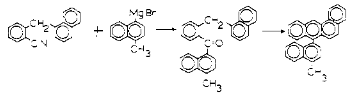
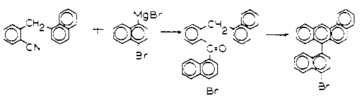
is possible through known reactions to transform II and IV into a very large variety of other new polycyclic compounds having a known substituent in a known position.



I II



III IV

EXPERIMENTAL

2-(1-Naphthylmethyl)phenyl 1-(4-Methyl)naphthyl Ketone (I). To the Grignard reagent prepared from 1.20 grams (0.05 gram-atom) of magnesium and 11 grams (0.05 mole) of 4-bromo-1-methylnaphthalene in 75 ml. of dry ether, 7.3 grams (0.03 mole) of 2-(1-naphthylmethyl)benzonitrile (*1*) in 100 ml. of benzene was added. The mixture was heated, and the solvent was removed by distillation until the boiling temperature of the solution reached 76° C., when the solution was allowed to reflux for 48 hours. The solution was cooled and decomposed with 50 ml. of 20% NH_4Cl. To the resulting mixture was added 100 ml. of benzene, 100 ml. of water, and 50 ml. of 40% H_2SO_4. The mixture was stirred and heated under reflux for 48 hours and worked up in the usual way. The product distilled at 280-2° C. (0.5 mm.), 12 grams (62%). Anal. Calcd. for $C_{29}H_{22}O$: C, 90.12, H, 5.74. Found: C, 89.87; H, 5.96.

The ketone failed to crystallize from chloroform, dioxane-ethanol (1 to 1), carbon tetrachloride, petroleum ether (30° to 60° C.), acetic acid, ethanol, and benzene-ethanol (1 to 1).

2-(1-Naphthylmethyl)phenyl 1-(2-Methyl)naphthyl Ketone (V). This compound was prepared essentially as was its isomer I. The Grignard reagent of 1-bromo-2-methylnaphthalene was allowed to react with 2-(1-naphthylmethyl)benzonitrile to give, after the usual hydrolysis and workup, 22% of the desired ketone, b.p. 275-6° C. (0.50 mm.) which on crystallization from ethanol melted at 127-8° C. Melting points were obtained using a Fisher-Johns melting point apparatus and are corrected; boiling points are not corrected. Anal. Calcd. for $C_{29}H_{22}O$: C, 90.12, H, 5.74. Found: C, 90.41; H, 5.97.

2-(1-Naphthylmethyl)phenyl 1-(4-Bromo)naphthyl Ketone. The Grignard reagent prepared from 1.9 grams (0.08 gram-atom) of magnesium and 22 grams (0.08 mole) of 1,4-dibromonaphthalene was allowed to react with 15 grams (0.06 mole) of 2-(1-naphthylmethyl)benzonitrile, and the product was worked up as described above. The product distilled at 305° to 310° C. (1 mm.), 5.2 grams (19%). The glass-like solid which formed on cooling was recrystallized from ethanol-benzene (9 to 1) four times, m.p. 120-1° C. Anal. Calcd. for $C_{28}H_{19}BrO$: C, 74.51; H, 4.24; Br, 17.71. Found: C, 74.01, H, 4.22; Br, 18.13.

7-[1-(4-Methyl)naphthyl]benz[*a*]anthracene. A mixture of 5.0 grams (0.013 mole) of 2-(1-naphthylmethyl)phenyl 1-(4-methyl)naphthyl ketone, 30 ml. of glacial HOAc, and 30 ml. of 48% HBr was heated under reflux for 72 hours. The mixture was worked up in the usual manner (*2*) and gave 3.3 grams (69%) of small white crystals, m.p. 171-2° C. from ethanol. Anal. Calcd. for $C_{29}H_{20}$: C, 94.53, H, 5.47. Found: C, 94.28; H, 5.50.

