## Internuclear Cyclisation. Part XXIII.<sup>1</sup> Formation and Rearrangement of 2-Methylisoindoline-1-spirocyclohexa-2',5'-diene-3,4'-dione. Synthesis of the Octahydro-derivative of an Unsaturated Dimer

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The decomposition of N-methyl-4'-(methylthio)benzanilide-2-diazonium salts (VIII) gives 2-methylisoindoline-1-spirocyclohexa-2'.5'-diene-3.4'-dione (IV) and methanethiol, rather than the corresponding thione and methanol. Similarly, 4'-methoxy-N-methylbenzanilide-2-diazonium sulphate (VIII; O for S) decomposes in <sup>18</sup>Oenriched water to give the dione (IV) with incorporation of <sup>18</sup>O. This spiro-dienone forming reaction does not intervene in Pschorr cyclisations since trans-2-amino-a-(2- and 4-methoxyphenyl)cinnamic acids give 1- and 3-methoxyphenanthrene-10-carboxylic acid in high yield.

Reduction of the spiro-dienone (IV) results in opening of the  $\gamma$ -lactam ring and aromatisation to biphenyls; thus its semicarbazone with potassium t-butoxide gave N-methylbiphenyl-2-carboxamide, and Clemmensen reduction gave 4'-hydroxy-N-methylbiphenyl-2-carboxamide (VII).

The octahydro-derivative [bi-(2-methyl-3-oxoisoindoline-1-spirocyclohex-4'-yl) (XIV)] of an unsaturated dimeric product, (11), of an earlier diazonium decomposition has been synthesised, thus confirming the structure of this and analogous dimers.

IN Part XXII<sup>1</sup> we showed that a major product of the copper-catalysed decomposition of N-methylbenzanilide-2-diazonium fluoroborate (I) was the unsaturated dimer (II). We now describe attempts at the independent synthesis of (II) and some related investigations. The most likely precursor for the dimer (II) was considered to be the spiro-cyclohexadiene (III) which should readily undergo allylic hydrogen abstraction, by t-butoxy-radicals for example.<sup>2</sup> The resulting stabilised cyclohexadienyl radical would be expected to dimerise to (II), as proposed for the above diazonium of treatment of its semicarbazone with potassium t-butoxide in boiling toluene. However rearrangement again occurred rapidly to give N-methylbiphenyl-2-carboxamide (88%), probably by the mechanism shown in (V) and (VI). If the cyclohexadiene (III) was formed it was aromatised by base too rapidly to be isolated. Therefore acidic reduction of the dienone (IV), which is itself remarkably stable to acid,<sup>4</sup> was attempted. However, Clemmensen reduction by the "two layer" method, to minimise exposure to acid, again resulted in smooth aromatisation of (IV), as shown,



decomposition reaction.<sup>1</sup> Furthermore, reduction of the readily available cyclohexadienone<sup>3</sup> (IV) appeared to provide an attractive route to the diene (III). An earlier attempt to effect this reduction for the corresponding N-ethyl compound under Wolff-Kishner conditions led to biphenyl-2-carboxylic acid.<sup>4</sup> Compound (IV) was therefore subjected to the milder conditions  $^{5}$ 

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<sup>1</sup> Part XXII, D. H. Hey, C. W. Rees, and A. R. Todd, J. Chem. Soc. (C), 1967, 1518.

<sup>2</sup> A. L. J. Beckwith and W. A. Waters, J. Chem. Soc., 1957, 1001.

to give 4'-hydroxy-N-methylbiphenyl-2-carboxamide (VII) quantitatively; the structure of (VII) was confirmed by independent synthesis.

Since reduction of dienone (IV) under both acidic and alkaline conditions gave rearranged products, the preparation of the analogous dienethione was attempted in the expectation that the corresponding dienethiol

<sup>&</sup>lt;sup>3</sup> D. H. Hey, J. A. Leonard, C. W. Rees, and A. R. Todd, J. Chem. Soc. (C), 1967, 1513.

<sup>4</sup> D. H. Hey, J. A. Leonard, T. M. Moynehan, and C. W. Rees, J. Chem. Soc., 1961, 232. <sup>5</sup> M. F. Grundon, H. B. Henbest, and M. D. Scott, J. Chem.

