of tetrahydrofuran under nitrogen. The mixture was held at 65° for 0.5 hr., then allowed to stand at room temperature for another hour. Ethyl acetate was added to decompose the excess hydride, followed by saturated sodium potassium tartrate. The solvents were separated from sludge by decantation, the latter extracted with hot alcohol, combined with the former, dried and distilled to give 18% of crude starting material (b.p. 48–53° (8 mm.), $n^{25}\text{D}$ 1.4435) and 2.48 g. of 3-amino-1-butanol, b.p. 73–74° (7 mm.) (reported[34] b.p. 82–85° (19 mm.)), $n^{25}\text{D}$ 1.4532–1.4543, 48% yield (based on unrecovered isoxazoline). A sample was distilled twice for analysis, precautions being taken to exclude water vapor and carbon dioxide.

Anal. Calcd. for $C_4H_{11}NO$: C, 53.89; H, 12.44. Found: C, 54.15; H, 11.97.

Reduction of Ethyl *dl*-β-Aminobutyrate.—Ethyl β-aminobutyrate (5.0 g., 0.0038 mole), prepared from 3-acetamidocrotonic ester[35] by reduction of the latter according to Skita with platinum oxide in ethanol containing a few drops of concentrated hydrochloric acid, followed by hydrolysis and re-esterification,[36] was reduced with lithium aluminum hydride in ether for 15 minutes according to Karrer.[37] Workup yielded an oil which was rectified in vacuum to give 2.11 g. of an aminoalcohol, b.p. 73° (7 mm.), $n^{25}\text{D}$ 1.4534–1.4543 (62%). The infrared of this material (neat) and that from isoxazoline showed little resolution but were superimposable, broad bands centered at 3.15, 6.29, 9.05, 9.40 μ. Samples of both amino alcohols were converted to identical bis-*p*-nitrobenzoyl derivatives, m.p. 155–156°, separately and on admixture. An analytical sample was recrystallized from ethanol (balls of tiny needles, m.p. 157°).

Anal. Calcd. for $C_{18}H_{17}N_3O_7$: C, 55.81; H, 4.42. Found: C, 55.91; H, 4.56.

The aminoalcohol was further characterized as the bisbenzoyl derivative, leaflets from ethanol-water, m.p. 112 112.5°.

Anal. Calcd. for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.40. Found: C, 72.36; H, 6.37.

MADISON, WISCONSIN

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(34) Bayer and Co., German Patent 247,144; *Chem. Zentr.*, **83**, 159 (1912).

(35) A. Skita and C. Wulff, *Ann.*, **453**, 206 (1927).

(36) E. Fischer and C. Roeder, *Ber.*, **34**, 3755 (1901).

(37) P. Karrer, P. Portmann and M. Suter, *Helv. Chim. Acta*, **31**, 1617 (1948).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

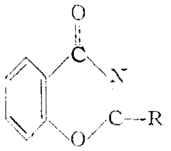
Experiments with 2-Aryl-1,3-benzoxaz-4-ones and with 2-Phenyl-2,3-dihydro-1,3-benzoxaz-4-one. A New Type of Thermochromic Compounds

BY AHMED MUSTAFA AND ALAA ELDIN ABDEL AZIZ HASSAN

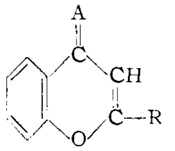
RECEIVED FEBRUARY 5, 1957

A number of new thermochromic di-(2-aryl)-1,3-benzoxaz-4-ylidenes (IVa-c) now have been prepared. Fission of the central ethylene linkage in IVa-c is brought about by the action of sulfur at 250° to yield the corresponding benzoxaz-4-thione derivatives (Va-c), respectively, and by the action of thionyl chloride followed by water in the case of IVa to give 2-phenyl-1,3-benzoxaz-4-one (Ia). The two new benzoxaz-4-one derivatives (Ib-c), needed in this investigation, have been synthesized. Whereas Ia, Ic, Va and/or Vc react with hydroxylamine hydrochloride in the presence of pyridine to give the corresponding oxime derivatives, they react with hydrazine hydrate to yield the corresponding 1,2,4-triazole derivatives (VIa-b), respectively. Treatment with organomagnesium compounds brought about addition to the carbonyl group in the case of Ic and cleavage of the hetero ring in the case of 2-phenyl-2,3-dihydro-1,3-benzoxaz-4-one (X).

