cularly, substituents on the nitrogen. Of the compounds synthesized and tested, only one had any activity [10-(4'-γ-diethylaminopropylamino)-phenylphenothiazine], and this was of a doubtful nature.

AMES, IOWA RECEIVED FEBRUARY 1, 1944

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE ETHYL CORPORATION]

Zinc Alkyls from Secondary Alkyl Halides

BY HAROLD SOROOS AND MORLEY MORGANA

Of zinc alkyls derived from secondary alkyl halides, the literature reports the preparation of only one, diisopropylzinc.[1] In the reported preparations of this compound, isopropyl iodide was added all at once to zinc or zinc–copper couple, and heat was applied. The yields were low, and mainly gaseous products were obtained. Recent attempts to repeat and confirm this work, by methods known to be successful for the preparation of zinc alkyls from primary halides, were unsuccessful.[2]

Recently, in studies conducted in this Laboratory, it was found that both diisopropylzinc[3] and di-*s*-butylzinc could be obtained in essentially as good yields as the zinc alkyls derived from primary alkyl halides, by a modification of Noller's procedure.[2] The method consists simply of adding a mixture of the secondary alkyl bromide and iodide slowly with stirring under controlled temperature conditions to an excess of zinc–copper couple, followed by distillation of the reaction mixture at as low a temperature and pressure as possible.

In contrast to the preparation of zinc alkyls from primary alkyl halides, the reaction with the secondary halides starts easily and proceeds smoothly if properly controlled. Only a trace of gas is formed, and the reaction mixture consists of a clear oily liquid[4] and the excess couple. Distillation of the reaction mixtures under reduced pressure gives the zinc alkyls in good yield.

Both compounds are spontaneously inflammable and somewhat less stable than the primary analogs, decomposing slowly in diffused daylight with the deposition of metallic zinc.

Experimental

Zinc–Copper Couple.—A wrought-iron alloy pot, flushed with nitrogen, was charged with 3319 g. (51 g. atoms) of zinc and 369 g. (3.55 g. atoms Cu, 2.11 g. atoms Zn) of Tobin bronze brazing rod, and loosely covered. The mass was heated to 600° with an oxy-acetylene torch and shaken vigorously for five minutes, maintaining the temperature at 600°. The melt was discharged into a one-inch iron pipe mold, cooled in air, and finally quenched in water. The rod was machined into turnings without the use of cutting oil. *Anal.*[5] Zn, 94.5; Cu, 5.86.

Diisopropylzinc.—To a 500-ml., 3-neck flask, equipped with a reflux condenser, an efficient stirrer, and a Hershberg dropping funnel, was added 104.5 g. (98.9 g. Zn, 1.5 g. atom) of zinc–copper couple turnings. The system was evacuated to 1 mm. while stirring and warming gently with a free flame, and then flushed several times with dry nitrogen. A trap cooled in dry-ice was connected to the outlet of the reflux condenser and a mixture of 61.5 g. (0.5 mole) of isopropyl bromide and 85.0 g. (0.5 mole) of isopropyl iodide was added to the dropping funnel. A water-bath at 50° was raised around the flask and the stirrer started. About 2 ml. of the alkyl halide mixture was added rapidly. Within two minutes, reaction had started as shown by a trace of white fumes, a darkening of the couple, and the oily appearance of the liquid on the walls of the flask. The 50° bath was replaced by a water-bath at 20°, and dropwise addition of the halides was started. The drop rate was adjusted so that addition was complete in five and one-half hours. At this rate not more than 0.5 ml. of liquid collected in the trap; a faster rate caused undue gas formation as shown by liquid in the dry-ice trap. After addition, stirring was continued for 30 minutes. The reaction mixture consisted of a clear, colorless, liquid and the almost black excess zinc–copper couple.