Soc., 1963, 1855.

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would give the required cyclohexadienyl radicals on treatment with triethyl phosphite (cf. ref. 6). 2-Amino-N-methyl-4'-(methylthio)benzanilide was therefore prepared in the standard way from p-methylthioaniline. Thermal decomposition of its diazonium sulphate (VIII;  $X = HSO_4$ ) gave, not the desired dienethione however, but the dienone (IV) (36%), identical with that from the analogous 4'-methoxy-compound. The normal ringclosed product, N-methyl-2-methylthiophenanthridin-6-one (IX) (30%), was also formed; its structure followed from comparison of its i.r. and n.m.r. spectra those of 2-methoxy-N-methylphenanthridinwith 6-one.<sup>3</sup> ‡

Formation of the dienone (IV) from the methylthiocompound (VIII) presumably results from initial ring closure of the decomposing diazonium ion to the sulphonium ion (X). This ion could then be attacked by water either at the ring carbon, to give the hemithioacetal (XI), followed by elimination of methanethiol, or at the S-methyl group to give the thione which is then hydrolysed to the dienone (IV) and hydrogen sulphide. The former path was indicated by the detection of methanethiol and the absence of hydrogen sulphide during the decomposition of (VIII). An attempt to



exclude water, to prevent formation of the hemi-thioacetal (XI), was made by decomposition of N-methyl-4'-(methylthio)benzanilide-2-diazonium fluoroborate (VIII;  $X = BF_4$ ) in dry acetone; however no thione could be detected and the dienone (IV) (23%) and the phenanthridinone (IX) (16%) were again isolated.

In view of these various complexities it was decided to attempt the synthesis of the octahydro-derivative<sup>1</sup> (XIV) of the dimer (II) where the possibility of aromatising rearrangements is absent. Catalytic hydrogenation of the dienone (IV) gave 2-methylisoindoline-1-spirocyclohexane-3,4'-dione (XII) which with sodium borohydride in methanol gave the cyclohexanol (XIII; X = OH). Conversion of this into a halide was difficult but the bromide (XIII; X = Br) was obtained by heating with phosphorus tribromide at 100°. A Wurtz

reaction on this bromide then gave compound (XIV) in high yield, identical with the hydrogenation product of the dimer (II). Since the structure of (IV) has previously been proved by independent synthesis,<sup>7</sup> this synthesis of the saturated dimer provides proof of the



structure of dimer (II) and, by analogy, of the other unsaturated dimers obtained in earlier catalysed diazonium fluoroborate decompositions and in those to be described in Part XXIV.

The above formation of the dienone (IV), rather than the corresponding dienethione, in the decomposition of N-methyl-4'-(methylthio)benzanilide-2-diazonium salts (VIII) must involve incorporation of water from the medium. This suggested that formation of (IV) from the corresponding 4'-methoxy-compound (VIII; O for S) probably also involved incorporation of water to give the hemiacetal (XI; O for S), rather than nucleophilic attack by water on the O-methyl group of the oxonium ion (X; O for S), as previously suggested.<sup>4</sup> This mechanism was therefore investigated further by diazotisation of 2-amino-4'-methoxy-N-methylbenzanilide and decomposition of the diazonium sulphate (VIII; O for S) in isotopically normal water (0.2% H<sub>2</sub><sup>18</sup>O) and in oxygen-18 enriched water  $(1.6\% H_2^{18}\overline{O})$ . Examination of the mass spectrum of the dienone (IV) showed more or less complete incorporation of oxygen-18. The ratio of M + 2: M peaks was increased, in the enriched solvent, by 1.1 and 1.8% in two separate experiments. For comparison the methylthiodiazonium sulphate (VIII;  $X = HSO_4$ ) was also decomposed in the oxygen-18 enriched water and the M + 2: M enrichment was 1.3%(theoretical =1.4%). Thus the methylthio- and methoxy-containing diazonium salts decomposed by the same mechanism.

The general tendency to form cross-conjugated spirodienones, such as (IV), in the decomposition of diazonium salts from 2-amino-2'- and 4'-methoxycompounds in the benzanilide series has been noted in our earlier papers.<sup>1,3</sup> This reaction often predominates

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<sup>&</sup>lt;sup>‡</sup> In this and the following papers phenanthridines are numbered systematically and not, as in previous papers, analogously to phenanthrene.

