poses the ether-phosphate XXI can be directly hydrolyzed, *vide infra*).

The main fraction (6.65 g., theory 7.03 g.) was collected at 125–131° (0.07 mm.). It was separated by further distillation into three fractions: (1) 2.6 g., b.p. 129–131° (0.07 mm.); (2) 2.5 g., b.p. 132–135° (0.1 mm.); and (3) residue, 0.6 g., which crystallized on standing.

Fractions 1 and 2 (total 5.1 g.) are essentially pure diethyl-(4-ethoxy-2,3,5,6-tetramethylphenyl) phosphate (XXI), $n^{25}D$ 1.4900, band at 7.9 μ. For analysis, fraction 2 was evaporatively distilled.

Anal. Calcd. for $C_{16}H_{27}O_5P$: C, 58.2; H, 8.2. Found: C, 58.7; H, 8.6.

Preparation of 2,3,5,6-Tetramethylhydroquinone-monoethyl Ether (Durohydroquinone-monoethyl ether) (XXVIII) from Duroquinone.—A mixture of duroquinone (0.95 g.) and triethyl phosphite (25 ml.) was kept 20 hr. at reflux temperature under nitrogen. The excess triethyl phosphite was removed under vacuum, and the residue was treated with 40 ml. of a 5% solution of potassium hydroxide in 95% ethanol. After *ca.* 20 hr. at reflux temperature the solution was treated with carbon dioxide. The durohydroquinone-monoethyl ether (XXVIII) (0.94 g., m.p. 122–124°, theory 1.1 g.) which precipitated was suitable for further work. The analytical sample had m.p. 123–124° (ethanol–water).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3. Found: C, 74.2; H, 9.4.

Attempts to Reduce Duroquinone (XIII) with Triethyl Phosphite.—(a) A solution of duroquinone in a 50:50 mixture of benzene–95% aq. ethanol was slowly added to a solution of triethyl phosphite in benzene at room temperature. After 48 hr. most of the duroquinone was recovered unchanged. (b) A mixture of duroquinone, triethyl phosphite, toluene and 95% ethanol was heated to reflux temperature for 20 hr. At least 50% of the duroquinone was recovered unchanged.

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[CONTRIBUTION NO. 520 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

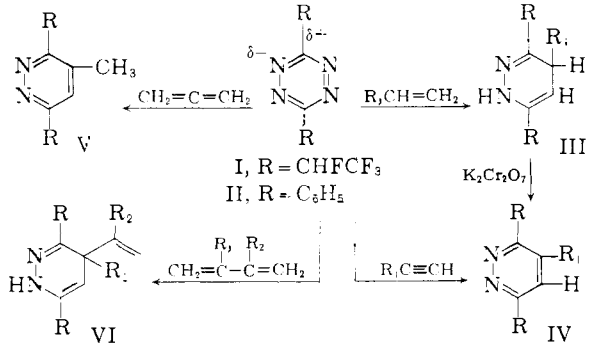
Reactions of Tetrazines with Unsaturated Compounds. A New Synthesis of Pyridazines

BY R. A. CARBONI AND R. V. LINDSEY, JR.

RECEIVED JANUARY 13, 1959

3,6-Bis-(polyfluoroalkyl)-*sym*-tetrazines were found to react with remarkable ease with a variety of unsaturated compounds, including styrenes, butadienes, acetylenes, aliphatic and alicyclic olefins, and allene to yield pyridazines. 3,6-Diphenyl- and 3,6-dimethyl-*sym*-tetrazines reacted similarly though less readily. The scope of this reaction and the nature of the products are discussed.

Although a number of synthetic routes to tetrazines have been reported,[1] little is known about their chemistry. In connection with our recent studies of the synthesis of 1,2-dihydro-3,6-bis-(polyfluoroalkyl)-*sym*-tetrazines from fluoroölefins and hydrazine,[2] it was discovered that these substances react easily with a variety of unsaturated compounds with the evolution of one mole of nitrogen to yield 3,6-disubstituted pyridazines. The reaction apparently proceeds by 1,4-addition of the —C=N—N=C— diene system of the tetrazine to the appropriate olefinic and acetylenic dienophiles.



