The Synthesis and Thermal and Photolytic Decomposition of 1,2-Dihydro-2,4,6-triphenyl-s-triazine[1a]

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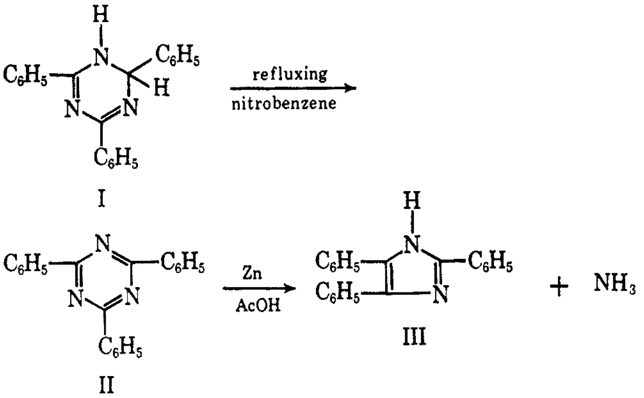
The synthesis of 1,2-dihydro-2,4,6-triphenyl-*s*-triazine (I) by the reduction of 2,4,6-triphenyl-*s*-triazine (II) with lithium aluminum hydride is described. The thermal and photolytic decomposition of pure I was found to give ammonia, toluene, benzonitrile, 2,4,5-triphenylimidazole (III), and II. A mechanistic interpretation of the decomposition is presented.

The synthesis of 1,2-dihydro-2,4,6-triphenyl-*s*-triazine (I) was first reported by Swamer, Reynolds, and Hauser[2] as a product formed in low yield from the treatment of benzonitrile with sodium hydride. In addition, these authors found that upon refluxing I in nitrobenzene or xylene, an almost quantitative yield of 2,4,6-triphenyl-*s*-triazine (II) was obtained. A second case pertinent to the present study is the reactions reported by Radziszewski[3a] and Cook and Jones[3b] in which 2,4,6-triaryl-*s*-triazines were reduced with zinc in alcoholic alkali or zinc in acetic acid to give the corresponding 2,4,5-triarylimidazoles and ammonia.



The preparation of I in good yields and the products from the thermal and photolytic decompositions of I are herein reported. It was found that I could be synthesized in an 85% yield by the reduction of II with lithium aluminum hydride in tetrahydrofuran. Further investigations indicated that II was not reduced by sodium hydride, but that it was reduced by lithium aluminum hydride in the presence of aluminum chloride[4] to give some III.

The thermal decompositions were carried out with solutions of I as well as with pure I. The thermal decomposition of pure I was carried out between 260 and 270° under an inert atmosphere, and the reaction was shown to be essentially complete within 10 min. The products of the thermal decomposition were identified as II, III, benzonitrile, toluene, and ammonia. Their yields are reported in Table I. The absence of hydrogen gas as a product of the decomposition was shown by mass spectrographic analysis of the decomposition gases. The presence of ammonia was shown qualitatively by both mass spectrographic and infrared analyses. The yield of ammonia was determined by passing the evolved gas into a standardized hydrochloric acid solution and subsequent titration. The quantities of II and III in the solid residue were obtained both by ultraviolet analysis and column chromatography, the latter providing pure samples of each for characterization. The identification and quantitative determination of benzonitrile was achieved both by column and gas chromatography. Toluene was not produced in sufficient quantity to permit its isolation in the pure state, but it was identified by means of its retention time in gas chromatographic analysis. Also, a sample was collected from the effluent gases from the gas chromatograph, and this was shown to have an infrared spectrum identical with that of toluene. The decomposition of I in nitrobenzene and xylene, which was noted by Swamer, *et al.*,[2] to be almost quantitative in its dehydrogenation to II, was examined further. The decomposition of I in refluxing nitrobenzene was carried out under an inert atmosphere and II was accounted for in a 98% yield. No evidence for hydrogen or ammonia evolution was obtained, nor for the formation of any benzonitrile. However, there was evidence for the reduction of the nitrobenzene from the infrared studies of the fractionated recovered solvent. On the other hand, a refluxing solution of I in xylene (6 hr) or in benzene (24 hr) under an inert atmosphere gave no evidence of any significant decomposition. However, if the attempted decomposition in xylene were carried out in air, some II was obtained. Thus, in nitrobenzene the solvent functioned as the oxidizing agent,[5] whereas in xylene the solvent appeared inert and the presence of oxygen enhanced the oxidation of I to II. The decomposition of I at 260° in Dow Corning 200 fluid (10 cstokes, 1% solution) gave evidence of the same products as those obtained by the decomposition of pure I at 260° except that the decomposition occurred at a much slower rate (60% in 30 hr, based on ammonia evolution).

The photolytic decomposition of I was carried out under an inert atmosphere in refluxing benzene over a 24-hr period, after which time the reaction had been completed. The products of the photolytic decomposition were identified as II, III, benzonitrile, toluene, and ammonia. Their yields are reported in Table I. A control, in which the solution was refluxed under identical conditions except for the absence of irradiation, gave no evolution of ammonia. The products

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[1] (a) This investigation was supported in part by a Research Corporation Grant and in part by a Public Health Service Research Grant from the National Cancer Institute, U. S. Public Health Service. (b) San Fernando Valley State College.

