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Synthesis of 2′-Cyanomethyl-2-biphenylcarboxylic Acid[1]

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The reaction product of diphenide (I) with potassium cyanide, previously described as 2′-cyanomethyl-2-biphenylcarboxylic acid (II), is in fact a phenanthrol derivative (V). The acid (II) is an intermediate in the reaction. These facts were proved by synthesis of II from I by an alternative, unambiguous method. In the last step of the synthesis, only boron tribromide is effective for hydrolysis of the ester (IX). This is the first time it has been employed as a hydrolyzing agent for an ester.

In contrast to previous results, 9-phenanthrol (III) was found to be a product of the calcium salt of V.

The previous paper[3] reported the preparation of diphenide (I) and its methoxyl derivatives from the corresponding diphenaldehydes or from the corresponding diphenic acids.

To convert these diphenides to 2′-cyanomethyl-2-biphenylcarboxylic acid (II) or its methoxyl derivatives, we had occasion to repeat the work of Chatterjee[4] in which the synthesis of 9-hydroxyphenanthrene (III) *via* II and then 2′-carboxy-2-biphenylylacetic acid (IV) was described. Consequently, our results and interpretation of the reaction differ from those reported by Chatterjee.[4]

The reaction path proposed by Chatterjee for the conversion of I to III is illustrated in Chart 1.

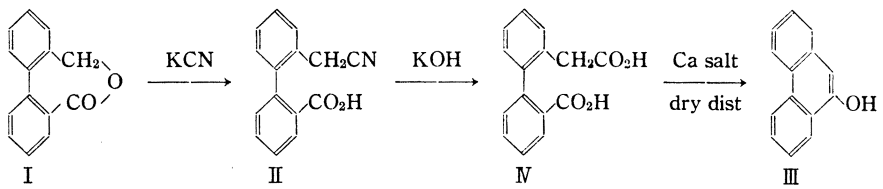

Chart 1

He deduced that a product (mp 240°, now named compound A) obtained by treatment of I with potassium cyanide had structure II based on elemental analysis of nitrogen only. The deduction seems to be supported by the fact that conversion of phthalide to 2-cyanomethylbenzoic acid was achieved under comparable conditions.[6] When we repeated the reaction we isolated a compound, $C_{15}H_9ON$ (mp 240—242°) with the same melting point as compound A. However, mass, ultraviolet (UV), and infrared (IR) spectroscopy showed that it was 10-hydroxy-9-phenanthrenecarbonitrile (V). This was confirmed by direct com-

1) This forms Part VIII[5] of "Studies on the Syntheses of Benzoheterocyclic Compounds," by S. Kobayashi.
2) Location: *78, Sho-machi-1-chome, Tokushima.*
3) S. Kobayashi, F. Senoo, M. Kihara, K. Sakata and A. Miura, *Chem. Pharm. Bull.* (Tokyo), **19**, 1262 (1971).
4) N. Chatterjee, *J. Ind. Chem. Soc.*, **12**, 418 (1935).
5) Part VII: S. Kobayashi and M. Kihara, *Tokushima Daigaku Yakugakubu Kenkyu Nempo* (Japan), **19**, 1 (1970).
6) W. Wislicenus, *Ann.*, **233**, 101 (1886).

parison of this compound with an authentic sample of V prepared by Mosby.[7] Therefore, we concluded that compound A has structure V. To confirm this we synthesized acid (II) by an alternative, unambiguous method as follows.

We attempted, unsuccessfully, to convert 2'-bromomethyl-2-biphenylcarboxaldehyde to II by way of 2'-bromomethyl-2-biphenylcarboxylic acid or 2'-cyanomethyl-2-biphenylcarboxaldehyde.[8] Then we selected 2'-hydroxymethyl-2-biphenylcarboxylic acid (VI) as starting material. Esterification of VI with diazomethane gave the desired ester (VII) in 44.2% yield, with a considerable amount of I. Bromination of VII with phosphorus tribromide afforded I and the corresponding bromo ester (VIII), mp 51.5—52.5°. The latter was treated with potassium cyanide, yielding methyl 2'-cyanomethyl-2-biphenylcarboxylate (IX), mp 38—39°, and V.

Hydrolysis of IX to an acid (II) must be carried out under conditions where there is no hydrolysis of the cyano group of IX and no cyclization of IX to V.

