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]

$$\mathrm{Ph_3SnH} \xrightarrow{\mathrm{Ar{-}NH_2}} \mathrm{Ph_3SnSnPh_3} + \mathrm{H_2}$$

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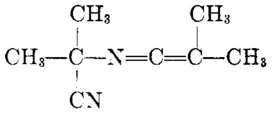
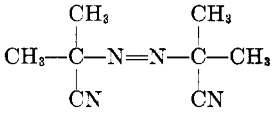
Lately it has been necessary to have a preparative method[3–6] for dimethyl-*N*-(2-cyano-2-propyl)-ketenimine (I). Previously we have employed[5,7]



$$\mathrm{CH_3{-}\underset{\displaystyle CN}{\overset{\displaystyle CH_3}{C}}{-}N{=}C{=}\overset{\displaystyle CH_3}{C}{-}CH_3}$$

I

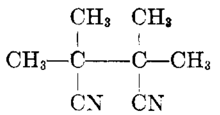
a procedure where 2,2′-azobisisobutyronitrile (II)



$$\mathrm{CH_3{-}\underset{\displaystyle CN}{\overset{\displaystyle CH_3}{C}}{-}N{=}N{-}\underset{\displaystyle CN}{\overset{\displaystyle CH_3}{C}}{-}CH_3}$$

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.



$$\mathrm{CH_3{-}\underset{\displaystyle CN}{\overset{\displaystyle CH_3}{C}}{-\!-}\underset{\displaystyle CN}{\overset{\displaystyle CH_3}{C}}{-}CH_3}$$

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.

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(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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The photolysis of II in inert solvents at room temperature using 365μ also produces I,[4–6] the molar conversion of II into I for a given solvent being essentially the same as for the thermal decomposition at *ca.* 80°. Because I is effectively stable under the conditions of the photodecomposition but is destroyed readily at *ca.* 80° in solution, it was expected that the photodecomposition of II would afford a preparative route for I giving higher yields than the thermal decomposition method with a less complicated procedure. The results obtained supported expectation.

The molar conversion of II into I during the photodecomposition of II is solvent dependent.[6] Benzene was picked as the reaction solvent as a compromise between the aim to obtain the maximum conversion[5,6] of II into I and the wish to carry out the photodecomposition in a convenient, small volume of solvent with moderate volatility.

Experimental

A solution of 164 g. (1.00 mole) of Porophor N (Recrystallized) 2,2′-azobisisobutyronitrile (II) in 0.80 l. of dry reagent grade thiophene-free benzene at *ca.* 45° in 1-l. round-bottom Pyrex flask, through which dry nitrogen (Matheson, Prepurified) bubbled, was placed in a 4-l. Pyrex beaker containing running tap water at 16 ± 2°. After a preliminary purge period of 30 min., during which some II precipitated, the reaction mixture was irradiated for 48 hr. with occasional stirring, by which time all the precipitate had dissolved and the nitrogen evolution had essentially stopped. Irradiation was carried out with the flask and water-jacket inside an aluminum enclosure using two Mazda type ME/D 250 watt extra-high pressure mercury vapor projection lamps of the rectangular metal box variety set *ca.* 20 cm. apart and aimed horizontally at the center of the solution *ca.* 15 cm. away. Each lamp was run with its supplied 6-mm.-thick glass window in place.[11] Following the irradiation, the reaction mixture was concentrated under reduced pressure, filtering off precipitate at intervals, pot temperature 15 ± 5°, the pressure being taken down to 0.5 mm. The precipitate, a total of 55 g., was impure tetramethylsuccinonitrile,[12] III, repeated crystallization from ethanol yielding a pure specimen, m.p. (uncor.) 169–170°, lit.-*e.g.*, 170°,[3] 168.5–169°,[5] and 167–168°.[8] Next the brown filtered concentrate was distilled at 0.2–0.3-mm. pressure, pot temperature 30–45°, yielding 48 g. of colorless liquid I, $n^{30}\text{D}$ 1.444_6, of 96 ± 1 mole % purity estimated from the refractive index and those of mixtures of I and III with known composition (yield, 35%). Two further distillations of this material at 0.2–0.3-mm. pressure, pot temperature 28–32°, collecting the middle 80% fraction gave a product comparable to that prepared before.[3,5] N.m.r. analysis[3] showed it to contain III as the only impurity and the purity to be at least 99.0 mole %, $n^{25}\text{D}$ and $n^{30}\text{D}$, respectively, 1.447_0 and 1.444_9 (lit., $n^{20.0}\text{D}$ 1.449_1,[3] $n^{25}\text{D}$ 1.4470–1.4473,[7] $n^{30.0}\text{D}$ 1.444_9[5]).

An attempt to repeat this photopreparation with similar experimental conditions, but using 0.80-l. of dry reagent grade cyclohexane in place of the benzene and employing vigorous mechanical stirring to keep the crystals of II in suspension, was unsuccessful. After irradiating for 48 hr. and concentrating the reaction mixture as before, the residual amount of I was only a trace. This is not surprising for both II and III are essentially insoluble in cyclohexane at 16 ± 2° and, at a given temperature, II in the solid state is considerably more thermally stable than when dissolved in an inert solvent.[6]

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[11] Examination using a Cary Model 11 spectrophotometer showed this window to be optically equivalent to *ca.* 12 mm. of Pyrex glass. Allowing for the water-jacket and reaction flask, the reaction mixture was estimated to be protected by the equivalent of *ca.* 16 mm. of Pyrex. This provides ample protection for the I formed.[8]

[12] Aside from I, this is the chief organic product of the photodecomposition of II in benzene solution at 25° using 365 μ radiation, and the photodecomposition of I under similar conditions yields II as the major product eg (P. E. Miller, N. Muller, P. Smith, and W. C. Tosch, unpublished analyses by the n.m.r. method[8]).

The Preparation of *s*-Triazine Derivatives Containing the N—O Bond. II.[1] Hydroxylamino Derivatives of *s*-Triazine

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A literature search revealed that hydroxylamino-*s*-triazines were only represented by two members: 2,4 - bis(*p* - chlorophenyl) - 6 - hydroxylamino-*s*-triazine[2] and 2,4-bis(trichloromethyl)-6-hydroxylamino-*s*-triazine.[3] The preparation of the latter compound involved the reaction of a chlorotriazine, 2-chloro-4,6-bis(trichloromethyl)-*s*-triazine, and hydroxylamine. This method was found to be quite useful and the compounds shown in Table I were prepared in this fashion. In those reactions where the replaceable chlorine was substituted by the hydroxylamino group, a large excess of hydroxylamine was required to obtain yields greater than 50%. The preparation of the various alkoxyamino derivatives shown in Table I followed well established procedures[4] for the preparation of aminotriazines from the corresponding halotriazines.

As a class, the unsubstituted and N-substituted hydroxylaminotriazines gave purple and sometimes dark green, blue, or black colors with ferric chloride; O-substituted derivatives did not. All of the compounds considered are white to pale lavender solids which usually melt with decomposition. The unsubstituted hydroxylaminotriazines generally showed some solubility in dilute warm acid or base; N- or O-substitution increased the alkali solubility considerably. None of the compounds tested reduced Fehling's or Tollens' reagents.

Experimental[5]

Materials and Methods.—With the exception of cyanuric chloride, which is available from the American Cyanamid

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[1] Part I; J. T. Shaw, *J. Org. Chem.*, in press.

[2] C. Grundmann and H. Schroeder, *Chem. Ber.*, **87**, 747 (1954).

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[5] All melting points are uncorrected. Microanalyses by Mr. John Kobliska and his staff.