[2] F. Swamer, G. Reynolds, and C. Hauser, *J. Org. Chem.*, **16**, 43 (1951).

[3] (a) B. Radziszewski, *Ber.*, **15**, 1493 (1882); (b) A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 278 (1941).

[4] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582 (1956).

[5] E. Lellman and W. Geller, *Ber.*, **21**, 1921 (1888).

Table I

Yield of Products Obtained from the Decomposition of I

Product	Thermal (pure I)		Photolytic	
	Wt, g[a]	Moles of product[b]/mole of I	Wt, g[c]	Moles of product[d]/mole of I
Ammonia	0.030	0.422	0.018	0.356
Toluene	0.044[e]	0.115	0.011[e]	0.040
Benzonitrile	0.250[f]	0.580	0.006[e]	0.020
Triphenylimidazole (III)	0.262[g]	0.211	0.132[h]	0.146
Triphenyltriazine (II)	0.710[i]	0.551	0.505[j]	0.538
Dihydrotriphenyltriazine (I)	0.027		0.047	
Unidentified materials	0.048		0.005	
Total	1.371		0.724	

[a] Obtained from 1.4720 g of I. [b] Based on 1.296 g of I (0.00417 mole). [c] Obtained from 0.9977 g of I. [d] Based on 0.946 g of I (0.00304 mole). [e] Value obtained from glpc. [f] Value obtained from glpc; 0.22 g was obtained from column chromatography. [g] Value obtained from ultraviolet analysis; 0.246 g was obtained from column chromatography (corrected for 94% chromatographic yield). [h] Value obtained from ultraviolet analysis; 0.133 g was obtained from column chromatography (corrected for 92% chromatographic yield). [i] Value obtained from ultraviolet analysis; 0.725 g was obtained from column chromatography (corrected for 94% chromatographic yield). [j] Value obtained from ultraviolet analysis; 0.535 g was obtained from column chromatography (corrected for 92% chromatographic yield).

from the photolysis and their yields were determined by methods similar to those used for the thermal decomposition, except that no quantitative determination of benzonitrile was attempted by column chromatography. It should be noted that the material accounted for in the photolytic decomposition (73%) is less than that in the thermal decomposition (93%). However, this difference in the total amount of material accounted for did not arise from a difference in the amount of solid isolated (photolysis 97% of thermal), nor from any substantial loss in the physical isolation of toluene (85% effective) or benzonitrile (97% effective) in the photolysis run.

To aid in substantiating that the decomposition was free radical in nature and, if so, to determine whether or not the reaction proceeded by a chain mechanism, a study of the effect of di-*t*-amyl peroxide on the decomposition of pure I was conducted at 193°. The competing side reaction, in which the peroxide abstracted hydrogens from I to give II, was corrected for by assuming that the ratio of II to III for the principal decomposition reaction in the peroxide-initiated reaction was the same as the ratio in the noninitiated decomposition study. Consequently, it was found that 37% of the total amount of II was produced by the competing side reaction, and that the principal decomposition reaction was accelerated by 20% as based upon the ammonia evolved.

Discussion

The thermal decomposition of pure I would appear to proceed by a free-radical mechanism rather than by an ionic mechanism. The free-radical mechanism is to be preferred on the following bases: the feasibility of the formation of ammonia and toluene *via* free radicals rather than ions arising from I or its derivatives, the necessity of high decomposition temperatures, the acceleration of the decomposition of I by di-*t*-amyl peroxide and by irradiation with ultraviolet light,[6] the realization of the same products from the thermal decomposition of I as obtained from the photolysis of I,[7] and the reduction of nitrobenzene when the latter is used as a solvent.[8] An attempt to confirm the free-radical mechanism by epr studies at 150 to 220° on pure I and its solutions (Dow Corning 200 fluid and diphenyl ether), however, gave no signals. Therefore, the failure to obtain signals would indicate that at these temperatures the steady-state concentration of the radicals was too low to be detected by epr. In addition to being a free-radical decomposition, it must also be concluded that a chain mechanism is involved. A chain mechanism is necessitated in order to account for the accelerating effect of di-*t*-amyl peroxide upon the decomposition.

It would appear from the identity of the products between the thermal and the photolytic decompositions that a similar free-radical mechanism applies to both. However, it is evident from the lower percentage recovery of products from the photolysis that the decomposition is complicated by additional side reactions. Therefore, the following discussion is concerned primarily with the mechanism of the thermal decomposition and relates to the photolytic decomposition only by implication.

The chain-initiating radicals for the decomposition could be those formed from the thermal excitation of a double bond within I[9] or the thermal cleavage of bonds within derivatives of I in which benzyl- and allyl-type radicals would be formed.

It is unlikely that the first propagating step in the chain mechanism for the decomposition involves any significant amount of net ring cleavage to yield such species as IV and V. This is substantiated by the fact that, when I was refluxed in nitrobenzene (bp 211°), II was formed in quantitative yields (98%). If any significant amount of net ring cleavage of I had occurred, a lower yield of II would have been obtained as well as the formation of some benzonitrile owing to the abstraction of hydrogen from species such as IV and V by nitrobenzene and subsequent detrimeri-

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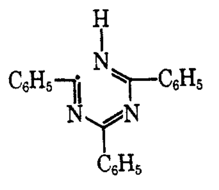
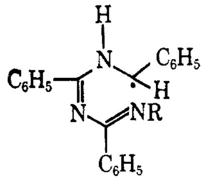
[6] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 36.