For distillation of the diisopropylzinc, one neck of the three-neck flask was stoppered, the other was equipped with a simple distillation head and thermometer, and the rubber sleeve of the stirrer was wired to the shaft. Three traps were placed in series, the first two being equipped with Vaseline-lubricated stopcocks, all being large enough so that freezing of the distillate would not cause plugging. With the first two traps at room temperature and the third in liquid nitrogen, the system was slowly evacuated to 1 mm. Low-boiling material was collected in the cold trap until ebullition ceased in the flask. The first two traps were then cooled in a dry-ice mixture at −65° and an oil-bath, placed around the flask, was heated rapidly to about 100°. The oil-bath was maintained at 90–140° for forty-five minutes until distillation was almost complete, at the end of which time it was raised to 200° to remove the last trace of product. It was necessary to maintain the oil pump on the system throughout, owing to some pyrolytic decomposition. Without the liquid nitrogen trap, an oil pump would not maintain a pressure of 1 mm. and the yield was lowered. The residue was a

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[1] Bohm (*J. Russ. Phys.-Chem. Soc.*, **31**, 46 (1899); *Chem. Zentr.*, **70**, 1, 1067 (1899)) reports obtaining diisopropylzinc in 25% yield from isopropyl iodide and zinc; Gladstone and Tribe (*J. Chem. Soc.*, **26**, 961 (1873)) obtained the compound in 13% yield from isopropyl iodide and zinc-copper couple; Ragosin (*J. Russ. Phys.-Chem. Soc.*, **24**, 549 (1892); *Ber.*, **26** (Ref.), 380 (1893)) obtained the compound by interaction of isopropyl iodide in ether with zinc and a small amount of sodium–zinc alloy.

[2] Noller, THIS JOURNAL, **51**, 594 (1929).

[3] The preparation of this compound was investigated in a study sponsored and supported by the National Advisory Committee for Aeronautics.

[4] The oily liquid is apparently the RZnX compound, which on subsequent heating disproportionates to R_2Zn and ZnX_2. It was necessary to heat the reaction mixtures at 1 mm. to considerably higher temperatures than required for distillation of the zinc alkyls alone before the latter distilled from the reaction mixtures. Also, the liquid was observed to be considerably more stable toward oxidation on exposure to air than the zinc alkyls.

[5] Spectrographic analysis of the zinc used in this preparation, kindly obtained for us by Dr. F. L. Howard of the National Bureau of Standards, showed the metal to contain trace amounts (less than 0.01%) of Au, Ba, Cd, Cu, Fe, Mg, Mn, Ni, Pb, and Si.

hard, gray cake. The yield of crude product was 64.2 g. (0.42 mole), or 85% based on the isopropyl halides.

The boiling points of a middle fraction of redistilled material at various pressures were obtained by distillation of a sample through a short Stedman column. The relation between temperature and pressure (in mm.) is given to within ±1.0 mm., which is within the accuracy of the measurements, by the equation $\log P = 7.987 - 1858/(t + 230)$.

Di-*s*-butylzinc.—By a procedure similar to that described above, di-*s*-butylzinc was prepared from 68.5 g. (0.5 mole) of *s*-butyl bromide, 92.0 g. (0.5 mole) of *s*-butyl iodide, and 140 g. (132 g. Zn, 2.0 g. atom) of zinc–copper couple. The starting temperature was 60°, and the reaction temperature 25°. The yield of crude product was 64.5 g. (0.36 mole), or 72%. On redistillation, the material distilled at 56° at 4 mm. *Anal.* Calcd. for $(C_4H_9)_2Zn$: Zn, 36.4. Found: Zn, 36.1.

Summary

Diisopropylzinc and di-*s*-butylzinc have been prepared from zinc–copper couple and secondary alkyl halides in good yield by a modification of the procedure usually used for preparation of the primary analogs.

