TABLE I

PHYSICAL AND ANALYTICAL DATA OF ENIMINES

Ethylenimines	No.	M. p., °C.	Yield, %	Formula	Percentage composition Calcd. C	Calcd. H	Found C	Found H
1-Benzyl-2-(*m*-nitrophenyl)-3-benzoyl	(I)	106	20	$C_{22}H_{18}N_2O_3$	73.72	5.06	73.80	5.24
1-Benzoyl-2-phenyl-3-(*p*-methylbenzoyl)	(II)	116	20	$C_{23}H_{21}NO$	84.37	6.47	84.11	6.78
1-Benzyl-2-(*p*-tolyl)-3-benzoyl	(III)	122	25	$C_{23}H_{21}NO$	84.37	6.47	84.20	6.61
α-Butylenimines								
1-Benzyl-2,4-diphenyl-4-hydroxy-	(IV)	93	85	$C_{23}H_{23}NO$	83.85	7.04	83.77	7.14
Propylenimines								
1-Benzyl-2,4,4-triphenyl-4-hydroxy-[a]	(V)	137	90	$C_{28}H_{25}NO$	85.90	6.44	85.51	6.68
1-Benzyl-2,4-diphenyl-4-(*p*-tolyl)-4-hydroxy-	(VI)	138	85	$C_{29}H_{27}NO$	85.89	6.71	85.67	6.81
	(VII)	117	80				85.69	6.84
1-Benzyl-2-(*p*-tolyl)-4,4-diphenyl-4-hydroxy-	(VIII)	143	95	$C_{29}H_{27}NO$	85.89	6.71	85.77	6.88

[a] Calcd.: N, 3.57. Found: N, 3.54.

for one hour. The reaction mixture was then poured into about 100 ml. of water and the solution made basic with dilute sodium hydroxide. This basic mixture was steam distilled until the distillate became clear (about one liter of distillate). The distillate was extracted with three 100-ml. portions of ether. The ether solution was washed several times with water and once with 0.1 *N* hydrochloric acid. After drying, the ether solution was evaporated to leave an oily residue.

The oily residue obtained from the oxidation of (IV) was dissolved in dilute alcohol and treated with phenylhydrazine to give 0.40 g. of the phenylhydrazone of acetophenone, m. p. 102°. When the oily residues resulting from the other experiments were touched with authentic crystals of the corresponding benzophenones they solidified and it was found that the enimine carbinol (V) gave 0.6 g. of benzophenone, (VI) gave 0.6 g. of phenyl *p*-tolyl ketone, (VII) gave 0.7 g. of phenyl *p*-tolyl ketone and (VIII) gave 0.8 g. of benzophenone. When about equal amounts of benzophenone and phenyl *p*-tolyl ketone are pressed together an oil results. These benzophenones were further identified by converting them to their corresponding phenylhydrazones.

When 2.0 g. of benzoin was oxidized in the same way, the steam-distillation distillate gave only 0.2 g. of benzil, m. p. 96°. The alkaline residue from the distillation step was acidified to precipitate 1.0 g. of solid acids which on several recrystallizations proved to be a mixture of benzoic acid and benzilic acid.

Miscellaneous Properties of Enimine Carbinols.—Carbinol (IV) was heated with phenylhydrazine in a mixture of 95% alcohol and acetic acid for thirty minutes. On cooling, the reaction mixture precipitated 75% of the starting material (IV).

When (V) was heated for ten minutes with an equivalent amount of benzoyl chloride in a pyridine solution, or in a benzene solution for two hours no reaction took place and the enimine carbinol was recovered unchanged.

These carbinols do not possess the unpleasant odor of the ketones from which they are derived. They are only slightly soluble in dilute mineral acids. When 1.0 g. of (V) was boiled for twenty minutes with 15% sulfuric acid only a small amount was changed (odor of benzaldehyde) and 0.6 g. of the starting material was recovered.

Summary

Ethylene imine ketones add the Grignard reagent to the carbonyl group to give a new class of compounds, enimine carbinols. These results may be taken as further evidence for the structures of the ethylene imine ketones, and as an indication of the stability of the ethylene imine ring and its inability to hinder the carbonyl reactions in such compounds.

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Derivatives of Phenanthrene. The Preparation of 9-Amino-, 9-Iodo- and 9-Fluorophenanthrene

BY M. A. GOLDBERG,[1] E. P. ORDAS[2] AND G. CARSCH[3]

In the course of our work on the synthesis of various halogenated phenanthryl amino alcohols as potential antimalarials,[4,5,6,7] it appeared desirable to prepare 9-iodo- and 9-fluorophenanthrene. 9-Fluorophenanthrene has not been previously described, and since the only previous preparation of 9-iodophenanthrene was not very satisfactory (reaction of 9-phenanthrylmagnesium bromide with iodine[8]), it seemed desirable to prepare these halogenated compounds from 9-phenanthrylamine.