3,6 - Bis - (1,2,2,2 - tetrafluoroethyl) - *sym*-tetrazine (I) reacts exothermically with styrene at room temperature to give a colorless, crystalline product, m.p. 131–132.5°, with the empirical formula $C_{14}H_{10}F_8N_2$ (III, R = $CHFCF_3$, R_1 = C_6H_5). The reaction can be moderated by cooling or by employing diluents such as ether or benzene. Completion of the reaction is signalled by the disappearance of the characteristic red or violet-red tetrazine color and by the cessation of nitrogen evolution. 3,6-Bis-difluoromethyl-*sym*-tetrazine[2] also reacts rapidly with styrene at room temperature while 3,6-bis-(3,3-difluoroallyl)-*sym*-tetrazine reacts somewhat more slowly. 3,6-Diphenyl-*sym*-tetrazine (II) and 3,6-dimethyl-*sym*-tetrazine behave in a similar manner, although the additions are slower and require higher temperatures. Thus, the reaction of II with styrene requires heating for 30 minutes at 75° for completion.

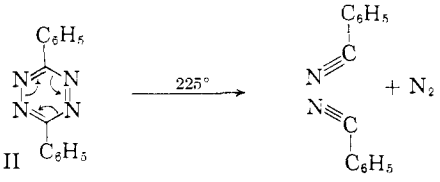
The enhanced reactivity of the fluoroalkyltetrazine derivatives toward many of the unsaturated compounds is undoubtedly associated with the electron-withdrawing effects of the polyfluoroalkyl groups which render the 3,6-positions more susceptible to attack by electron-rich olefins.

Dienophiles containing electron-releasing substituents were found to facilitate the reaction, while those with electron-attracting groups exhibited a retarding effect. Thus, isobutyl vinyl ether, butadiene, isoprene and 2,3-dimethylbutadiene reacted immediately with I at room temperature to give the corresponding dihydropyridazine derivatives. With acrylonitrile and acrolein, prolonged heating at 70° was required to complete the reaction. Negatively polysubstituted olefins such as maleic anhydride, maleic acid, diethyl azodiformate and tetracyanoethylene, which are nor-

(1) J. G. Erickson, P. F. Wiley and V. P. Wystrach, "The Chemistry of Heterocyclic Compounds," Vol. X, "The 1,2,3- and 1,2,4-triazines, Tetrazines, and Pentazines," Interscience Publishers, Inc., New York, N. Y., 1956, Chapter IV.

(2) R. A. Carboni and R. V. Lindsey, Jr., THIS JOURNAL, **80**, 5793 5793 (1958).

mally powerful dienophiles in the Diels-Alder reaction, failed to react with either I or II. When the temperature was raised to 225° in an attempt to bring about addition of these dienophiles, 3,6-diphenyl-*sym*-tetrazine (II) underwent a smooth decomposition to benzonitrile with the loss of one molecule of nitrogen.

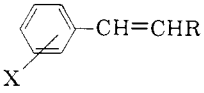


II

Additional evidence for the electronic effect of substituents on the reactivity of the dienophile was obtained by treating aliquots of 3,6-diphenyl-*sym*-tetrazine (II) in benzene with *p*-methoxystyrene, styrene, β-methylstyrene, *o*-methoxy-β-methylstyrene, *p*-methoxy-β-methylstyrene, ethyl *p*-methoxycinnamate and stilbene. Each of the mixtures and a control were heated at 100° in a sealed tube. The reaction was followed qualitatively by the disappearance or diminution of the characteristic red-violet tetrazine color relative to the control. The relative reactivities in descending order are shown in Table I.

TABLE I

RELATIVE REACTIVITY OF STYRENE DERIVATIVES

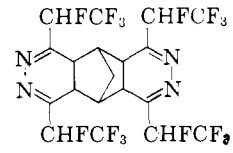


X = *p*-OCH_3, R = H >
X = H, R = H >>
X = *p*-OCH_3, R = CH_3 >
X = *o*-OCH_3, R = CH_3 >
X = H, R = CH_3 >>>
X = *p*-OCH_3, R = $COOC_2H_5$ or
X = H, R = C_6H_5

The latter two substances showed no detectable reactivity under these conditions. The observed order is in accord with the concept that the reaction proceeds by attack of the olefins of higher electron density upon the relatively electron-poor carbons of the tetrazine.

