$$2R_3SnN(C_2H_5)_2 + CO_2 + H_2O \longrightarrow (R_3Sn)_2CO_3 + 2(C_2H_5)_2NH \quad (3)$$

$$(R = C_2H_5,\ n\text{-}C_3H_7,\ \text{or}\ n\text{-}C_4H_9)$$

Infrared absorptions characteristic to the diethylaminotin grouping, Sn—N$(C_2H_5)_2$, were observed at 1290 (m), 1173 (vs), 1010 (s), 880 (s), and 780 (s) cm.$^{-1}$, all being common to the three trialkyl(diethylamino)tins herein described. These bands completely disappeared on exposure of the sample to air for several minutes on a sodium chloride plate, when characteristic bands of organotin carbonate appeared at 1560–1520 (vs), 1370 (vs), 1070 (m), and 840 (m) cm.$^{-1}$ instead.

These results show that the organotin–nitrogen bonding is rather stable to heating, as indicated by no change upon distillation, but is highly reactive toward proton-containing reagents.

Experimental

Analyses.—A microelementary analysis for carbon and hydrogen was given up because of the too high sensitivity of the sample to air (equation 3). As soon as a sealed ampoule was cut, diethylamine which was recognized by the strong odor vaporized.

Nitrogen was analyzed by titration according to equation 2: an exactly weighed sealed ampoule containing about 2.0 g. of the sample was crushed with a glass rod in 30 ml. of standardized 0.5 *N* hydrochloric acid, and the excess acid was back-titrated with 0.5 *N* sodium carbonate with methyl orange as an indicator.

Tin analyses were carried out according to Farnsworth and Pekola.[9] In this case the vaporization of diethylamine has no effect on the analytical values of tin.

Triethyl(diethylamino)tin.—A tetrahydrofuran solution of diethylaminomagnesium bromide prepared from 2.9 g. (0.12 g.-atom) of magnesium, 10.9 g. (0.1 mole) of ethyl bromide, and 7.3 g. (0.1 mole) of diethylamine in 50 ml. of tetrahydrofuran was added dropwise to a solution of 14.5 g. (0.06 mole) of triethyltin chloride[10] (b.p. 86–88°/9 mm.) dissolved in 50 ml. of tetrahydrofuran. An exothermic reaction was observed during this procedure. After refluxing for 4 hr. the solvent was distilled and the reaction product was fractionated under reduced pressure. A fraction boiling at 72–88°/11 mm. was collected; yield, 10.5 g. (63%). Redistillation gave 9.5 g. of an analytically pure fraction boiling at 114–117°/23 mm. All procedures were carried out in a nitrogen atmosphere. This sample gave a negative Beilstein test for halogen. The product was stored in sealed ampoules under nitrogen.

Anal. Calcd. for $C_{10}H_{25}NSn$: Sn, 42.69; N, 5.04. Found: Sn, 42.64, 42.98, 42.45; N, 4.92.

Tri-*n*-propyl(diethylamino)tin and tri-*n*-butyl(diethylamino)tin were also obtained in about 70% yields by an analogous way from tri-*n*-propyltin chloride[10] (b.p. 122–123°/10 mm.) and tri-*n*-butyltin chloride[10] (b.p. 130–132°/4 mm.), respectively.

Tri-*n*-propyl(diethylamino)tin had b.p. 118–120°/13 mm.

Anal. Calcd. for $C_{13}H_{31}NSn$: Sn, 36.97; N, 4.36. Found: Sn, 37.41; N, 3.95.

Tri-*n*-butyl(diethylamino)tin distilled at 124–134°/8 mm.

Anal. Calcd. for $C_{16}H_{37}NSn$: Sn, 32.77; N, 3.87. Found: Sn, 32.62; N, 3.40.

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[9] M. Farnsworth and J. Pekola, *Anal. Chem.*, **31**, 410 (1959).

[10] K. A. Kocheskov, *Ber.*, **66**, 1661 (1930).

