyric	151·5° (150°)	$C_{13}H_{18}O_2N_4S$	19·1	19·0

Figures in parentheses indicates m.p.s of corresponding benzyl analogs.[4]

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[2] G. K. Hughes and F. Lions, *J. Proc. Roy. Soc., N.S.W.* **71**, 209 (1938).
[3] J. Walker, *J. Chem. Soc.* 1996 (1949).
[4] J. Berger, *Acta Chem. Scand.* **8**, 427 (1954).