ml. of anhydrous diethyl ether was added dropwise with stirring (in an atmosphere of nitrogen) over a period of two hours to a suspension of sodium amalgam sand containing 35 g. (1.5 gram atoms) of sodium and 25 g. (0.125 gram atom) of mercury dispersed in 300 ml. of refluxing anhydrous diethyl ether. The same procedure was followed as described in "a." Acidulation of the aqueous layer with 174 ml. of concentrated hydrochloric acid yielded 150 g. (92%) of 5-chloro-2-thiophenecarboxylic acid.

Preparation of 5-Bromo-2-thienylsodium and 5-Bromo-2-thiophenecarboxylic Acid from Sodium and 2-Bromothiophene.—Following the procedure described in "a" above, 41 g. (0.25 mole) of 2-bromothiophene was reacted with 13.5 g. (0.59 gram atom) of sodium and the mixture worked up as before: eighteen grams (35%, of a red oil separated which crystallized on cooling. White needles of 5-bromo-2-thiophenecarboxylic acid were obtained by sublimation, m. p. 140.5–141.5°.[8,9] The observed neutral equivalent was 202 (calcd. 207). A mixed melting point with an authentic sample (m. p. 141–141.5°) of 5-bromo-2-thiophenecarboxylic acid[7] gave no depression.

Preparation of 5-Iodo-2-thienylsodium and the Corresponding 5-Iodo-2-thiophenecarboxylic Acid from Sodium and 2-Iodothiophene.—Following the procedure described in "a" above, 55 g. (0.25 mole) of 2-iodothiophene was treated with 9 g. (0.38 gram atom) of sodium and worked up as before. Twenty-one grams (33%) of a red oil separated from solution which crystallized on cooling. White needles of 5-iodo-2-thiophenecarboxylic acid were obtained by sublimation, m. p. 132.5–133.5°.[8,10] The observed neutral equivalent was 250 (calcd. 253).

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Summary

2-Thienylsodium has been prepared in yields of 60–89% from an alkyl or aryl halide, sodium amalgam, and thiophene, and in yields of 84% from 2-chlorothiophene and sodium amalgam.

2-Chloro-, 2-bromo- and 2-iodothiophenes have been metalated with sodium without replacement of the halo- atom, and the 5-halo-2-thienyl sodium compounds so formed were carbonated to give 2-chloro-, 5-bromo- and 5-iodo-2-thiophenecarboxylic acids in yields of 70, 35 and 33%, respectively. With 70% sodium amalgam, instead of sodium, the yield of 5-chloro-2-thiophenecarboxylic acid was 92%. Diethyl ether was the only solvent which gave satisfactory results. A decrease in solvent volume resulted in lower yields, but increases in the rate of reaction were noted. The reaction proceeded satisfactorily at 30–40°, but above 50° normal replacement of the halogen atom by sodium occurred.

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[10] Rinkes, *Rec. trav. chim.*, **53** [4], 640 (1934), lists m. p. of 133–134° for 5-iodo-2-thiophenecarboxylic acid.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

Aromatization Studies. VI. Aminobiphenyls and Naphthylamines

BY E. C. HORNING, M. G. HORNING AND E. JANE PLATT[1]

The preparation of alkyl anilines from alkylcyclohexenones, by aromatization of the corresponding azines, was described in a previous paper.[2] This method provides a way of obtaining amines with alkyl substituents whose character or position are such that the compound would be difficult or impossible to obtain by ordinary aromatic substitution routes. Further investigation of this method has now shown that it can be applied also to the preparation of aminobiphenyls and naphthylamines; it appears therefore to be generally applicable in the aromatic series.

The aminobiphenyls obtained were 3-amino-5-methyl-4′-methoxy-biphenyl, 3-amino-5-methyl-2′,3′-dimethoxybiphenyl and 3-amino-5-methyl-3′,4′-dimethoxybiphenyl. The azines were prepared from the corresponding arylcyclohexenones,[3] and the aromatization was carried out in triethylbenzene with a 5% palladium–carbon catalyst. The amines were isolated in the form of their acetyl derivatives. The yields were uniformly in the vicinity of 50%, as in the case of alkylanilines,[2] but we have as yet no information on the fate of the rest of the material or on the mechanism of the reaction.

The tetralones which were converted to the corresponding aminonaphthalenes were tetralone-1, 7-methyltetralone-1 and 7-ethyltetralone-1. 7-Substituted tetralones may be obtained readily by the usual succinoylation method from benzene derivatives, and this route offers a means of obtaining many 7-substituted 1-naphthylamines. The yields here were lower (about 20%), although this appeared to be due more to difficulties in isolation of pure acetyl derivatives than to the aromatization itself.

The aromatization of these azines in a boiling solvent at a moderate temperature (214°) with a reflux period of only thirty minutes indicates the high degree of effectiveness of Hartung's palladium–carbon catalyst[4] in aromatization reactions.

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Experimental

All melting points are corrected. Analyses are by Miss Sarah H. Miles.

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[1] Rohm and Haas Research Assistant.

[2] Horning and Horning, THIS JOURNAL, **69**, 1907 (1947).

[3] Horning and Field, *ibid.*, **68**, 384 (1946).

[4] "Organic Syntheses," **26**, 77 (1946).

