solution of 55 mg (0.48 mmol) of methanesulfonyl chloride in 0.5 mL of dichloromethane. The resulting solution was stirred at 0 °C for 7 min, diluted with 15 mL of dichloromethane, and poured into 5 mL of a mixture of equal parts of 10% potassium hydroxide aqueous solution and saturated sodium chloride aqueous solution. The aqueous phase was extracted with 5 mL of dichloromethane, and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo to give 110 mg of a white solid. This solid was dissolved in 0.5 mL of methanol and stirred with an aqueous solution of 1.4 g sodium tetrafluoroborate (12.7 mmol) in 6 mL of water for 1 h. The resulting solution was extracted with chloroform (2 × 10 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo to give 102 mg of a white solid. This material was recrystallized from ether–dichloromethane (3:2) to give 74 mg (61%) of the tetrafluoroborate salt **28** as white crystals: mp 162–163 °C; IR ($CHCl_3$) 3040, 2960, 2880, 1460 cm^{-1}; NMR ($CDCl_3$) δ 0.85–2.50 (m, 18 H), 2.50–3.60 (m with qu at 2.97, J = 11 Hz, 2 H, NCH, methylene CH), 3.60–4.60 (m, with qu at 4.27, J = 10 Hz, 3 H, NCH), 4.60–5.00 (m, 1 H, NCH); ^{13}C NMR ($CDCl_3$) δ 13.79 (q), 17.53 (t), 19.42 (t), 20.10 (t), 21.26 (t), 22.33 (t), 27.04 (t), 27.58 (t), 30.15 (t), 35.00 (t), 64.13 (d), 65.88 (d), 71.66 (d).

Anal. Calcd for $C_{13}H_{24}NBF_4$: C, 55.50; H, 8.60. Found: C, 54.61; H, 8.83.

***rel*-(1*S*,4*R*,7*S*,11*R*)-11-Propyl-1-azatricyclo[5.4.0.0^{1,4}]undecane Tetrafluoroborate (29).** To a solution of 78 mg (0.37 mmol) of amino alcohol **27** in 0.43 mL of dry dichloromethane cooled in an ice bath under argon was added 0.13 mL (0.93 mmol) of triethylamine in one portion followed by the addition of a solution of 47 mg (0.41 mmol) of methanesulfonyl chloride in 0.43 mL of dichloromethane. The resulting solution was stirred at 0 °C for 7 min, diluted with 20 mL of dichloromethane, and poured into 4 mL of a mixture of equal parts of 10% potassium hydroxide aqueous solution and saturated sodium chloride aqueous solution. The aqueous phase was extracted with 5 mL of dichloromethane, and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo to give 92 mg of a yellow solid. This material was dissolved in 0.4 mL of methanol and stirred with a solution of 1.2 g (10.9 mmol) of sodium tetrafluoroborate in 4 mL of water for 1 h. The resulting solution was extracted with dichloromethane (2 × 15 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated to give 90 mg (86%) of the tetrafluoroborate salt **29** as a yellow oil: IR ($CHCl_3$) 3040, 2960, 2880, 1470 cm^{-1}; NMR ($CDCl_3$) δ 0.80–3.40 (m, 19 H), 3.40–4.40 (m, 5 H), 4.70–5.07 (m, 1 H, NCH); ^{13}C NMR ($CDCl_3$) δ 13.74 (q), 15.44 (t), 19.57 (t), 20.34 (t), 22.53 (t), 25.78 (t), 29.94 (t), 30.44 (t), 56.66 (t), 63.11 (d), 66.66 (d), 74.57 (d).

Formation of Amino Ketone 19 via Grignard Addition to Amino Ester 24. To a solution of 97 mg (0.38 mmol) of amino ester **24** in 0.4 mL of dry ether under argon was added dropwise 1.5 mL of a solution of 1.28 M (5 equiv) ethylmagnesium bromide in ether. The resulting solution was stirred at room temperature for 6 h and transferred via syringe into a vigorously stirred mixture of 15 mL of dichloromethane, 10 mL of water, and approximately 5 g of ice. The resulting mixture was diluted with 30 mL of dichloromethane and separated. The aqueous phase was extracted with two 10-mL portions of dichloromethane, and the combined organic layers were dried and concentrated in vacuo to give 77 mg of a pale-yellow oil. This material was chromatographed over 8 g of silica gel [eluted with methanol (2% concentrated ammonium hydroxide)–chloroform; 8:92] to give 59 mg (65%) of a pale-yellow oil, which was identical by NMR and TLC [silica gel, methanol (2% concentrated ammonium hydroxide)–chloroform; 12:88] with amino ketone **19** prepared as described above.