7-[1-(4-Bromo)naphthyl]benz[*a*]anthracene. A mixture of 1.0 gram (0.0022 mole) of 2-(1-naphthylmethyl)phenyl 1-(4-bromo)naphthyl ketone, 15 ml. of 48% HBr, 15 ml. of glacial HOAc, and 50 ml. of acetic anhydride was heated under reflux for 18 hours. The mixture was worked up in the usual way and gave 0.7 gram (78%) of colorless cubes, m.p. 184-5° C. from ethanol-benzene (90 to 10). Anal. Calcd. for $C_{28}H_{17}Br$: C, 77.60; H, 3.95; Br, 18.44. Found: C, 77.85; H, 3.86; Br, 18.03.

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N-Coumarin Analogs: 7-Amino-4-Substituted Carbostyrils

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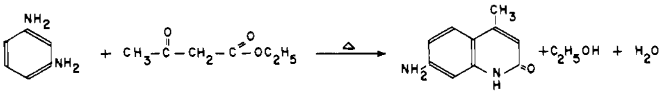
An efficient and simple method has been devised for the synthesis of substituted 7-amino carbostyrils. The acetyl derivatives and the proton magnetic resonance spectrum of compound I has been described.

THE condensation of β-keto esters with 1,3-polyhydroxy phenols in the presence of trifluoroacetic acid to form coumarins has been reported (*4*).

Nitrogen analogs of the coumarins, classified as carbostyrils, may be prepared in excellent yields by a very simple process, without a catalyst, to give 7-amino-4-substituted carbostyrils. Carbostyrils have been prepared by many methods all adequately documented by Rodd (*2*); however, only one of the compounds, 7-amino-4-methylcarbostyril, presented here has been prepared previously (*3*) by a different and less efficient method.

The essential data on the compounds prepared by this simplified method are given in Table I as the I to V series. The reaction for compound I may be considered to be the general course of the reaction for all members of the series.



I

The acetylated derivatives of the members of the I to V series are described in Table II with the optical characteristics of the several members of the series. The compounds are all powerful blue fluorescers.

The proton magnetic resonance spectrum of compound I has been determined, and peaks located at 2.31, 5.71, 5.99, 6.43, 6.49, 7.37, and 11.17 p.p.m. (δ) were found. The spectrum confirms the postulated structure of the compound.

When alcoholic solutions of each of the members of the series were allowed to react with symmetrical trinitrobenzene, only compounds I and III reacted to give stable Burgundy red colored π-complexes whose preparation is described in the experimental portion of this report as compounds I_A and III_A.

When representative 3-hydroxyphenols were heated with β-keto esters in the absence of a catalyst, no coumarins could be isolated. However, substitution of 3-(*N*,*N*-dimethylamino)-phenol or 3-aminophenol for *m*-phenylenediamine in the reaction with ethyl acetoacetate gave 7-dimethylamino-4-methylcoumarin (VI) and 7-hydroxy-4-methylcarbostyril (VII), respectively.

Fluorescence data on the several members of the series are given in Table III.

EXPERIMENTAL

Preparation of I to V Series. One-tenth mole of *m*-phenylene diamine and 0.1 mole of the β-keto ester were mixed and heated together in a flask immersed in a Fisher Hi-Temp oil bath for 18 hours at 150° C. At the end of the reaction period, 100 to 200 ml. of water was added to the flask. The contents were heated on a hot plate to the boiling temperature of the water. The mixture was then chilled, filtered, and the precipitate dried in air. Compounds I and III were purified by taking them up in hot morpholine and then precipitating the compounds with heptane. This process was repeated for a second and third recrystallization. Compounds II and IV were purified several times from boiling absolute ethanol.

Crude compound V was extracted with benzene and the residue was purified from boiling absolute ethanol. Data on these compounds are given in Table I.

Acetylated Derivatives of I to V Series. One-gram samples of the compounds were treated with 7 ml. of acetic anhydride and one drop of concentrated sulfuric acid. The compounds, when worked up in the usual manner, were purified by taking them up in ethyl acetate and then precipitating them with heptane. The compounds are described in Table II.

Complexes I_A and III_A. One gram of symmetrical trinitrobenzene was dissolved in 100 ml. of absolute ethanol.