[7] (a) C. Walling, ref 6, p 544; (b) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1, 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1954, p 9.

[8] W. Huckel, "Theoretical Principles of Organic Chemistry," Vol. 1, Elsevier Publishing Co., New York, N. Y., 1955, p 801.

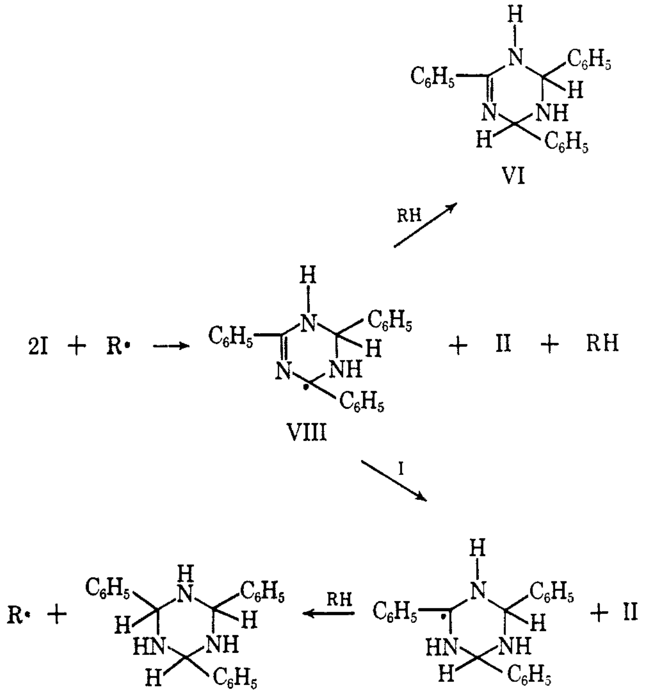
[9] (a) A. F. Trotman-Dickenson, "Free Radicals," John Wiley and Sons, Inc., New York, N. Y., 1959, p 119; (b) H. Gilman, "Organic Chemistry, An Advanced Treatise," Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1943, p 630.


IV


V

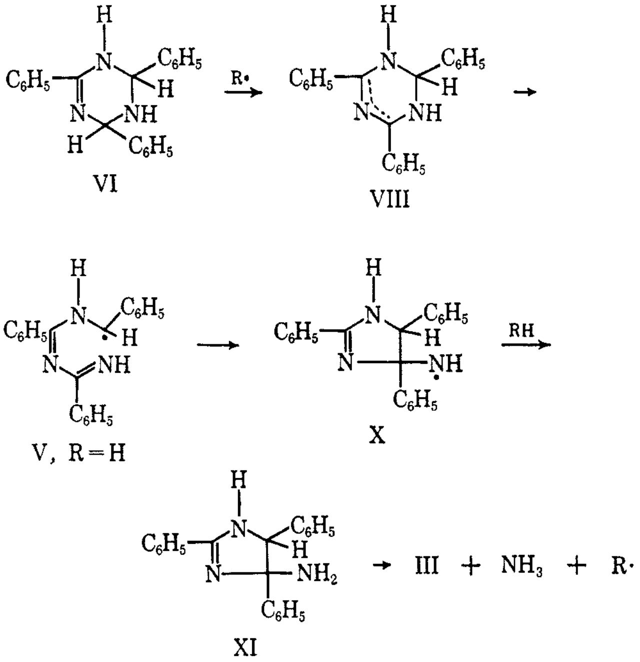
zation to benzonitrile. Further experimental evidence supporting the absence of ring cleavage of I as a major decomposition route is the relative yield of products resulting from the thermal decomposition of I in Dow Corning 200 fluid and the photolytic decomposition of I in benzene compared with that from the decomposition of pure I. Owing to the dilute nature of the solutions of I, any IV or V formed would have had a much longer life in the solutions than in the pure form, and hence they would have been more subject to fragmentation and detrimerization. This would have led to a decrease in the relative amount of II formed and an increase in the amount of benzonitrile. Experimentally this was not found to be the case (benzonitrile was not determined quantitatively in the case of the Dow Corning 200 fluid). Therefore, in view of the evidence against fragmentation, it is postulated that the first propagating step (Scheme I) consists of the disproportionation of I to form ultimately the tetrahydro-2,4,6-triphenyl-*s*-triazine (VI) and the hexahydro-2,4,6-triphenyl-*s*-triazine (VII) *via* precursors VIII and IX, respectively. The tetrahydro compound VI has been previously suggested as one of the species by which III is formed in the reduction of II with sodium amalgam and alcohol, and the hexahydro compound VII has been postulated as a possible species through which II is obtained in the nitridation of benzaldimine.[10] The above disproportionation is also similar to that of 1-phenyl-3,4-dihydroisoquinoline, which has been reported to disproportionate without added catalyst to 1-phenylisoquinoline and 1-phenyl-1,2,3,4-tetrahydroisoquinoline.[11] Many other disproportionations have also been reported but which require the presence of an added catalyst in order to proceed at a feasible rate.[12]