Steric considerations were also found to play an important role in determining the reactivity of the dienophile. Alkenes of the type $RCH{=}CH_2$ were more active than non-terminal olefins. Thus, acrolein reacted more rapidly with compound I than did crotonaldehyde. It is evident from Table I that styrene derivatives with a terminal methylene group are more reactive than any of the β-substituted styrenes. The highly hindered tetramethylethylene added to compound I only with difficulty despite the high electron density about the double bond. Two equivalents of I were readily consumed in the reaction with bicycloheptadiene. Chemical analyses and a molecular weight determination indicated that the product, presumably VII, has the empirical formula $C_{19}H_{12}F_{16}N_4$.

Cyclopentene underwent exothermic addition to compound I at room temperature while cyclohexene required heating at reflux for 3 hours. This behavior probably reflects the greater relief



VII

from angular strain resulting from saturation of the double bond in the cyclopentene ring compared to that obtained by saturation of the double bond of the 6-membered ring.[3]

The pyridazine structure for the products was established by elemental and spectral analyses and by comparing the physical properties of some of the products with those of known pyridazines. The data for some of these pyridazine derivatives are given in Table II.

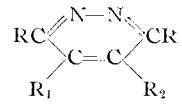
When the tetrazines were treated with acetylenes or allenes, the corresponding pyridazines were obtained directly. Thus, 3,6-diphenylpyridazine (m.p. 228–229°), 3,4,6-triphenylpyridazine (m.p. 176–177.5°) and tetraphenylpyridazine (m.p. 196–197°) were obtained from II and acetylene, phenylacetylene and diphenylacetylene, respectively. Reaction of allene with I gave the corresponding 3,6-bis-(fluoroalkyl)-4-methylpyridazine (V). The pyridazines were also obtained by oxidation of the dihydro derivatives which formed when olefins were employed instead of acetylenes. For example, styrene reacted rapidly with 3,6-diphenyl-*sym*-tetrazine at 100° to yield a mass of yellow crystals, m.p. 182–186°. The dihydrotriphenylpyridazine (III, R = C_6H_5) was found by chemical and spectral analyses to be contaminated with a small quantity of the dihydrotetrazine. When the product was oxidized with potassium dichromate in acetic acid, a small amount of red-violet diphenyltetrazine separated. Workup of the main component in the acetic acid gave the colorless 3,4,6-triphenylpyridazine, m.p. 176–177.5°, whose infrared spectrum was identical to that of the product obtained from phenylacetylene. Smith[4] has reported that the condensation of desylacetophenone with hydrazine gave 3,4,6-triphenyl-1,2-dihydropyridazine as a yellow solid, m.p. 186–188°. Subsequent oxidation gave the colorless pyridazine, m.p. 173–175°.[4,5]

The ultraviolet spectra of the pyridazines obtained in this study resemble the absorption patterns of previously reported substituted pyridazines. These data are given in Table III. The dihydropyridazines obtained from the tetrazines and an olefin exhibited a strong >NH absorption at 3 μ in the infrared spectrum, thus excluding the expected azine structure as the major product. The dihydropyridazines obtained from the reactions of 3,6-diphenyl(II) and 3,6-bis-(tetrafluoroethyl)-*sym*-tetrazine(I) with acrylonitrile each exhibit a moderately strong conjugated nitrile band at 4.55 and 4.53 μ, respectively. The diphenyl derivative shows strong peaks at 3.48 and 3.57 μ which are attributed to saturated CH_2 stretching vibrations. It thus appears that the 1,4-dihydro-

(3) R. B. Turner and R. H. Garner, THIS JOURNAL, **80**, 1424 (1958); H. C. Brown, J. H. Brewster and H. Schechter, *ibid.*, **76**, 467 (1954).
(4) A. Smith, *Ann.*, **289**, 310 (1896).
(5) S. Capuano, *Gazz. chim. ital.*, **68**, 527 (1938).