A weak base, such as sodium bicarbonate or 2,4,6-collidine-lithium iodide,[9] appeared suitable for this purpose. However, use of either base for the hydrolysis gave only the cyclized product (V) instead of II in good yield. The explanation for this must be that the basic reagent attacks the activated methylene group in preference to the ester group and the resulting methine carbanion undergoes a Dieckmann-type condensation as shown in Chart 2, since II, which was obtained from IX as described below, did not cyclize with sodium bicarbonate under the same conditions. This mechanism is consistent with that of formation of the cyclized product on hydrolysis of methyl 2'-nitro-2-biphenylylacetate with a base.[10] The formation of V from VIII described above can also be interpreted as involving IX as an intermediate.

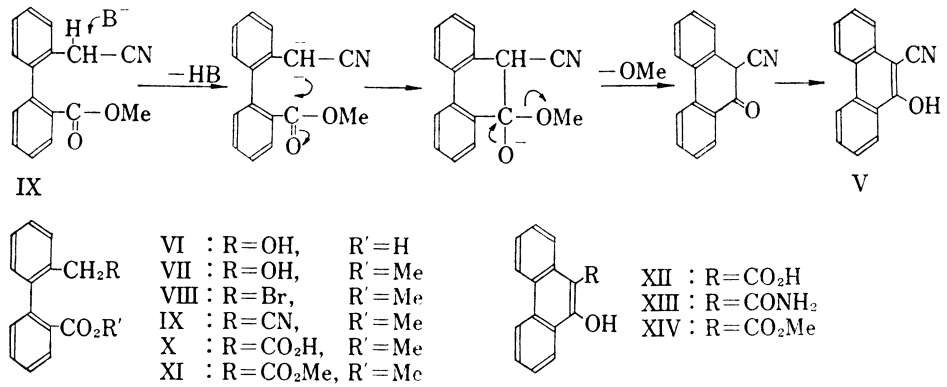

Chart 2

A second unsuccessful attempt to achieve the reaction was made using acid catalysts, such as hydrochloric, perchloric,[11] and methanesulfonic acid.[12] On treatment of IX with 0.5N hydrochloric acid in alcohol the starting material was revovered unchanged. Use of perchloric acid[11] in tetrhydrofuran afforded IV and I. On refluxing IX with methanesulfonic acid[12] in formic acid IV was obtained with a new product, mp 84—86°, which was deduced to be methyl 2'-methoxycarbonyl-2-biphenylylacetic acid (X) from its IR spectrum. In the hydrolysis of IX it is of interest that in contrast to basic reagents which afforded a Dieck-

7) W.L. Mosby, *J. Org. Chem.*, **24**, 421 (1959).
8) The results will be reported elsewhere.
9) F. Elsinger, J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, **43**, 113 (1960).
10) C.W. Muth, J.C. Ellers and O.F. Folmer, *J. Am. Chem. Soc.*, **79**, 6500 (1957).
11) J. Schmidlin, G. Anner, J.-R. Billeter, K. Heusler, H. Ueberwasser, P. Wieldand and A. Wettstein, *Helv. Chim. Acta*, **40**, 2291 (1957).
12) B. Loev, *Chem. Ind.*, **1964**, 193 .

mann-type condensation product (V), acidic ones attacked the cyano group and the ester group to give a diacid (IV).

Finally, we selected boron tribromide,[13,14] a demethylation agent for phenolic methyl ethers, as a suitable, neutral reagent for the hydrolysis. Excess boron tribromide was used because of the presence of the cyano group[15] and a new compound, $C_{15}H_{11}O_2N$, melting at 123—124.5°, was obtained from IX in 44.3% yield. Its mass spectrunum, IR, and nuclear magnetic resonance (NMR) spectrum showed that it was II. This is the first time that boron tribromide has been employed for hydrolysis of an ester.

The melting point of V, prepared by repeating the reaction of Chatterjee[4] is the same as that of compound A, but differs from that of II, which we obtained by this unambiguous method. Thus the compound A must have structure V. Furthermore, II was found to be an intermediate in the conversion of I to V, since when II was heated with potassium cyanide at 180° it gave V quantitatively.

