Thermolysis of Substituted 1-Acetoxybenzotriazoles. Carbon-to-Oxygen Migration of an Alkyl Group

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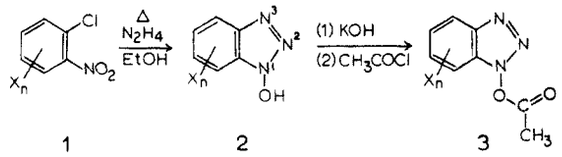
In examining the pyrolysis of 1-acetoxybenzotriazoles (**3**), it was found that tetrachloro substitution moderated the reaction favorably. At 350–400° under vacuum, 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole (**4a**) gave a primary product with spectral properties suggestive of 2-methoxy-3,4,5,6-tetrachlorophenylisocyanate (**5a**), which was identified chemically by conversion with methanol into the carbamate (**6a**) and by ammonia to the correspondingly substituted urea (**7a**). The unique translocation of the R group of the original ester to alkoxy in the product was checked by variation in R and by variation in the alcohol (R'OH) used to convert the primary product into carbamate. The possible mechanism of the new rearrangement has been investigated using carbonyl-^{18}O-labeled 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole (**10**), whereby it was established that the carbonyl oxygen appears in the methoxy group (**12**), suggesting a pathway such as **4** → **8** → **9** → **5**. Suitable controls were applied to show that the oxygens in **10** did not become equivalent. The position of the oxygen-18 was determined by the mass spectral fragmentation of labeled product **7a**.

In connection with the study of azirines,[1-3] the irradiation of substituted benzotriazoles[4] suggests a route to benzazirines, which have not yet been isolated but have been postulated as intermediates.[5,6] In the related formation of benzocyclopropenes from substituted 3H-indazoles and in the thermal rearrangement of the latter, diradical intermediates have been detected.[7] We were guided by these precedents and also by the reported oxidation of 1-aminobenzotriazoles with lead tetraacetate, which results in nitrogen evolution and benzyne-derived products.[8]

As generators of diradical (or possibly carbene) intermediates the 1-hydroxybenzotriazoles appeared to offer an advantage since they are already at an oxidation level which should facilitate the liberation of gas (N_2, N_2O, H_2O) on heating. Descriptions of 1-hydroxybenzotriazoles as explosive[9-11] support this judgment. The synthesis of substituted 1-hydroxybenzotriazoles (**2**) was accomplished by the general method[12-15] of heating the appropriately substituted *o*-nitrohalobenzene (**1**) with hydrazine hydrate in ethanol under reflux. In this manner, the following compounds were made: 1-hydroxybenzotriazole,[12,15] 4,5-dichloro-1-hydroxybenzotriazole, 5,6-dichloro-1-hydroxybenzotriazole,[14] 1-hydroxy-4,5,6-trichlorobenzotriazole, 1-hydroxy-4,6,7-trichlorobenzotriazole, 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole, and 6-bromo-1-hydroxybenzotriazole. The increasing degree of chlorine substitution in this series was intended to moderate the thermal decomposition and to stabilize



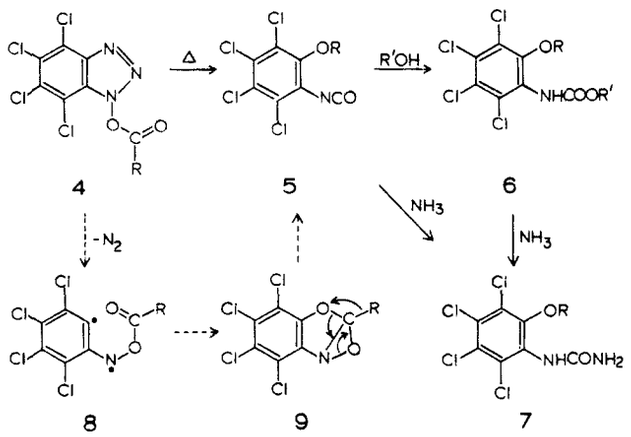
1 2 3

the benzene ring toward rearrangement, especially since such substitution had been employed favorably in thermal cyclization reactions involving loss of nitrogen from 3,4,5,6-tetrachlorobenzo-2-diazo 1-oxide.[16] However, attempts to control the thermal decomposition process of these compounds were not successful. All of the substituted 1-hydroxybenzotriazoles decomposed violently at 200–210° to carbonaceous material.

Further modification was therefore sought by means of the acetylation of the 1-hydroxybenzotriazoles. The general procedure,[14] which involved the formation and isolation of the potassium salt and then reaction of the salt with acetyl chloride in acetone, produced the seven 1-acetoxybenzotriazoles (**3**) corresponding to the 1-hydroxybenzotriazoles listed above. Two features regarding spectroscopic properties in this series are of special interest. The infrared maximum corresponding to the C=O stretch was found at relatively high frequency, within the range 1795–1825 cm^{-1} in Nujol. The absorption frequencies for the model compounds acetone oxime O-acetate and benzophenone oxime O-acetate, 1773 and 1782 cm^{-1},[17] respectively, are confirmatory for the structure of the 1-acetoxybenzotriazoles (**3**) and indicative of the electron-withdrawing power of the heterocyclic ring system. The proton magnetic resonance corresponding to the acetate methyl group was relatively invariant, τ 7.43–7.48 ($CDCl_3$), for all of the 1-acetoxybenzotriazoles unsubstituted on the 7 position, whereas the τ value for the methyl protons of 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole (**4a**) was 7.86 ppm. In this compound, because of the bulky 7 substituent, conformations in which the acetoxy group lies above (or below) the plane of the aromatic ring system are probably favored on a time average and hence the protons

(1) N. J. Leonard and B. Zwanenburg, *J. Amer. Chem. Soc.*, **89**, 4456 (1967).
(2) N. J. Leonard, E. F. Muth, and V. Nair, *J. Org. Chem.*, **33**, 827 (1968).
(3) V. Nair, *ibid.*, **33**, 2121 (1968).
(4) E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, **90**, 1923 (1968).
(5) M. Appl and R. Huisgen, *Ber.*, **92**, 2961 (1959).
(6) R. Huisgen and M. Appl, *ibid.*, **91**, 12 (1958).
(7) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967), and references therein.
(8) (a) C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 296 (1964); (b) *Chem. Commun.*, 192 (1965); (c) C. W. Rees and R. C. Storr, *ibid.*, 193 (1965).
(9) H. Goldstein and R. Voegeli, *Helv. Chim. Acta*, **26**, 475 (1943).
(10) B. Vis, *Rec. Trav. Chim. Pays-Bas*, **58**, 847 (1939).
(11) A. Mangini, *Gazz. Chim. Ital.*, **66**, 675 (1936).
(12) T. Zincke and P. Schwarz, *Ann.*, **311**, 329 (1900).
(13) R. Nietzki and E. Braunschweig, *Ber.*, **27**, 3381 (1894).
(14) E. Müller and W. Hoffmann, *J. Prakt. Chem.*, **111**, 293 (1925).
(15) E. Müller and G. Zimmermann, *ibid.*, **111**, 277 (1925).
(16) (a) R. Huisgen, G. Binsch, and H. König, *Chem. Ber.*, **97**, 2868 (1964); (b) *ibid.*, **97**, 2884, 2893 (1964).
(17) O. Exner and M. Horák, *Chem. Listy*, **52**, 1613 (1958).