SCHEME I



The tetrahydro compound VI may be converted to final products by one of two possible routes. One route is the free-radical-initiated fragmentation of VI to benzonitrile and benzaldimine or derivatives of the latter. The second route is the free-radical-initiated cleavage and rearrangement of VI as shown in Scheme II. Evidence against fragmentation lies in the fact that it is reported[13] that benzaldehyde and ammonia react to form a trimer, namely the hydrobenzamide, which can be converted by heat to the dihydro derivative of III and ultimately to III. Thus, it would appear that cyclization rather than fragmentation is favored in the case of benzaldehyde and ammonia, and therefore, in the case at hand, it would appear unnecessary to postulate the formation of any discrete fragments which would ultimately be required to recombine. Secondly, it is reported that in the isolation of aldimines there is a strong tendency for polymerization to highly colored, gummy resins.[14] In the present study no polymers or resins were formed. Therefore, in summary, the rearrangement of VI as indicated in Scheme II should be a more favorable route than the fragmentation of VI. The elimination of ammonia from species XI could be comparable to that involved in the thermal elimination of ammonia from 1,2-diphenylethylamine (see Experimental Section), or it is conceivable that X could rearrange in-

SCHEME II



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[10] H. H. Strain, *J. Am. Chem. Soc.*, **49**, 1558 (1927).

[11] C. I. Brodrick and W. F. Short, *J. Chem. Soc.*, 2587 (1949).

[12] (a) C. Mannich and G. Heilner, *Ber.*, **55**, 365 (1922); (b) P. W. Neber, G. Knoller, K. Herbst, and A. Trissler, *Ann.*, **471**, 113 (1929); (c) F. Bohlmann, *Ber.*, **85**, 390 (1952); (d) R. P. Linstead, *Ann. Rept. Progr. Chem.* (Chem. Soc., London), **33**, 305 (1936).

[13] M. M. Sprung, *Chem. Rev.*, **26**, 297 (1940).

[14] T. L. Tolbert and B. Houston, *J. Org. Chem.*, **28**, 695 (1963).

tramolecularly[15] or with intermolecular assistance to yield III and the amino radical.[16] Either possibility would result in a chain-propagating step.

The necessity of postulating the existence of the hexahydro compound VII is due to the formation of toluene and benzonitrile, as well as the production of ammonia in an amount greater than that of III. A second alternative for the formation of these compounds is the fragmentation of precursors of VII such as VI, VIII, IX, or even I. However, this alternative would have the disadvantage of anticipating the formation of discrete radicals such as the benzyl radical and the amino radical, which would have to have a sufficiently long lifetime to abstract hydrogens from other species, or in the case of the benzyl radical, to dimerize to form bibenzyl. However, no bibenzyl was isolated in any of the experiments, and therefore it would appear necessary to exclude any route which would lead to the formation of the discrete benzyl radical. In view of this, the hexahydro compound VII has the advantage of being able to disproportionate intramolecularly in a concerted manner to yield benzonitrile, toluene, and ammonia owing to the presence of all necessary hydrogens within the ring.

The above proposed disproportionation mechanism for I to yield II, VI, and VII is consistent with the quantitative experimental data. Theoretical stoichiometric considerations of the disproportionation and the subsequent rearrangement of VI and VII to products give calculated values for the products which are within 5% of the experimental values except for toluene, which was isolated in only half of the theoretical yield. Also, the conversion of a small amount (5%) of open-chain isomer IV to benzonitrile is necessitated. Benzonitrile, under the experimental conditions of the decomposition, will not trimerize to form II. The presence of additional II in the decomposition of I did not alter the distribution of products.

The laboratory synthesis of VI and a study of its decomposition would have greatly enhanced the elucidation of the decomposition of I, but attempts at the synthesis and isolation of VI have thus far been unsuccessful.

Experimental Section[17]

Apparatus A.—Apparatus A consisted of a ₸ flask of appropriate size attached to a head. To the head was attached a 50-ml buret as well as an outlet tube which led to a gas buret *via* a three-way stopcock and a micro cold trap. When solutions of I were involved, a reflux condenser was incorporated into the apparatus.

Apparatus B and Associated Method.—Apparatus B consisted of a ₸ flask of appropriate size attached to a head which contained a gas-inlet tube for argon and an outlet tube for evolved gases. The inlet tube extended to the bottom of the flask and the outlet tube led into an inverted 250-ml erlenmeyer flask contained within a 600-ml beaker. When solutions of I were involved, a condenser was incorporated into the apparatus. In each run the system was thoroughly flushed with argon after the sample was introduced, but before the inverted flask and beaker were installed. The inverted flask and part of the 600-ml beaker were filled with a total of 400 ml of a standardized hydrochloric acid (normality known accurately near 0.01 *N*). After the run the system was cooled to room temperature and again flushed with argon to sweep any evolved gases into the acid solution. Titration of aliquots of the acid solution to the methyl red end point enabled the moles of ammonia evolved to be calculated.

1,2-Dihydro-2,4,6-triphenyl-s-triazine (I).—A boiling solution of 20.0 g (0.065 mole) of triphenyltriazine (II)[3b] in 600 ml of purified tetrahydrofuran was added over a 10-min period to a cold (0°) slurry of 15 g (0.40 mole) of lithium aluminum hydride in 50 ml of purified tetrahydrofuran. The resulting mixture was stirred for approximately 40 hr at 30° after which the excess tetrahydrofuran was distilled off, and 500 ml of ether was added. Ice water (200 ml) was added until the residue was gelatinous, and then the ether phase was decanted, washed to neutrality with warm saturated ammonium chloride solution and warm water, dried rapidly, and permitted to stand to yield crystals of I. Recrystallization from chloroform–pentane gave a total of 17.2 g (86%): mp 175.0–177.0° (lit.[2] 14% yield, mp 171–172°); nmr spectrum ($CDCl_3$), 4 H multiplet at τ 1.96 (*ortho* aromatics, conjugated), 11 H multiplet at τ 2.50 (aromatics), 1 H singlet at τ 3.75 (benzyl), and 1 H broad band at τ 4.80 (amino).