However, the preparation of large quantities of 9-phenanthrylamine presented some difficulty. The best reported methods are those of Bachmann and Boatner[9] as modified by Krueger and Mosettig,[10] involving Beckmann rearrangement of the oxime of 9-acetylphenanthrene, and that of

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[1] Present address: Pepsodent Division, Lever Bros. Co., Chicago, Illinois.

[2] Present address: The Velsicol Corporation, Chicago, Illinois.

[3] Present address: 600 S. Michigan Avenue, Chicago, Illinois.

[4] Schultz, Goldberg, Ordas and Carsch, *J. Org. Chem.*, **11**, 307 (1946).

[5] Schultz, Goldberg, Ordas and Carsch, *ibid.*, **11**, 314 (1946).

[6] Schultz, Goldberg, Ordas and Carsch, *ibid.*, 320 (1946).

[7] Schultz, Goldberg, Ordas and Carsch, *ibid.*, 329 (1946).

[8] Zalkind and Lubinskaia, *Ber.*, **61B**, 269 (1928).

[9] Bachmann and Boatner, THIS JOURNAL, **58**, 2097 (1936).

[10] Krueger and Mosettig, *J. Org. Chem.*, **5**, 313 (1940).

Fieser, Jacobsen and Price,[11] consisting of a bromination of phenanthrene in methanolic solution to give 9-phenanthrylamine by way of 9-phenanthrol.

Neither of these methods is as satisfactory as might be desired, the yield by the first method being 23–25% and by the second method being about 21% based on phenanthrene taken. Even allowing for the phenanthrene recovered in the latter method, the yield is only about 40% based on phenanthrene consumed and the procedure suffers the disadvantage of not being readily adaptable to large-scale runs.

Accordingly, the following series of reactions was investigated

$$\underset{\text{I}}{\text{RH}} \xrightarrow{\text{Br}_2} \underset{\text{II}}{\text{RBr}} \xrightarrow{\text{CuCN}} \underset{\text{III}}{\text{RCN}} \longrightarrow \underset{\text{IV}}{\text{RCO}_2\text{H}} \xrightarrow{\text{SOCl}_2}$$

$$\underset{\text{V}}{\text{RCOCl}} \xrightarrow{\text{NaN}_3} \underset{\text{VI}}{\text{RCON}_3} \longrightarrow \underset{\text{VII}}{\text{RNCO}} \longrightarrow \underset{\text{VIII}}{\text{RNH}_2}$$

R = 9-phenanthryl-

Phenanthrene (I) was brominated to 9-bromophenanthrene (II) by the procedure of May and Mosettig.[12] The 9-bromophenanthrene was converted to 9-cyanophenanthrene by an adaptation of the Bachmann and Boatner modification of the method of Mosettig and van de Kamp.[13] The hydrolysis of the 9-cyanophenanthrene to 9-phenanthroic acid (IV) was carried out in ethylene glycol monoethyl ether. The phenanthroic acid was converted to the acid chloride (V) by reaction with thionyl chloride and then to the acyl azide (VI) by treatment with sodium azide. The azide was decomposed to give the isocyanate (VII) which was not isolated but hydrolyzed to 9-phenanthrylamine (VIII).

In spite of the number of reactions involved, the over-all yield in this synthesis is quite good (54%).

By diazotization of the amine so prepared and reaction with potassium iodide, 9-iodophenanthrene was prepared. The diazotization presented some difficulty. A suspension of finely divided 9-phenanthrylamine in hydrochloric acid was found not to diazotize in the presence of nitrous acid. No better results were obtained when a suspension of previously precipitated amine hydrochloride (prepared by the reaction of 9-phenanthrylamine in ether or benzene with dry hydrogen chloride) was treated with sodium nitrite. The desired reaction took place readily however when a dioxane solution of the 9-phenanthrylamine was run into cold dilute acid and the resulting mixture treated immediately with sodium nitrite.

By diazotization and treatment with fluoboric acid, 9-phenanthrylamine fluoborate was prepared. This substance decomposed smoothly in dry dioxane to yield 9-fluorophenanthrene.

Experimental

9-Bromophenanthrene.—This was prepared according to the directions of May and Mosettig.[12] The crude product was distilled *in vacuo* and was then found to be sufficiently pure for the subsequent steps. The phenanthrene used in this preparation was purified by partial oxidation with chromic acid followed by vacuum distillation and crystallization from alcohol as described by Bachmann[14] and by Durland and Adkins.[15] Material so treated had a melting point of 97–99°. The yield from the bromination of 960 g. of this phenanthrene was 1066 g. (77%); m. p. 59–60°.