SCHEME I



a, R=CH_3, R'=CH_3; b, R=CH_3, R'=C_2H_5; c, R=C_2H_5, R'=CH_3

experience a shielding effect compared with the methyl protons in the other compounds. 1-Acetoxy-4,5,6,7-tetrachlorobenzotriazole, which was selected as the prototype for the thermal decomposition study, was also prepared unequivocally by the action of ketene on 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole in acetone at 0°.

The pyrolysis of 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole, $C_8H_3Cl_4N_3O_2$ (**4a**), was carried out *in vacuo* by subliming the compound into an area heated at about 400° (Scheme I). The crude pyrolysis product was obtained as an oil, the most characteristic spectral feature of which was a very strong infrared absorption band at 2220 cm^{-1} suggestive of an isocyanate grouping. The band was retained after partial purification of the oil by vacuum distillation.

Reaction with methanol furnished a crystalline product, $C_9H_7Cl_4NO_3$, corresponding to loss of nitrogen and addition of the elements of methanol to the original **4a**. The infrared maximum at 1725 cm^{-1} ($CHCl_3$) was indicative of a carbamate grouping, and the seven hydrogens per molecule were fully accounted for in the nmr spectrum, which showed two singlets at τ 6.10 and 6.19 ($CDCl_3$) of three hydrogens each, characteristic of CH_3O, and one exchangeable proton at 3.57, characteristic of NH. The feature at first surprising was the indication of *two* methoxyl groups; however, one methoxyl group was already indicated in the suspected isocyanate precursor by the strong nmr signal at τ 6.02. The second methoxyl was obviously introduced in the conversion of isocyanate to methyl carbamate. The mass spectrum of the product resulting from pyrolysis followed by methanol treatment was confirmatory of the $C_9H_7Cl_4NO_3$ formula, showing peaks at *m/e* 317 (M^+), 319 $(M + 2)^+$, and 321 $(M + 4)^+$ in relative abundances 1.00:1.25:0.65, which are close to the expected ratios (1:00:1.31:0.64) for a Cl_4-containing molecule.[18] The mass spectral fragmentation pattern included the loss of Cl· [*m/e* 282 $(M - 35)^+$, 284 $[(M + 2) - 35]^+$, and 286 $[(M + 4) - 35]^+$, in relative abundance 1.00:1.00:0.40 (close to theoretical for a Cl_3-containing fragment, 1.00:1.00:0.32)];[18] the loss of CH_3O· [286 $(M - 31)^+$, 288 $[(M + 2) - 31]^+$, and 290 $[(M + 4) - 31]^+$; the loss of CH_3OH: 285 $(M - 32)^+$, 287 $[(M + 2) - 32]^+$, and 289 $[(M + 4) - 32]^+$; and the loss of ·$COOCH_3$ [258 $(M - 59)^+$, 260 $[(M + 2) - 59]^+$, and 262 $[(M + 4) - 59]^+$, *inter alia*. These analytical and spectroscopic features limited the structure to that of methyl *N* - (2 - methoxy - 3,4,5,6 - tetrachlorophenyl)-carbamate (**6a**), which in turn required that the initial pyrolysis product, which posessed tetrachlorophenyl, methoxyl, and isocyanate groupings, be 2-methoxy-3,4,5,6-tetrachlorophenylisocyanate (**5a**).

Treatment of the pyrolysis product in methylene chloride with ammonia yielded a urea derivative identical with the compound $C_8H_6Cl_4N_2O_2$ obtained from the carbamate **6a** and methanolic ammonia under pressure, hence N-(2-methoxy-3,4,5,6-tetrachlorophenyl)-urea (**7a**). The elemental analysis and the infrared spectrum were in accord with this assignment. The mass spectrum, which provided further confirmation of the structure, was also useful in delineating the mechanism of the pyrolytic rearrangement, as will be described in detail subsequently. When the pyrolysis product from **4a** was treated with ethanol in place of methanol the corresponding ethyl carbamate derivative was obtained, as indicated by the infrared spectrum and by conversion to the substituted urea **7a** with ammonia in ethanol under pressure.

In order to provide independent confirmation that the R group initially attached to carbonyl in **4** ends up on the ether oxygen in **5**, the pyrolysis of 1-propionoxy-4,5,6,7-tetrachlorobenzotriazole (**4c**) was investigated under the same conditions. The crude pyrolysis product showed infrared absorption at 2220 cm^{-1} typical for isocyanate. Treatment with methanol converted it into a carbamate ($\nu_{max}^{CHCl_3}$ 1740 cm^{-1}) of molecular formula $C_{10}H_9Cl_4NO_3$. The nmr spectrum exhibited a singlet at τ 6.20 ($CDCl_3$) characteristic of CH_3O and a triplet–quartet combination at 8.60, 5.90 indicative of CH_3CH_2O, with a broad signal at 3.47 for NH. The structural assignment as methyl N-(2-ethoxy-3,4,5,6-tetrachlorophenyl)carbamate (**6c**) was confirmed chemically by conversion with ammonia to a urea derivative, $C_9H_8Cl_4N_2O_2$, which still possessed the ethoxyl group, hence N-(2-ethoxy-3,4,5,6-tetrachlorophenyl)urea (**7c**). The formula and structure of **6c** were also confirmed by the mass spectrum, which showed peaks at *m/e* 331 (M^+), 333 $(M + 2)^+$, and 335 $(M + 4)^+$ in relative abundances 1.00:1.27:0.62,[18] respectively. The mass spectral fragmentation pattern included the loss of C_2H_4 [*m/e* 303 $(M - 28)^+$, 305 $[(M + 2) - 28]^+$, and 307 $[(M + 4) - 28]^+$ in relative abundances 1.00:1.27:0.61]; the loss of Cl· [296 $(M - 35)^+$, 298 $[(M + 2) - 35]^+$, 300 $[(M + 4) - 35]^+$ in relative abundances 1.00:0.91:0.32]; and the loss of ·$COOCH_3$ $(M - 59)^+$, of $CO_2 + CH_2$ $(M - 58)^+$, and of C_2H_4 + ·$COOCH_3$ $(M - 87)^+$, although departure from the theoretical abundance ratios[18] for the +2 and +4 peaks in the last three cases indicates the presence of some double peaks, *i.e.*, alternate fragmentation processes.