2-Aryl-1,3-benzoxaz-4-ones (Ia-c) bear a structural resemblance to flavone (IIa), the former having in the hetero ring the system —CR=N— in place of CR=CH— in the latter. This has stimulated us to investigate the analogy between I and II in their chemical reactions.

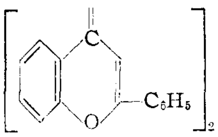


Ia, R = C_6H_5
b, R = $C_6H_4CH_3$-*p*
c, R = $C_6H_4OCH_3$-*p*

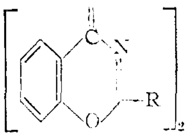


IIa, A = O; R = C_6H_5
b. A = S; R = C_6H_5

Diflavylene (III) shows remarkable physical and chemical properties; it forms light yellow crystals at the temperature of liquid air, at room temperature they are yellow, the melt is ruby-red and the color of the hot solutions varies from orange-red to deep red depending on concentrations.[1] Under pressure, it shows piezochromic properties,[2] changing from yellow to dark red. We now have found that di-(2-aryl)-1,3-benzoxaz-4-ylidenes (IVa-c) show thermochromic properties: dilute solutions of IVa in ethyl benzoate and/or in diphenyl ether are yellow at 0° and orange-red at the boiling point of the solvent; the phenomenon is reversible. Strong thermochromic effects also were observed with powdered solid IVa (yellow at 0° ←→ deep red at 260°).



III



IVa, R = C_6H_5; b, R = $C_6H_4CH_3$-*p*;
c, R = $C_6H_4OCH_3$-*p*

III shows remarkable behavior toward thionyl chloride, followed by the action of water[3] and toward the action of elementary sulfur[4]; fission of the central ethylene bond occurs and IIa and IIb are formed, respectively. We now have found that IVa behaved analogously; fission of the central ethylene linkage in IVa-c is brought about by the action of sulfur at 250° to yield the corresponding benzoxaz-4-thione derivatives (Va-c), respectively, and by the action of thionyl chloride followed by the action of water in the case of IVa to give Ia.

Whereas IIa reacts with hydroxylamine hydrochloride to give the corresponding oxazole deriva-

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(1) A. Schönberg and S. Nickel, *Ber.*, **64**, 2325 (1931).

(2) A. Schönberg, A. F. A. Ismail and W. Asker, *J. Chem. Soc.*, 442 (1946).

(3) A. Schönberg and W. Asker, *ibid.*, 272 (1942).

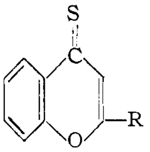
(4) A. Schönberg, *Ber.*, **58**, 1793 (1925).

tive,[5] Ia and Ic react readily with the same reagent, under the same conditions, to give the corresponding oxime derivatives. The latter are also formed by the action of the same reagent on the thione derivatives (Va and Vc, respectively).[6]

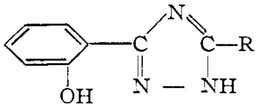
Phenylhydrazine reacts with flavone to form the pyrazole derivative,[5] but 2,4-dinitrophenylhydrazine reacts with flavone in acid solution to give the corresponding hydrazone derivative.[7] We now have found that Ia reacts readily with phenylhydrazine to give the hydrazone derivative.

It has been established that the action of hydrazine on 2-methylchromone[8] and on chromone itself[5b] leads to the formation of pyrazole derivatives and not hydrazones of the chromones in question as previously described.