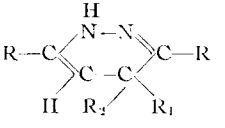
TABLE II

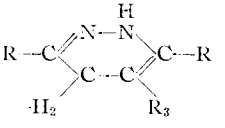
SUBSTITUTED PYRIDAZINE DERIVATIVES



R	R_1	R_2	R_3	M.p., °C.	Solvent	B.p., °C. (mm.)	Formula	$n^{25}D$	Analyses, %, Calcd. values / Found values			
$-CHFCF_3$	C_6H_5	H		65–67	EtOH–H_2O	.....	$C_{14}H_8F_8N_2$		N 7.87	F 42.67		
									N 7.78	F 43.00		
C_6H_5	C_6H_5	H		176–177.5	EtOH	.....	$C_{22}H_{16}N_2$		C 85.68	H 5.23	N 9.09	
									C 85.89	H 5.27	N 9.09	
C_6H_5	C_6H_5	C_6H_5		196–197	EtOH	.....	$C_{28}H_{20}N_2$		C 87.47	H 5.24	N 7.29	
									C 87.33	H 5.36	N 7.32	
C_6H_5	H	H		228–229	DMF	.....	$C_{16}H_{12}N_2$		C 82.73	H 5.21	N 12.06	
									C 82.75	H 5.26	N 11.84	
$CHFCF_3$	$CH=CH_2$	H		.....	.....	65 (0.9)	$C_{16}H_{16}F_8N_2$		C 39.22	H 1.98	F 49.65	N 9.15
									C 39.66	H 2.29	F 50.20	N 9.02
$CHFCF_3$	CH_3	H		.....	.....	66 (1.6)	$C_9H_6F_8N_2$		C 36.75	H 2.06	N 9.53	
									C 36.00	H 2.29	N 9.69	
C_6H_5	CN	H		162–163	EtOH	.....	$C_{17}H_{11}N_3$		C 79.36	H 4.31	N 16.33	
									C 78.59	H 4.13	N 15.91	

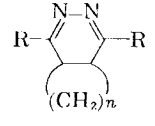
SUBSTITUTED DIHYDROPYRIDAZINES





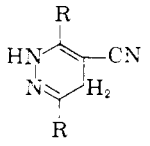
$CHFCF_3$	.....	.....	C_6H_5	131–132.5	Pentane–ether	.....	$C_{14}H_{10}F_8N_2$		C 46.96	H 2.81	F 42.43	N 7.82
									C 46.85	H 2.98	F 42.12	N 7.89
$CHFCF_3$	CH_3	C_6H_5	.....	101–103	Pentane–ether	.....	$C_{15}H_{12}F_8N_2$		N 7.53	F 40.83		
									N 7.96	F 40.69		
$CHFCF_3$	.....	.....	$C=CH_2$ CH_3	.....	.....	57 (0.7)	$C_{14}H_{10}F_8N_2$	1.4078	C 41.00	H 3.13	F 47.18	N 8.70
									C 40.94	H 3.13	F 48.13	N 9.05
$CHFCF_3$	CH_2	$C=CH_2$ CH_3	.....	.....	.....	76 (1.1)	$C_{12}H_{12}F_8N_2$	1.4200	C 42.86	H 3.60	F 45.21	N 8.33
									C 43.10	H 3.56	F 45.36	N 8.86
$CHFCF_3$	..	.....	CN	.....	CH_2Cl_2–petr. ether	.....	$C_9H_5F_8N_3$		N 13.68			
									N 13.54			
C_6H_5	...	.....	CN	190–191	EtOH	.....	$C_{17}H_{13}N_3$		C 78.74	H 5.05	N 16.21	
									C 78.44	H 5.04	N 15.95	
CH_3	CH_3	$CH=CH_2$	.....	.....	.....	70 (1)	$C_9H_{11}N_2$		C 71.95	H 9.40	N 18.65	
									C 72.18	H 9.72	N 18.93	

POLYCYCLIC PYRIDAZINE DERIVATIVES

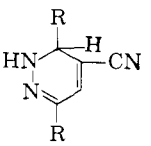


$CHFCF_3$	[4]	.....	.....	.....	Pentane	.....	$C_{12}H_{12}F_8N_2$		N 8.35	N 8.21		
$CHFCF_3$	[5]	.....	.....	86–88	Petr. ether	.....	$C_{11}H_{10}F_8N_2$		F 47.17	F 46.29		
VII	.....	223° (when sample dropped on hot block)			Toluene	.....	$C_{18}H_{12}F_{16}N_4$		N 9.33	N 9.45		

pyridazine structure VIII is the predominant one, though the 1,6-dihydro derivative IX may be present to a lesser extent. When VIIIb is oxidized to the corresponding pyridazine, the intensity of the nitrile band is markedly diminished, presumably due to the electron-withdrawing effect of the pyridazine ring. The product from the tetrazine–



VIIIa, R = $CHFCF_3$
b, R = C_6H_5

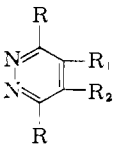


IX

styrene reaction is probably also the 1,4- and/or the 1,6-dihydropyridazine.