Tetrachloro-*o*-anisidine, mp 90–91°, prepared by chlorination of *o*-methoxyacetanilide,[19] was treated with phosgene and triethylamine in benzene solution.

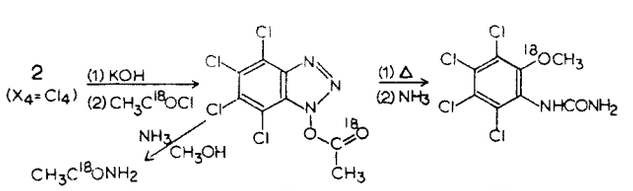
(18) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 17.

(19) E. Bureš and B. Havlínová, *Časopis Českoslov. Lékárnictva*, **9**, 101 129, 153 (1929); *Chem. Zentr.*, II, 1402 (1929).

Reaction of the resulting 2-methoxy-3,4,5,6-tetrachlorophenyl isocyanate (**5a**), ν_{max} 2220 cm^{-1}, with methanol gave authentic methyl N-(2-methoxy-3,4,5,6-tetrachlorophenyl) carbamate (**6a**) (70% yield), mp 181–182°, identical in all respects with the product obtained *via* the pyrolysis of **4a** (→ **5a** → **6a**). By this independent synthesis the structures of all of the compounds under consideration have been fully secured.

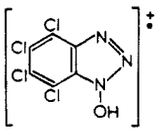
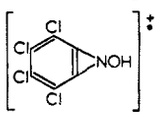
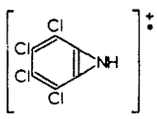
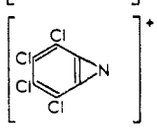
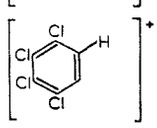
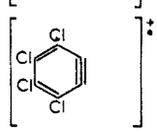
The mechanism of the thermal rearrangement, **4** → **5**, is of interest especially since it involves the unique translocation of the R group in the original ester to alkoxy in the product. A logical initiation of the process would be by loss of nitrogen to give the diradical **8**.[4-7,20] Rehybridization and electron pairing could lead to the strained intermediate **9**, which is a bicyclic oxaziridine. Rearrangements of oxaziridines are well documented,[21-23] and the N–O bond is usually expected to cleave first under conditions of high temperature, although C–O bond cleavage has also been observed. Formation of product **5** can be envisaged as resulting from migration of the alkyl group from carbon to oxygen and sequential or concerted bond cleavage and bond formation shown in **9**. The representations in **8** and **9** are not to be considered restrictive, especially since the homolytic *vs.* heterolytic details of the process are not available. If the thermal rearrangement followed the pathway indicated, it can be seen that the carbonyl oxygen of 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole (**4a**) would appear in the methoxyl group of the isocyanate **5a**. This is subject to test by ^{18}O labeling.

First we examined the mass spectra of the rearranged products **6** and **7** to decide which compound would offer the better fragmentation pattern to enable us to locate ^{18}O. After careful study of all the spectra obtained we decided to follow the rearrangement from carbonyl-^{18}O-labeled 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole (**10**) to the corresponding ^{18}O-labeled N-(2-methoxy-3,4,5,6-tetrachlorophenyl)urea. Treatment of the potassium salt of 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole **2** (X_n = Cl_4) with acetyl-^{18}O chloride, 90% enrichment, yielded **10**. The mass spectrum was first compared with that (see Figure 1) of unlabeled material (**4a**), which showed peaks at *m/e* 313 (M^+), 315 $(M + 2)^+$, and 317 $(M + 4)^+$, in relative abundances 1.00:1.24:0.67, corresponding to the molecular ion(s) of a Cl_4-containing molecule.[18] The major fragment ions may be rationalized as shown in Table I. The mass spectrum of carbonyl-^{18}O-labeled 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole (**10**) exhibited similar major fragments (see Figure 2), but calculations based on relative abundances for a Cl_4-containing molecule suggested the presence of $C^{18}OCH_3$, $C^{18}OCH_2D$, $C^{18}OCHD_2$, and $C^{18}OD_3$ moieties and of minor oxygen-16 components, mainly $C^{16}OCHD_2$ and $C^{16}OCD_3$.



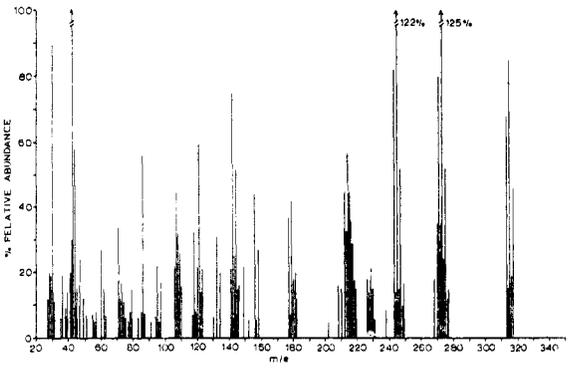
(20) W. Kirmse and L. Horner, *Ann.*, **614**, 1 (1958).
(21) L. S. Kaminsky and M. Lamchen, *J. Chem. Soc.*, 2128 (1967).
(22) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957).
(23) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **30**, 3427 (1965).

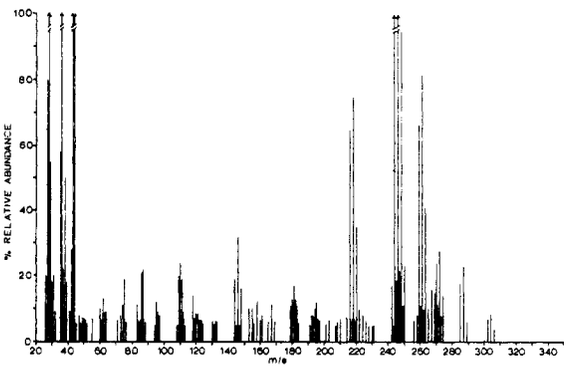
TABLE I
FRAGMENTATION OF
1-ACETOXY-4,5,6,7-TETRACHLOROBENZOTRIAZOLE (**4a**) AT 70 eV