Attempted Hydrogenolysis of Amines with Triphenyltin Hydride[1]

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Received May 31, 1962

It has been reported that allylamine[4] (I) and benzylamine[5] (II), *n*-butylamine and *n*-hexylamine[6] are hydrogenolyzed to the parent hydrocarbons, propylene, toluene, butane and hexane, respectively, using triphenyltin hydride (III). Ammonia was claimed as one product of the reactions and hexaphenylditin (IV) was also isolated.

In attempting to repeat these results it was found that I or II with III does give IV and a steady evolution of gas. However, no propylene (using vapor phase chromatography), toluene (using vapor phase chromatography and infrared analysis), or ammonia (Nessler's reagent) could be detected. In the reaction of II with III, a considerable amount of benzene was formed. These results are in direct contrast to the successful reports of van der Kerk and Noltes, who, however, failed to identify positively the expected propylene and ammonia.[7] These results are also in sharp contrast to those of Kupchik and Connolly. The latter reported that a superimposable infrared spectrum of toluene was obtained from the first drops of distillate of the reaction mixture, which is difficult to understand. We were unable to find any trace of toluene. Benzene invariably accompanies the reaction of benzylamine with triphenyltin hydride and therefore should have been present in the first drops of distillate. Again, no positive evidence for ammonia was provided.

In the course of our attempts to hydrogenolyze carbon–nitrogen bonds, we also examined *p*-toluidine, *N*-methylbenzylamine, and *N*,*N*-dimethylbenzylamine. In these experiments IV and a gas were always obtained, but no hydrocarbon nor ammonia (see Experimental). In the case of *p*-toluidine and III, which was carried out in a sealed tube, the gas was not condensable at −80°. Qualitatively, the rate of formation of IV

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[1] This work was supported by O.O.R. Project No. 2440, Department of the Army Project No. DA-30-069-ORD-2851 and Grant DA-ORD-31-124-61-G39, U. S. Army Research Office (Durham).

[2] Taken from the dissertation submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[3] To whom inquiries should be sent.

[4] J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Middlesex, England, 1958, p. 115.

[5] E. J. Kupchik and R. E. Connolly, *J. Org. Chem.*, **26**, 4747 (1961).

[6] J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind.* (London), 294 (1959).

[7] In a private communication from G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, the earlier hydrogenolyses are refuted.

decreased in the order of greater substitution of the amine group—*i.e.*, 3° < 2° < 1°. These results suggest that III is being catalytically decomposed to IV and hydrogen.[8,9]

$$Ph_3SnH \xrightarrow{Ar—NH_2} Ph_3SnSnPh_3 + H_2$$

Experimental

Allylamine and III.—To a round bottom flask equipped with a stirrer, reflux condenser, gas inlet tube, and gas exit tube leading from the top of the condenser to a trap containing 95% ethanol kept at −78° were added 32.2 g. (0.092 mole) of triphenyltin hydride and 2.6 g. (0.046 mole) of allylamine. Evolution of a gas was observed on mixing. The reaction mixture was stirred under a nitrogen atmosphere til solidification was complete. The contents of the trap gave a negative test with Nessler's reagent for ammonia, no characteristic brown-red color being observed. The solid in the flask was recrystallized from benzene, m.p. 230–232°. It did not depress the melting point on admixture with an authentic sample of IV.

In a second experiment, using the same procedure as described above, 20 g. (0.057 mole) of III and 1.62 g. (0.029 mole) of I were used. Any possible propylene being evolved was led from the top of the condenser into a trap containing 1-hexene kept at −78°, but no propylene was detected upon running the trap contents into a vapor phase chromatograph.

Benzylamine and III.—The procedure of Kupchik and Connolly was followed. The first few drops of distillate collected showed bands in the infrared (cm.$^{-1}$) at 3077, 3021, 1961, 1815, 1754, 1715, 1529, 1479, 1393, 1247, 1175, 1036, 850, 680, which excludes toluene[10] and confirms benzene. Further distillation and subsequent infrared analyses still showed no evidence for toluene.

