tive index of chloroform and gave a positive carbylamine test. The remainder of the reaction mixture was heated on the steam-bath until all the ethanol distilled off. The residue was treated with 20% sulfuric acid and extracted with chloroform. The solvent was removed from the extract and the residue distilled yielding a colorless liquid (26 g.), b. p. 158°, $n^{20}D$ 1.4388. This liquid when treated with alcoholic ammonia yielded an amide, m. p. 95–96°. These properties agree closely with those of ethyl dichloroacetate.

Treatment of hexachloroacetone in a similar manner yielded chloroform and ethyl trichloroacetate.

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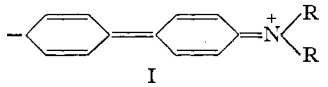
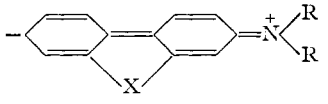
Synthesis of Some Substituted Biphenyls

BY RUSSELL MELBY, ROBERT K. BROWN AND REUBEN B. SANDIN

It has recently been found that 4-dimethylaminobiphenyl shows carcinogenic activity when fed to male rats.[1] Recent work[2] has also shown that 4-acetylaminobiphenyl is a carcinogenic compound. In view of these findings, the present authors consider it possible that the biological activity of certain derivatives of biphenyl, fluorene and fluorene analogs[1] is in some way associated with the resonating quinoid structures[3] such as I and II. It was therefore considered of interest to prepare the 2-methyl and 2′-methyl derivatives of 4-acetylaminobiphenyl in order to find out the effect, if any, of hindering groups[4] on carcinogenicity. These compounds might also be considered as "open" analogs of the carcinogen 2-acetylaminofluorene.



I



X = CH_2, O, S, S → O

II

In this communication is reported the preparation of 2-methyl-4-acetylaminobiphenyl and some intermediates of the 2′-methyl isomer which have not been reported in the literature.

(1) Miller, Miller, Sandin and Brown, *Cancer Research*, **9**, 504 (1949).

(2) Unpublished work by E. C. Miller and J. A. Miller.

(3) The interesting work of Haddow, Harris, Kon and Roe, *Trans. Roy. Soc. (London)*, **A241**, 147–195 (1948), on 4-aminostilbene and derivatives suggests that one of the requirements for biological effectiveness is an unbroken conjugation of the amino group with both nuclei.

(4) For excellent articles on the effect of hindering groups on the resonance structures of biphenyl derivatives involving coplanarity, see (a) O'Shaughnessy and Rodebush, THIS JOURNAL, **62**, 2906 (1940); (b) Sherwood and Calvin, *ibid.*, **64**, 1350 (1942); (c) Friedel, Orchin and Reggel, *ibid.*, **70**, 199 (1948). In the case of 2,2′-dimethylbiphenyl,[4a] the resonance band is practically eliminated. For that reason 2,2′-dimethyl-4-acetylaminobiphenyl may prove to be an interesting compound biologically. Further work along this line is contemplated.

Experimental Part[5]

2′-Methyl-4-acetylaminobiphenyl.—The reaction of diazotized *p*-nitroaniline with toluene in the presence of alkali, according to the procedure of France, Heilbron and Hey,[6] afforded a 12% yield of crude 4-nitro-2′-methylbiphenyl. It was purified by distillation under diminished pressure, followed by recrystallization from ethyl alcohol. Reduction of the nitro compound with stannous chloride gave the amine, b. p. 194–195° at 24 mm.; yield 60%. The base formed a hydrochloride which was recrystallized from water; m. p. 285° dec.

Anal. Calcd. for $C_{13}H_{14}NCl$: Cl, 16.1. Found: Cl, 15.9, 16.1.

The pure amine (b. p. 190° at 23 mm.) was liberated from the salt by the regular procedure.

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.2; H, 7.2. Found: C, 85.3; H, 7.1.

The acetyl derivative (yield 80%) was crystallized from aqueous alcohol; m. p. 143–144° (reported[6] 146–147°). Further crystallization did not raise the m. p.

2-Methyl-4-acetylaminobiphenyl.—The reaction of diazotized 2-amino-5-nitrotoluene with benzene in the presence of alkali[7] gave a 15% yield of 2-methyl-4-nitrobiphenyl; m. p. 55–56° (reported[7] 56–57°). The amine (yield 80%), produced from the nitro compound by stannous chloride reduction, gave a hydrochloride which was crystallized from water; m. p. 270° dec.

Anal. Calcd. for $C_{13}H_{14}NCl$: Cl, 16.1. Found: Cl, 15.5, 15.6.

The pure amine (b. p. 178° at 12 mm.) was liberated from the salt.

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.2; H, 7.2. Found: C, 85.7; H, 7.2.

The acetyl derivative was obtained in 90% yield. It was crystallized from dilute alcohol; m. p. 125°.

Anal. Calcd. for $C_{15}H_{15}ON$: C, 80.0; H, 6.7. Found: C, 80.6; H, 6.7.

Acknowledgment.—The authors express their appreciation to the Canadian Cancer Society for financial help in connection with this work. We are also grateful to Drs. J. A. Miller and E. C. Miller of the McArdle Memorial Laboratory. Madison, Wisconsin, for determining the carcinogenic properties of 2- and 2′-methyl-4-acetylaminobiphenyl. Their results will be published elsewhere.

(5) Melting points are uncorrected.

(6) France, Heilbron and Hey, *J. Chem. Soc.*, 1283 (1939).

(7) Bamberger, *Ber.*, **28**, 403 (1895).

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N-Substituted-2-iminazolidones

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It is the purpose of this paper to describe a new and more convenient method for the preparation of 1,3-dialkyl-2-iminazolidones. These substances are also known as 1,3-dialkyl-2-ketotetrahydroiminazoles, and as N,N′-dialkylethylene ureas.

In general the method consists of heating a slight molar excess of urea with a 1,2-diamine having at least one replaceable hydrogen on each nitrogen, without solvent to a temperature at