We now have investigated the action of hydrazine hydrate on Ia and on Va and believe, by analogy, that the reaction product is the 1,2,4-triazole derivative VIa. Similarly, VIb is obtained upon treatment of Ic with the same reagent. VIa-b are colorless compounds, soluble in aqueous sodium hydroxide solution and give violet color with ferric chloride.

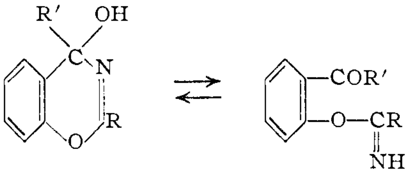


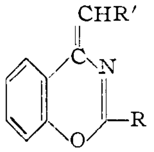
Va, R = C_6H_5;
b, R = $C_6H_4CH_3$-*p*;
c, R = $C_6H_4OCH_3$-*p*



VIa, R = C_6H_5;
b, R = $C_6H_4OCH_3$-*p*

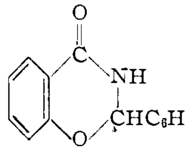
Recently, Mustafa and co-workers[9] have shown that in contrast to 2-phenyl-3,1-benzoxaz-4-one, which underwent hetero ring opening with phenylmagnesium bromide, Ia reacted with the same reagent to yield 2,4-diphenyl-4-hydroxy-1,3-benzoxazine (VIIa) which could also be present in equilibrium with the open form VIIIa. 2-Phenyl-4-benzal-1,3-benzoxazine (IXa) was obtained when Ia was treated with benzylmagnesium chloride. Similar results now have been obtained when 2-(*p*-methoxyphenyl)-1,3-benzoxaz-4-one (Ic) was allowed to react with phenylmagnesium bromide and with benzylmagnesium chloride, followed by hydrolysis, yielding 2-(*p*-methoxyphenyl)-4-phenyl-4-hydroxy-1,3-benzoxazine (VIIb), which could also be present in equilibrium with the open form VIIIb, and 2-(*p*-methoxyphenyl)-4-benzal-1,3-benzoxazine (IXb), respectively. That VIIb and IXb are not identical in structure is indicated by the analytical results; furthermore, VIIb is colorless and contains an active hydrogen atom, while IXb is yellow and contains no active hydrogen atom. The behavior of Ia and Ic toward Grignard reagents is comparable to that of flavone.[10]



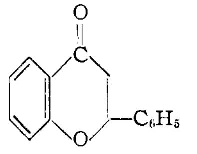


VIIa, R = R′ = C_6H_5 VIII IX
b, R = $C_6H_4OCH_3$-*p*; R′ = C_6H_5

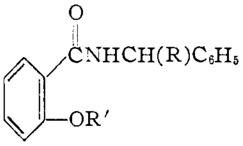
In this connection, we have also investigated the behavior of 2-phenyl-2,3-dihydro-1,3-benzoxaz-4-one (X), which bears structural resemblance to flavanone (XI), toward the action of organomagnesium compounds. Thus, whereas XI reacts with both aliphatic[11] and aromatic Grignard reagents[12] to form chromanols which can be dehydrated to α-chromenes, X undergoes hetero ring opening with phenylmagnesium bromide and with methylmagnesium iodide to yield colorless products, believed to have structures like XIIa-b, respectively. XIIa-b are soluble in aqueous sodium hydroxide solution and give violet color with alcoholic ferric chloride. They form insoluble acetyl derivatives (XIIc-d) in aqueous sodium hydroxide solution when allowed to react with acetic anhydride. When an acetic acid solution of XIIa is boiled with hydrochloric acid, salicylamide was obtained.



X



XI



XIIa, R = C_6H_5; R′ = H
b, R = CH_3; R′ = H
c, R = C_6H_5; R′ = $COCH_3$
d, R = CH_3; R′ = $COCH_3$

Methods of Preparation.—The new 2-aryl-1,3-benzoxaz-4-ones (Ib-c) now have been obtained after the procedure of Titherley[13] by treatment of O-*p*-methylbenzoyl- and O-*p*-methoxybenzoylsalicylamides, respectively, with hydrogen chloride gas in boiling anisole.