Thus, since compound A has been shown not to have structure II, Chatterjee's conclusion that the hydrolysis product (mp 295°, now named compound B) of compound A is IV must be incorrect. In fact, the melting point (295°) of compound B is different from that (171—172°) reported for IV by Marvel and Patterson.[16] The latter value is probably correct, since we obtained IV melting at 167—169° by saponification of the corresponding diester (XI) with potassium hydroxide. In this hydrolysis a by-product (mp 148—153°) was isolated as brown needles. The structure of this compound was not suggested by Marvel and Patterson.[16] Since IX underwent cyclization to V during hydrolysis with a base, as described above, the by-product is probably 9-phenanthrol (III), a product of the Dieckmann condensation of XI. This was confirmed by direct comparison of the compound with an sample of III prepared by an alternative method.[17]

Compound B seemed likely to be 10-hydroxy-9-phenanthrenecarboxylic acid (XII) or its amide (XIII), since compound B was obtained by hydrolysis of compound A or V with potassium hydroxide as reported by Chatterjee.[4] However, XII could not be prepared by saponification of the corresponding ester (XIV), obtained by the Dieckmann condensation of XI with sodium methoxide, because XII readily underwent decarboxylation.[18] Furthermore, the amide (XIII) melting at 181—184°, prepared by treatment of XIV with ammonia, was found to be different from compound B. Finally, hydrolysis of V with potassium hydroxide under the conditions reported by Chatterjee[4] gave the potassium salt of V melting at 301—305° and a trace of III. The former seems to be compound B from the similarity in their melting points.

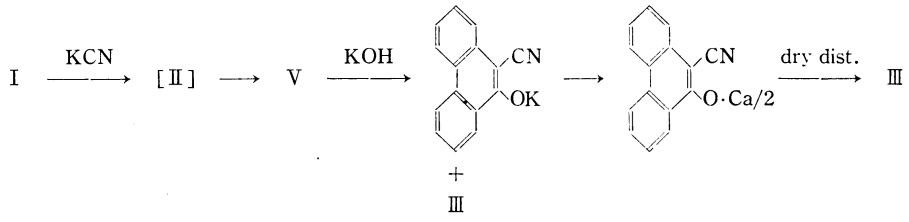

Chart 3

13) J.F.W. McOmie and D.E. West, "Organic Syntheses" Vol. 49, ed. by K.B. Wiberg, John Wiley and Sons, Inc. New York, N.Y. 1969, p. 50.
14) Z. Horii, T. Momose and Y. Tamura, *Chem. Pharm. Bull.* (Tokyo), **13**, 797 (1965); These authors reported that demethylation of η-pyrromycinone O-trimethyl ether with this reagent gave η-pyrromycinone together with η-pyrromycinonic acid.
15) J.F.W. McOmie, M.L. Watts and D.E. West, *Tetrahedron*, **24**, 2289 (1968).
16) C.S. Marvel and L.A. Patterson, *J. Am. Chem. Soc.*, **63**, 2218 (1941).
17) R.G.R. Bacon and S.C. Rennison, *Chem. Ind.*, **1966**, 812.
18) I.M. Hunsberger, R. Ketcham and H.S. Gutowsky, *J. Am. Chem. Soc.*, **74**, 4839 (1952).

The potassium salt of V was converted to the corresponding calcium salt, which in turn was dry distilled to afford III characterized as its picrate, as described by Chatterjee.[4] Therefore, the reaction path from I to III reported by Chatterjee (see Chart 1) is corrected to that shown in Chart 3.

Experimental[19]

Reaction of I with Potassium Cyanide——A mixture of I (500 mg) and KCN (400 mg) was heated in a sealed tube at 180° for 3 hr. Then water was added to the reaction mixture and the aqueous solution was washed with ether and acidified with 15% HCl to give brown precipitates. These were recrystallized from benzene and then toluene to afford V as white needles, mp 240—242° (reported[7] mp 247—249°). *Anal.* Calcd. for $C_{15}H_9ON$: C, 82.17; H, 4.14; N, 6.39. Found: C, 82.14; H, 4.24; N, 6.23. IR ν_{max}^{KBr} cm^{-1}: 3230 (OH), 2250 (C≡N). Mass Spectrum *m/e*: 219 (M^+). UV λ_{max}^{EtOH} mμ (log ε): 247 (4.68), 254 (4.66), 262 (4.59), 287 (4.12), 299 (3.96), 320 (3.95), 342 (3.86), 359 (3.87). This sample was identical with an authentic sample of V prepared by Mosby.[7]