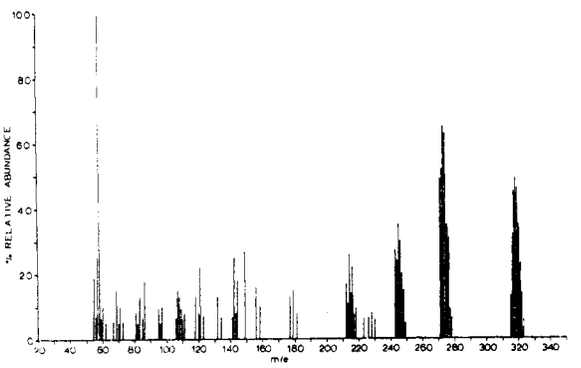
	m/e		Relative abundance
	271	$(M - 42)^+$	1.00
	273	$[(M + 2) - 42]^+$	1.25
	275	$[(M + 4) - 42]^+$	0.65
	CH_2CO = 42		
	243	$(M - 70)^+$	1.00
	245	$[(M + 2) - 70]^+$	1.22
	247	$[(M + 4) - 70]^+$	0.63
	$CH_2CO + N_2$ = 70		
	227	$(M - 86)^+$	1.00
	229	$[(M + 2) - 86]^+$	1.07
	231	$[(M + 4) - 86]^+$	0.39
	$CH_2CO + N_2 + O$ = 86		
	226	$(M - 87)^+$	1.00
	228	$[(M + 2) - 87]^+$	1.16
	230	$[(M + 4) - 87]^+$	0.83
	$CH_2CO + N_2 + OH$ = 87		
	213	$(M - 100)^+$	1.00
	215	$[(M + 2) - 100]^+$	1.34
	217	$[(M + 4) - 100]^+$	0.86
	$CH_2CO + N_2 + NO$ = 100		
	212	$(M - 101)^+$	1.00
	214	$[(M + 2) - 101]^+$	1.27
	216	$[(M + 4) - 101]^+$	0.80
	$CH_2CO + N_2 + NOH$ = 101		

At this stage a check was made to ascertain whether the oxygen-18 enrichment was contained only in the carbonyl function of the 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole and that no mechanism was readily available for translocation of the label in the ether oxygen. The oxygen-18-labeled compound was ammonolyzed using ammonia in methanol, giving 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole and acetamide. The mass spectrum of the former at 13.5 eV showed M (271), M + 2, M + 4, and M + 6 positive ions in the ratio of 1.00:1.30:0.65:0.27 relative abundance. For comparison, the mass spectrum at 14 eV of unlabeled 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole showed M (271), M + 2, M + 4, and M + 6 positive ions in the ratio of 1.00:1.30:0.66:0.30 relative abundance, indicating that the 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole portion of the oxygen-18-labeled acetate did not contain the heavy isotope. That the label was still at the site of the carbonyl oxygen in the acetate was confirmed by the mass spectrum of the acetamide ammonolysis product (**11**), which gave prominent peaks at *m/e* 44 (15%), 46 (>100), 61 (17), 62 (47), 63 (49), 64 (20), compared with unlabeled acetamide similarly formed: *m/e* 44 (100%), 59 (75), 60 (25).

The mass spectrum of N-(2-methoxy-3,4,5,6-tetrachlorophenyl)urea (**7a**) showed peaks at *m/e* 302 (M^+), 304 $(M + 2)^+$ and 306 $(M + 4)^+$, in relative abundances 1.00:1.21:0.57 (see Figure 3). The major fragment ions containing oxygen are at $(M - 32)^+$, $(M - 43)^+$, $(M - 44)^+$, and $(M - 58)^+$. The last three have retained only one oxygen, which is the one attached to the aromatic ring, barring unprecedented rearrangements. It will be seen from Table II that the +2 and +4 fragments in each case provide an internal check, by means of the abundance ratios compared with the







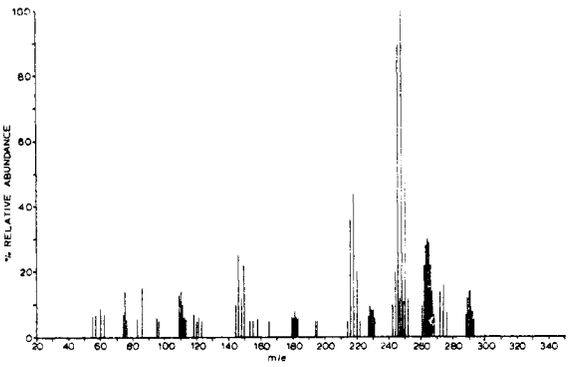
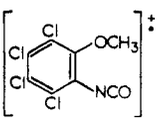
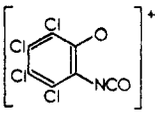
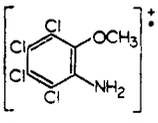
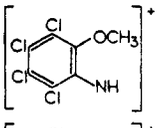
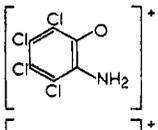
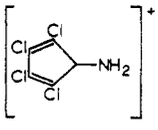


Figure 1 (upper left).—Mass spectrum of 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole (**4a**) at 70 eV.
Figure 2 (lower left).—Mass spectrum of carbonyl-^{18}O-labeled 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole (**10**) at 70 eV.
Figure 3 (upper right).—Mass spectrum of N-(2-methoxy-3,4,5,6-tetrachlorophenyl)urea (**7a**) at 70 eV.
Figure 4 (lower right).—Mass spectrum of ^{18}O-labeled N-(2-methoxy-3,4,5,6-tetrachlorophenyl)urea (**12**) at 70 eV.

TABLE II

FRAGMENTATION OF N-(2-METHOXY-3,4,5,6-TETRACHLOROPHENYL)UREA (**7a**) AT 70 eV

	m/e	Relative abundance	
	285	$(M - 17)^+$	1.00
	287	$[(M + 2) - 17]^+$	1.28
	289	$[(M + 4) - 17]^+$	0.30
	$NH_3 = 17$		
	270	$(M - 32)^+$	1.00
	272	$[(M + 2) - 32]^+$	1.16
	274	$[(M + 4) - 32]^+$	0.58
	$NH_3 + CH_3 = 32$		
	259	$(M - 43)^+$	1.00
	261	$[(M + 2) - 43]^+$	1.22
	263	$[(M + 4) - 43]^+$	0.61
	HNCO = 43		
	258	$(M - 44)^+$	1.00
	260	$[(M + 2) - 44]^+$	1.37
	262	$[(M + 4) - 44]^+$	1.25
	$H_2NCO = 44$		
	244	$(M - 58)^+$	1.00
	246	$[(M + 2) - 58]^+$	1.00
	248	$[(M + 4) - 58]^+$	0.90
	$HNCO + CH_3 = 58$		
	216	$(M - 86)^+$	1.00
	218	$[(M + 2) - 86]^+$	1.15
	220	$[(M + 4) - 86]^+$	0.54
	$HNCO + CH_3 + CO = 86$		