IVa-c have been obtained by the action of copper bronze on the corresponding 2-aryl-1,3-benzoxaz-4-thiones[14] (Va-c), respectively, which may be prepared by treating Ia-c with phosphorus pentasulfide.[15] IVa also has been obtained by the action of copper bronze[14] on the product resulting by treatment of Ia with thionyl chloride.

Experimental

2-Aryl-1,3-benzoxaz-4-ones (Ib-c). O-Aroylsalicylamides.—O-*p*-Toluoyl- and O-*p*-methoxybenzoylsalicylamides were obtained by treating a solution of 5 g. of salicylamide in 20 ml. of dry pyridine with 5.5 g. of *p*-toluoyl chloride and with 6 g. of *p*-methoxybenzoyl chloride, respectively. The reaction mixture was heated on a steam-bath for 1 hr., poured into ice-cold water and the resulting solids (yield 85, 89%, respectively) collected and worked up as follows:

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(5) (a) W. Baker and V. S. Butt, *J. Chem. Soc.*, 2142 (1949); (b) W. Baker, J. B. Harborne and W. D. Ollis, *ibid.*, 1303 (1952).

(6) *Cf.* the formation of flavone oxime by the action of hydroxylamine hydrochloride on thioflavone in presence of pyridine (ref. 5b).

(7) R. Mozingo and H. Adkins, THIS JOURNAL, **60**, 669 (1938).

(8) E. Koenigs and J. Freund, *Ber.*, **80**, 143 (1947).

(9) A. Mustafa, W. Asker, M. Kamel, A. F. A. Shalaby and A. E. A. E. Hassan, THIS JOURNAL, **77**, 1612 (1955).

(10) E. R. Watson, K. B. Sen and V. R. Medhi, *J. Chem. Soc.*, **107**, 1477 (1915); I. M. Heilbron, D. H. Hey and A. Lowe, *ibid.*, 1380 (1936).

(11) K. v. Auwers and F. Krollpfeiffer, *Ber.*, **47**, 2591 (1914).

(12) A. Lowenbein, *ibid.*, **57**, 1517 (1924).

(13) A. W. Titherley, *J. Chem. Soc.*, **97**, 200 (1910).

(14) A. Schönberg, O. Schütz and O. Nickel, *Ber.*, **61**, 1375 (1927).

(15) H. Simonis and L. Hervici, *ibid.*, **50**, 787 (1917).

O-*p*-Toluoylsalicylamide forms colorless crystals from ethyl alcohol, m.p. 213°. It gives yellow color with sulfuric acid, no color with alcoholic ferric chloride solution and is insoluble in cold aqueous sodium hydroxide solution (10%) but soluble on boiling.

Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.59; H, 5.10; N, 5.48. Found: C, 70.32; H, 4.90; N, 5.60.

O-*p*-Methoxybenzoylsalicylamide forms colorless crystals from dilute ethyl alcohol, m.p. 198°. It gives greenish-yellow color with sulfuric acid and behaves similarly toward ferric chloride and sodium hydroxide solutions.

Anal. Calcd. for $C_{15}H_{13}NO_4$: C, 66.42; H, 4.80; N, 5.17. Found: C, 66.23; H, 4.72; N, 5.15.

2-*p*-Tolyl-1,3-benzoxaz-4-one (Ib) was obtained in 72% yield by treating a clear solution of 5 g. of O-*p*-toluoylsalicylamide in 30 ml. of freshly distilled anisole with a stream of dry hydrogen chloride for a few minutes after the procedure described by Titherley[13] for the preparation of Ia. Ib forms colorless crystals from a mixture of petroleum ether (b.p. 80–100°), m.p. 113°. It does not give color with alcoholic ferric chloride solution and is insoluble in aqueous sodium hydroxide solution.

Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.95; H, 4.64; N, 5.90. Found: C, 76.10; H, 4.52; N, 5.56.

