Proton Magnetic Resonance Spectra of Some Tetrazoles, Triazoles, and Tetrazolium and Triazolium Salts[1]

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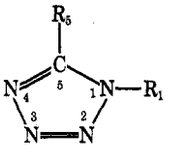
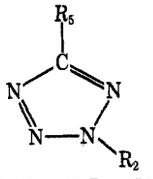
Structural assignments of 1,5- and 2,5-disubstituted tetrazoles and 1,3,5- and 3,4,5-trisubstituted 1,2,4-triazoles can be made on the basis of their proton magnetic resonance spectra. The 2-alkyl substituents in tetrazoles and the 1-alkyl substituents in triazoles are further downfield than the 1- and 4-alkyl substituents, respectively. Different isomers of phenyl-substituted triazole and tetrazole derivatives can be distinguished by the absence (or degree) of an anisotropic effect on the ortho protons.

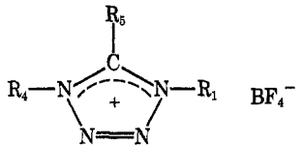
A previous paper[3] dealt with the synthesis of some 1,5- and 2,5-disubstituted tetrazoles and 1,3,5- and 3,4,5-trisubstituted 1,2,4-triazoles and their tetrazolium and triazolium salts. Pmr data obtained for compounds of Tables I and II allow a comparison of the triazole and tetrazole derivatives investigated and assignment of structure.



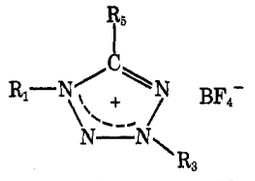
1, R_1 = Et; R_5 = Me
2, R_1 = R_5 = Et
3, R_1 = Me; R_5 = vinyl
4a, R_1 = H; R_5 = Ph
5, R_1 = Me; R_5 = Ph
6, R_1 = Et; R_5 = Ph



4b, R_2 = H; R_5 = Ph
7, R_2 = Et; R_5 = Ph



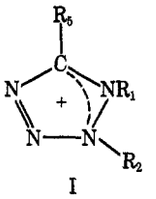
8, R_1 = R_4 = Et; R_5 = Me
9, R_1 = R_4 = Et; R_5 = Ph



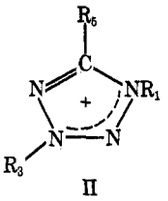
10, R_1 = R_3 = Et; R_5 = Ph

The pmr data of the tetrazoles and tetrazolium salts are reported in Table I. The observed chemical shift of the CCH_3 resonance at δ 2.53 in **1** agrees with the CCH_3 resonance at 2.58 reported for 1,5-dimethyltetrazole.[4] The pmr spectrum of **2** shows that the NCH_2 resonance at 4.32 and the NCH_2CH_3 at 1.47 are more deshielded than the CCH_2 resonance at 2.91 and the CCH_2CH_3 at 1.35. Phenyl protons ortho to the tetrazole ring of **4** and **7** are deshielded by 0.5–0.6 ppm relative to the meta and para protons. This deshielding effect was not observed in **6**, **9**, or **10**. Although there is no deshielding in **6**, **5** exhibits deshielding of 0.3 ppm. These results are consistent with greater deshielding for smaller groups ortho to the phenyl group on the tetrazole ring which allows a greater degree of coplanarity of tetrazole and phenyl rings. The difference in chemical shift between ortho and para–meta protons of **5** in deuteriochloroform (0.2 ppm) was smaller than that observed in deuterioacetonitrile (0.3 ppm). Fraser and Hague[5] have reported that the pmr spectrum of **5** in deuteriochloroform (TMS) showed a NCH_3 resonance at 4.16 and showed ortho, para, and meta protons on the phenyl ring at 7.64 with no deshielding effect.