Formation of Amino Ketone 20 via Grignard Addition to Amino Ester 25. To a solution of 104 mg (0.41 mmol) of amino ester **25** in 0.4 mL of dry ether under argon was added dropwise 1.5 mL of a 1.278 M ethylmagnesium bromide in ether (4.7 equiv). The resulting solution was stirred at room temperature for 8 h and transferred via syringe into a vigorously stirred mixture of 10 mL of dichloromethane, 10 mL of water, and about 5 g of ice. The resulting mixture was diluted with 30 mL of dichloromethane and separated. The aqueous phase was extracted with two 10-mL portions of dichloromethane, and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo to give 82 mg of a pale-yellow oil, which was a mixture of amino ketone **20** and unreacted amino ester **25** by NMR, IR, and TLC [silica gel, methanol (2% concentrated ammonium hydroxide)–chloroform, 12:88; alumina, ethyl acetate–hexane, 1:9]. Attempts to purify this crude material by chromatography over 10 g of neutral activity III alumina (eluted with ethyl acetate–hexane, 2:98) resulted in isomerization of amino ketone **20** to a mixture of **20** and **19**. Signals due to **20** were visible at δ 0.70–2.80 and δ 3.00–3.80 (m, 3 H, NCH) in NMR spectra ($CDCl_3$) of the crude product mixture.

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Registry No. **2**, 83024-10-6; **3**, 83024-11-7; **7**, 75534-05-3; **8**, 78688-77-4; **9**, 78688-79-6; **10**, 82979-13-3; **11**, 82979-14-4; **12**, 78167-73-4; **13**, 82979-15-5; **15**, 82979-16-6; **16**, 83024-07-1; **17**, 82979-17-7; **18**, 82979-18-8; **19**, 82979-19-9; **20**, 83024-08-2; **21**, 82979-20-2; **22**, 83024-09-3; **23**, 78167-66-5; **24**, 82979-21-3; **25**, 83024-12-8; **26**, 82979-22-4; **27**, 83024-13-9; **28**, 82979-24-6; **29**, 83024-15-1; 1-bromo-2-butanone, 816-40-0.

Reactivity of Tetracyanoethylene Oxide toward Heteroaromatic Compounds. Synthesis and Structure of Heterocyclic Dicyanomethylides

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Tetracyanoethylene oxide (TCNEO) was allowed to react with 17 heterocyclic derivatives, mainly azoles. Only in ten cases the reaction affords the corresponding dicyanomethylide. The structure of these compounds was established by IR and ^1H NMR spectroscopies. The reactivity of heterocycles toward TCNEO increases with basicity and decreases with steric hindrance. A bidimensional plot of our results and those of the literature shows a clear frontier between reactive and unreactive heterocycles.

Tetracyanoethylene oxide (TCNEO) is a powerful and interesting reagent. Contrary to normal epoxides, TCNEO is not attacked by electrophilic reagents because of the presence of the strong electron-withdrawing cyano groups, but, for this same reason, it easily reacts with nucleophlic reagents.[1] Linn et al.[1-3] have examined the reactivity of

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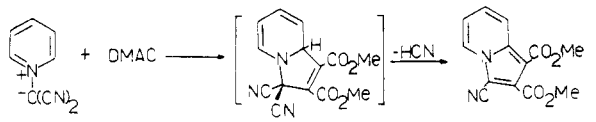
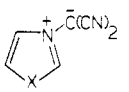
Scheme I

Scheme II



TCNEO toward different nucleophiles. Of special interest is the reaction with nitrogenated tertiary aromatic bases, like pyridine (1), 3- and 4-picoline (2, 3), pyrazine (4), and isoquinoline (5, Scheme I). The reaction affords stable *N*-dicyanomethylides, which react as 1,3-dipoles in cycloaddition reactions. Thus, the reaction between the pyridinium dicyanomethylide (1a) and dimethylacetylenedicarboxylate (DMAC) yields 1,2-dicarbomethoxy-3-cyanopirrocoline (Scheme II).

In 1968, Boekelheide and Fedoruk[4] extended this reaction to the azoles, preparing in this manner the dicyanomethylides of 1-methylimidazole (6) and thiazole (7).