9-Cyanophenanthrene.—In a two-liter Claisen flask equipped with a stirrer and thermometer was placed 1066 g. of the above 9-bromophenanthrene. The bromophenanthrene was melted and heated, with stirring, to 250°. One hundred fifty grams of cuprous cyanide was then added and the temperature raised to 280°. The temperature was held at 280° until the reaction set in (about fifteen minutes) as indicated by a rapid temperature rise. Heating was then discontinued, the thermometer removed (the temperature rises well over 360°) and 276 g. more of cuprous cyanide added over a period of about fifteen minutes with continued stirring but without additional heating. A very dark, clear liquid resulted. After stirring for an additional one-half hour, the 9-cyanophenanthrene was distilled *in vacuo* immediately from the still molten reaction mixture; b. p. 200–220° (2–4 mm.). The yield was 729 g. (87%), m. p. 104.5–106°.

9-Phenanthroic Acid.—To a hot solution of 350 g. of the 9-cyanophenanthrene in 1400 cc. of ethylene glycol monoethyl ether was added a solution of 350 g. of potassium hydroxide in 160 cc. of water. The solution was refluxed while a slow stream of carbon dioxide–free air was bubbled through it until one ml. of 0.1 *N* hydrochloric acid was not neutralized within five minutes by the exit air carrying the liberated ammonia. About six hours was required to reach this condition.

The solution was then cooled somewhat and poured into a stirred solution of 610 cc. of concentrated hydrochloric acid in 5250 cc. of water. After standing overnight, the precipitated 9-phenanthroic acid was filtered off and washed thoroughly with water; yield 374 g. (98%); m. p. 246–248°.

After one recrystallization from glacial acetic acid, a sample melted at 252–253°.

9-Phenanthroyl Chloride.—A mixture of 300 g. of the crude 9-phenanthroic acid, 300 cc. of dry benzene, and 300 cc. of thionyl chloride was refluxed for two hours, during which time a clear solution was obtained. The solvent and excess reagent were removed *in vacuo* at 100° and the residue recrystallized from benzene–hexane. Light tan-colored needles were obtained, m. p. 101–102°; yield 295 g. (91%). A sample, after recrystallization from benzene–hexane (carbon), was obtained as colorless needles, m. p. 103–104°, lit.[16] 101.5–102°.

9-Phenanthroyl Azide.—To a cold (0–5°) solution of 75 g. of sodium azide in 200 cc. of water and 500 cc. of dioxane was added 200 g. of 9-phenanthroyl chloride in small portions over a period of fifteen minutes. The mixture was stirred at 0–5° for one-half hour after all the acid chloride had been added. About 700 cc. of ice-water was then added and stirring continued for an additional half hour. The precipitated azide was then filtered off, washed with ice-water, and dried *in vacuo* over concentrated sulfuric acid. The yield of practically colorless micro-crystalline material was 201 g. (98%); m. p., explodes 95°.

9-Phenanthrylamine.—To 150 g. of the 9-phenanthroyl azide was added 750 cc. of sodium-dried dioxane and the mixture warmed gently. Reaction set in almost at once with evolution of nitrogen and was kept going at a mod-

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[11] Fieser, Jacobsen and Price, THIS JOURNAL, **58**, 2163 (1936).

[12] May and Mosettig, *J. Org. Chem.*, **11**, 15 (1946).

[13] Mosettig and van de Kamp, THIS JOURNAL, **54**, 3328 (1932).

[14] Bachmann, *ibid.*, **57**, 555 (1935).

[15] Durland and Adkins, *ibid.*, **59**, 135 (1937).

[16] Mosettig and van de Kamp, *ibid.*, **55**, 2995 (1933).

erate rate by immersing the flask in warm water (40–50°) when the gas evolution slowed and by chilling in an ice-bath when it became too vigorous. When the reaction rate permitted, the mixture was placed in a water-bath the temperature of which was gradually raised to 100°, at which temperature the reaction was at an end and a clear solution was obtained.

To the solution of 9-phenanthryl isocyanate was added 325 cc. of concentrated hydrochloric acid and the mixture refluxed on the water-bath for one hour. About 500 cc. of water was then added, the mixture cooled, and the 9-phenanthrylamine hydrochloride filtered off and washed with water.

The wet amine hydrochloride was suspended in hot water and decomposed with ammonium hydroxide. The 9-phenanthrylamine melted at 135–137.5°; yield 93%.

9-Iodophenanthrene.—To a solution of 202 cc. of concentrated hydrochloric acid in 2100 cc. of water previously cooled to 0° in an ice–salt-bath was added a solution of 60 g. of the crude 9-phenanthrylamine in 200 cc. of dioxane. The amine solution was added in a steady thin stream to the well-stirred acid solution.