2′-Hydroxymethyl-2-biphenylcarboxylic Acid (VI)——The acid (VI) was prepared by saponification of I as described in the previous paper.[3]

Methyl 2′-Bromomethyl-2-biphenylcarboxylate (VIII)——A mixture of VI (2.237 g) and diazomethane (from 10 g of nitrosomethylurea) in dry ether (150 ml) was stood at −5° for 2 hr. Evaporation of the solvent and trituration of the residue (2.47 g) with ether gave I (892 mg), mp 132—133°, as white plates. The ether solution which was separated from I was submitted to preparative thin-layer chromatography (TLC) on silica gel using benzene–acetone (5: 1, v/v) as developing solvent. Elution of the material of *Rf* 0.5—0.7 gave I (239 mg, total 1.131 g, in 54.9% yield). Elution of the material of *Rf* 0—0.5 gave VII as a colorless oil (1.050 g) in 44.2% yield. IR $\nu_{max}^{Liquid\ film}$ cm^{-1}: 3500 (OH), 1725 (C=O). Mass Spectrum *m/e*: 210 (M-MeOH)$^+$. This peak corresponds to the molecular ion peak of I. The ester (VII) could not be purified further, since it readily changed to I on vacuum distillation or chromatography on Al_2O_3.

A mixture of VI (136 mg) in dry benzene (4 ml) and PBr_3 (1.3 ml) was stood at room temperature overnight. Then the solvent was evaporated off and ether (5 ml) and cold water (5 ml) were added to the residue. The mixture was extracted with ether. The extracts were washed with 1% Na_2CO_3 and then water and then dried and evaporated to give a colorless oil (142 mg). This was submitted to preparative TLC using SiO_2–benzene. Elution of material with an *Rf* of about 0.3 with ether gave a trace of I. Material with an *Rf* of about 0.4—0.6 was eluted with ether. The eluate afforded a colorless oil (118 mg, 68.8%, over-all yield, 30.4%), which was triturated with ether–petr. ether to give VIII, mp 51.5—52.5°, as colorless cubes. *Anal.* Calcd. for $C_{15}H_{13}O_2Br$: C, 59.03; H, 4.03. Found: C, 58.59; H, 4.30. IR ν_{max}^{KBr} cm^{-1}: 1725 (C=O). Mass Spectrum *m/e*: 304 (M^+), 306 (M+2)$^+$. NMR ($CDCl_3$) τ: 1.90—2.07 (1H, multiplet, aromatic proton), 2.39—2.95 (7H, multiplet, aromatic protons), 5.63 and 5.78 (2H, a pair of AB type doublets, J=10.0 Hz, -C_6H_4-CH_2-Br), 6.40 (3H, singlet, -CO_2CH_3).

In the second run, in which VII was not isolated in a pure state but was used as material in the next reaction, the over-all yield of VIII from VI was 55.0%; a mixture of ethereal diazomethane solution (from 21 g of nitrosomethylurea) and VI (10.200 g) was stood at −5° for 2 hr. After evaporation of the ether, the residue was triturated with benzene (50 ml) to afford I (352 mg). The benzene solution, which was separated from I was mixed with PBr_3 (5 ml) and kept at room temperature for 38 hr. Repetition of the treatment described above gave I (1.114 g) and VIII (7.501 g).

Methyl 2′-Cyanomethyl-2-biphenylcarboxylate (IX)——To a solution of KCN (470 mg) in dimethylsulfoxide (DMSO) (15 ml) was added VIII (2.000 g) in DMSO (25 ml). The mixture was stirred for 12 min at room temperature and then acidified with 9% HCl and extracted with ether. It was evaporated and the residue was triturated with ether to give crude V (127 mg) as white needles. The ethereal mother liquor gave a pale yellow oil (1.510 g), which was submitted to preparative TLC using SiO_2–benzene. Elution of material of about *Rf* 0.1—0.6 and crystallization of this material from ether gave IX as colorless prisms (1.156 g, 70.2%), mp 38—39° (from ether). *Anal.* Calcd. for $C_{16}H_{13}O_2N$: C, 76.47; H, 5.22; N, 5.57. Found: C, 76.53; H, 5.21; N, 5.46. IR ν_{max}^{KBr} cm^{-1}: 2250 (C≡N), 1717 (C=O). Mass Spectrum *m/e*: 251 (M^+). NMR ($CDCl_3$) τ: 1.90—2.07 (1H, multiplet, aromatic proton), 2.39—3.00 (7H, multiplet, aromatic protons), 6.38 (3H, singlet, -CO_2CH_3), 6.51 (2H, singlet, -C_6H_4-CH_2-CN).