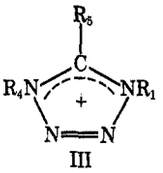
Quaternization of 1,5-disubstituted tetrazoles with alkyl halides has been reported[6] to give 1,4,5-trisubstituted tetrazolium salts (III). Three possibilities exist: 1,2,5-trisubstituted (I), 1,3,5-trisubstituted (II), and 1,4,5-trisubstituted (III) tetrazolium salts. Alkaline degradation[6a] of the methiodide of 5-methyl-1-phenyltetrazole to phenyl azide and methylamine supports structure III.



I

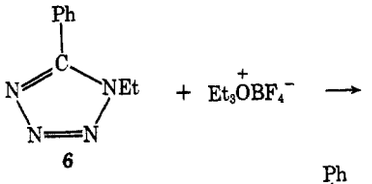


II

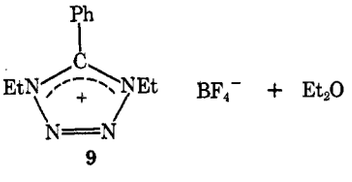


III

It appeared that the structure of 1,4,5-trisubstituted tetrazolium salts might be elucidated by physical methods rather than by chemical degradation. The model compound selected was 1,4-diethyl-5-phenyltetrazolium fluoroborate (**9**), synthesized by quaternizing 1-ethyl-5-phenyltetrazole (**6**) with triethyloxonium fluoroborate. The only isomer isolated exhibited in its pmr spectrum a triplet at 1.53, a quartet at 4.47, and



6



9

a singlet at 7.72 with relative areas of 6:4:5 corresponding to six equivalent methyl protons at positions 1 and

(1) Taken from the dissertation of L. A. Lee in partial fulfillment of the requirements for the Ph.D. degree, Howard University, 1970.

(2) Author to whom correspondence should be addressed at Polaroid Corp., Cambridge, Mass. 02139.

(3) L. A. Lee, R. Evans, and J. W. Wheeler, *J. Org. Chem.*, **37**, 343 (1972).

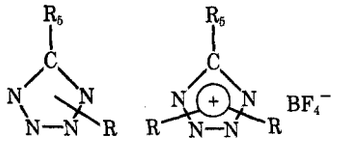
(4) J. H. Markgraf, W. T. Bachmann, and D. P. Hollis, *ibid.*, **30**, 3472 (1965).

(5) R. R. Fraser and K. E. Hague, *Can. J. Chem.*, **46**, 2855 (1968).

(6) (a) G. F. Duffin, J. D. Kendall, and H. R. J. Waddington, *Chem. Ind. (London)*, 1355 (1955); (b) F. R. Benson, L. W. Hartzel, and W. I. Savell, *J. Amer. Chem. Soc.*, **73**, 4457 (1951); (c) R. M. Herbst and K. G. Stone, *J. Org. Chem.*, **22**, 1139 (1957).

TABLE I

PMR DATA[a] OF TETRAZOLES AND TETRAZOLIUM SALTS

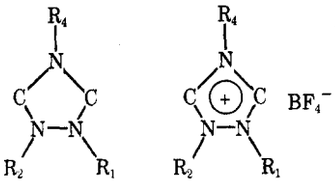


Compd	Solvent	Ph Ortho	Ph Meta–para	NCH_2	CCH_2	NCH_3	C_5CH_3
1	*b*			4.39 q, J = 7		1.47 t, J = 7	2.53 s
8	*b*			4.59 q, J = 7		1.62 t, J = 7	2.89 s
2	*b*			4.32 q, J = 7	2.91 q, J = 7	1.47 t, J = 7	1.35 t, J = 7
3	*b*				6.31 q[e]	4.18 s	
					5.86 q[f]		
4	*c*	7.68 m	7.14 m				
5	*d*	7.78 m	7.60 m			4.18 s	
	b	7.85 m	7.58 m			4.18 s	
6	*b*	7.64 m		4.49 q, J = 7		1.51 t, J = 7	
9	*b*	7.72 s		4.47 q, J = 7		1.53 t, J = 7	
7	*b*	8.15 m	7.55 m	4.72 q, J = 7		1.61 t, J = 7	
	c	7.65 m	7.15 m	4.54 q, J = 7		1.53 t, J = 7	
10	*b*	7.68 m		4.88 q, J = 7; 4.64 q, J = 7		1.72 t, J = 7; 1.61 t, J = 7	