theoretical ratios (1.00:1.31:0.64) for Cl_4-containing units, as to whether the fragment pictured is solely or partly responsible for the *m/e* values observed. The molecular ion peak for the ^{18}O-labeled N-(2-methoxy-3,4,5,6-tetrachlorophenyl)urea, which was obtained from carbonyl-^{18}O-labeled 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole (**10**), was diffuse (304–309) because of the presence of deuterated species as in the starting material **10**. Moreover, the $(M - 17)^+$ peaks suffered from the same difficulty in attempted analysis. In the case where the fragment ion contained no hydrogen (or deuterium), as in $(M - 32)^+$, corresponding to the loss of NH_3 and $CH_3\cdot$ (see Table II), the relative abundance ratios for *m/e* 272, 274, and 276 of 1.00:1.14:0.53 provided a reasonably accurate indication that one of the two oxygens present in the fragment ion was ^{18}O. The $(M - 43)^+$ peak corresponding to loss of HNCO from the parent ion was diffuse (261–268) due to the presence of deuterium in this fragment, but if $HNC^{18}O$ had been lost there should have been a strong peak at $(M - 45)^+$ (Figure 4), or *m/e* 259. Since the peak at *m/e* 259 was only 3.5% in relative abundance (100% for base peak), this provides strong indication that the ^{18}O label was not lost from the major fragment but was retained on the aromatic ring. The main proof for the ^{18}O atom being attached to the aromatic ring came from the fact that the $(M - 58)^+$ fragment ion (see Table II) contained ^{18}O (*ca.* 10:1 over ^{16}O) and showed satisfactory relative abundance ratios for *m/e* 246, 248, and 250 of 1.00:1.11:0.54. Additionally, in the mass spectrum of the unlabeled urea product **7a** (Table II) there were peaks corresponding to $[(M - 58) - 28]^+$. It was unknown initially whether the 28 loss was due to CO or CNH_2. In the mass spectrum of the oxygen-18-labeled urea product the main peaks appeared at $[(M - 58) - 30]^+$. Thus the 30 loss can only be due to $C^{18}O$, giving *m/e* 216, 218, and 220 in the relative abundance ratios of 1.00:1.24:0.66.

TABLE III

SUBSTITUTED 1-HYDROXYBENZOTRIAZOLES (2)

Compound[a]	Registry no.	Mp, °C[b]	Yield, %	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
1-Hydroxybenzotriazole[e]		158	90	$C_6H_5N_3O$						
4,5-Dichloro-1-hydroxybenzotriazole	18355-00-5	213	85	$C_6H_3Cl_2N_3O$	35.32	1.48		35.35	1.47	
5,6-Dichloro-1-hydroxybenzotriazole		210[c]	66	$C_6H_3Cl_2N_3O$						
1-Hydroxy-4,5,6-trichlorobenzotriazole	18355-01-6	210	67	$C_6H_2Cl_3N_3O$	30.22	0.84		30.34	1.03	
1-Hydroxy-4,6,7-trichlorobenzotriazole	18355-02-7	210	6[d]	$C_6H_2Cl_3N_3O$	30.22	0.84	17.62	30.24	0.84	17.53
1-Hydroxy-4,5,6,7-tetrachlorobenzotriazole	18226-02-3	213	40	$C_6HCl_4N_3O$	26.40	0.37	15.39	26.35	0.58	15.64
6-Bromo-1-hydroxybenzotriazole	18355-04-9	208–209	66	$C_6H_4BrN_3O$	33.68	1.88	19.63	33.60	2.06	19.31

[a] All colorless needles. [b] All melt with violent decomposition. [c] Lit.[14] mp 194–196°. [d] The main product was 2,3,5,6-tetrachlorophenylhydrazine. [e] See ref 12 and 15.

TABLE IV

SUBSTITUTED 1-ACETOXYBENZOTRIAZOLES (3)

Compound[a]	Registry no.	Mp, °C	Yield, %	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Ir[b] $\nu_{C=O}$, cm^{-1}	Nmr[c] CH_3, τ
1-Acetoxybenzotriazole	18355-05-0	104–105	62	$C_8H_7N_3O_2$	54.22	3.98	54.57	4.06	1805	7.48
1-Acetoxy-4,5-dichlorobenzotriazole	18355-06-1	116.5–117.5	74	$C_8H_5Cl_2N_3O_2$	39.06	2.09	39.10	2.12	1795	7.45
1-Acetoxy-5,6-dichlorobenzotriazole		150.5–151.5[d]	70	$C_8H_5Cl_2N_3O_2$					1800	7.47
1-Acetoxy-4,5,6-trichlorobenzotriazole	18355-07-2	174	50	$C_8H_4Cl_3N_3O_2$	34.25	1.44	34.30	1.71	1805	7.43
1-Acetoxy-4,6,7-trichlorobenzotriazole	18355-08-3	119.5–120.5	48	$C_8H_4Cl_3N_3O_2$	34.25	1.44	34.29	1.58	1825	
1-Acetoxy-4,5,6,7-tetrachlorobenzotriazole		197.5–199.5	71	$C_8H_3Cl_4N_3O_2$	30.51	0.96	30.36	0.79	1825	7.86
1-Acetoxy-6-bromobenzotriazole	18355-10-7	135	60	$C_8H_6BrN_3O_2$	37.52	2.36	37.52	2.34[e]	1815	7.45

[a] All colorless needles. [b] Nujol mull. [c] $CDCl_3$ containing TMS. [d] Lit.[14] mp 150°. [e] Calcd for N, 16.41. Found: N, 16.69.

With the oxygen-18-labeled N-(2-methoxy-3,4,5,6-tetrachlorophenyl)urea definitely established as possessing structure **12**, any mechanism to be satisfactory must account for the facts that the oxygens in the original 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole retain their nonequivalence during the thermolysis process and that the carbonyl oxygen ends up attached to the aromatic ring in the ether function. The product structures also require alkyl migration from the original carbonyl carbon to the final ether oxygen. The formal sequence which we have proposed, *i.e.*, **4 → 8 → 9 → 5**, fully satisfies these requirements, but it cannot be regarded as exclusive since other sequences may be devised which are satisfactory to varying extents. It should be emphasized that we have accounted for the structure and have offered a possible route of formation of the compound, 2-methoxy-3,4,5,6-tetrachlorophenyl isocyanate, which makes up about 50% of the crude thermolysis product of 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole. The spectral characteristics of the crude product indicate the presence of additional materials which suggest the operation of alternative pathways following the initial triazole ring opening[4] and rearrangements of the kind encountered with oxaziridines.[21]

Experimental Section[24]

General Synthesis of Substituted 1-Hydroxybenzotriazoles (2).—The appropriate chloronitrobenzene (5 g) was dissolved in 15–20 ml of hot ethanol, and 5 g of 85% hydrazine hydrate was added. The mixture was heated under reflux for 3 hr and cooled. The precipitate was filtered, dissolved in hot water, and the 1-hydroxybenzotriazole derivative was precipitated with hydrochloric acid. The crude product was decolorized with charcoal and recrystallized from 50% ethanol or methanol. In the reaction of hydrazine hydrate with 2,5-dibromonitrobenzene, the reflux period was 5 hr. With pentachloronitrobenzene, benzene was added to the reaction mixture to retain solubility. Following the reflux period, the solvents were evaporated *in vacuo*, 50 ml of 5% aqueous potassium hydroxide was added, the undissolved pentachlorophenylhydrazine was removed by filtration, and 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole was precipitated with concentrated hydrochloric acid. The properties of the substituted 1-hydroxybenzotriazoles are shown in Table III.