Anal. Calcd for $C_{21}H_{17}N_3$: C, 81.00; H, 5.50; N, 13.50. Found: C, 81.08; H, 5.47; N, 13.33.

Reduction of II with Lithium Aluminum Hydride in the Presence of Aluminum Chloride.—A warm solution of 10.0 g (0.0324 mole) of triphenyltriazine (II) in 375 ml of purified tetrahydrofuran was added over a 5-min period to a cold (0°) slurry of 5 g (0.13 mole) of lithium aluminum hydride and 5.7 g (0.044 mole) of aluminum chloride in 40 ml of purified tetrahydrofuran. The reaction mixture was stirred for 43 hr at approximately 55° after which the excess tetrahydrofuran was distilled off and 200 ml of ether was added. Ice water (100 ml) was added until the residue was gelatinous, and then the ether phase was decanted, washed to neutrality, dried rapidly, and permitted to stand to yield 1.52 g of 2,4,5-triphenylimidazole (III), mp 274–277°.

Decomposition of the Dihydrotriazine I for Gas Analysis.—Apparatus A was equipped with a ₸ test tube (14 × 130 mm) as the flask. A typical run was as follows. Into the tube was placed 0.8306 g (0.00367 mole) of the dihydrotriazine I and the system was flushed thoroughly with argon. After adjusting the system to atmospheric pressure and thermostating the cold trap (24°), the tube was immersed in a 230° bath which was raised to 265° within 10 min (approximately 95% of the gas had evolved). The application of heat was continued for 1 hr and then the system was cooled to room temperature. A total of 20.2 cc (STP) of gas was collected (0.000902 mole and 91% of that determined by titration). Mercury from the buret attached to the head was then permitted to flow into the system to displace all of the gas into the gas buret. Samples of the gas were then submitted for infrared and mass spectrographic analyses. The infrared spectrum gave evidence only for ammonia. The mass spectrograph showed masses of 16 and 17 (ammonia), 28 (nitrogen), 40 (argon), 43 (acetone), and 83 (chloroform).

Decomposition of the Dihydrotriazine I for Glpc Analysis.—The thermal decomposition for the gas chromatographic studies was carried out in the microreactor accessory[18] for a Perkin-Elmer Model 154-D vapor fractometer equipped with a Ucon Polyglycol LB-550-X column. The microreactor was adapted for the decomposition by reversing the flow of the carrier gas through the reactor tube by exchanging the inlet and the outlet tubes at the reactor valve, and by installing a septum holder and a needle guide on the top of the reactor tube. The exposed tubes and valves were heated by a heating tape so as to minimize the condensation of liquid products. A sample of the dihydrotriazine I (weighed accurately within the 200- to 400-mg range) contained in a test tube (6 × 20 mm) was placed on the disk within the reactor tube, and the reactor was assembled and flushed with the helium carrier gas. The flow of the carrier gas was then stopped at the exit as well as at the source, the microreactor was heated rapidly to approximately 260°, and after a

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[15] O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 305 (1962).

[16] (a) P. Davis, M. G. Evans, and W. C. E. Higginson, *J. Chem. Soc.*, 2563 (1951); (b) H. Seaman, P. J. Taylor, and W. A. Waters, *ibid.*, 4690 (1954); (c) C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. E. Mochel, *J. Am. Chem. Soc.*, **81**, 1489 (1959).

[17] All melting points are corrected. Unless otherwise stated, magnesium sulfate was employed as a drying agent. The infrared spectra were determined with either a Beckman IR-8, IR-7, or IR-5 spectrophotometer. The ultraviolet spectra were determined with a Cary Model 14 or a Perkin-Elmer Model 202 recording spectrophotometer. The mass spectra were obtained with a CEC, Model 21-620, mass spectrometer. The nmr and epr studies were carried out by Varian Associates, Palo Alto, Calif.

[18] (a) R. J. Kokes, H. Tobin, Jr., and P. H. Emmett, *J. Am. Chem. Soc.*, **77**, 5860 (1955); (b) Perkin-Elmer Accessory Data Sheet VPC-AC-004-60, Instrument Division, Perkin-Elmer Corp., Norwalk, Conn.

10-min reaction time, the flow of the carrier gas was resumed with subsequent chromatography of the products. The vapor fraction due to toluene was collected in carbon tetrachloride to provide a solution which gave a spectrum (90–100% expanded scale, Beckman IR-7) which corresponded to that of toluene. After the liquid decomposition products had been chromatographed, the flow of the carrier gas was once again interrupted and a control sample of toluene and benzonitrile was injected through the septum installed on the top of the microreactor tube. After 10 min at approximately 260°, the flow of the carrier gas was resumed and the control sample was chromatographed. The quantitative analysis of the toluene and the benzonitrile was obtained by the area calibration method.