TABLE III

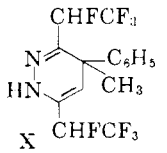
ULTRAVIOLET SPECTRA OF SUBSTITUTED PYRIDAZINES



R	R_1	R_2	λ_{max},[a] mμ	ϵ_{max}
$-CHFCF_3$	C_6H_5	H	318	430
			261	6400
			(227)	5340
$-CHFCF_3$	CH_3	H	312	300
			247.5	590
			210	6470
$-CHFCF_3$	$-CH=CH_2$	H	326	310
			252.5	9490
C_6H_5	H	H	280	29,000
C_6H_5	C_6H_5	C_6H_5	260	26,880
C_6H_5	CN	H	278	26,730
CH_3[b]	$-COOEt$	$-COOEt$	274	2290
			240.5	1820
			231	2880
OCH_3[c]	CH_3	H	283	2100
Cl[c]	H	H	305	400
			370	1300
			210	10,000
H[c]	H	H	311	308
			248	1590
			243	1650

[a] The values in parentheses refer to inflection points or shoulders. [b] W. L. Mosby, *J. Chem. Soc.*, 3997 (1957). [c] K. Eichenberger, R. Rometsch and J. Druey, *Helv. Chim. Acta*, **37**, 1298 (1954).

On the other hand, the >NH absorption at 2.93 μ of the dihydropyridazine from I and α-methyl-

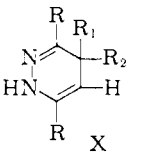


X

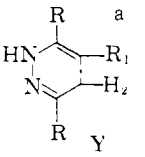
styrene is strong evidence in favor of structure X, since the possibilities of tautomerism which characterize the products from vinyl-type olefins are excluded. The ultraviolet absorption data for a number of dihydropyridazines obtained during this investigation are summarized in Table IV. These data are similar to the absorption data reported for other substituted dihydropyridazines. The absorption maxima near the 300 mμ region for most of the derivatives may be associated with the cyclic hydrazone structure shown in VII, IX or X.[6]

TABLE IV

ULTRAVIOLET SPECTRA OF SUBSTITUTED DIHYDROPYRIDAZINES



X



Y

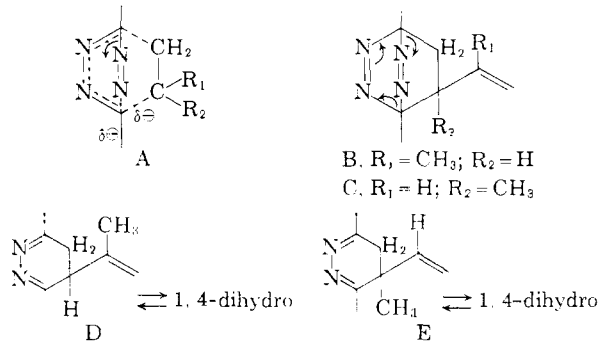
R	R_1	R_2	λ_{max}, mμ[b]	ϵ_{max}
$CHFCF_3$	$-CH=CH_2$	H	317	2300
$CHFCF_3$	$-C(CH_3)=CH_2$	H	292 (215–225)	2030
$CHFCF_3$	$-C(CH_3)=CH_2$	CH_3	304	1890
$CHFCF_3$	C_6H_5	H	292	2040
			(228)	8950
$CHFCF_3$	C_6H_5	CH_3	303 (273, 266, 259)	2050
C_6H_5	C_6H_5	H	363	7090
			(310)	7090
			240	17,890
C_6H_5	CN	H	365	7500
			263	19,950
			242	17,350
CH_3	$COOC_2H_5$	$COOC_2H_5$[c]	318	5600
			243	5370
			210	5500

[a] Structure Y is generally favored when R_2 = H. [b] The values in parentheses refer to inflection points or shoulders. [c] W. L. Mosby, *J. Chem. Soc.*, 3997 (1957).