[a] δ values are in ppm relative to TMS. J values in Hz. Abbreviations used are s, singlet; t, triplet; q, quartet; m, multiplet. [b] CD_3CN. [c] DMSO-d_6. [d] $CDCl_3$. [e] Pair of doublets, J_{AX} = 17, J_{AB} = 2.5 Hz. [f] Pair of doublets, J_{BX} = 10, in addition to Hx at 6.90 as a pair of doublets.

TABLE II

PMR DATA[a] OF TRIAZOLES AND TRIAZOLIUM SALTS



Compd	Solvent	Ph Ortho	Ph Meta–para	N_1CH_2	N_4CH_2	3 and 5 CCH_2	N_1CH_3	N_4CH_3	C_3CH_3	C_5CH_3
11	*b*			3.96 q, J = 7			1.32 t, J = 7		2.31 s	2.18 s
12	*b*			3.90 q, J = 7		2.60 m[e]	1.28 m[f]		1.28[f]	1.28[f]
14	*c*	8.27 m	7.56 m							
13	*b*	8.12 m	7.60 m	4.28 q, J = 7			1.48 t, J = 7			
18	*b*	7.74 m		4.13 q, J = 7	4.13 q, J = 7		1.47 t, J = 7	1.05 t, J = 7		
16	*d*	7.52 m			4.13 q, J = 7			1.05 t, J = 7		
15	*d*	7.60 m						3.70 s		
17	*b*	7.72 m		4.22 q, J = 7			1.47 t, J = 7	3.58 s		

[a] δ, J, and abbreviations as in Table I. [b] CD_3CN. [c] DMF-d_6. [d] $CDCl_3$. [e] Two overlapping quartets appearing as five lines. [f] Three overlapping triplets appearing as four lines.

4, four equivalent methylene protons at positions 1 and 4, and five phenyl protons at position 5. This pmr spectrum strongly suggests that quaternization occurred at position 4, affording the symmetrical 1,4,5-trisubstituted tetrazolium salt, in accord with chemical evidence.[6a] Analogous results were observed for **8** and have been reported for the methiodide of 1-methylimidazole,[7] protonated imidazoles, and benzimidazoles in sulfuric acid.[8]

The quaternization of 2,5-disubstituted tetrazoles has not been reported. When 2-ethyl-5-phenyltetrazole (**7**) was treated with triethyloxonium fluoroborate, only one isomer was isolated. Its pmr spectrum shows that the two ethyl groups are affected by a positive charge distributed between nitrogen atoms at positions 1, 2, and 3 within the tetrazole ring as are the ethyl groups in **8**, its methylene and methyl protons being deshielded by 0.20 and 0.15 ppm compared with the parent compound **1**. Deshielding of the ethyl groups in **9** appears to be negligible because most of the charge is localized in the phenyl ring through resonance in spite of steric hindrance.

The appearance of two quartets for the CH_2 groups and two triplets for the CH_3 groups eliminates the 2,3-substituted isomer as that compound is symmetrical and would have equivalent groups, leaving the only possibilities either the 1,3 or the 1,2 isomers. Although arguments can be made on the basis of chemical shifts, neither the pmr spectrum nor the mass spectrum allows an unequivocal assignment of this compound as either the 1,2- or 1,3-diethyl-5-phenyltetrazolium salt. Attempts to prove the structure by chemical reduction of the salt were unsuccessful.