Table III. Fluorescence Data on Members of I to V Series[a]

No.	Excitation Maximum λ, μ	Excitation Slit Width, μ	Emission Maximum λ, μ	Emission Slit Width, μ	Emission, Electron Volts
I	354	5.5	404	4.2	3.06884
II	355	6.0	413	8.0	3.00196
III	350	4.0	415	10.0	2.98749
IV	402	10.0	410	10.0	3.02393
V	358	12.0	442	12.0	2.80500

[a] All measurements were taken on a Hitachi recording spectrophotometer Model MPF-2A in spectrograde methanol at concentration of 1 p.p.m. except for compound III, whose concentration was two parts.

Table I. 7-Amino-4-Substituted Carbostyrils from *m*-Phenylenediamine

No.	β-Keto Ester Used	Yield, %	M.P., ° C.	Formula	Calculated C	Calculated H	Calculated N	Found C	Found H	Found N
I	Ethylacetoacetate	100	281.5–282	$C_{10}H_{10}N_2O$	68.94	5.78	16.08	68.78	5.64	15.87
II	Ethyl-2-benzyl acetoacetate	83	288.5–290	$C_{17}H_{16}N_2O$	77.24	6.10	10.59	77.32	6.31	10.44
III	Ethyl-2-methyl acetoacetate	45	328–329	$C_{11}H_{12}N_2O$	70.19	6.42	14.88	69.94	6.28	14.72
IV	Ethylbenzoyl acetate	100	334–336	$C_{15}H_{12}N_2O$	76.25	5.11	11.85	76.08	5.04	11.94
V	Ethyl-*o*-anisoyl acetate	56	249–251	$C_{16}H_{14}N_2O$	72.16	5.22	10.52	72.04	5.34	10.60

I. 7-Amino-4-methylcarbostyril, lit. (*3*) 270.4–272° C.
II. 7-Amino-3-benzyl-4-methylcarbostyril.
III. 7-Amino-3,4-dimethylcarbostyril.
IV. 7-Amino-4-phenylcarbostyril.
V. 7-Amino-4(2-methoxy phenyl)carbostyril.

Table II. Acetylated Derivatives and Spectral Characteristics of I to V Series

No.	Acetylated Carbostyrils Formula	M.P., ° C.	N Calcd.	N Found	Ultraviolet Absorption Maxima in Mμ (log ε)[a]	Infrared Absorption Maxima in the Range of 3500 to 1500 cm.$^{-1}$[b]
I	$C_{12}H_{12}N_2O_2$	360	12.95	12.68	239(4.22);255(4.17);359(4.23)	3438;3320;3200;1610;1550
II	$C_{19}H_{18}N_2O_2$	301–302	9.14	9.42	235(4.37);275(4.26);354(4.37)	3460;3370;1616;1550;1511
III	$C_{13}H_{14}N_2O_2$	360	12.16	12.32	229(4.07);350(4.01);354(4.00)	3480;3340;1628;1550;1510
IV	$C_{17}H_{14}N_2O_2$	259.5–261	10.06	9.78	233(4.01);255(3.97);351(3.94)	3460;3300;3200;1626;1530;1511
V	$C_{18}H_{16}N_2O_3$	196–198	9.08	8.84	236(4.11);347(4.10)	3550;3230;1625-B;1533;1518

[a] The ultraviolet spectra were taken on a Bausch and Lomb Spectronic-505. [b] Infrared spectra were taken on a Beckman IR-8 using a KBr pellet; B means broad.

Twenty milliliters of this filtered solution was mixed with 20 ml. of a filtered solution containing the compound (1 gram dissolved in 100 ml. of absolute ethanol). The mixtures were chilled to give Burgundy red colored crystals. The compounds were recrystallized once from ethanol: I_A, m.p. 148° C. (decomposed); Anal. calcd. $C_{16}H_{13}N_5O_7$: N, 18.05; Found: N, 17.88; III_A, m.p. 183° C. (decomposed); Anal. calcd. $C_{17}H_{15}N_5O_7$: N, 17.45; Found: N, 17.70.

Compound VI. When 0.1 mole of 3-(*N,N*-dimethylamino) phenol was mixed with 0.1 mole of ethyl acetoacetate and treated under the same conditions used to prepare the I to V series, a 65% yield of 7-(dimethylamino)-4-methyl coumarin was obtained. The compound was purified by taking up the substance in the ethyl acetate and precipitating the material with heptane. The process was repeated twice additionally, m.p. 139.5° C. [lit. 144° C. (*1*)]. Dilute solutions of hydrochloric acid dissolve the compound to give a reddish solution.