Conjugated dienes also functioned as dienophiles. Thus, when butadiene, isoprene and 2,3-dimethylbutadiene were added to an ether solution of the fluoroalkyl tetrazine (I) at room temperature, the characteristic red color disappeared and the corresponding dihydropyridazine with an unsaturated sidechain was formed. The reaction of isoprene with 3,6-dimethyl-*sym*-tetrazine was also examined to determine which end of the unsymmetrical diene reacted. If it is assumed that the reactions described in this paper proceed by attack of the dienophile at the electron-poor 3-carbon *via* a transition state such as A, then a predominant steric effect would favor the formation of the pyridazine D with isoprene, *via* an intermediate such as B, whereas pyridazine E would be expected (*via* C) from the addition of isoprene to give the most stable carbonium ion.

Chemical and spectral evidence clearly indicated that the 4-vinyl dihydropyridazine E was formed in preponderance over the 4-isopropenyl derivative D. The infrared spectra of the dimethyltetrazine–isoprene product showed a strong peak at 11.0 μ and weaker one at 10.2 μ, which is associated with a vinyl group. Furthermore, the product could not be oxidized to the corresponding pyridazine

(6) An absorption maximum at 292 mμ (log ε 4.19) has been reported to be characteristic of hydrazones tautomeric with cyclic azo compounds; G. Fodor, *Ber.*, **76B**, 334 (1943); S. S. Cohen, THIS JOURNAL, **79**, 4400 (1957).



with potassium dichromate and acetic acid under conditions similar to those employed for the oxidation of the butadiene and styrene adducts (III → IV). Thus, attack occurs *via* the most stable carbonium ion.

Experimental[7]

3,6-Bis-(1,2,2,2-tetrafluoroethyl)-*sym*-tetrazine (I).—The preparation and properties of I, as well as of other fluoroalkyl and fluoroalkenyl-*sym*-tetrazines used in this present work have been described in an earlier paper.[2]

3,6-Diphenyl-*sym*-tetrazine (II).—1,2-Dihydro-3,6-diphenyl-*sym*-tetrazine was prepared from benzimido ethyl ester hydrochloride and hydrazine by the method of Pinner.[8] The yellow dihydro derivative was easily oxidized to the corresponding blue-red tetrazine II, m.p. 195°, lit.[7] 192°, with nitric acid in acetic acid.[2]

3,6-Dimethyl-*sym*-tetrazine.[9,10]—A mixture of 172 g. (1.4 moles) of ethyl iminoacetate hydrochloride and 400 ml. of absolute ethanol was placed in a Morton flask under a nitrogen atmosphere and cooled to −50°. A solution of 48 g. (1.5 moles) of anhydrous hydrazine in 100 ml. of absolute ethanol was added with rapid stirring over the course of 30 minutes while the temperature was maintained at −60 to −30°. The mixture was stirred at −50° for an additional 30 minutes, then at room temperature for 17 hours.

The mixture containing the dihydrotetrazine derivative was poured into a solution of 138 g. (2 moles) of sodium nitrite in 3 l. of ice-water along with 300 ml. of dichloromethane. Glacial acetic acid (100 g.) was added with stirring during 30 minutes. After an additional hour, gas evolution was complete and the blue-red organic layer was separated. The aqueous phase was extracted repeatedly with dichloromethane. The combined dichloromethane extracts were washed with 250 ml. of 5% potassium carbonate and dried over calcium chloride. Most of the dichloromethane was removed by distillation through a packed column. The deep red-purple residue was placed on a chromatography column packed with 1 kg. of activated alumina[11] and the red 3,6-dimethyltetrazine was eluted with ether. The ether was removed from the eluate by distillation through a column. Upon cooling, the residue crystallized. After recrystallization from petroleum ether, 14 g. (18%) of 3,6-dimethyltetrazine was obtained in two crops as deep-red, very volatile leaflets, m.p. 73–73.5°, lit.[10] 74°.

Reactions of 3,6-Disubstituted *sym*-tetrazines with Unsaturated Compounds.—The following procedures are typical of those employed in the preparation of pyridazine derivatives whose properties are summarized in Table II.