<sup>&</sup>lt;sup>6</sup> C. Walling and M. S. Pearson, J. Amer. Chem. Soc., 1964,

<sup>86, 2262.</sup> <sup>7</sup> D. H. Hey, J. A. Leonard, and C. W. Rees, J. Chem. Soc.,

over ring closure to give phenanthridinones. It was therefore of interest to seek the analogous reaction in cases where the amide bridge is replaced by other groups. It was noted that in Pschorr's extensive study of 2-amino- $\alpha$ -phenylcinnamic aids, yields of the phenanthrene-9-carboxylic acids were sometimes lower than average when there were methoxy-groups in the  $\alpha$ -phenyl ring.<sup>8</sup> Therefore trans-2-amino- $\alpha$ -(2- and 4-methoxyphenyl)cinnamic acids were prepared and the decomposition of their diazonium salts under Pschorr's original, and our standard, conditions carefully investigated (see Experimental section). In the 4-methoxyphenyl case the only product detected was 3-methoxyphenanthrene-10-carboxylic acid, which was isolated in high yield (80-100%, lit., 8 50%). With the 2-methoxyphenyl compound 1-methoxyphenanthrene-10-carboxylic acid was again isolated in high yields (80-85%, lit.,  $^{8}$  55%) though a small amount of a gum was always formed. This could not be purified, but it showed no chemical or spectroscopic properties of a ketone, and no spiro-dienone analogous to those formed in the benzanilide series could be detected. Thus the formation of dienones does not extend to the spiro-indene system, possibly because of the greater rigidity of the olefinic bridging group.

## EXPERIMENTAL

For general directions see Part XXI.<sup>3</sup>

Reduction of 2-Methylisoindoline-1-spirocyclohexa-2',5'diene-3,4'-dione (IV).-(a) Modified Wolff-Kishner reducduction (with Dr. A. R. Todd). The dienone was converted into its semicarbazone (V), colourless needles from ethanol, m.p. 229-233° (decomp.) (Found: N, 19.6. C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub> requires N, 19.85%), which could be reconverted into the dienone (IV) with nitrous fumes.<sup>9</sup> The semicarbazone (1 g.), dry toluene (12 ml.), and potassium t-butoxide (1 g.) were heated under reflux in an apparatus attached to a gas burette. A rapid evolution of nitrogen occurred and the reaction was complete in 1.5 hr. The mixture was cooled and poured into 2n-hydrochloric acid (75 ml.) and the toluene layer was separated. The aqueous layer was extracted with ether and the combined organic layers were washed with water and dried. Removal of the solvents gave N-methylbiphenyl-2-carboxamide (0.7 g., 94%) which crystallised from benzene in yellow needles, m.p. 167-168°, mixed m.p. with an authentic specimen, 168-169° (lit.,<sup>10</sup> 165-167°), v<sub>max.</sub> 3317 (N-H) and 1634 cm.<sup>-1</sup> (amide C=O).

(b) Clemmensen reduction. Zinc dust (1 g.), mercuric chloride (100 mg.), concentrated hydrochloric acid (2 drops), and water (1 ml.) were shaken together for 5 min. The aqueous layer was decanted and the amalgamated zinc covered with water (1.5 ml.) and concentrated hydrochloric acid (1.5 ml.). The dienone (IV) (0.5 g.) in toluene (15 ml.) was added and the solution refluxed with stirring for 6 hr. The solution was diluted with water and continuously extracted with ether. The ether was dried and evaporated and the residue sublimed to give 4'-hydroxy-N-methyl-biphenyl-2-carboxamide (0.5 g., 100%) as needles, m.p. 190° (Found: C, 73.5; H, 5.9; N, 6.1. C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub> requires C, 74.0; H, 5.8; N, 6.2%)  $\nu_{max}$  3275 (N-H) and

1620 cm.<sup>-1</sup> (amide C=O). This was identical with the product from 4'-hydroxybiphenyl-2-carboxylic acid on treatment with thionyl chloride followed by methylamine.