Material of about *Rf* 0—0.1 eluted with ether gave white needles of crude V (49 mg, total 176 mg), which was recrystallized from acetone to afford V (139 mg) as white needles, mp 239—241°. *Anal.* Calcd. for $C_{15}H_9O_2N$: C, 82.17; H, 4.14; N, 6.39. Found: C, 81.91; H, 3.97; N, 6.55. IR ν_{max}^{KBr} cm^{-1}: 3240 (OH), 2230 (C≡N). This sample was identical with an authentic sample of V from Mosby.

19) All melting points are uncorrected. IR spectra were taken on Hitachi EPI-G2, UV spectra on Hitachi EPS-2, NMR spectra on Varian A-60 using TMS as an internal standard, and mass spectra on Hitachi RMU-6E.

Hydrolysis of Methyl 2′-Cyanomethyl-2-biphenylcarboxylate (IX)——(A) By Basic Reagents: (a) By $NaHCO_3$: A mixture of IX (12 mg) in MeOH (2 ml) and 0.5N $NaHCO_3$ (0.1 ml) was refluxed for 30 min. On working up in the usual way white needles of V (9 mg, 86.0%) were obtained.

(b) By LiI and 2,4,6-Collidine[9]: To LiI (400 mg) in 2,4,6-collidine (8 ml) IX (100 mg) was added and the mixture was refluxed under N_2 for 6.5 hr. After working up in the usual way the crude V (93 mg) was recrystallized from acetone as white needles (45 mg, 62.7%), mp 240—242°.

(B) By Acidic Reagents: (a) By HCl: A mixture of IX (32 mg), MeOH (5 ml), and 0.5N HCl (1 ml) was stood at 0° for 1 hr and then at room temperature for 135 days. A colorless oil (27 mg) was obtained by standard procedures from the reaction mixture. It gave a spot in the same position as IX on TLC.

(b) By $HClO_4$[11]: A mixture of IX (55 mg) in tetrahydrofuran (THF) (5 ml) and 6N $HClO_4$ (1 ml) was stood at room temperature for 140 days. Standard treatment of the mixture gave 50 mg of V. In the second run, a mixture of IX (130 mg) in THF (15 ml) and 6N $HClO_4$ (5 ml) was refluxed for 30.5 hr. Then water was added and the mixture was extracted with ether. The extracts gave a brown oil (160 mg), which was submitted to preparative TLC using SiO_2–benzene. Elution of material of *Rf* 0—0.4 with ether and crystallization of the material from ether gave IV (20 mg) as white cubes, mp 166.5—168°. Elution of material of *Rf* 0.5—1.0 afforded I (12 mg) as white cubes.

(c) By CH_3SO_3H and HCO_2H[12]: A solution of IX (50 mg) in CH_3SO_3H (20 ml) and 90% HCO_2H (5 ml) were refluxed for 105 hr. After removal of the solvent and addition of water the mixture was extracted with ether. The extracts were submitted to preparative TLC using SiO_2–(benzene–acetone). Elution of material of *Rf* 0.1—0.3 with ether gave IV (18 mg, 43.2%) as white cubes, mp 165—168° (from ether-petr. ether). IR ν_{max}^{KBr} cm^{-1}: 1715 (C=O of RCH_2CO_2H), 1675 (C=O of $R'C_6H_4CO_2H$). The acid was found to be identical with an authentic sample of IV spectra. On elution of material of *Rf* 0.3—0.4 with ether 19 mg (42.9%) of X were obtained as white prisms, mp 84—86° (from EtOH). *Anal.* Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.39; H, 5.10. IR ν_{max}^{KBr} cm^{-1}: 1725 (C=O of $RC_6H_4CO_2CH_3$), 1700 (C=O of $R'CH_2CO_2H$). Mass Spectrum *m/e*: 270 (M^+).