Although two mass spectral studies have been published recently on the fragmentation pattern of tetra-

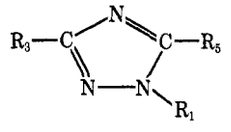
(7) C. G. Oberberger, J. C. Salamone, and S. Yaroslavsky, *J. Org. Chem.*, **30**, 3580 (1965).

(8) H. A. Staab and A. Mannschreck, *Tetrahedron Lett.*, **No. 20**, 913 (1962).

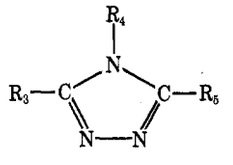
zoles,[5,9] tetrazolium salts have not been studied. Fraser and Hague[5] showed that the 1- and 2-methyltetrazoles could be differentiated by mass spectrometry. Similarly the 1- and 2-ethyl isomers (**6** and **7**) can be differentiated on the basis of their mass spectra. The 1-ethyl isomer shows a stronger parent ion and a peak at *m/e* 118 that is not observed for the 2-ethyl. Mass spectra of the tetrazolium salts **9** and **10** were essentially the same as those of the parent tetrazoles at 200° showing no peaks above *m/e* 175. The observation of an ion at *m/e* 118 in the mass spectrum of 1,2- (or 1,3-) diethyl-5-phenyltetrazolium fluoroborate (**10**) suggests the presence of 1-ethyl-5-phenyltetrazole. This evidence is in accord with pmr data which eliminates the 2,3-diethyl isomer as a possible product of quaternization as it would give only the 2-ethyl isomer.

Spectra of the tetrazolium salts **9** and **10** at 150° on an LKB-9000 instrument showed two peaks at higher *m/e* than the parent tetrazoles at 174. Both salts gave a peak at *m/e* 203, corresponding to the tetrazolium cation itself, as well as a peak at *m/e* 222, corresponding to that cation plus a fluorine or the original fluoroborate salt minus boron trifluoride.

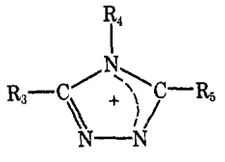
Nmr Correlations of *sym*-Triazoles and Triazolium Salts.—Pmr data of some triazoles and triazolium salts are reported in Table II. The pmr spectrum of **11**



11, $R_3 = R_5 = Me$; $R_1 = Et$
12, $R_1 = R_3 = R_5 = Et$
13, $R_1 = Et$; $R_3 = R_5 = Ph$
14a, $R_1 = H$; $R_3 = R_5 = Ph$



14b, $R_4 = H$; $R_3 = R_5 = Ph$
15, $R_4 = Me$; $R_3 = R_5 = Ph$
16, $R_4 = Et$; $R_3 = R_5 = Ph$



17, $R_4 = Me$; $R_1 = Et$; $R_3 = R_5 = Ph$
18, $R_1 = R_4 = Et$; $R_3 = R_5 = Ph$

shows a quartet at 3.96, triplet at 1.32 for the NCH_2CH_3 group, and two singlets at 2.31 and 2.18 for C_3CH_3 and C_5CH_3. Assignment of the peak at 2.18 to C_5CH_3 was made on the basis of the shielding effect of the adjacent ethyl group. Compound **12** shows a quartet at 3.90 for the NCH_2 protons and a multiplet (two quartets with almost identical chemical shifts) at 2.60 for CH_2 protons at C_3 and C_5 and a multiplet consisting of four peaks with additional splittings accounting for the three methyl groups at C_3, C_5, and N, at 1.28.

The phenyl proton resonances in 1,3,5-trisubstituted 1,2,4-triazoles and 1,3,4,5-tetrasubstituted 1,2,4-triazolium salts also exhibit an anisotropy effect of the heterocyclic ring on the ortho protons of the phenyl ring, as observed in the previously discussed tetrazole and tetrazolium salts. The phenyl protons ortho to the triazole ring of **14a** and **14b** and **13** are deshielded by 0.5–0.6 ppm relative to the meta and para protons.