6a, X = NMe
7a, X = S

Following this work, the dicyanomethylides of other nitrogenated tertiary bases were described. These included 3*H*-pyrazolines,[5] pyridazine (8),[6] 4,4'-bipyridyl (6, as the bis ylide),[7] and 1,2,3-triazines.[8]

The aim of the present work is to explore the generality of this reaction in order to establish the influence of structural factors in the nitrogenated nucleophilic reagent on the reaction. Thus, TCNEO was allowed to react with an extensive series of azoles having different structural characteristics around the reactive nitrogen atom and with some six-membered heterocycles not previously reported.

Table I. Yields of Dicyanomethylides

compd	heterocycle	pK_a[c]	yield, %
10	2-picoline	5.97[9]	2
11	quinoline	4.94[9]	2
12	1-methylpyrazole	2.09[10]	
13	1,2-dimethylimidazole	7.4–8.3[11]	?[a]
14	1-phenylimidazole	5.83[12]	74
15	1-methylbenzimidazole	5.57[9]	57
16	1-ethylbenzimidazole	5.57[b]	66
17	1,2-dimethylbenzimidazole	5.8–6.5[11]	
18	isoxazole	−2.97[9]	
19	1-ethyl-1,2,3-triazole	1.25[9]	73
20	benzothiazole	1.20[13]	
21	1-ethylbenzotriazole	0.2 to −0.4[14]	21
22	2-methylbenzotriazole	−3.9[13]	
23	1-methyl-1,2,4-triazole	3.20[15]	10
24	1-phenyl-1,2,4-triazole	1.90[16]	19
25	4-phenyl-1,2,4-triazole	2.10[16]	76
26	4,4'-bi-1,2,4-triazolyl	−0.8 to −1.2[17]	

[a] A fast reaction is observed, yielding a polymeric mass which could not be analyzed. [b] It was assumed that the substitution of a methyl by an ethyl has no influence on the basicity. [c] Conjugated acid of the heterocycle.

Results

Table I summarizes the studied heterocycles, their pK_a values, and the reaction yields. The reaction was carried out by mixing equimolar amounts of the base and TCNEO dissolved in ethyl acetate or ether at 0 °C or at room temperature. Highly reactive compounds (yields up to 50%) react in a similar way whatever the conditions may be; however, with less reactive compounds better yields and purer products were obtained at room temperature in ether rather than in ethyl acetate. Higher reaction temperatures cause tars by polimerization of TCNEO.

The structure of the ylides was established by spectroscopic methods. The infrared spectra of these compounds exhibit, in addition to the typical bands of each system, a strong doublet due to the cyano groups at 2130–2160 and 2180–2200 cm^{-1}, characteristic of a high degree of ionic character. This absorption was observed for trimethylammonium,[18] triphenylphosphonium,[19] and pyridinium[1] (1a) dicyanomethylides. In ^1H NMR spectra all signals are shifted to low field relative to the neutral base, because of the presence of a positive charge on the ring.

Structures were established by analogy with quaternization results of the corresponding heterocycles.[15] The position of the $C(CN)_2$ group was further confirmed by comparing the chemical shifts of the ylides with those of the free bases and those of the quaternary salts. Table II summarizes the chemical shifts, measured in Me_2SO-d_6 as the solvent, of the azole ring protons of the dicyanomethylides (a) and the available quaternary salts (b). In parentheses are given the calculated deshielding shifts relative to the neutral base, measured in the same solvent.

In all cases similar effects were observed for each heterocycle. The aromatic protons of the *N*-phenyl and the benzo-condensed rings could not be analyzed at 60 MHz, but the shift to low field can be observed relative to the free bases. The proton located between the two nitrogen atoms, which has the highest positive character, shows the highest deshielding effect. Concerning the other two protons of the ring, the proton located α to the nitrogen atom which bears the dicyanomethyl group is the most