(c) Catalytic reduction. The dienone (IV) (3 g.) in ethanol (300 ml.) was hydrogenated over 20% palladised charcoal (1 g.) until hydrogen (600 ml.) had been absorbed. The solution was filtered through Celite and evaporated. The residue crystallised from benzene-light petroleum to give prisms of 2-methylisoindoline-1-spirocyclohexane-3,4'-dione (XII) ( $2\cdot1$  g.), m.p. 173-175°,  $v_{max}$  1676 ( $\gamma$ -lactam C=O) and 1713 cm.<sup>-1</sup> (cyclohexanone C=O). Sodium borohydride (1 g.) in methanol (140 ml.) was added dropwise to the dione (XII) ( $2\cdot0$  g.) in methanol (200 ml.) and the mixture was stirred for 2 hr. The solution was diluted with water, the methanol was removed under reduced pressure, and the aqueous solution was continuously extracted with ether. Crystallisation from acetone-light petroleum gave 4'-hydroxy-2-methylisoindoline-1-spirocyclohexan-3-one

(XIII; X = OH) (90%) as fine needles, m.p. 145—146° (Found: C, 72.4; H, 7.1; N, 6.4.  $C_{14}H_{17}NO_2$  requires C, 72.7; H, 7.4; N, 6.1%),  $v_{max}$  3389br (OH) and 1680 cm.<sup>-1</sup> (y-lactam C=O).

Bi-2-methyl-3-oxoisoindoline-1-spirocyclohex-4'-yl (XIV). —The above cyclohexanol (XIII; X = OH) (0.02 g.) was heated on a steam-bath with phosphorus tribromide (2 ml.) for 1 hr. The mixture was poured into water, neutralised with 2N-aqueous potassium hydroxide, and extracted with ether. The extracts were washed with water, dried (CaSO<sub>4</sub>), and evaporated to give the crude cyclohexyl bromide as a colourless oil,  $v_{max}$ . 1680 cm.<sup>-1</sup> ( $\gamma$ -lactam C=O). The oil in dry ether was refluxed with sodium wire (0.02 g.) for 1 hr., and the solution was filtered and evaporated to give the bis-cyclohexyl compound (XIV) (0.015 g., 80%), m.p. and mixed m.p. above 360°, with an identical i.r. spectrum to that of the octahydro-derivative of bi-(2-methyl-3-oxoisoindoline-1-spirocyclohexadien-4'-yl) (II).<sup>1</sup>

2-Amino-N-methyl-4'-(methylthio)benzanilide. --- 4'-Methylthio-2-nitrobenzanilide. o-Nitrobenzoyl chloride (40 g.) in dry ether (40 ml.) was added dropwise to a solution of p-methylthioaniline (31 g.) in dry pyridine (150 ml.) with ice-cooling. After heating on a steam-bath for 1 hr. the ether was removed and the mixture was poured into water. The precipitate was washed with water, dried, and crystallised from ethanol to yield 4'-methylthio-2-nitrobenzanilide (55 g., 100%) as yellow needles, m.p. 160° (Found: C, 58·2; H, 4·4; N, 9·6. C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>S requires C, 58·3; H, 4·2; N, 9·7%),  $v_{max}$ . 3262 (amide N-H) and 1649 cm.<sup>-1</sup> (secondary amide C=O).

N-Methyl-4'-methylthio-2-nitrobenzanilide. 4'-Methylthio-2-nitrobenzanilide (48 g.) in acetone (600 ml.) and 10% aqueous sodium hydroxide (600 ml.) was boiled under reflux and dimethyl sulphate (60 ml.) added dropwise. The mixture was boiled for 0.5 hr., cooled, and poured into water. Crystallisation of the precipitate from benzene-light petroleum gave N-methyl-4'-methylthio-2-nitrobenzanilide (43 g., 90%) as yellow prisms, m.p. 143—144° (Found: C, 59.4; H, 4.6; N, 9.4.  $C_{15}H_{14}N_2O_3S$  requires C, 59.6; H, 4.7; N, 9.3%),  $\nu_{max}$ . 1644 cm.<sup>-1</sup> (tertiary amide C=O).