2-*p*-Methoxyphenyl-1,3-benzoxaz-4-one (Ic).—Similarly, Ic was obtained in 68% yield by treating a solution of 5 g. of O-*p*-methoxybenzoylsalicylamide in 40 ml. of anisole with a stream of hydrogen chloride as described above. Ic forms colorless crystals from ethyl alcohol, m.p. 168°. It is insoluble in aqueous sodium hydroxide solution and gives no color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.35; N, 5.53. Found: C, 70.88; H, 4.14; N, 5.41.

2-Aryl-1,3-benzoxaz-4-thiones (Va-c). General Procedure.—The thiones were prepared by refluxing a benzene solution of 1 g. of each of Ia-c with 1 g. of phosphorus pentasulfide for 3 hr. The reaction mixture was filtered while hot, the benzene was evaporated and the oily residue was washed several times with cold light petroleum (b.p. 40–60°). The solidified mass was then worked up as follows: 2-phenyl-1,3-benzoxaz-4-thione (Va) was crystallized from petroleum ether as orange crystals, m.p. 128°, yield 71%. It gives orange color with sulfuric acid and is insoluble in aqueous sodium hydroxide solution.

Anal. Calcd. for $C_{14}H_9NOS$: N, 5.81; S, 13.38. Found: N, 5.72; S, 13.58.

2-*p*-Tolyl-1,3-benzoxaz-4-thione (Vb) was crystallized from petroleum ether (b.p. 60–90°) as orange crystals, m.p. 155°, yield 78%. It gives yellow color with sulfuric acid.

Anal. Calcd. for $C_{15}H_{11}NOS$: C, 71.14; H, 4.35; N, 5.53; S, 12.65. Found: C, 70.78; H, 4.15; N, 4.92; S, 12.34.

2-*p*-Methoxyphenyl-1,3-benzoxaz-4-thione (Vc) formed orange crystals from petroleum ether (b.p. 60–90°), m.p. 148°, yield 62%. It gives orange-red color with sulfuric acid.

Anal. Calcd. for $C_{15}H_{11}NO_2S$: N, 5.20; S, 11.90. Found: N, 4.99; S, 11.72.

Di-(2-aryl)-1,3-benzoxaz-4-ylidenes (IVa-c). General Procedure.—These were obtained by refluxing a solution of 1 g. of each of Va-c in 40 ml. of dry xylene with 1 g. of copper bronze for 6 hr. The reaction mixture was filtered off, concentrated and cooled. The crystals that separated out were collected. No molecular weight determination could be carried as the compounds (IVa-c) are difficultly soluble. Di-2-phenyl-1,3-benzoxaz-4-ylidene (IVa) was crystallized from xylene, as yellow crystals, m.p. 269°, yield *ca.* 68%. It gives yellow color with sulfuric acid.

Anal. Calcd. for $C_{28}H_{18}N_2O_2$: C, 81.16; H, 4.35; N, 6.76. Found: C, 80.92; H, 4.16; N, 6.95.

Di-2-(*p*-tolyl)-1,3-benzoxaz-4-ylidene (IVb) formed yellow-orange crystals, m.p. 288°, yield *ca.* 71%. It gives yellow color with sulfuric acid and is insoluble in aqueous sodium hydroxide solution.

Anal. Calcd. for $C_{30}H_{22}N_2O_2$: C, 81.45; H, 4.98; N, 6.33. Found: C, 81.24; H, 4.76; N, 6.25.

Di-2-(*p*-methoxyphenyl)-1,3-benzoxaz-4-ylidene (IVc) was crystallized from xylene as orange-yellow crystals, m.p. 282°, yield *ca.* 61%. It gives yellow color changing to violet with sulfuric acid.

Anal. Calcd. for $C_{30}H_{22}N_2O_4$: C, 75.94; H, 4.64; N, 5.91. Found: C, 75.74; H, 4.26; N, 5.67.