Decomposition of the Dihydrotriazine I for Ammonia Titration.—Into the flask (25 ml) of apparatus B was packed 1.4720 g (0.00473 mole) of the dihydrotriazine I. The flask and its contents were heated from 235 to 270° over a 2-hr period and then cooled to room temperature, after which approximately 3.5 cc[19] of gas remained undissolved in the inverted flask. After flushing the system, the titration of 10-ml aliquots of the acid solution indicated that 0.00176 mole of ammonia had been evolved.

Column Chromatographic Separations.—The semisolid residue remaining from the above decomposition was triturated with three 3-ml portions of distilled pentane. The pentane extract was placed on 30 g of alumina (Harshaw, Al-0101P, activity II[20]) and eluted with eluent which progressed in composition from pure pentane through ether to pure methanol. At 10% ether in pentane, 0.22 g of benzonitrile was obtained and identified by its infrared spectrum and its hydrolysis to benzoic acid. At other eluent compositions little or no material was obtained.

The solid remaining from the above pentane trituration was filtered and dried to yield 1.0470 g, mp 220–227°. A portion (0.5026 g) of the solid was placed as a solid on 200 g of alumina (Harshaw, Al-0101P, activity II[20]) and eluted to give four fractions: (1) 2,4,6-triphenyl-*s*-triazine (II), 0.3257 g, mp 238.5–240.0°, 15% ether in pentane; (2) 1,2-dihydro-2,4,6-triphenyl-*s*-triazine (I), 0.0122 g, mp 165–167°, 100% ether; (3) unidentified material, 0.0215 g, mp 199.5–203.0°, 100% ether; and (4) 2,4,5-triphenylimidazole (III), 0.1106 g, mp 278.0–279.0°, 100% ether. The 2,4,5-triphenylimidazole (III) was identified by its mixture melting point with an authentic sample and by its picrate, mp 238–239° (lit.[21] mp 235°).

Decomposition of the Dihydrotriazine I in Nitrobenzene.—Into the flask (50 ml) of apparatus B were placed 1.4696 g (0.00472 mole) of the dihydrotriazine I and 30 ml of distilled nitrobenzene. After the solution had been refluxed for 46 hr, the system was cooled to room temperature to give no evidence of any water-insoluble gas in the inverted flask. After flushing the system, the titration of 10-ml aliquots of the acid solution indicated that no ammonia had been evolved.

The solid which had crystallized from the nitrobenzene upon standing at room temperature was filtered, washed with pentane, and dried to yield 1.2283 g of triphenyltriazine (II), mp 236.5–240.0°. A control showed that 0.2095 g of II was soluble in 30 ml of nitrobenzene (total II formed: 1.4378 g, 98.5%). The nitrobenzene filtrate was fractionally distilled (bp $C_6H_5NO_2 > C_6H_5CN > C_6H_5NH_2$) to yield initial fractions which gave infrared spectra having absorption bands at 3450, 3370, 1275, 995, and 875 cm^{-1} ($C_6H_5NH_2$) in addition to the bands due to nitrobenzene. No absorption band was observed at 2225 cm^{-1} ($C{\equiv}N$).

Decomposition of the Dihydrotriazine I in Dow Corning 200 Fluid.—Into the flask (100 ml) of apparatus A were placed 0.7435 g (0.00239 mole) of the dihydrotriazine I and 75 ml of Dow Corning 200 fluid, 10 cstokes. After bubbling argon gas through the mixture and the system, the system was adjusted to atmospheric pressure, the cold trap was thermostated (0°), and the solution was heated at 250–270° for 30 hr. After cooling the system to room temperature, a total of 10.8 cc (STP, 0.000482 mole, and 60% relative to that obtained from the thermal decomposition of pure I) of gas had been collected. Dow Corning 200 fluid from the buret attached to the head was then permitted to flow into the system to displace all of the gases into the gas buret. An infrared spectrum of the gases was identical with that of ammonia except for an additional band at 1310 cm^{-1}.

The contents of the system were removed (odor of benzonitrile was detected) and kept at −5° for 48 hr to yield 0.4873 g of solid (washed with cold toluene and pentane), mp 227.0–230.0°. A portion (0.2608 g) of the solid was placed as a solid on 100 g of alumina (Harshaw, Al-0101P, neutral, activity I[20]) and eluted to give two major fractions: (1) 2,4,6-triphenyl-*s*-triazine (II), 0.1868 g, mp 236.0–237.0°, 25% ether in pentane; and (2) 2,4,5-triphenylimidazole (III), 0.0483 g, mp 275–277°, 100% ether.

Decomposition of the Dihydrotriazine I in Xylene.—A solution of 0.4924 g of the dihydrotriazine I in 10.0 ml of redistilled xylene was refluxed in an argon atmosphere for 5.8 hr. After standing overnight, 0.3743 g of solid had crystallized, mp 174–176°. No triphenyltriazine (II) crystals were evident. The supernatant solution was evaporated under reduced pressure at 35° to yield 0.0793 g of solid, mp 196.5–222°.

A solution of 0.4897 g of the dihydrotriazine I in 10.0 ml of redistilled xylene was refluxed in an atmosphere of moving air for 5.8 hr. After standing overnight, 0.3786 g of solid had crystallized: mp 172–200°. Evident throughout the solid were long needles of the triphenyltriazine (II), mp 234–236°. The supernatant solution was evaporated under reduced pressure at 35° to yield 0.0527 g of solid, mp 195–235°.