TABLE I

AZINES OF KETONES

Ketone	Formula	M. p., °C.	Yield, %	Analyses, % C Calcd.	C Found	H Calcd.	H Found
Derivative of 2-cyclohexen-1-one							
3-Methyl-5-(*p*-methoxyphenyl)-	$C_{28}H_{32}O_2N_2$	190.5–191.5	58	78.47	78.43	7.53	7.50
3-Methyl-5-(3′,4′-dimethoxyphenyl)-	$C_{30}H_{36}O_4N_2$	168–170[a]	64[b]	73.74	73.79	7.43	7.21
3-Methyl-5-(2′,3′-dimethoxyphenyl)-	$C_{30}H_{36}O_4N_2$	175–176[c]	52[d]	73.74	73.89	7.43	7.17
Tetralone-1	$C_{20}H_{20}N_2$	142–143[e,f]	66[g]	...	...	..	..
7-Methyltetralone-1	$C_{22}H_{24}N_2$	146–147[h]	50	83.50	83.63	7.64	7.50
7-Ethyltetralone-1	$C_{24}H_{28}N_2$	102–103[h]	25[i]	83.67	83.68	8.19	8.07

[a] Recrystallized from aqueous acetic acid. [b] Reflux period 3.3 hours. [c] Recrystallized from cyclohexanebenzene. [d] Reflux period one hour. Water was added to the solution, and the supernatant liquor decanted after cooling. The residue was treated with 100 ml. of boiling methanol to yield a crystalline product. [e] Reported, 143–144°. Blout, Eager and Gofstein, THIS JOURNAL, 68, 1983 (1946). [f] Recrystallized from cyclohexane. [g] Reflux period two hours. [h] Recrystallized from methanol. [i] Reflux period one hour; water was added to yield the product.

TABLE II

ACETYL DERIVATIVES OF AMINES

Amine	M. p., °C.	Yield, %	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
3-Amino-5-methyl-4′-methoxybiphenyl	158–159[a]	54	$C_{16}H_{17}O_2N$	75.26	6.71	75.29	6.67
3-Amino-5-methyl-2′,3′-dimethoxybiphenyl	118–118.5[a]	53	$C_{17}H_{19}O_3N$	71.56	6.71	71.57	6.76
3-Amino-5-methyl-3′,4′-dimethoxybiphenyl	108–109[b]	55	$C_{17}H_{18}O_3N$	71.56	6.71	71.72	6.71
1-Aminonaphthalene	158–159[a]	15	$C_{12}H_{11}ON$				
7-Methyl-1-aminonaphthalene	180–181[a]	16	$C_{13}H_{13}ON$	78.36	6.57	78.44	6.50
7-Ethyl-1-aminonaphthalene	149–150[a]	21	$C_{14}H_{15}ON$	78.84	7.09	78.84	7.06

[a] Recrystallized from cyclohexane–ethyl acetate. [b] Recrystallized from benzene–ethyl acetate.

Preparation of Azines. 3-Methyl-5-(*p*-methoxyphenyl)-2-cyclohexen-1-one Azine.—A mixture of 10.8 g. of 3-methyl-5-(*p*-methoxyphenyl)-2-cyclohexen-1-one, 1.9 g. of 85% hydrazine hydrate and 1 drop of concentrated hydrochloric acid, in 30 ml. of ethanol, was maintained under reflux for one hour. The product crystallized from solution during the reflux period; the yield was 6.3 g. (58%) of yellow azine, m. p. 186–189°. Recrystallization from methanol gave a sample melting at 190.5–191.5°, with shrinking.

The yields, properties, and analyses of the azines prepared are described in Table I. The general method of preparation was modified in each case as described in the footnotes.

Aromatization of Azines.—The aromatization reaction was carried out in the same fashion for all azines, but the method of isolation of the resulting aromatic amines varied. In cases where the hydrochlorides of the amines were water-insoluble, it was not possible to use the previously described method.[3] A typical aromatization is described.

A mixture of 5.0 g. of 3-methyl-5-(*p*-methoxyphenyl)-2-cyclohexen-1-one azine, 1.5 g. of 5% palladium–carbon catalyst,[4] and 15 ml. of triethylbenzene was heated under reflux for thirty minutes. After cooling, the catalyst was removed by filtration, and washed with 15 ml. of warm benzene.

In this case, the solution was added to 200 ml. of water containing 15 ml. of concentrated hydrochloric acid and steam-distilled. The aqueous solution was chilled and filtered to remove 3.5 g. of crystalline hydrochloride, m. p. 230–232° (dec.). The hydrochloride was treated with 50 ml. of 5% sodium hydroxide solution and 50 ml. of ether. The alkaline solution was extracted with ether, and the combined ether solutions washed and dried. After evaporation, the residue was acetylated by adding 15 ml. of pyridine and 10 ml. of acetic anhydride. This mixture, after standing overnight, was poured into 100 ml. of ice water and the crystalline material removed by filtration. The yield and properties of the product are in Table II.

In the case of the other two aminobiphenyls, the isolation procedure followed that described previously.[3]

The alkylnaphthylamines could not be extracted satisfactorily from ether with aqueous acid. In consequence, the benzene–triethylbenzene solution was treated immediately with 25 ml. of pyridine and 15 ml. of acetic anhydride. After standing overnight, the solution was poured into water and steam-distilled. On cooling, the product separated in part as a colorless, crystalline precipitate, and in part as a gummy, dark mass. The gum was removed mechanically, and the crystalline material collected separately. It was found in each case that the crystalline material was of a high state of purity, and that a smaller amount of additional considerably less pure material could be obtained by treatment of the gum with appropriate solvents. The yields given in Table II represent only the yield of pure material obtained directly.

Summary

The aromatization of several 3-methyl-5-aryl-2-cyclohexen-1-one and tetralone-1 azines to the corresponding 3-amino-5-methylbiphenyls and 1-aminonaphthalenes, using a palladium–carbon catalyst in boiling triethylbenzene, is described. This method has been applied previously to the synthesis of alkyl anilines; it is apparently general for the aromatic series.

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