(9) D. M. Forkey and W. R. Carpenter, *Org. Mass Spectrom.*, **2**, 433 (1969).

The pmr spectrum of **13** indicated that the C-5 phenyl ortho protons are less deshielded relative to the meta and para protons due to steric hindrance with the ethyl group, in contrast to the unhindered phenyl group at C-3. A study of the areas of phenyl protons resonances (1:4 rather than 2:3) suggests the presence of an anisotropic effect on the ortho protons of the phenyl group at C-3 and its decrease or absence at C-5. The pmr spectra of **15** and **16** and their triazolium salts exhibited multiplets at 7.60, 7.52, 7.72, and 7.74 with areas of five protons indicating that both phenyl groups at C-3 and C-5 are prevented from attaining coplanarity with the triazole ring. Similar observations of magnetic anisotropy have been observed in the pmr spectra of substituted phenyl pyrazoles.[10]

The ethyl group at position 1 with resonances at 4.28 (N_1CH_2) and 1.48 ($N_1CH_2CH_3$) in **13** is more deshielded than the ethyl group in position 4 of **16** (N_4CH_2 at 4.13 and $N_4CH_2CH_3$ at 1.05) by 0.15 and 0.43 ppm for the methylene and methyl resonances. This observation is reasonable since the 3-phenyl group in the 1 isomer can effectively conjugate with the triazole ring, thus deshielding the ethyl group *via* resonance and inductive effects. Partial deshielding is possible by the sterically hindered 5-phenyl group. Because of steric hindrance in **16**, there is a smaller deshielding effect due to the loss of coplanarity of both phenyl groups. The fact that the chemical shift difference for the methyl group is greater than the methylene group suggests that the methyl group positioned between the rings reflects ring current effects of the phenyl groups. Similar results are also observed in **18** whose pmr spectrum shows a multiplet for the phenyl protons at 7.74 and a quartet at 4.13 for CH_2 groups at 1 and 4 with no chemical shift difference and triplets at 1.47 and 1.05 for N_1CH_3 and N_4CH_3.

As the 1 substituent is changed from H (**4a**, **4b**) to Me (**5**) to Et (**6**) in 5-phenyltetrazole, the anisotropy effect is decreased. As expected, the anisotropy effect is greater in 2-ethyl-5-phenyltetrazole (**7**) than in 1-ethyl-5-phenyltetrazole (**6**) because of ideal resonance conjugation and the absence of steric hindrance between the phenyl and tetrazole ring. The loss of the anisotropy effect in 1,2- or 1,3-diethyl-5-phenyltetrazolium fluoroborate (**10**) indicates the presence of steric inhibition to resonance between the phenyl and tetrazole ring. Similar effects were observed for 1-ethyl-3,5-diphenyl-1,2,4-triazole (**13**) and 4-ethyl-3,5-diphenyl-1,2,4-triazole (**16**).

Experimental Section[11]

Proton magnetic resonance spectra were taken on a Varian Associates A-60 or HR-60 spectrometer. Positions are reported in parts per million from tetramethylsilane (δ). A Beckman IR-5 or IR-8 spectrophotometer with sodium chloride optics was used for all ir spectra. Mass spectra were recorded on a Bendix Model 12-101 time-of-flight mass spectrometer at 70 eV using a liquid or solid inlet system and an LKB-9000 instrument.

1- and 2-Ethyl-5-phenyltetrazole (6 and 7).—A solution of 5-phenyltetrazole[12] (50.0 g, 0.342 mol), sodium hydroxide (18.0 g, 0.45 mol), and diethyl sulfate (52.73 g, 0.342 mol) in 500 ml of distilled water was stirred at reflux temperature for 12 hr. The

(10) L. G. Tensmeyer and C. Ainsworth, *J. Org. Chem.*, **31**, 1878 (1966); B. M. Lynch and Y. Y. Hung, *Can. J. Chem.*, **42**, 1605 (1964).