In the reaction of 5 g of 2,3,5,6-tetrachloronitrobenzene with 5 g of hydrazine hydrate in 15 ml of ethanol, after a reflux period of 1 hr, the mixture solidified. The precipitate, which was filtered and washed with ethanol and ether, was a mixture of 2,3,5,6-tetrachlorophenylhydrazine and the hydrazine salt of 1-hydroxy-4,6,7-trichlorobenzotriazole, yield 3.16 g. When the crude mixture (250 mg) was heated at 0.5 mm and 130–135°, the **2,3,5,6-tetrachlorophenylhydrazine** sublimed, mp 173–173.5°, yield 180 mg.

Anal. Calcd for $C_6H_4Cl_4N_2$: C, 29.27; H, 1.62; N, 11.38. Found: C, 29.31; H, 1.73; N, 11.52.

The residue remaining after sublimation (30 mg) was recrystallized from ethanol, yielding the **hydrazine salt of 1-hydroxy-4,6,7-trichlorobenzotriazole,** mp 206–207°.

Anal. Calcd for $C_6H_6Cl_3N_5O$: C, 26.64; H, 2.23; N, 25.89. Found: C, 26.98; H, 2.34; N, 25.98.

General Procedure for Acetylation of the Substituted 1-Hydroxybenzotriazoles.—The substituted 1-hydroxybenzotriazole (5 g) was dissolved in 50 ml of ethanol and treated with 20 ml of an ethanol solution containing an equimolar amount of potassium hydroxide. The crystallized potassium salt of 1-hydroxybenzotriazole was filtered, dried, and used without further purification. In several cases the ethanolic solution had to be concentrated to cause precipitation of the potassium salt. To a suspension of 0.01 mol of the potassium salt in 30 ml of anhydrous acetone was then added 0.012 mol of acetyl chloride. The mixture was heated under reflux for 30 min and poured into 1.5 l. of ice water. The acetyl derivative was collected by filtration, dried, and recrystallized from benzene. It could be reconverted into the 1-hydroxy compound by treatment with aqueous ammonia in methanol. The properties of the acetoxy derivatives are shown in Table IV.

1-Propionoxy-4,5,6,7-tetrachlorobenzotriazole (4c).—The propionate ester of 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole was

(24) All melting points are corrected; boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer grating spectrophotometer, Model 337. Nmr spectra were obtained on a Varian Associates Model A-60 spectrometer using tetramethylsilane (TMS) as an internal standard. We are indebted to Mr. R. Thrift for these determinations, to Mr. J. Nemeth and his associates for the microanalyses, and to Mr. Joseph Wrona for the mass spectra determinations using an Atlas Model CH_4 low resolution spectrometer.

obtained similarly to the acetate ester. The crude product was purified by recrystallization from petroleum ether (bp 40–60°), colorless needles: mp 122–123°, yield 50%; ν_{max}^{Nujol} 1820 cm^{-1} (C=O); nmr ($CDCl_3$) τ 8.58 (t, CH_3), 7.09 (q, CH_2).

Anal. Calcd for $C_9H_5Cl_4N_3O_2$: C, 32.86; H, 1.53; N, 12.77. Found: C, 32.94; H, 1.66; N, 13.06.

1-Ethoxycarbonyloxy-4,5,6,7-tetrachlorobenzotriazole was made in a similar manner from the potassium salt of 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole and ethyl chloroformate and was recrystallized from benzene–hexane, colorless needles: mp 100°, yield 86%; ν_{max}^{Nujol} 1810 cm^{-1} (C=O); nmr ($CDCl_3$) τ 8.50 (t, CH_3), 5.42 (q, CH_2).

Anal. Calcd for $C_9H_5Cl_4N_3O_3$: C, 31.33; H, 1.46; N, 12.18. Found: C, 31.39; H, 1.43; N, 12.17.

1-Methoxy-4,5,6,7-tetrachlorobenzotriazole.—1-Hydroxy-4,5,6,7-tetrachlorobenzotriazole (2.0 g, 7.3 mmol) was dissolved in 20 ml of hot ethanol. A solution of 0.44 g of potassium hydroxide in 10 ml of ethanol was added, followed by 2.0 g of methyl iodide. As the suspension was heated under reflux for 2 hr the solid gradually went into solution. When the solution was cooled the precipitate which formed was collected by filtration, washed with water, and recrystallized from ethanol, colorless needles: mp 139–140°, yield 1.42 g (67%); nmr ($CDCl_3$) τ 5.50.

Anal. Calcd for $C_7H_3Cl_4N_3O$: C, 29.30; H, 1.05; N, 14.64. Found: C, 29.16; H, 1.06; N, 14.73.

1-Ethoxy-4,5,6,7-tetrachlorobenzotriazole.—A similar procedure using excess ethyl iodide and a reflux time of 3 hr produced the ethyl ether, colorless needles: mp 105–106°; yield 66%; nmr ($CDCl_3$) τ 8.43 (t, CH_3), 5.27 (q, CH_2).

Anal. Calcd for $C_8H_5Cl_4N_3O$: C, 31.93; H, 1.67; N, 13.96. Found: C, 31.91; H, 1.82; N, 14.13.

Pyrolysis of 1-Acetoxy-4,5,6,7-tetrachlorobenzotriazole (4a).—The pyrolysis *in vacuo* was effected in a vertical tube, the lower part of which was a sublimation area heated at 200–210° and the upper part, a decomposition area filled with Pyrex wool and heated at 400°. The top of the tube was bent horizontally and through it the products were vented into a cooled flask for collection. The side arm of the flask was evacuated at 0.025 mm. From 600 mg (1.9 mmol) of 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole was obtained 120–130 mg of crude pyrolysis product as an oil, ν_{max}^{film} 2220 cm^{-1}. While an attempt to purify the oil by freezing at −70° was unsuccessful, distillation *in vacuo* was partially successful. The distillate retained the infrared band at 2220 cm^{-1} and the analysis was indicative of, but not fully satisfactory for, the elemental composition $C_8H_3Cl_4NO_2$, corresponding to **2-methoxy-3,4,5,6-tetrachlorophenylisocyanate (5a)**.

Anal. Calcd for $C_8H_3Cl_4NO_2$: C, 33.49; H, 1.05; N, 4.88. Found: C, 34.93; H, 1.20; N, 5.10.