IVa also was obtained by the following procedure: one gram of Ia was treated with 15 ml. of freshly distilled thionyl chloride on a steam-bath for 20 hr.; the excess of thionyl chloride was distilled off. The residue was dissolved in 30 ml. of dry xylene and refluxed with 1 g. of copper bronze for 6 hr. The xylene solution was filtered hot and concentrated; on cooling IVa (*ca.* 0.42 g.) separated out. It was filtered off and recrystallized from xylene, m.p. 269°; identified as IVa (m.p. and mixed m.p.).

Experiments with Thermochromic Substances.—The color changes, which are all reversible, were obtained in layers of solution 1 cm. in depth. The solutions were heated nearly to the boiling point (heating lasted only for a few seconds) and then cooled immediately. The expansion of the volume of the solutions with temperature was taken into consideration.

Ethyl benzoate (Schering–Kahlbaum) was purified by shaking it with sodium carbonate for 24 hr., followed by filtration and distillation.

Action of Thionyl Chloride.—One gram of IVa was refluxed with 30 ml. of thionyl chloride for 6 hr.; the excess of thionyl chloride was distilled off completely (pump) and the residual oil was dissolved in benzene and shaken with water at 30° for 30 minutes. The benzene layer was evaporated and the residual oil was solidified on scratching and crystallized from petroleum ether, m.p. 106°; identified as Ia (m.p. and m.p. determination). The yield was *ca.* 68%.

Action of Sulfur.—One gram of IVa was ground with 0.5 g. of sulfur, and the mixture was heated at 250° (bath-temp.) for 10 minutes, allowed to cool, powdered and extracted repeatedly with petroleum ether (b.p. 100–120°). The extract was concentrated, cooled, filtered from precipitated sulfur and was concentrated further and cooled. Va was obtained; identification was carried out by m.p. and m.p. determination with an authentic specimen (see above).

Behavior of 2-Aryl-1,3-benzoxaz-4-ones toward: (a) Hydroxylamine Hydrochloride.—A solution of 1 g. of each of Ia and Ic in 40 ml. of ethyl alcohol was treated with 0.3 g. of hydroxylamine hydrochloride and five drops of freshly distilled pyridine for 4 hr. (steam-bath). The cooled reaction mixture was poured into ice-cold water, acidified with dilute hydrochloric acid; the deposit formed was filtered (*ca.* 0.75 g., 0.64 g., respectively), and crystallized from alcohol as colorless crystals.

2-Phenyl-1,3-benzoxaz-4-one oxime melts at 135°, gives no color with alcoholic ferric chloride and is soluble in aqueous sodium hydroxide solution.

Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.20; N, 11.76. Found: C, 70.26; H, 4.05; N, 11.92.

The above oxime derivative was similarly prepared by the action of hydroxylamine hydrochloride on Va, as described above, in almost quantitative yield. Identification was carried out by m.p. and mixed m.p. determination.

2-(*p*-Methoxyphenyl)-1,3-benzoxaz-4-one oxime formed colorless crystals (*ca.* 0.73 g.), m.p. 140°. Its behavior toward ferric chloride and sodium hydroxide simulates that of the oxime of Ia.

Anal. Calcd. for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.47; N, 10.45. Found: C, 66.92; H, 4.31; N, 10.55.

(b) **Phenylhydrazine.**—A mixture of 1 g. of Ia and 1 g. of phenylhydrazine and 40 ml. of absolute ethyl alcohol was refluxed for 3 hr. Working up the reaction mixture gave colorless crystals from ethyl alcohol (*ca.* 0.67 g.) of 2-phenyl-1,3-benzoxaz-4-one phenylhydrazone derivative, m.p. 130°. It is insoluble in aqueous sodium hydroxide solution and gives no color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{20}H_{15}N_3O$: C, 76.69; H, 4.79; N, 13.42. Found: C, 76.36; H, 4.38; N, 13.21.

(c) **Hydrazine Hydrate.**—A solution of 1 g. of each of Ia and Ic in 50 ml. of absolute ethyl alcohol was treated with 0.30 g. of hydrazine hydrate. The reaction mixture was heated (steam-bath) for 15 minutes and kept aside overnight at room temperature. It was diluted with water and the colorless crystals, so obtained, were collected.