2-Amino-N-methyl-4'-(methylthio)benzanilide. The above nitro-compound (10 g.) in ethanol (200 ml.) was hydrogenated over 20% palladised charcoal (1 g.) until hydrogen

- <sup>8</sup> R. Pschorr, O. Wolfes, and W. Buckow, Ber., 1900, 23, 162.
- <sup>9</sup> D. H. Hey and D. S. Morris, J. Chem. Soc., 1948, 2319.
- <sup>10</sup> T. Mukai, Bull. Chem. Soc. Japan, 1959, **32**. 272.

(2·2 l.) had been absorbed. Filtration through Celite and evaporation of the solvent yielded an oil which crystallised from ethanol to give the *amine* (5·0 g., 56%), m.p. 77—77.5° (Found: C, 65·8; H, 6·1; N, 10·6.  $C_{15}H_{16}N_2OS$  requires C, 66·1; H, 5·9; N, 10·3%),  $\nu_{max}$ . 3440, 3340 (NH<sub>2</sub>), and 1640 cm.<sup>-1</sup> (tertiary amide C=O).

Decomposition of the Diazonium Sulphate from 2-Amino-N-methyl-4'-(methylthio)benzanilide (VIII;  $X = HSO_A$ ). The amine (3 g.) in water (130 ml.) and sulphuric acid (7 ml.) was diazotised at 0° with sodium nitrite (1 g.) in water. After stirring at  $0^{\circ}$  for 1 hr., urea (0.5 g.) was added and the solution was heated to  $70^{\circ}$  and held at this temperature for 1 hr. Methanethiol, but not hydrogen sulphide (lead acetate paper), was evolved and a solid separated. This was extracted with chloroform and the extracts were washed with water, dried, and evaporated. The crystalline residue was recrystallised from benzene-light petroleum (b.p. 80-100°) to give needles of 2-methylisoindoline-1-spirocyclohexa-2',5'-diene-3,4'-dione (IV) (0.7 g.), m.p. and mixed m.p. 222-223°. The mother-liquor from the recrystallisation was evaporated and the resultant gum was chromatographed on alumina. Elution with benzeneether and ether gave a yellow solid which crystallised from benzene-light petroleum (b.p. 80-100°) to give N-methyl-2-methylthiophenanthridin-6-one (IX), (0.85 g., 30%) as needles, m.p. 135-136° (Found: C, 70.8; H, 6.0.  $C_{15}H_{13}NOS$  requires C, 70.6; H, 5.1%)  $\nu_{max}$  1641 cm.<sup>-1</sup>. The nuclear magnetic resonance spectrum showed  $\tau 2.0$ — 3.0 (7H, aromatic), 6.2 (3H, N-Me), and 7.4 (3H, S-Me). Elution with 10% methanol in ether, and recrystallisation as above, gave more dienone (0.2 g., 36% in all), m.p. and mixed m.p. 222-223°.

Decomposition of the Diazonium Fluoroborate from 2-Amino-N-methyl-4'-(methylthio)benzanilide (VIII;  $X = BF_4$ ).—The amine (2 g.) was diazotised and converted with sodium fluoroborate in the usual way into its diazonium fluoroborate (1.9 g.). The latter was decomposed in dry acetone (MgSO<sub>4</sub>, then CaSO<sub>4</sub>) with copper powder to yield a gum which was chromatographed on alumina. Elution with benzene-ether and ether gave a yellow solid which crystallised from benzene-light petroleum to give N-methyl-2-methylthiophenanthridin-6-one (IX) (0.3 g., 16%), m.p. and mixed m.p. 135—136°. Further elution with ether gave a yellow solid which crystallised from benzenelight petroleum to give 2-methylisoindoline-1-spirocyclohexa-2',5'-diene-3,4'-dione (IV) (0.4 g., 23%), m.p. and mixed m.p. 222—223°.

