2,4-Dinitrophenylhydrazone of II. The same procedure described for I was used to prepare the 2,4-dinitrophenylhydrazone of II which was recrystallized from ethyl acetate–hexane, m.p. 157–8° C. dec.

1,1-Diacetoxy-4,4,4-trinitrobutane, II. METHOD A. A solution containing 10 ml. of anhydrous ether, 3.0 grams (0.019 mole) of 1,1-diacetoxy-2-propene, 2.9 grams (0.019 mole) of trinitromethane and 2.7 grams (0.019 mole) of boron trifluoride etherate was stirred at ambient temperature for 8 hours. The dark brown reaction mixture was dissolved in 25 ml. of ether and was washed with four 25-ml. portions of water. The ether solution was dried with anhydrous magnesium sulfate, filtered, and evaporated to a dark red, viscous sirup which was extracted with two 25-ml. portions of boiling hexane. The hexane solution was cooled overnight in the refrigerator to yield 1.85 grams of orange crystals (32% yield). The product was decolorized with activated charcoal in ether solution and was crystallized by adding hexane to give white crystals melting at 60° to 70° C.

NMR spectrum in deuterochloroform with TMS reference: C_1 proton at 3.18τ (triplet, J = 45 cps), C_2 protons at 7.76τ (quartet, J = 4.5 cps), C_3 protons at 6.80τ (triplet, J = 8.4 cps), and acetyl protons at 7.96τ (singlet). The integral was consistent with the assignment of protons. Infrared spectrum (KBr): 3.40(3) C—H; 5.72(s) C=O; 6.30(3), 7.72(m), 12.48(s) NO_2; 8.05(s), 8.32(s) ester C—O; 9.92 microns (m).

METHOD B. Compound III was prepared by a previously reported procedure (3) for the synthesis of acylals. To a solution containing 2.0 grams (0.010 mole) of I in 10 ml. of acetic anhydride was added 2 drops of 96% sulfuric acid. The mixture was stirred at ambient temperature for 15 hours, then poured into 100 ml. of water, and stirred for 15 minutes. The pale yellow oily lower organic phase was extracted with 25 ml. of ether, and the ether phase was washed with two 100-ml. portions of 5% sodium bicarbonate solution. The organic phase was dried with anhydrous magnesium sulfate, filtered, and evaporated to give 2.9 grams (97% of theory) of III which was recrystallized from ether-hexane to give white needle crystals, m.p. 69–70° C. The infrared and NMR spectra of III prepared by this method were identical to those of III prepared by method A.

1,1-Diacetoxy-3-methyl-4,4,4-trinitrobutane, IV. METHOD A. This compound was prepared by the procedure used for III, but the product could not be crystallized. The yellow oil which was obtained (4.0 grams, 73%) was identified as IV by elemental analysis, and infrared and NMR spectra.

NMR spectrum in deuterochloroform with TMS reference: C_1 proton at 3.14θ (doublet of doublets, J = 6 cps, 4 cps), C_2 protons at 7.80θ (multiplet), C_3 proton at 6.62τ (quintet, J = 6 cps), 3-methyl protons at 8.52τ (doublet, J = 6 cps), acetyl protons at 7.93τ (two singlets separated by 3 cps). The integral was consistent with the assignment of protons. The acetyl protons appeared as two distinct signals each integrating for three protons. The two signals probably arise from rotational conformations present in this compound, whereas they are not evident in III. Infrared spectrum (neat): 3.35(w), 3.40(w) C—H; 5.65(s) C=O; 6.25(s), 7.70(m), 12.50(m) NO_2; 8.80(s), 8.32(s) ester C—O; 9.90μ(m).

METHOD B. The same procedure described for the synthesis of III by method B was used for the synthesis of IV by this method. IV was obtained in 51% yield, and the infrared and NMR spectra were identical to IV prepared by method A.

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Synthesis of Substituted 7-(1-Naphthyl)benz[*a*]anthracenes

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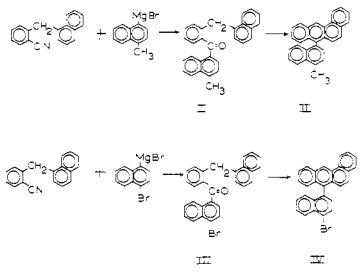
By known procedures, three new ketones and two new benz[*a*]anthracene derivatives were prepared and characterized. Per cent yields, boiling and/or melting points, and elemental analyses are given.

POLYCYCLIC aromatic compounds are at the forefront of the most exciting chemical research being done today. These compounds provide interesting models for studies in organic synthesis and physical organic chemistry including spectroscopic studies of various sorts, as well as physiological activity–molecular structure correlations. Many of the structures one would like to have are either unavailable or very difficult to prepare with the desired substituent in the proper position in the polycyclic ring system. The synthesis of two new important polycyclic aromatic compounds is reported. One compound, 7-[1-(4-methyl)naphthyl]benz[*a*]anthracene (II), contains an electron repelling methyl group, while the second compound, 7-[1-(4-bromo)naphthyl]benz[*a*]anthracene (IV), contains an electron attracting bromine atom. The position of the substituent in each case is known, and most importantly, it

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.



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