3,6-Bis(1,2,2,2-tetrafluoroethyl)-4-phenyl-1,4-dihydropyridazine.—To 3 g. of styrene was added gradually a solution of 1.2 g. (0.0043 mole) of 3,6-bis-(1,2,2,2-tetrafluoroethyl)-*sym*-tetrazine[2] in a mixture of diethyl ether and pentane. An immediate reaction occurred with the evolution of nitrogen and the gradual disappearance of the red tetrazine color. Toward the end of the addition, the mixture was gently heated to the boiling point to complete the reaction, and some fresh pentane was added to the warm mixture. On cooling, 0.9 g. (60%) of the colorless dihydropyridazine separated. One recrystallization from a 5:1 pentane–ether mixture gave colorless needles, m.p. 131–132.5°.

Anal. Calcd. for $C_{14}H_{10}F_8N_2$: N, 7.82; F, 42.43; mol. wt., 358. Found: N, 7.89; F, 42.12; mol. wt., 365.

3,6-Bis-(1,2,2,2-tetrafluoroethyl)-4-methyl-4-isopropenyl-1,4-dihydropyridazine.—The tetrazine I (5 g., 0.0177 mole) was added in portions to an excess (5 g.) of 2,3-dimethyl-1,3-butadiene. After each addition, a slightly exothermic reaction occurred with the evolution of nitrogen and the disappearance of the red tetrazine color. The mixture was heated at 50° for five minutes, then allowed to stand overnight at room temperature. Fractionation of the reaction product yielded 3.7 g. (62%) of a colorless liquid, b.p. 74–76° (1.1 mm.), $n^{25}D$ 1.4198.

Anal. Calcd. for $C_{12}H_{12}N_2F_8$: C, 42.86; H, 3.60; N, 8.33; F, 45.21. Found: C, 43.10; H, 3.56; N, 8.86; F, 45.36.

3,6-Diphenyl-5-cyano-1,4-dihydropyridazine.—Ten grams (0.043 mole) of 3,6-diphenyl-*sym*-tetrazine was heated with an excess of acrylonitrile in toluene at 100° for five days. The red-violet color of the tetrazine diminished appreciably during this period. On cooling the mixture a crop (6.1 g.) of yellow crystals separated, m.p. 190–191°.

Anal. Calcd. for $C_{17}H_{13}N_3$: C, 78.74; H, 5.05; N, 16.21. Found: C, 78.44; H, 5.04; N, 15.95.

When the mother liquor was concentrated and cooled, an additional 1.07 g. of the same product was obtained (total yield 64%).

3,4,5,6-Tetraphenylpyridazine.—A mixture of 1 g. (0.0043 mole) of 3,6-diphenyl-*sym*-tetrazine, 0.85 g. (0.0047 mole) of diphenylacetylene and 25 ml. of toluene was heated at reflux for three days. The solution, which had lost its red color, was concentrated and cooled. There was obtained 1.15 g. (86%) of colorless tetraphenylpyridazine, m.p. 196–197°.

Anal. Calcd. for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.33; H, 5.36; N, 7.32.

3,6-Diphenyl-4-cyanopyridazine.—The following example illustrates the procedure employed for the oxidation of the dihydro derivatives to the corresponding pyridazines. A mixture of 2.6 g. (0.01 mole) of 3,6-diphenyl-5-cyano-1,4-dihydropyridazine and 1.2 g. (1 oxygen equivalent) of potassium dichromate dihydrate in 50 ml. of acetic acid and 10 ml. of water was heated at 100° for 1 hour. On cooling the solution there was obtained 2.2 g. (85% yield) of 3,6-diphenyl-4-cyanopyridazine, m.p. 162–163°.

Anal. Calcd. for $C_{17}H_{11}N_3$: N, 16.33. Found: N, 15.94.

The NH peak present in the infrared spectra of the dihydropyridazine was absent in that of the oxidized product.

WILMINGTON 98, DELA.

(7) All melting points are uncorrected.

(8) A. Pinner, *Ann.*, **297**, 221 (1897); *Ber.*, **26**, 2128 (1893).

(9) We are indebted to Dr. J. K. Williams for this preparation.

(10) 3,6-Dimethyl-1,2-dihydro-*sym*-tetrazine was prepared in 5% yield by Th. Curtius, A. Darapsky and E. Müller, *Ber.*, **48**, 1614 (1915), by heating acetonitrile and anhydrous hydrazine in alcohol for several days. The corresponding tetrazine, m.p. 74°, was subsequently obtained by oxidation.

(11) Woelm anionotropic, activity grade I aluminum oxide was employed.