On the basis of nmr the isocyanate corresponded to at least 50% of the crude. The nmr spectrum showed a strong signal for OCH_3 at τ 6.02 (in $CDCl_3$), but an additional signal at 8.48 and a weak, complex pattern at 7.13–8.82. The results of various forms of chromatography suggested that chemical conversions were probably taking place during such a process and indicated the presence of at least two components. The reactivity of the crude product was consistent with the presence of an isocyanate group, and this observation was utilized in the preparation of characterizable derivatives from the pyrolysis product.

Methyl N-(2-Methoxy-3,4,5,6-tetrachlorophenyl)carbamate (6a).—The crude pyrolysis product (500 mg) from 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole was dissolved in 10 ml of methanol, and the solvent was removed *in vacuo*. Methanol (4 ml) was added to the brown semisolid residue, and the mixture was filtered immediately. After purification of the precipitate with charcoal in hot methanol 40 mg of colorless needles were obtained: mp 183.5–184°; $\nu_{max}^{CHCl_3}$ 3400, 2925, 2825, 1725, 1550, 1480, 1450, 1400, 1370, 1330, 1240, 1070, and 1020 cm^{-1}; nmr ($CDCl_3$) τ 6.10 (3 H, CH_3O), 6.19 (3 H, CH_3O), and 3.57 (1 H, NH).

Anal. Calcd for $C_9H_7Cl_4NO_3$: C, 33.89; H, 2.21; N, 4.39; Cl, 44.46. Found: C, 34.16; H, 2.25; N, 4.48; Cl, 44.01.

N-(2-Methoxy-3,4,5,6-tetrachlorophenyl)urea (7a).—A sample of the compound described above (50 mg), mp 183°, which resulted from treatment of the acetate pyrolysis product with methanol, was dissolved in 25 ml of anhydrous methanol. The solution was placed in a glass pressure tube and saturated with ammonia while cooling in an ice bath. While the solution was cooled further in Dry Ice–acetone the tube was sealed. After the sealed tube had been heated at 100° for 10 hr it was allowed to stand overnight. The solvent was evaporated *in vacuo* to dryness, and the residue was recrystallized from methanol, yielding 36 mg (75%) of N-(2-methoxy-3,4,5,6-tetrachlorophenyl)urea, colorless needles: subl pt >250°; ν_{max}^{Nujol} 3490, 3330, 3250, 3160, 1660, and 1019 cm^{-1}.

Anal. Calcd for $C_8H_6Cl_4N_2O_2$: C, 31.61; H, 1.99; N, 9.22. Found: C, 31.83; H, 2.25; N, 9.16.

N-(2-Methoxy-3,4,5,6-tetrachlorophenyl)urea was also obtained directly by dissolving the acetate pyrolysis product (200 mg) in 30 ml of methylene chloride and passing in gaseous ammonia. The gray precipitate was filtered, decolorized with charcoal in hot methanol, and recrystallized from methanol as colorless needles: subl pt >250°; yield 18 mg; infrared spectrum identical with that described above.

When the acetate pyrolysis product was treated with ethanol in place of methanol the infrared spectrum showed the disappearance of the 2220-cm^{-1} maximum and the appearance of new maxima at 3400–3200 (br) and 1715 cm^{-1}. When the ethanol solution was saturated with ammonia and then heated in a sealed tube for 10 hr at 100°, the urea derivative isolated was identical in all respects with the product obtained by treatment of the pyrolysis product directly with ammonia or by following the methanol treatment with ammonia.

Pyrolysis of 1-Propionoxy-4,5,6,7-tetrachlorobenzotriazole (4c).—The pyrolysis of 600 mg was carried out under conditions identical with those employed with the 1-acetoxy derivative. The crude oily product (45 mg) showed ν_{max}^{film} 2220 cm^{-1}.

Methyl N-(2-Ethoxy-3,4,5,6-tetrachlorophenyl)carbamate (6c).—The crude propionate pyrolysis product (500 mg) was dissolved in 5 ml of methanol and the solvent was then removed *in vacuo*. The residue was recrystallized from hexane–methylene chloride as colorless needles: mp 162–163°; yield 100 mg; $\nu_{max}^{CHCl_3}$ 3400, 2975, 2948, 1740, 1549, 1495, 1450, 1440, 1420, 1380, 1355, 1240, 1074, 1024, 950, and 860 cm^{-1}; nmr ($CDCl_3$) τ 8.60 (t, CH_3), 6.20 (s, OCH_3), 5.90 (q, CH_2), 3.47 (br, NH).

Anal. Calcd for $C_{10}H_9Cl_4NO_3$: C, 36.07; H, 2.72; N, 4.21. Found: C, 36.16; H, 2.64; N, 4.48.

N-(2-Ethoxy-3,4,5,6-tetrachlorophenyl)urea (7c).—The crude propionate pyrolysis product (100 mg) was dissolved in 20 ml of methylene chloride and gaseous ammonia was passed in. The resulting suspension was evaporated *in vacuo* and the residue was recrystallized from methanol: mp 252.5°; yield 20 mg; ν_{max}^{Nujol} 3425, 3325, 3250, 1670, 1610, 1570, 1530, 1460, 1440, 1390, 1370, 1350, 1225, 1026.

Anal. Calcd for $C_9H_8Cl_4N_2O_2$: C, 33.98; H, 2.53; N, 8.81. Found: C, 34.43; H, 2.55; N, 8.70.

Pyrolysis of Carbonyl-^{18}O-labeled 1-Acetoxy-4,5,6,7-tetrachlorobenzotriazole (10).—In three practice runs the sequence 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole → 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole → 2-methoxy-3,4,5,6-tetrachlorophenylisocyanate → N-(2-methoxy-3,4,5,6-tetrachlorophenyl)urea was carried out starting with 250 mg of acetyl chloride and following the directions described above.

When the method was sufficiently standardized, 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole-carbonyl-^{18}O was prepared from 250 mg of acetyl-^{18}O chloride, 90% enrichment (Research Products Department of Miles Laboratories, Inc.). The yield of crude material was 96%. After recrystallization from benzene, pure material was obtained in 55% yield: mp 196°; ν_{max}^{Nujol} 1825 (C=^{16}O) and 1795 cm^{-1} (C=^{18}O), ratio ~1.10; nmr (CCl_4) τ 7.90 (s). In the mass spectrum the following peaks were observed in the region of the molecular ion: *m/e* 315 (13% relative abundance), 316 (32), 317 (45), 318 (50), 319 (46), 320 (35), 321 (23), 322 (14), 323 (5.5), indicating some replacement of hydrogen by deuterium. A portion of 500 mg of 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole-carbonyl-^{18}O was pyrolyzed under conditions identical with those described for the unlabeled compound, yielding 79 mg of pyrolysis product, ν_{max}^{film} 2220 cm^{-1}. The crude pyrolysis product was subjected immediately to reaction with gaseous ammonia in methylene chloride. Yield was sacrificed for purity of the oxygen-18-labeled N-(2-methoxy-3,4,5,6-tetrachlorophenyl)urea (12) isolated (*ca.* 3 mg), and this product was subjected to mass spectrometric analysis, as described in the discussion, to prove the location of the oxygen-18.