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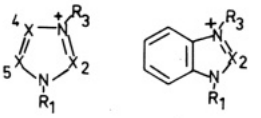
Table II. Proton NMR Results[a,d]



compd	R_1	R_3	X-2	X-4	X-5	chemical shift,[c] δ H_2	H_4	H_5	R_1	R_3
14a	C_6H_5	$C(CN)_2$	CH	CH	CH	9.75 (1.45)	8.27 (1.07)	7.90 (0.12)		
14b[20]	C_6H_5	CH_3	CH	CH	CH	9.68 (1.38)	7.92 (0.72)	8.25 (0.47)		3.96 (CH_3)
15a	CH_3	$C(CN)_2$	CH	benzo		9.75 (1.47)[b]			4.07 (CH_3)	
16a	C_2H_5	$C(CN)_2$	CH	benzo		9.80 (1.52)			4.49 (CH_2) (0.26)	1.55 (CH_3) (0.18)
15b	CH_3	CH_3	CH	benzo		9.70 (1.42)			4.17 (CH_3)	4.17 (CH_3)
19a	C_2H_5	$C(CN)_2$	N	CH	CH		8.65 (0.95)	8.37 (0.27)	4.50 (CH_2) (0.07)	1.50 (CH_3) (0.05)
19b[21,c]	CH_3	CH_3	N	CH	CH		8.46 (0.62)	8.46 (0.38)	4.32 (CH_3)	4.32 (CH_3)
21a	C_2H_5	$C(CN)_2$	N	benzo					4.91 (CH_2) (0.13)	1.63 (CH_3) (0.08)
23a	CH_3	$C(CN)_2$	CH	CH	N	10.08 (1.81)	9.17 (1.39)		3.98 (CH_3) (0.15)	
24a	C_6H_5	$C(CN)_2$	CH	CH	N	10.82 (1.52)	9.42 (1.17)			
25a	C_6H_5	$C(CN)_2$	CH	N	CH	10.55 (1.38)		9.60 (0.43)		
25b	C_6H_5	CH_3	CH	N	CH	10.81 (1.64)		9.72 (0.55)		4.22 (CH_3)

[a] Solvent was Me_2SO-d_4 unless indicated otherwise. [b] From 1-ethylbenzimidazole. [c] Solvent D_2O. [d] Numbers in parentheses are the calculated deshielding shifts (in parts per million) relative to the shifts of the neutral bases.

deshielded. This indicates that the positive charge is mainly localized on the $C(CN)_2$-substituted nitrogen atom.

Discussion

Formation of the ylides involves the nucleophilic attack of a "pyridinic" nitrogen atom of the azole on the oxirane ring.

It is assumed that two main factors determine the reactivity of heterocycles toward the TCNEO: the nucleophilicity of the nitrogen atom and the steric hindrance around it. The nucleophilicity of the heterocycle depends on the reagent; however, its variation parallels the basicity, and pK_a values have often been used as a measure of the nucleophilicity. It has been shown[13] that the nucleophilic reactivity of aromatic heterocycles with five- or six-membered rings increases monotonically with the pK_a.

The importance of steric hindrance of a methyl substituent α to the nitrogen atom or of the hydrogen peri in the benzo-condensed system is, for the quaternization reactions, greater in the six-membered than in the five-membered series. This is presumably due to an increase in the value of the external angle in the five-membered series.

In benzo-condensed derivatives the reduction of the reactivity is mainly due to steric causes in six-membered rings and to electronic causes in the five-membered ones.[13] This conclusion was verified in this work. The formation of ylides is more sensitive to steric effects than the methylation reaction, since in some cases the quaternization product has been isolated, and the ylide has not formed, for instance, with the benzothiazole.[13] Thus the 2-picoline (**10**) and quinoline (**11**) are weakly reactive compounds while *N*-alkylbenzimidazoles are highly reactive compounds comparable with the corresponding *N*-alkylimidazoles, and the reaction fails only when there is steric hindrance (e.g., 1,2-dimethylbenzimidazole, **17**). The pyrazole derivative **12** is an unreactive compound since two factors contribute: a low pK_a and the steric hindrance of the N_1-methyl group.

The presence of electron pairs adjacent to the reactive nitrogen atom (α effect) increases the nucleophilicity but not the basicity (as noted in the diazines[13]). This effect can be observed in the series of azoles when the reactivities of the triazoles **19** and **25** are compared with those of triazoles **23** and **24**, and specially when the reactivity of the benzothiazole **20** is compared with that of benzotriazole **21**, the pK_a of which is lower than the pK_a of most unreactive heterocycles.