(C) By BBr_3[13]: A solution of IX (299 mg) in CH_2Cl_2 (15 ml) was mixed with BBr_3 (300 mg) in CH_2Cl_2 (3 ml) at room temperature and refluxed for 3.5 hr. Further BBr_3 (300 and then 100 mg) was added at 1 hr intervals. Then cold water (10 ml) was added and the mixture was extracted with ether. The extracts were evaporated to dryness and crystallized from ether–petr. ether to afford II (125 mg, 44.3%) as white cubes, mp 123—124.5° (now named the α-form). *Anal.* Calcd. for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.67; N, 5.90. Found: C, 75.84; H, 4.60; N, 5.64. IR ν_{max}^{KBr} cm^{-1}: 3250—2500 (OH), 2250 (C≡N), 1720, 1682 (C=O); $\nu_{max}^{CHCl_3}$ cm^{-1}: 3050—2500 (OH), 2250 (C≡N), 1700 (C=O). Mass Spectrum *m/e*: 237 (M^+). NMR ($CDCl_3$) τ: −0.05 (1H, singlet, $-CO_2H$), 1.83—2.03 (1H, multiplet, aromatic proton), 2.27—3.03 (7H, multiplet, aromatic protons), 6.58 (2H, singlet, $-C_6H_4-CH_2CN$). $[\alpha]_D^{15}$ 0° (*c*=1.69, dioxane).

The solution in ether–petr. ether which was separated from II (α-form) was evaporated to give white cubes of II (65 mg), mp 129—131° (now named the β-form). *Anal.* Calcd. for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.67; N, 5.90. Found: C, 75.71; H, 4.76; N, 5.79. IR ν_{max}^{KBr} cm^{-1}: 3080—2500 (OH), 2250 (C≡N), 1690 (C=O); $\nu_{max}^{CHCl_3}$ cm^{-1}: 3050—2500 (OH), 2250 (C≡N) 1700 (C=O). Mass Spectrum *m/e*: 237 (M^+). $[\alpha]_D^{15}$ 0° (*c*=0.52, dioxane). The two substances (II, α- and β-forms) seem to be dimorphic forms of one compound for the following reasons: (1) the C,H, and N contents of the two were identical, (2) the mass spectra of the two were identical, (3) both forms were optically inactive, and (4) the IR spectra of the two forms in the crystalline state (KBr) were significantly different in the carbonyl region, but those in $CHCl_3$ or $CHCl_3$–Et_3N were identical over the range from 4000 to 400 cm^{-1}.

In the second run, the yield of II from IX was 67.3% by the same procedure.

2′-Carboxy-2-biphenylylacetic Acid (IV)——(A) From XI with 20% KOH in EtOH: A mixture of XI (300 mg), EtOH (20 ml), and 20% KOH (20 ml) was refluxed for 2 hr. Treatment of the mixture by standard procedures afforded brown crystals (258 mg), which were recrystallized from ether–petr. ether to give IV (193 mg, 71.4%), mp 167—169° (reported[16] mp 171—172°). *Anal.* Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.24; H, 4.80. IR ν_{max}^{KBr} cm^{-1}: 1715 (C=O of RCH_2CO_2H), 1675 (C=O of $R'C_6H_4-CO_2H$).

The ether–petr. ether solution which was separated from IV gave III, which was characterized as its picrate (8 mg), mp 184—185° (from ether). The picrate was identical with an authentic sample judging from its mixed melting point and IR spectrum.

(B) From XI with 10% NaOH[16]: A mixture of XI (150 mg) and 10% NaOH (1.2 ml) was heated at 100° for 3 hr. The alkaline solution was washed with ether, acidified with HCl, and extracted with ether. The extracts gave IV (79 mg, 58.4%), mp 167—168°. This material was identical with a sample prepared by method (A).

The washing ether separated from the alkaline solution gave III (15 mg, 16.3%) as red needles, mp 148—152° (from benzene under N_2). Its picrate had mp 184—185°. The phenol (III) and its picrate were each identical with an authentic sample.