DETROIT, MICHIGAN RECEIVED FEBRUARY 19, 1944

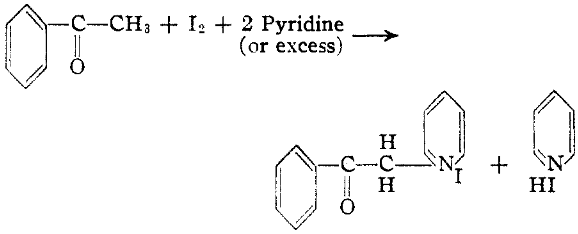
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

The Reaction of Iodine with Some Ketones in the Presence of Pyridine

BY L. CARROLL KING

In an investigation of the reactions of compounds containing reactive hydrogen atoms with iodine in the presence of a base it was observed that acetophenone, 1-naphthyl methyl ketone, 1-anthryl methyl ketone and propiophenone react directly with one mole of iodine and two moles (or excess) of pyridine to give excellent yields of 1-phenacylpyridinium iodide, 1-(1-naphthoylmethyl)-pyridinium iodide, 1-(1-anthroylmethyl)-pyridinium iodide and 1-(α-methylphenacyl)-pyridinium iodide, respectively, and, in each case, pyridine hydroiodide.

If acetophenone is used as an example the reaction may be formulated as follows



1-Phenacylpyridinium iodide has been reported.[1] It was further characterized by conversion to the known 1-phenacylpyridinium perchlorate.[2,3] 1-(α-Methylphenacyl)-pyridinium iodide was also characterized by conversion to the known 1-(α-methylphenacyl)-pyridinium perchlorate.[4]

It has been demonstrated previously that 1-phenacylpyridinium bromide[2,5] and 1-(α-methylphenacyl)-pyridinium bromide[3] can be cleaved by means of aqueous alkali to give benzoic acid. The 1-phenacylpyridinium iodide and the 1-(α-methylphenacyl)-pyridinium iodide described in this article when treated with aqueous sodium hydroxide also gave excellent yields of this substance.

The characterization of 1-(1-naphthoylmethyl)-pyridinium iodide and of 1-(1-anthroylmethyl)-pyridinium iodide depends on the mode of formation, the analysis, and on the fact that after treatment with aqueous alkali the respective 1-naphthoic and 1-anthroic acids were isolated in good yield from the cleavage products.[6]

In three of the four reactions carried out 74–92% yields (based on the ketones) of the expected substituted β-ketoalkylpyridinium iodides were obtained and in every case 87–95% of the expected yields of pyridine hydroiodide were observed. 1-(α-Methylphenacyl)-pyridinium iodide was obtained in only 41% yield. The low yield in this case was due to the solubility characteristics of this compound. When the 1-(α-methylphenacyl)-pyridinium compound was isolated as the perchlorate a 64% yield was obtained.

When excess pyridine was used as the solvent, the formation of the substituted β-ketoalkylpyridinium iodides, by means of the above reaction, proceeded smoothly with twenty to thirty minutes heating on the steam-bath and the reaction was complete after standing overnight. In most cases a solid began to separate soon after the heating was started. This substance consisted of pyridine hydroiodide and usually contained some of the substituted β-ketoalkylpyridinium iodide. In the four instances discussed in this paper, it was not found advantageous to use solvents other than an excess of the base when effecting this synthesis.

Preliminary experiments indicate that the above reaction is of value for the synthesis of derivatives of various nitrogeneous bases, particularly in those cases where an intermediate halogen compound is difficult to obtain. These experi-

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(1) F. Krohnke, *Ber.*, **66B**, 1386 (1933).

(2) E. Schmidt and H. VanArk, *Archiv. Pharm.*, **238**, 331 (1900).

(3) Krohnke, *Ber.*, **66**, 604 (1933).

(4) F. Krohnke, *ibid.*, **69**, 921 (1936).

(5) Babcock, Nakamura and Fuson, THIS JOURNAL, **54**, 4407 (1932); Babcock and Fuson, *ibid.*, **55**, 2949 (1933); E. Bamberger, *Ber.*, **20**, 3344 (1887).

(6) Krohnke[3] prepared 1-(1-naphthoylmethyl)-pyridinium bromide and showed that after treatment with aqueous alkali 1-naphthoic acid could be obtained from the cleavage products.