3-(*o*-Hydroxyphenyl)-5-phenyl-1,2,4-triazole (VIa) formed colorless crystals from benzene, m.p. 204°, yield *ca.* 82%. VIa is soluble in aqueous sodium hydroxide solution and gives violet color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{14}H_{11}N_3O$: C, 70.88; H, 4.64; N, 17.72. Found: C, 70.61; H, 4.42; N, 17.90.

VIa was similarly prepared by the action of hydrazine hydrate on 1 g. of Va, as described above, in an almost quantitative yield. Identification was carried out by m.p. and mixed m.p. determination.

3-(*o*-Hydroxyphenyl)-5-(*p*-methoxyphenyl)-1,2,4-triazole (VIb) formed colorless crystals from ethyl alcohol, m.p. 186°, yield *ca.* 79%. It behaves in a similar manner to VIa toward ferric chloride and sodium hydroxide solutions.

Anal. Calcd. for $C_{15}H_{13}N_3O_2$: C, 67.41; H, 4.87; N, 15.73. Found: C, 67.52; H, 4.65; N, 15.80.

Action of Grignard Reagents on Ic. (a) **Phenylmagnesium Bromide.**—To a solution of phenylmagnesium bromide (prepared from 0.9 g. of magnesium and 9 g. of bromobenzene in 50 ml. of dry ether) was added a solution of 1.5 g. of Ic in 50 ml. of dry benzene. The ether was evaporated and the reaction mixture heated for 3 hr. on a steam-bath. After the mixture had stood overnight at room temperature, it was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution and extracted with ether. The precipitate which separated from the ether–benzene mixture was crystallized from benzene–light petroleum as colorless crystals, m.p. 122°, yield *ca.* 0.89 g.

Anal. Calcd. for $C_{21}H_{17}NO_3$: C, 76.13; H, 5.13; N, 4.23; active H, 0.30. Found: C, 75.68; H, 4.96; N, 4.15; active H, 0.27.

2-(*p*-Methoxyphenyl)-4-phenyl-1,3-benzoxazine (VIIa) is easily soluble in benzene and hot ethyl alcohol, difficultly soluble in light petroleum and insoluble in cold aqueous sodium hydroxide solution. It gives red color with sulfuric acid. The alcoholic solution of VIIb does not become colored when treated with alcoholic ferric chloride solution.

(b) **Benzylmagnesium Chloride.**—To a Grignard solution of benzylmagnesium chloride (prepared from 0.8 g. of magnesium, 5.5 g. of benzyl chloride and 50 ml. of dry ether) was added a solution of 1 g. of Ic in 40 ml. of benzene. The reaction mixture was worked up in the usual manner. The oily product, obtained upon evaporation of the ethereal extract, solidified after working with light petroleum. 2-(*p*-Methoxyphenyl)-4-benzal-1,3-benzoxazine (IXb) was obtained as yellow crystals from petroleum ether, yield 0.68 g., m.p. 126°.

Anal. Calcd. for $C_{22}H_{17}NO_2$: C, 80.73; H, 5.20; N, 4.28. Found: C, 80.62; H, 4.91; N, 4.05.

IXb is easily soluble in chloroform and benzene, difficultly soluble in cold petroleum ether and insoluble in cold aqueous sodium hydroxide solution; it gives an orange red color with sulfuric acid.

Action of Grignard Reagents on X. (a) **Phenylmagnesium Bromide.**—To a solution of phenylmagnesium bromide was added 1 g. of X[13] in 30 ml. of dry benzene. The reaction mixture was worked up as described above. The oily residue, obtained on evaporation of the ethereal extract, solidified on scratching and cooling. N-Benzohydrylsalicylamide (XIIa) was crystallized from petroleum ether (b.p. 100–120°) as colorless crystals, m.p. 140°, yield 0.64 g.