In a second experiment, beginning with 22.5 g. (0.064 mole) of triphenyltin hydride and 3.6 ml. (0.032 mole) of II in which ammonia was particularly sought, a water-trap for the evolved gases contained no ammonia, (Nessler's reagent).

***p*-Toluidine and III.**—Beginning with 2.15 g. (0.020 mole) of *p*-toluidine and 8.0 g. (0.023 mole) of III, stirring at 150° for 1 hr. and at 190° for another 2 hr., throughout under a nitrogen atmosphere, evolution of gas was observed and solidification proceeded during the course of the reaction, but no positive test for ammonia was observed throughout this time.

No toluene was determined in the distillate, only benzene. Similar results were obtained in a sealed tube experiment at 80–150°.

***N*-Methylbenzylamine and III.**—In two separate experiments, with 7.00 g. of III and 1.21 g. of *N*-methylbenzylamine each, no methylamine could be determined by means of the Rimini test. It was noted that hydrogen was evolved only at a higher temperature (~100°) for the secondary amine.

***N*,*N*-Dimethylbenzylamine and III.**—With this amine, using the procedure outlined in detail earlier, no test for secondary amine could be determined from 1.35 g. of *N*,*N*-dimethylbenzylamine and 7.0 g. of III, by means of the Simon and the nickel dithiocarbonate tests. Again, it was noted that with the tertiary amine, decomposition of III took place at a still higher temperature (~130–150°).

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(8) In ref. 7 van der Kerk, Noltes, and Luijten give evidence for the stoichiometry.

(9) We wish to express our gratitude to Drs. van der Kerk, Noltes, and Luijten for making their experimental work known to us prior to publication.

(10) Comparisons were made with spectra as follows: American Petroleum Institute Research Project No. 44, Serial No. 308 (benzene) and No. 498 (toluene).

The Photochemical Preparation of Dimethyl-*N*-(2-cyano-2-propyl)ketenimine from 2,2′-Azobisisobutyronitrile[1]

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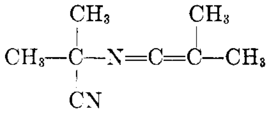
Received June 25, 1962

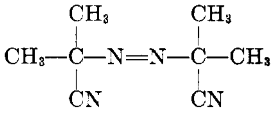
Lately it has been necessary to have a preparative method[3–6] for dimethyl-*N*-(2-cyano-2-propyl)ketenimine (I). Previously we have employed[5,7]



$$CH_3—\underset{CN}{\overset{CH_3}{C}}—N=C=\overset{CH_3}{C}—CH_3$$

I

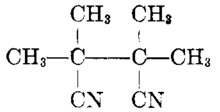
a procedure where 2,2′-azobisisobutyronitrile (II)



$$CH_3—\underset{CN}{\overset{CH_3}{C}}—N=N—\underset{CN}{\overset{CH_3}{C}}—CH_3$$

II

was thermally decomposed in an inert solvent, cyclohexane, at *ca.* 80° until the concentration of I had reached its maximum value,[4,8–10] whereupon the reaction mixture was quenched by cooling to *ca.* 10° and I isolated after filtering off the precipitate, which was largely all the tetramethylsuccinonitrile (III) formed and the undecomposed II.



$$CH_3—\underset{CN}{\overset{CH_3}{C}}——\underset{CN}{\overset{CH_3}{C}}—CH_3$$

III

The chief disadvantages of this method are that it gives low yields (*ca.* 15%),[5,7] requires care to keep the reaction under control, and demands a knowledge of the approximate time when the maximum concentration of I is reached.

(1) Supported by grants from Esso Research and Engineering Company and the United States Public Health Service, Division of General Medical Sciences.

(2) In partial fulfilment of the requirements for Graduation with Distinction.

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