(11) All compounds listed in Tables I and II except **6**, **7**, **8**, **9**, **15**, and **17** are reported in ref 3.

(12) W. G. Finnegan, R. A. Henry, and R. Lofquist, *J. Amer. Chem. Soc.*, **80**, 3908 (1958).

reaction mixture was then concentrated to one-third volume under reduced pressure at 65° and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, concentrated, and distilled giving 19.90 g (30%) of 2-ethyl-5-phenyltetrazole (7): bp 77–78° (0.20 mm); ir (neat) 1575 (s), 1555 (s), 1374 (s), 1342 (s), 786 (s), 730 (s), 715 (s), 690 (s), and 653 cm^{-1} (w).

Anal. Calcd for $C_9H_{10}N_4$: C, 62.05; H, 5.79; N, 32.17; mol wt, 174. Found: C, 62.11; H, 5.72; N, 32.23; mol wt, 174 (mass spectrometry).

The still pot residue that solidified after cooling was recrystallized from ethanol affording 6.05 g (10%) of 1-ethyl-5-phenyltetrazole[13] (6): mp 70–71°; ir (KBr) 1451 (s), 1170 (s), 1114 (s), 1076 (s), 776 (s), 735 (s), 694 (s), and 650 cm^{-1} (s).

1,4-Diethyl-5-phenyltetrazolium Fluoroborate (9).—A solution of 1-ethyl-5-phenyltetrazole (6) (5.00 g, 0.03 mol) and triethyloxonium fluoroborate (5.46 g, 0.03 mol) in ethylene chloride (50 ml) was stirred at reflux temperature for 4 hr. The solvent was removed under reduced pressure and the remaining residue was washed with ether. Recrystallization from ethanol gave 4.15 g (59%) of 1,4-diethyl-5-phenyltetrazolium fluoroborate (9): mp 131–132°; ir (KBr) 1486 (s), 1449 (m), 1100–1000 (vs), 770 (s), 742 (s), 717 (s), and 691 cm^{-1} (s).

Anal. Calcd for $C_{11}H_{15}BF_4N_4$: C, 45.54; H, 5.21; N, 19.32. Found: C, 45.93; H, 5.43; N, 19.41.

1,2- or 1,3-Diethyl-5-phenyltetrazolium Fluoroborate (10).—A solution of 2-ethyl-5-phenyltetrazole (7) (5.00 g, 0.03 mol) and triethyloxonium fluoroborate (5.46 g, 0.03 mol) in ethylene chloride (50 ml) was stirred at reflux temperature for 4 hr. The product was isolated in the same manner as the tetrazolium salt described above. Compound 10 (5.5 g, 78%) was recrystallized from ethanol to give a white crystalline solid which had a melting point of 71–72°: ir (KBr) 1605 (m), 1477 (s), 1449 (s), 1100–1000 (vs), 802 (m), 781 (s), 773 (s), 747 (s), 728 (s), and 694 cm^{-1} (s).

Anal. Calcd for $C_{11}H_{15}BF_4N_4$: C, 45.54; H, 5.21; N, 19.32. Found: C, 45.37; H, 5.30; N, 19.26.

1,4-Diethyl-5-methyltetrazolium Fluoroborate (8).—1-Ethyl-5-methyltetrazole (5.00 g, 0.045 mol) was added dropwise to a magnetically stirred solution of triethyloxonium fluoroborate (8.47 g, 0.045 mol) in ethylene chloride (50 ml). The reaction temperature was maintained at 25–35° by means of a cooling bath. After the addition was complete, the reaction mixture was stirred at 25° for 4 hr. The solvent was then removed under pressure at 40° leaving a 4.50 g (88%) of hygroscopic 8: mp 129–130° after recrystallization from ethanol; ir (solid film) 1575 (m), 1445 (s), 1111–1000 (s), 722 (m), 689 (w), and 665 cm^{-1} (m).