Reaction of 1-Hydroxy-4,5,6,7-tetrachlorobenzotriazole (2, X_n = Cl_4) with Ketene.—As an alternative synthesis of the substituted 1-acetoxybenzotriazoles and as a check on their structural assignments, the 1-hydroxybenzotriazoles could be acetylated with ketene. For example, through a solution of 100 mg of 1-hydroxy-4,5,6,7-tetrachlorobenzotriazole in 50 ml of acetone

cooled at 0° was passed excess ketene in a stream of dry nitrogen. The solution was then poured into ice water, and the precipitate was collected by filtration and dried, yield 98 mg (85%) of 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole. Following recrystallization from benzene, the compound had mp 197.5–199.5° and was identical in all respects (ir, etc.) with the sample obtained by acetylation using the potassium salt and acetyl chloride, as described above.

Chlorination of *o*-Methoxyacetanilide (*o*-Acetanisidide).—Dry chlorine was passed through a solution of *o*-acetanisidide in glacial acetic acid, and upon completion of the reaction the solution was poured into ice water. The precipitated material was recrystallized from ethanol as colorless needles of 2-methoxy-3,4,5,6-tetrachloroaniline, mp 224–225° (lit.[19] mp 227.5°), with the correct elemental analysis for $C_9H_7Cl_4NO_2$, nmr ($CDCl_3$ τ 7.78 (s, CH_3CO), 6.13 (s, CH_3O).

Reaction of 2-Methoxy-3,4,5,6-tetrachloroaniline with Phosgene Followed by Methanol.—To a solution of 200 mg of 2-methoxy-3,4,5,6-tetrachloroaniline in 20 ml of anhydrous benzene and 0.5 ml of anhydrous triethylamine was added 4 ml of a 12.5% solution of phosgene in benzene, and the reaction mixture was maintained at ambient temperature for 1 hr. The solvent was evaporated *in vacuo*, the residue was treated with anhydrous ether, and triethylamine hydrochloride was removed by filtration. Ether was evaporated from the filtrate under reduced pressure, leaving a half-solid residue which showed very strong infrared absorption at 2220 cm^{-1}. The residue was treated with 10 ml of methanol, and from this solution pure methyl N-(2-methoxy-3,4,5,6-tetrachlorophenyl)carbamate crystallized, yield 170 mg (70%), mp 181–182°, undepressed on admixture with a sample of methyl N-(2-methoxy-3,4,5,6-tetrachlorophenyl)carbamate (**6a**). The infrared spectra of the samples from the two sources were identical.

Registry No.—**4a,** 18355-09-4; **4c,** 18425-98-4; **5a,** 18355-11-8; **6a,** 18355-12-9; **6c,** 18355-13-0; **7a,** 18355-14-1; **7c,** 18355-15-2; **10,** 18346-74-2; **12,** 18346-75-3; 2,3,5,6-tetrachlorophenylhydrazine, 18355-16-3; hydrazine salt of 1-hydroxy-4,6,7-trichlorobenzotriazole, 18355-17-4; 1-ethoxycarbonyloxy-4,5-6,7-tetrachlorobenzotriazole, 18355-18-5; 1-methoxy-4,5,-6,7-tetrachlorobenzotriazole, 18355-19-6; 1-ethoxy-4,5,6,7-tetrachlorobenzotriazole, 18355-20-9.

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The Structures of Two Diastereoisomeric Sulfoxides. 3,5-Dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one 4-Oxides

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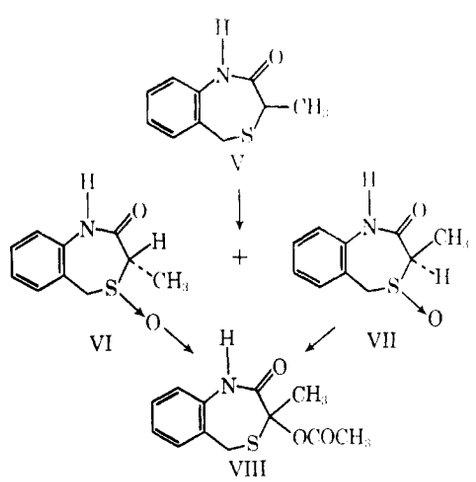
The sodium metaperiodate oxidation of 3,5-dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one gave two diastereoisomeric sulfoxides with mp 220–223 and 246–248°, respectively. The crystal structure of the major product (mp 220–223°) has been determined and the 3-methyl group has been shown to be *trans* to the sulfoxide oxygen atom. The crystals are monoclinic, with $a = 13.20 \pm 0.02$ Å, $b = 4.71 \pm 0.01$ Å, $c = 17.16 \pm 0.03$ Å and $\beta = 113°15' \pm 15'$. There are four molecules of $C_{10}H_{11}NO_2S$ in the space group $P2_1/c$. The structure has been refined to an R factor of 0.09 on 1427 reflections, obtained photographically. The detailed geometry of the molecule in the crystal is described. In boiling acetic anhydride solution both sulfoxides interconvert and rearrange to 3-acetoxy-3,5-dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one.

In the course of the study of 4,1-benzothiazepines, a new class of heterocyclic compounds[2] with interesting pharmacological properties, the Pummerer rearrangement[3] of sulfoxides was investigated as a method for the introduction of an acetoxy group on the carbon next to sulfur. In the 3-methyl series, we encountered the problem of separation and structure determination of two diastereoisomeric sulfoxides. This was resolved as follows.

The sodium metaperiodate oxidation[4] of racemic 3,5-dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one (V), the synthesis[2] of which is fully described in the Experimental Section, gave two diastereoisomeric sulfoxides in a ratio of 3:1. They were separated by chromatography on a silica gel column. The major product was eluted first with 15% ethyl acetate–85% benzene mixture. The minor product was eluted subsequently with 75% ethyl acetate–25% benzene mixture and pure ethyl acetate. The structure of the major product was elucidated by X-ray analysis and determined as that of the *trans*-sulfoxide VI.



The X-Ray Analysis of the *trans*-Sulfoxide VI.—The crystals of VI are transparent needles belonging to the monoclinic system with $a = 13.20 \pm 0.02$ Å,

(1) (a) University of Illinois. (b) Alfred P. Sloan Research Fellow. (c) Hoffmann-La Roche.

(2) M. Uskoković, G. Grethe, J. Iacobelli, and W. Wenner, *J. Org. Chem.*, **30**, 3111 (1965).

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