Compound VII. A mixture of 0.1 mole of *m*-amino phenol and 0.1 mole of ethyl acetoacetate was treated under the same conditions use to prepare the I to V series. The compound was purified by taking it up in tetrahydrofuran and then precipitating it with heptane. The process was repeated for a second recrystallization, yield 96%, m.p. >300° C.

Dilute hydrochloric acid solutions show no effect on the compound and indicate that the amino group of *m*-phenol is now the substituted amide group of 7-hydroxy-4-methylcarbostyril. Anal. calcd. $C_{10}H_9NO_2$: C, 68.55; H, 4.67; N, 7.99; Found: C, 68.37; H, 4.49; N, 8.22.

ACKNOWLEDGMENT

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Aziridine Adducts of α, β-Unsaturated Nitriles

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The aziridine adducts of crotononitrile, 2-methyleneglutaronitrile, cinnamonitrile, and methacrylonitrile were prepared. The products obtained were 3-(1-aziridinyl)butyronitrile, 2-(1-aziridinylmethyl)glutaronitrile, 3-(1-aziridinyl)3-phenylpropionitrile, and 3-(1-aziridinyl)2-methyl propionitrile, respectively. Aziridine also reacted with allyl cyanide, yielding a product identical with the aziridine adduct of crotononitrile. Apparently, allyl cyanide rearranges to crotonitrile in the presence of aziridine, and then aziridine adds to the crotonitrile. All of the adducts polymerized readily in aqueous media in the presence of zinc fluoborate.

THE reaction of aziridine with acrylonitrile, acrylamide, methyl acrylate, crotonamide, and methyl crotonate were reported by Bestian (*3*). In some of these reactions, either sodium methylate or metallic sodium was employed as the catalyst. Yoshida and Naito reported that in this type of reaction the aziridine group added to the β-carbon of the double bond to form the aziridine adducts (*5*).

The present authors prepared the adducts of aziridine (I) and crotononitrile (II), 2-methylene glutaronitrile-(acrylonitrile dimer) (III), cinnamonitrile (IV), and methacrylonitrile (V). The products obtained were 3-(1-aziridinyl)butyronitrile (VI), 2-(1-aziridinylmethyl)glutaronitrile (VII), 3-(1-aziridinyl)-3-phenylpropionitrile (VIII), and 3-(1-aziridinyl)-2-methylpropionitrile (IX), respectively. VI and VII required only heat to complete the reaction, whereas VIII and IX required heating in the presence of catalytic amounts of metallic sodium. The reaction of aziridine with allyl cyanide was also tried. The product obtained had the same boiling point, infrared spectrum, and refractive index as that obtained from the reaction of aziridine with crotononitrile. Apparently, allyl cyanide rearranges to crotononitrile in the presence of the aziridine (a base), and then aziridine adds to the crotononitrile to give the identical compound. The rearrangement of allyl cyanide to crotononitrile in the presence of alkali is well known (*1*).

Infrared spectra of VI, VII, VIII, and IX showed the typical absorption band for $C \equiv N$ at 2257 to 2262 $cm.^{-1}$. All four compounds had sharp, intense bands in the region 1259 to 1274 $cm.^{-1}$, characteristic of the aziridine ring (*4*). The cinnamonitrile adduct had bands at 1605 and 1590 $cm.^{-1}$ and also at 756 and 698 $cm.^{-1}$, attributed to the benzene ring.

The polymerization of some *N*-substituted aziridines has been studied by Barb (*2*). Compounds VI, VII, VIII, and IX polymerized in aqueous solutions in the presence of $Zn(BF_4)_2$. In all cases, water insoluble polymers formed rapidly at room temperature.

EXPERIMENTAL

3-(1-Aziridinyl)butyronitrile (VI). Compound I (50.0 grams, 1.16 moles) was added dropwise with stirring to a flask containing II (67.0 grams, 1.0 mole). There was no temperature change. The solution was heated at reflux for 9 hours and the product distilled, yielding 53.7 grams