Methyl 10-Hydroxy-9-phenanthrenecarboxylate (XIV)——A mixture of XI (117 mg) in dry benzene (12 ml) and MeONa (from 27 mg of Na) was refluxed under N_2 for 3 hr. The reaction mixture was acidified with HAcO, diluted with water and extracted with ether. The extracts were washed with 1% Na_2CO_3,

dried and evaporated to dryness. The crude product (103 mg) thus obtained was recrystallized from MeOH to give XIV (68 mg, 65.5%) as white needles, mp 88—89° (reported[18] 90.6—91.2°). *Anal.* Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 75.89; H, 4.89. IR ν_{max}^{KBr} cm^{-1}: 1640 (C=O in chelation).

10-Hydroxy-9-phenanthrenecarbonamide (XIII)——A solution of XIV (40 mg) in dry MeOH (25 ml) was saturated with dry NH_3 at −16° for 40 min. The mixture was heated in a sealed tube at 80° for 6 hr. After removal of the solvent under reduced pressure the crude sample of XIII (28 mg, 74.5%, mp 178—181°) was recrystallized from benzene as white needles, mp 181—184°. *Anal.* Calcd. for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.67; N, 5.90. Found: C, 76.23; H, 4.78; N, 6.07. IR ν_{max}^{KBr} cm^{-1}: 3452 (OH), 3300, 3150 (NH), 1655 (C=O). Mass Spectrum *m/e*: 237 (M^+).

Treatment of V with Alkaline——(A): Using the method of Chatterjee,[4] a mixture of V (150 mg) and 30% KOH (20 ml) was refluxed for 15.5 hr. The reaction mixture was filtered and the resulting solid was washed with water to give pale yellow needles (130 mg), mp 301—305° (decomp.). The needles (90 mg) were dissolved in warm water (40 ml) and the solution was acidified with 36% HCl and extracted with ether. Evaporation of the solvent gave yellow crystals (58 mg, mp 235—239°), which were shown to be identical with V by the mixed melting point test. Therefore, the needles (mp 301—305°) are the potassium salt of V.

The filtrate separated from the needles was acidified with 36% HCl and extracted with ether. The extracts were triturated with ether to give V (50 mg). Picric acid in ether was added to the ethereal mother liquor and the picrate of III was obtained, mp 178—181°. This was shown to be identical with an authentic sample by the mixed melting test and comparison of IR spectra.

(B): Unsuccessful attempt to prepare IV from V by the method of Pecherer, *et al.*[20]; a mixture of V (50 mg) in MeOH (4 ml) and 30% KOH (6.5 ml) was refluxed for 24 hr. After treatment of the mixture by usual procedures the nitrile (V) (23 mg), mp 238—241°, was recovered unchanged.

9-Phenanthrol (III)——(A) From 9-Bromophenanthrene: Following the method of Bacon, *et al.*[17] 9-methoxyphenanthrene (1.197 g, 98.8%) was obtained from 9-bromophenanthrene (1.500 g). It had mp 92—93° (from petr. ether) (reported[17] mp 94.5—95.5°). *Anal.* Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.40; H, 5.58.

A mixture of 9-methoxyphenanthrene (200 mg), HAcO (13.5 ml), and 47% HBr (2.6 ml) was heated in a sealed tube at 100° for 4 hr. The crude needles of III (163 mg) were recrystallized from benzene–petr. ether to afford pale brown needles (82 mg, 44.0%), mp 148—152° (reported mp 152—154°,[17] 153°,[4] 153—155°,[21] 156—157°,[22]). *Anal.* Calcd. for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.45; H, 5.41. Its picrate had mp 187—188° (from ether) (reported[4] mp 185°). *Anal.* Calcd. for $C_{14}H_{10}O \cdot C_6H_3N_3O_7$: C, 56.74; H, 3.10; N, 9.93. Found: C, 56.47; H, 2.80; N, 9.72.

(B) By Dry Distillation of the Ca salt of V: The nitrile (V) (100 mg) was dissolved in 0.05% $Ca(OH)_2$ with heating and the hot solution was filtered. The grey precipitate (61 mg) separated from the filtrate was dry distillated under reduced pressure (below 1 mmHg) to give 14 mg of a yellow oil (bp 125—243°). This was submitted to preparative TLC using SiO_2–benzene to afford red crystals (3 mg). They were characterized as the picrate of III, mp 181—183° (from ether) by the mixed melting point test and comparison of the IR spectrum with that of authentic material.

Alternatively the calcium salt (5 mg) of V was obtained by addition of 20% $Ca(NO_3)_2$ to the potassium salt of V (7 mg).

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