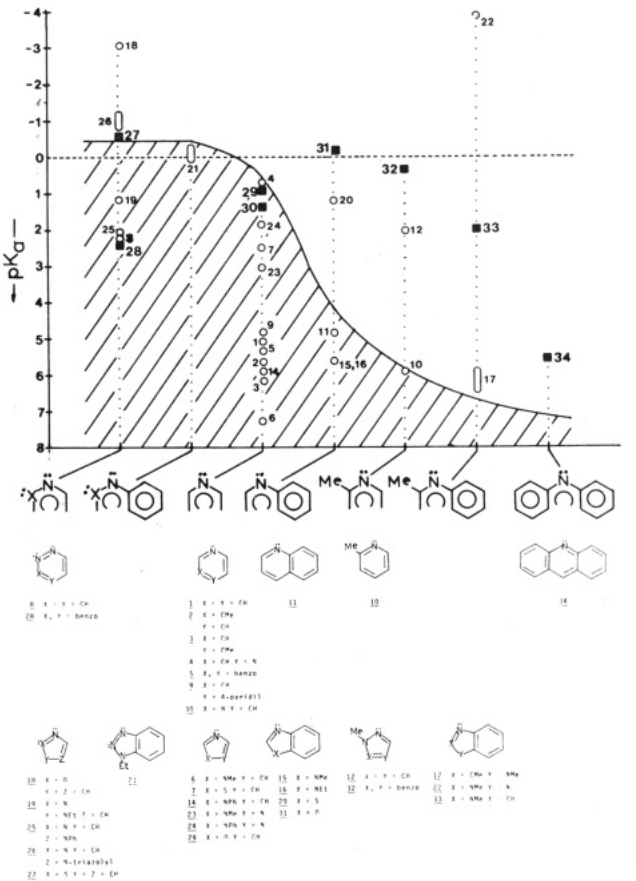


Figure 1. Reactivity of heterocyclic compounds toward TCNEO: open circles correspond to experimental results; elongated circles along the *y* axis correspond to uncertainties in the pK_a values; black squares correspond to predicted reactivities.

These considerations about the reactivity of heteroaromatic compounds in the formation of dicyanomethylides are based on isolated products and on reaction times and not on kinetic rates. The reactivities can be graphically represented in a two-dimensional plot as shown in Figure 1, with the pK_a values as the ordinate. The abcissa represents the various structural types arranged at arbitrary intervals in order of decreasing reactivity. The

classification of structures takes into account the factors (α effect, steric hindrance, benzo fusion) which influence reactivity. The curve in Figure 1 represents a boundary between reactive and nonreactive compounds. Within each structural type, the reactivity increases with increasing pK_a; thus the lower the point on the ordinate, the greater the reactivity. For the purpose of this representation, reactivity is defined by the appearance of a precipitate from ether solution before 96 h. The literature data concerns exclusively positive results, i.e., isolated dicyanomethylides. The reactivities are represented in Figure 1 (pK_a values of the corresponding heterocycles in parentheses): pyridine [**1**[1] (5.23)],[9] 3-picoline [**2**[1] (5.68)],[9] 4-picoline [**3**[1] (6.02)],[9] pyrazine [**4**[1] (0.65)],[9] isoquinoline [**5**[1] (5.40)],[9] 1-methylimidazole [**6**[4] (7.33)],[9] thiazole [**7**[4] (2.53)],[9] pyridazine [**8**[6] (2.33)],[9] 4,4′-bipyridyl [**9**[7] (4.82)].[9]

On the basis of the diagram it is now possible to predict the reactivity of heterocycles toward TCNEO by knowing their pK_a. Thus, it can be predicted (noted in Figure 1 by black squares) that the isothiazole **27** (pK_a – 0.51)[9] will not react, or at least it will do so only with difficulty, the cinnoline **28** (pK_a 2.42)[9] will react easily on the N_2-nitrogen atom, the oxazole **29** (pK_a = 0.80)[9] will react with difficulty as will the pyrimidine **30** (pK_a = 1.30),[9] and the benzoxazole **31** (pK_a = –0.13),[9] 1-methylindazole **32** (pK_a = 0.42),[22] 2-methylindazole **33** (pK_a = 0.02),[22] and acridine **34** (despite its quite high basicity, pK_a = 5.60[9]) will not react.

Experimental Section

General Methods. Melting points were determinated in a Büchi 510 D apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 257 spectrometer. Proton NMR spectra were recorded at 60 MHz on a Varian T-60A spectrometer with Me_2SO-d_6 as the solvent. Chemical shifts are reported as δ values (parts per million) relative to tetramethylsilane as an internal standard.