Decomposition of the Dihydrotriazine I in the Presence of Di-*t*-amyl Peroxide.[22]—Apparatus B was modified by incorporating a microburet into the head so as to permit the peroxide to drop into the decomposition flask. The dihydrotriazine I (3.0167 g, 0.00970 mole) was heated at 193° until the solid had totally melted (time zero). The di-*t*-amyl peroxide (0.40 g.) was then added dropwise over a period of 500 sec after which the bath was removed. After flushing the system, the titration of 10-ml aliquots of the acid solution indicated that 0.00179 mole of ammonia had been evolved. The residue remaining in the flask was thoroughly triturated five times with distilled pentane and dried to yield 2.6973 g of solid, mp 195–215°. The analysis of the solid by ultraviolet absorbance (226, 270, and 302 mμ) gave the following composition by weight: dihydrotriazine I, 46.5%; triphenyltriazine (II), 41.5%; and triphenylimidazole (III), 12.0%.[23]

A reference run for the above was carried out under identical conditions except with the absence of the peroxide. The dihydrotriazine I (3.0153 g, 0.00970 mole) was found to yield 0.00159 mole of ammonia and 2.7718 g of solid, mp 161–200°. The analysis of the solid by ultraviolet absorbance gave the following composition by weight: dihydrotriazine I, 64.0%; triphenyltriazine (II), 24.5%; and triphenylimidazole (III), 11.5%.

A control run employing the peroxide (0.40 g) in the absence of the dihydrotriazine I was carried out under conditions identical with those above with no change in the hydrochloric acid titer.

Photolysis of the Dihydrotriazine I.—A solution of 0.9977 g (0.00321 mole) of the dihydrotriazine I in 100 ml of purified benzene contained in a quartz flask attached to apparatus B was irradiated (with reflux) by a Hanovia 450-w high-pressure mercury lamp for 24 hr. After flushing the system, the titration of 10-ml aliquots of the acid solution indicated that 0.00108 mole of ammonia had been evolved (91% relative to the thermal decomposition).

The benzene solution was evaporated under reduced pressure at room temperature to yield 0.6848 g of solid, mp 223.5–227.0°. A portion (0.2680 g) of the solid was placed as a solid on 100 g of alumina (Harshaw, Al-0101P, neutral, activity I–II[20]) and eluted to give two major fractions: (1) 2,4,6-triphenyl-*s*-triazine (II), 0.1921 g, mp 235–236°, mmp with authentic sample 235.5–237°, 25% ether in pentane; and (2) 2,4,5-triphenylimidazole (III), 0.0477 g, mp 275–276°, mmp with authentic sample 276–277.5°, 100% ether. Unidentified chromatographic residues totaled 0.0053 g.

In another run similar to the above, the benzene solution was fractionated through a 35-cm Podbielniak-type column (0.7-ml holdup). After completion of the distillation, the column was

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[19] This gas may have been due to ammonia which had been evolved and had not yet been absorbed in the acid solution.

[20] H. Brockmann and H. Schodder, *Ber.*, **B74**, 73 (1941).

[21] R. Weidenhagen, R. Herrmann, and H. Wegner, *ibid.*, **B70**, 575 (1937).

[22] Synthesized by the method of N. A. Milas and D. M. Surgenor [*J. Am. Chem. Soc.*, **68**, 643 (1946)] and provided by Dr. Carl J. Olsen.

[23] Based on the ratio of triphenyltriazine (II) to triphenylimidazole (III) from the reference run with the absence of peroxide, it can be shown that in the presence of peroxide 37% of II arose from hydrogen abstraction from the dihydrotriazine I by the peroxide.

rinsed with a 1.0- and a 0.5-ml portion of benzene to give a total liquid residue of 4.8 ml in the pot. Analysis by glpc showed that approximately 0.011 g of toluene and 0.006 g of benzonitrile were present in the liquid residue.

A control identical with the above photolysis run, except that the solution was refluxed without irradiation, gave no change in the hydrochloric acid titer. Other control experiments showed that (1) no additional ammonia was evolved after 24 hr; (2) under the conditions of the photolysis, both triphenyltriazine (II) and triphenylimidazole (III) were stable and benzonitrile did not cyclize to triphenyltriazine (II); and (3) toluene and benzonitrile in benzene could be photolyzed and recovered as above in 85 and 97% yields, respectively.

Effect of Added Triphenyltriazine (II) upon the Decomposition of I.—A mixture of 0.9304 g (0.0030 mole) of the dihydrotriazine I and 1.8609 g (0.00602 mole) of the triphenyltriazine (II) contained in the flask of apparatus A was decomposed for 1.75 hr to yield 20.6 cc (STP) of gas (91.5% relative to that obtained from pure I). The pentane extract of the residue upon evaporation gave 0.1480 g of benzonitrile (106% relative to that obtained from pure I).