Anal. Calcd for $C_6H_{13}BF_4N_4$: C, 31.67; H, 5.76; N, 24.63. Found: C, 31.48; H, 5.25; N, 24.25.

4-Methyl-3,5-diphenyl-1,2,4-triazole (15).—*N*-Methylbenzamide (54.05 g, 0.40 mol) was treated with phosphorus pentachloride (83.30 g, 0.40 mol) and benzhydrazide (54.46 g, 0.40 mol) in chloroform (200 ml) by the method of Scheuing and Walach[14] yielding 59.20 g (63%) of 4-methyl-3,5-diphenyl-1,2,4-triazole (15): mp 242–243° (lit.[14] mp 243°) after recrystallization from ethanol; ir (KBr) 1464 (s), 1064 (m), 1020 (w), 1005 (m), 769 (s), 727 (s), and 687 cm^{-1} (s).

4-Methyl-1-ethyl-3,5-diphenyl-1,2,4-triazolium Fluoroborate (17).—A stirred solution of 4-methyl-3,5-diphenyl-1,2,4-triazole (2.35 g, 0.01 mol) and triethyloxonium fluoroborate (1.90 g, 0.01 mol) in ethylene chloride (50 ml) at reflux temperature for 2 hr gave 3.30 g (94%) of 17: mp 148–149°; ir (solid film) 1608 (m), 1100–1000 (vs), 794 (m), 733 (m), and 697 cm^{-1} (s). The isolation procedure used was described previously for compound 8.

Anal. Calcd for $C_{17}H_{18}BF_4N_3$: C, 58.15; H, 5.17; N, 11.97. Found: C, 58.20; H, 5.26; N, 11.90.

Registry No.—**1**, 3641-05-2; **2**, 3641-06-3; **3**, 15284-40-9; **4a**, 3999-10-8; **5**, 20743-50-4; **6**, 24433-71-4; **7**, 31818-94-7; **8**, 32827-41-1; **9**, 32675-44-8; **10**, 32675-45-9; **11**, 32675-46-0; **12**, 32675-47-1; **13**, 32675-48-2; **14a**, 2039-06-7; **15**, 32272-86-9; **16**, 32675-51-7; **17**, 32675-52-8; **18**, 32675-53-9.

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Reactions of Pyrrole with Isocyanates. Preparation and Reactions of *N*-Ethoxycarbonylpyrrole-2-carboxamide and Pyrrole-1,2-dicarboximide

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Treatment of pyrrole with ethoxycarbonyl isocyanate in toluene yields *N*-ethoxycarbonylpyrrole-2-carboxamide (1), which is readily hydrolyzed to either pyrrole-2-carboxamide or pyrrole-2-carboxylic acid and cyclized to pyrrole-1,2-dicarboximide (8). Reaction of 8 with ammonia gives *N*-carbamoylpyrrole-2-carboxamide (10) and its N-tosylation followed by hydrolysis affords *N*-tosylpyrrole-2-carboxamide (13), which is found to be identical with the compound formed from pyrrole and tosyl isocyanate in dioxane. Pyrrolylpotassium reacts with ethoxycarbonyl isocyanate in tetrahydrofuran to form, after acidification, *N*-ethoxycarbonylpyrrole-1-carboxamide (2).

The reactions of pyrrole with phenyl isocyanate[1] and trichloroacetyl isocyanate[2] are known to yield the corresponding derivatives of pyrrole-2-carboxamide. Of these, *N*-phenylpyrrole-2-carboxamide has been shown to react further with phenyl isocyanate, in the presence of triethylamine, to form *N*-phenylpyrrole-1,2-dicarboximide (7).[3] Unexpectedly, in view of the higher reactivity of the 2 position of pyrrole toward electrophilic reagents,[4] treatment of pyrrole with tosyl isocyanate in dioxane has been reported to lead to *N*-tosylpyrrole-3-carboxamide.[5]

In analogous reactions of enamines with ethoxycarbonyl isocyanate, the initial products have been shown

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