Diazotisation and Decomposition of 2-Amino-4'-methoxy  $and\ -4'-methyl thio-N-methyl benzanilide\ in\ Isotopically\ Normal$ and in <sup>18</sup>O-Enriched Water.—The amine (1 g.) was dissolved in a warm mixture of sulphuric acid (1 ml.) and <sup>18</sup>O-enriched water  $(1.6\% H_2^{18}O, 15 ml.)$ . The solution was cooled to  $0^{\circ}$  and diazotised with sodium nitrite (0.32 g.) in <sup>18</sup>O-enriched water (2 ml.). After stirring at  $0^{\circ}$  for 1 hr. the mixture was warmed to  $70^\circ$  and maintained at this temperature for 1 hr., when the decomposition was complete. The solution was cooled and the product was filtered off, washed with water, and dried. Recrystallisation from benzene-light petroleum (b.p. 80-100°) gave, in each case, 2-methylisoindoline-1-spirocyclohexa-2',5'-diene-3,4'-dione (IV) as needles, m.p. 222-223°, identical (mixed m.p. and i.r. spectra) with the product of the same reactions in isotopically normal water. The methoxy-compound decomposition in enriched water was run in duplicate. The mass

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spectra of all five specimens of (IV) were recorded on an A.E.I. MS 9 spectrometer and the relative amounts of the parent (M) and M + 2 ions determined by the height of the trace, using two galvanometers of sensitivity ratio 100:1.

trans-2-Amino- $\alpha$ -(2- and 4-methoxyphenyl)cinnamic Acids. —These were prepared by reduction of the corresponding nitro-compounds with ammoniacal ferrous sulphate.<sup>8</sup> The latter acid was obtained in two polymorphic forms (u.v. and i.r. spectra): colourless needles, m.p. 175°, and yellow needles, m.p. 149°. The former was converted into the latter by boiling in water. Pschorr *et al.*<sup>8</sup> reported only the yellow form. Catalytic hydrogenation of *trans*-2-nitro- $\alpha$ -(2-methoxyphenyl)cinnamic acid over 10% palladised charcoal gave 2-hydroxy-3-(2-methoxyphenyl)-3,4-dihydroquinoline (100%) as needles, m.p. 183—184° (Found: C, 75·5; H, 5·7. C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub> requires C, 75·9; H, 6·0%),  $v_{max}$ . 3220, 3140 (N-H), and 1680 cm.<sup>-1</sup> ( $\delta$ -lactam C=O).

Decomposition of the Diazonium Salts from trans-2-Amino- $\alpha$ -(2-methoxyphenyl)cinnamic Acid.—(a) Decomposition of the diazonium sulphate by Pschorr's method.<sup>8</sup> The amine (1 g.) was diazotised in aqueous sulphuric acid and the diazonium solution decomposed with copper powder (0.5 g)as described by Pschorr et al.<sup>8</sup> Aqueous sodium hydroxide was added, and the solution was filtered and acidified to give the crude product. Extraction with ether gave more product (0.84 g. in all) which contained one major and one minor component (t.l.c.) and did not give a test with Brady's reagent. Crystallisation from ethanol gave 1-methoxyphenanthrene-10-carboxylic acid (0.81 g., 85%)as yellow needles, m.p. 215° (lit., 8 215°). The minor component was separated as a yellow gum (0.04 g.) by chromatography on silica gel.

(b) Thermal decomposition of the diazonium sulphate. The above diazonium sulphate was decomposed by keeping the solution at  $70^{\circ}$  for 1 hr. in the absence of copper. The separated solid was collected, washed with water, and recrystallised to give 1-methoxyphenanthrene-10-carboxylic acid (81%), m.p. 215°. Chromatography as before gave the same gum (0.03 g.) which gave a negative test with Brady's reagent.

(c) Decomposition of the diazonium fluoroborate. The amine (1 g.) was converted into its pale yellow diazonium fluoroborate (1.3 g.) in the standard way, and this was decomposed in acetone with copper powder (0.5 g.) to give crude product (0.98 g.) on filtration and evaporation. The same products were formed (t.1.c.) and crystallisation and chromatography as before gave 1-methoxyphen-anthrene-10-carboxylic acid (85%), m.p. 215°, and the gum (0.03 g.). No positive test was obtained with Brady's reagent.

Decomposition of the Diazonium Salts from trans-2-Amino- $\alpha$ -(4-methoxyphenyl)cinnamic Acid.—In a series of experiments exactly parallel to those described for the 2-methoxyphenyl isomer the only product detected (t.l.c.) was 3-methoxyphenanthrene-10-carboxylic acid, m.p. 239° (lit.,<sup>8</sup> 239°), isolated in 88, 80, and 100% yield respectively. Negative tests with Brady's reagent were obtained. throughout.

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