Anal. Calcd. for $C_{20}H_{17}NO_2$: C, 79.21; H, 5.61; N, 4.62. Found: C, 79.20; H, 5.46; N, 4.32.

XIIa is easily soluble in benzene and hot alcohol, difficultly soluble in light petroleum and soluble in cold aqueous sodium hydroxide; it gives an orange-red color with alcoholic ferric chloride solution.

Acetylation.—A solution of 0.5 g. of XIIa in 30 ml. of acetic anhydride was refluxed for 2 hr. The reaction mixture was poured into cold water, and the solid, so obtained after cooling, was filtered off, washed thoroughly with water and crystallized from alcohol as colorless crystals (*ca.* 0.39 g.), m.p. 148°. The acetyl derivative XIIc is insoluble in cold aqueous sodium hydroxide solution and gives no color with ferric chloride. It gives an orange-red color with sulfuric acid.

Anal. Calcd. for $C_{22}H_{19}NO_3$: C, 76.52; H, 5.51; N, 4.06. Found: C, 76.50; H, 5.34; N, 3.82.

Action of Hydrochloric Acid on XIIa.—A solution of 1 g. of XIIa in 40 ml. of glacial acetic acid was treated with 5 ml. of concentrated hydrochloric acid. The reaction mixture was refluxed for 3 hr., cooled, poured into ice-cold water and neutralized with sodium carbonate. It was extracted with ether, dried and evaporated. The solid residue was crystallized from ethyl alcohol as colorless crystals (*ca.* 0.41 g.), m.p. 136°; identified as salicylamide (m.p. and mixed m.p.).

Anal. Calcd. for $C_7H_7NO_2$: C, 61.31; H, 5.10; N, 10.21. Found: C, 61.42; H, 4.96; N, 10.12.

(b) **Methylmagnesium Iodide.**—A solution of 1 g. of XIIa in 40 ml. of dry benzene was added to methylmagnesium iodide (prepared from 0.9 g. of magnesium, 3.6 g. of methyl iodide and 50 ml. of dry ether); the reaction mixture was refluxed on a steam-bath for 3 hr., allowed to stand overnight at 25° and worked out as usual. N-(α-Phenylethyl)-salicylamide (XIIb) was crystallized from light petroleum as colorless crystals, m.p. 103°, yield 0.51 g.

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.68; H, 6.22; N, 5.81. Found: C, 74.46; H, 5.98; N, 5.85.

XIIb is easily soluble in benzene and hot alcohol, difficultly soluble in light petroleum and soluble in cold aqueous sodium hydroxide solution; it gives yellow color with sulfuric acid. The alcoholic solution of XIIb gives violet color with alcoholic ferric chloride solution.

Acetylation.—The acetyl derivative XIId was similarly prepared as previously described in the case of XIIc. It was obtained in colorless crystals from chloroform–light petroleum mixture, m.p. 98°, yield 82%. It was insoluble in aqueous sodium hydroxide solution and gives no color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{17}H_{17}NO_3$: C, 72.08; H, 6.00; N, 4.94. Found: C, 71.78; H, 5.82; N, 5.00.

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[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

Relative Reactivities of Polynuclear Aromatic Systems. The Solvolysis of α-Arylethyl Chlorides[1]

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The rates of reaction, activation energies and entropies were determined for the SN1 solvolysis of 13 different α-arylethyl chlorides, $ArCHClCH_3$, in 80% or 90% aqueous acetone. The relative reactivities, referred to 25° and 80% aqueous acetone, correlate satisfactorily with various theoretical parameters, but compounds with an "α-naphthalene-like" structure react slower than predicted.

Although polynuclear aromatic hydrocarbons have played an important part in organic chemical theories, an experimental knowledge of the relative reactivities of polycyclic aromatic systems is very scanty. This is in contrast to the theoretical treatment accorded these systems, particularly in

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[1] Taken from a dissertation submitted by Miss Nan Shieh to the Graduate School of Bryn Mawr College in partial fulfillment of the requirements for the Ph.D. degree, June, 1957.