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.

THE RESEARCH LABORATORIES
DOMINION RUBBER COMPANY, LIMITED
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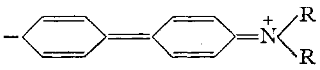
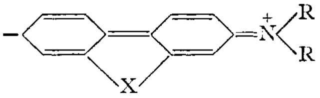
Synthesis of Some Substituted Biphenyls

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.

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.

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(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.

(5) Melting points are uncorrected.

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

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

DEPARTMENT OF CHEMISTRY
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N-Substituted-2-iminazolidones

BY ARTHUR E. MARTELL AND ALBERT E. FROST

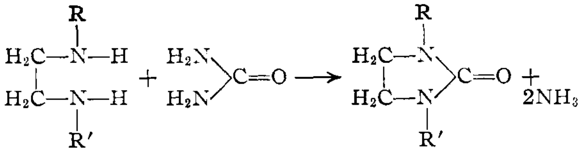
It is the purpose of this paper to describe a new and more convenient method for the preparation of 1,3-dialkyl-2-iminazolidones. These substances are also known as 1,3-dialkyl-2-ketotetrahydroiminazoles, and as N,N′-dialkylethylene ureas.

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

Table I

Compound	B. p., °C.	Mm.	M. p., °C.	% yield	N Analyses, % Calcd.	Found
1,3-Dicyclohexyl-2-iminazolidone	165–166	1	92–94	80	11.19	10.91
1,3-Dibutyl-2-iminazolidone	137–140	3	. . .	81	14.14	14.36
1,3-Dioctyl-2-iminazolidone	195–200	3	5–6	80	9.02	9.30
1,3-Didodecyl-2-iminazolidone	245–252	2	48–49	76	6.63	6.36
1,3-Dibenzyl-2-iminazolidone	183–186	1	93–94	80	10.53	10.43

which ammonia is rapidly evolved, according to the equation



Although the reaction of urea with amines to produce substituted ureas is well known, the only reaction between diamines and urea previously described was reported by Clarke[1] as a method of preparing polymers of interest as synthetic fibers.

A previous synthesis of 2-imidazolidones was described by Boon,[2] who treated the diamines with phosgene. He reported approximately equal yields of the cyclic urea and of the carbonyl chloride, so that, at best, yields of less than 50% were obtained. In the present investigation, the yield is in general about 80% of the theoretical amount.

Data for the five substances now prepared are shown in Table I. Of these the only one previously reported is the dibenzyl derivative, prepared by Lob[3] from phosgene. In this case our data agree very closely to the physical constants which he reported.

The general procedure for the preparation of these substances is given herewith.

One-tenth mole of the diamine is heated in a glass vessel with 0.125 mole of urea with a free flame until vigorous evolution of ammonia takes place. The heating is continued until this slows down to a negligible rate (ten to fifteen minutes). The product is then vacuum distilled and, if crystalline, is recrystallized from absolute alcohol.

Acknowledgment.—The authors express their appreciation to the F. C. Bersworth Laboratories of Framingham, Massachusetts, for financial support for this research.

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(1) Clarke, British Patent 530,267, Dec. 9, 1940.

(2) Boon, *J. Chem. Soc.*, 307 (1947).

(3) Lob, *Rec. trav. chim.*, **55**, 866 (1936).

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The Reduction of Sulfonyl Chlorides to Mercaptans with Lithium Aluminum Hydride

By C. S. Marvel and P. D. Caesar

The reduction of aliphatic and aromatic sulfonyl chlorides to mercaptans with lithium aluminum hydride has been realized. There is no previous record of the use of this reagent for a reduction of this type.

The reaction may proceed according to the following stoichiometrical equation, although in the preliminary experiments shown here a two- to threefold excess of lithium aluminum hydride was used to assure a positive reaction. Ethyl ether was employed as the solvent.

$$2RSO_2Cl + 3LiAlH_4 \longrightarrow LiAlCl_2(SR)_2 + 6H_2 + 2LiAlO_2$$

Initial attempts to reduce arylsulfonamides and diarylsulfones, using ethyl ether as a solvent, proved fruitless. It seems probable that use of a higher boiling solvent such as tetrahydrofuran may improve this reaction.

***p*-Thiocresol and *n*-Butyl Mercaptan.**—These compounds were prepared under the general conditions for lithium aluminum hydride reduction described by Nystrom and Brown.[1] The reductions were carried out at 35° for one and one-half hours.

From 5 g. (0.026 mole) of *p*-toluenesulfonyl chloride and 4 g. (0.1 mole) of lithium aluminum hydride there was obtained 1.6 g. (50% based on *p*-toluenesulfonyl chloride) of *p*-thiocresol, m. p. 42.5–43.5°, alone and when mixed with an authentic sample of *p*-thiocresol.

From 4 g. (0.025 mole) of 1-butanesulfonyl chloride and 3 g. (0.08 mole) of lithium aluminum hydride there was isolated 2.2 g. (45% based on 1-butanesulfonyl chloride) of mercury *n*-butyl mercaptide; m. p. 84–85°, reported m. p. 85–86°.[2] This was obtained by distilling the ether, mercaptan and some of the water from the reaction mixture, after decomposition of the lithium aluminum complex, into a suspension of mercuric oxide in alcohol.

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(1) R. F. Nystrom and W. G. Brown, This Journal, **69**, 1197 (1947).

(2) E. Wertheim, *ibid.*, **51**, 3661 (1929).

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Proton Exchange between Ammonia and Ammonium Ion in Liquid Ammonia[1]

By C. J. Nyman, Si-Chang Fung and H. W. Dodgen

In the explanation of data observed on the exchange of protons between ND_3 and $B_2H_6 \cdot 2NH_3$, it was postulated by Burg[2] that the exchange of protons between ammonia molecules and ammonium ions was rapid. Several properties of the ammonium ion in liquid ammonia caused the authors to consider the possibility of this reaction being slow. The fact that the conductance[3] of the ammonium ion in this solvent is similar to that of lithium indicates that the proton is not nearly so mobile as in aqueous solution. Like-

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(1) This project supported in part by the State College of Washington Committee on Research.

(2) A. B. Burg, This Journal, **69**, 747 (1947).

(3) E. C. Franklin and C. A. Kraus, *ibid.*, **27**, 191 (1905); *Am. Chem. J.*, **23**, 277 (1900).