To the suspension of 9-phenanthrylamine hydrochloride was then added *at once* a solution of 24.8 g. of sodium nitrite in 104 cc. of ice-cold water while maintaining the temperature between -5 and $+5°$ and with vigorous agitation. Stirring was continued for one hour at 0° after the addition of the sodium nitrite to complete the reaction, producing a suspension of yellow, difficultly soluble diazonium salt.

A solution of 8 g. of urea in a little water was added and stirring continued for an additional hour. A solution of 64 g. of potassium iodide in 160 cc. of water was then added, the ice-bath removed, and stirring continued until the gummy precipitate had thoroughly coagulated. The reaction mixture was then allowed to stand overnight.

The precipitate was then filtered off, dissolved in benzene, and the benzene solution washed with a solution of sodium bisulfite, then with 5% aqueous sodium hydroxide, and finally with water. The washed benzene solution was filtered and evaporated to dryness. The residue was distilled *in vacuo*, b. p. 190–205° (4 mm.). The distillate, amounting to 50.4 g. was crystallized from alcohol (about 1500 cc.) to yield 43 g. (45%) of pale yellow needles; m. p. 91–92°, lit.[8] 87°.

Anal. Calcd. for $C_{14}H_9I$: I, 41.8. Found: I, 41.9.

By chromic acid oxidation of a sample of the 9-iodophenanthrene, phenanthrene-9,10-quinone, m. p. 204–205°, was formed.

9-Iodophenanthrene Picrate.—Hot alcoholic solutions of 9-iodophenanthrene and picric acid were mixed and the picrate which separated on cooling was recrystallized twice from alcohol to yield orange needles; m. p. 140–141°, lit.[8] 137°.

Anal. Calcd. for $C_{20}H_{12}IN_3O_7$: N, 7.88. Found: N, 7.80.

9-Fluorophenanthrene.—Seventy-five grams of 9-phenanthrylamine was diazotized by the procedure described under the preparation of 9-iodophenanthrene. Urea was not added to destroy excess nitrous acid, however.

To the diazonium salt suspension was added a solution of 30.2 g. of boric acid in 81.5 g. of 48% hydrofluoric acid and stirring continued for one hour at 0–5°. The suspension of diazonium fluoborate was then stoppered and placed in a refrigerator at 5° overnight.

The precipitated fluoborate was then filtered with suction, washed with ice-water and dried in a vacuum desiccator, first over sulfuric acid, finally over phosphorus pentoxide. It was noted that the diazonium fluoborate could not be washed with alcohol and ether according to the usual technique. The alcohol appeared not only to dissolve large amounts of the material but to cause the residue to become quite tarry. Considerable coupling of the diazonium salt appeared to take place. However, the fluoborate was satisfactorily washed with cold water and proved to be sufficiently stable to permit drying at room temperature for several days.

The dry diazonium fluoborate was suspended in 500 cc. of sodium-dried dioxane and decomposed by refluxing for one-half hour. About 400 cc. of dioxane was then distilled off and the remaining solution poured into water. The crude fluorophenanthrene was extracted with ether, the ethereal solution washed with 5% sodium hydroxide solution, then with water. The washed ethereal solution was filtered and evaporated to dryness. The residue was distilled *in vacuo*, b. p. 145–155° (3–4 mm.). The distillate amounted to 32 g. of light-colored oil which rapidly solidified; m. p. 49–51°. The distilled fluorophenanthrene was dissolved in hexane, treated with carbon, filtered, and chilled overnight. The solution was filtered, removing a small amount of precipitated high-melting material (over 200°), and evaporated to a very small volume. After the addition of 100–150 cc. of petroleum ether (20–40°) and chilling overnight, 23 g. (30%) of colorless crystals was obtained; m. p. 51–52°.

Anal. Calcd. for $C_{14}H_9F$: F, 9.69. Found: F, 9.65.

Chromic acid oxidation of a sample of the fluorophenanthrene gave phenanthrene-9,10-quinone, m. p. 204–205°.

9-Fluorophenanthrene picrate, yellow needles, m. p. 107–107.5°.

Anal. Calcd. for $C_{20}H_{12}FN_3O_7$: N, 9.88. Found: N, 9.63.

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The nitrogen analyses herein reported (picrates of 9-iodophenanthrene and 9-fluorophenanthrene) were done by Dr. T. S. Ma.

Summary

An improved preparation of 9-phenanthrylamine has been described.

The diazo reaction has been applied to the preparation of 9-iodophenanthrene and 9-fluorophenanthrene, the latter a compound not previously reported.

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