Thermal Decomposition of 1,2-Diphenylethylamine.—Purified 1,2-diphenylethylamine (8.6739 g, 0.044 mole) contained in the flask (25 ml.) of apparatus B was refluxed for 21 hr. After flushing the system, the titration of 10-ml aliquots of the acid solution indicated that 0.0232 mole of ammonia had been evolved. That the gas was ammonia was shown in a second experiment in which the gas was collected and identified by its infrared spectrum. A portion (4.1758 g) of the residue remaining in the flask was dissolved in ether and extracted with 10% hydrochloric acid to yield ultimately 1.6028 g of recovered 1,2-diphenylethylamine. The neutral fraction gave 2.3021 g of material which was separated by column chromatography into several compounds of which the major ones were 1,2-diphenylethane, stilbene, and deoxybenzoin. Their identification was based upon their infrared spectra and mixture melting point with authentic samples.

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Fluorinated 1,2,3-Triazolines

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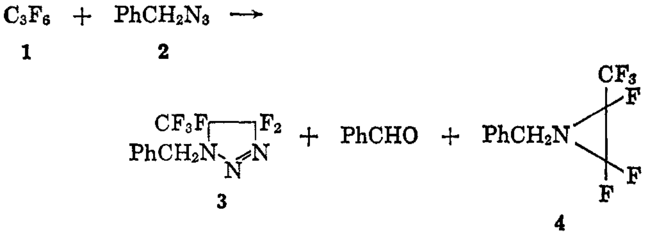
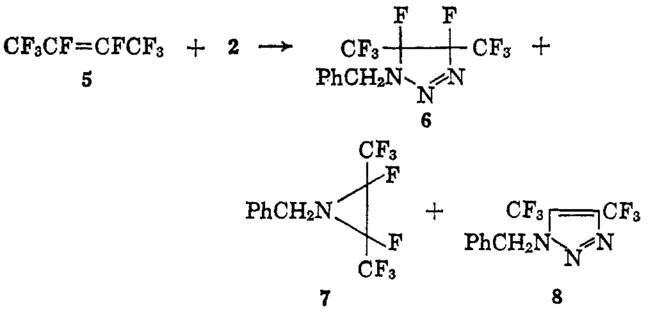
Benzyl azide reacted slowly with perfluoropropene and perfluorobutene-2 at 150° to produce the triazolines **3** and **6**, respectively. The triazolines have been defluorinated to the triazoles, **10** and **8**, and have been pyrolyzed on glass beads to the corresponding aziridines, **4** and **7**. The pyrolysis of **3** on nickel balls gives an unusual type of cleavage wherein both nitrogen and difluorocarbene are eliminated, leaving N-benzyltrifluoroacetimidoyl fluoride as the major product. Difluorocarbene was isolated as tetrafluoroethylene. When tetramethylethylene was present, the difluorocarbene was trapped as 1,1-difluorotetramethylcyclopropane.

The condensation of organic azides with olefins to produce 1,2,3-triazolines has been studied extensively.[1] However, the use of perfluorinated olefins has not yet been described. The present investigation involves the condensation of benzyl azide with perfluoropropene and perfluorobutene-2.

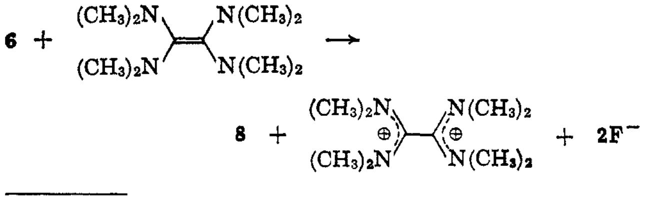
Perfluoropropene (1) reacts with benzyl azide (2) to produce 1-benzyl-4,4,5-trifluoro-5-trifluoromethyl-1,2,3-triazoline (3) in 85% yield based on the benzyl azide present. Benzaldehyde and N-benzyl-2,2,3-trifluoro-2-trifluoromethylaziridine (4) were also detected by gas chromatography as minor products.



Perfluorobutene-2 (5) reacts with 2 under the same conditions to give 1-benzyl-4,5-difluoro-4,5-bistrifluoromethyl-1,2,3-triazoline (6) in 65% yield. N-Benzyl-2,3-difluoro-2,3-bistrifluoromethylaziridine (7) and 1-benzyl-4,5-bistrifluoromethyl-1,2,3-triazole (8) were formed in 7 and 5% yield, respectively. Benzaldehyde, 6%, and benzyl azide, 2%, were also detected as constituents of the product mixture. The mechanism by which 8 was formed was not determined. Its structure was confirmed by an alternate synthesis from benzyl azide and hexafluorobutyne-2. The triazole was also formed by extracting two fluorine atoms from 6 with tetrakis(dimethylamino)ethylene (9), a compound capable of halogen abstractions.[2]



$$CF_3C{\equiv}CCF_3 + 2 \longrightarrow 8$$



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[1] (a) K. Alder and G. Stein, *Ann.*, **485**, 211 (1931); (b) R. Fusco, G. Bianchetti, and D. Pocar, *Gazz. Chim. Ital.*, **91**, 849, 933 (1961); **92**, 1040 (1962); *Chem. Ber.*, **96**, 802 (1963); (c) J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964); (d) L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat, and R. L. Hale, *Chem. Ind.* (London), 1556 (1964); (e) P. Scheimer, *J. Org. Chem.*, **30**, 7 (1965); (f) R. Huisgen, L. Möbius, and G. Szeimies, *Chem. Ber.*, **98**, 1138, 1153 (1965).

[2] W. Carpenter, *J. Org. Chem.*, **30**, 3082 (1965).