Tetracyanoethylene oxide (TCNEO) was prepared by reaction of tetracyanoethylene with hydrogen peroxide after the method of Linn.[23]

Preparation of Dicyanomethylides. Method A. To a solution of the heterocyclic compound in the minimum quantity of ethyl acetate cooled at 0 °C was added an equimolar amount of TCNEO in ethyl acetate (1 mmol/mL). The reaction mixture was kept at 0 °C until the product precipitated (2–5 min). The crude product was filtered off and recrystallized.

Method B. To a solution of 0.01 mol of the heterocyclic compound in 50 mL of ether was added an equimolecular amount of TCNEO in 50 mL of ether. The reaction mixture was kept at room temperature for a variable period of time (24–72 h). Then the crude product was filtered off and recrystallized.

Method A was tried with all compounds, and method B was employed when method A failed.

2-Methylpyridinium-1-dicyanomethylide (10a). The compound was prepared by method B with a reaction time of 24 h: yield 2%; mp 197–198 °C (from ethanol); IR (KBr) 2180, 2150 (CN) cm^{-1}; NMR 2.50 (s, CH_3), 7.56–7.70 (m, H-3 and H-5), 8.30 (m, H-4 and H-6).

Anal. Calcd for $C_9H_7N_3$: C, 68.77; H, 4.49; N, 26.74. Found: C, 69.01; H, 4.32; N, 27.12.

Quinolinium-1-dicyanomethylide (11a). The compound was prepared by method B with a reaction time of 24 h: yield 2%; mp 241–242 °C (from ethanol); IR (KBr) 2190 and 2150 (CN) cm^{-1}; NMR 7.66–8.37 (m, aromatic protons), 9.27 (m, H-2).

Anal. Calcd for $C_{12}H_7N_3$: C, 74.60; H, 3.65; N, 21.75. Found: C, 74.83; H, 3.67; N, 21.78.

1-Phenylimidazolium-3-dicyanomethylide (14a). The compound was prepared by method A: yield 74%; mp 210–212 °C (from ethanol); IR (KBr) 2180 and 2120 cm^{-1}; NMR 7.90 (m, Ph and H-5), 8.27 (t, J = 2.0 Hz, H-4), 9.75 (t, J = 2.0 Hz, H-2).

Anal. Calcd for $C_{12}H_8N_4$: C, 69.00; H, 3.84; N, 26.92. Found: C, 68.77; H, 3.88; N, 26.65.

1-Methylbenzimidazolium-3-dicyanomethylide (15a). The compound was prepared by method A: yield 57%; mp 250–252 °C (from ethanol); IR (KBr) 2180 and 2130 cm^{-1}; NMR 4.07 (s, CH_3), 7.60–7.80 (m, aromatic protons), 9.75 (s, H-2).

Anal. Calcd for $C_{11}H_8N_4$: C, 67.33; H, 4.10; N, 28.55. Found: C, 66.90; H, 3.96; N, 28.32.

1-Ethylbenzimidazolium-3-dicyanomethylide (16a). The compound was prepared by method A: yield 66%; mp 224–225 °C (from ethanol); IR (KBr) 2180 and 2135 cm^{-1}; NMR 1.55 (t, J = 7.0 Hz, CH_3), 4.49 (q, J = 7.0 Hz, CH_2), 7.60–8.03 (m, aromatics), 9.80 (s, H-2).

Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.55; H, 4.79; N, 26.65. Found: C, 68.21; H, 4.85; N, 26.64.

1-Ethyl-1,2,3-triazolium-3-dicyanomethylide (19a). The compound was prepared by method A: yield 73%; mp 176–177 °C (from ethanol); IR (KBr) 2190 and 2160 (CN) cm^{-1}; NMR 1.50 (t, J = 7.0 Hz, CH_3), 4.50 (q, J = 7.0 Hz, CH_2), 8.37 (d, J = 1.0 Hz, H-5), 8.65 (d, J = 1.0 Hz, H-4).

Anal. Calcd for $C_7H_7N_5$: C, 52.16; H, 4.37; N, 43.45. Found: C, 52.18; H, 4.46; N, 44.38.

1-Ethylbenzotriazolium-3-dicyanomethylide (21a). The compound was prepared by method B with a reaction time of 24 h: yield 21%; mp 160–161 °C (from ethanol); IR (KBr) 2190 and 2150 (CN) cm^{-1}; NMR 1.63 (t, J = 7.5 Hz, CH_3), 4.91 (q, J = 7.5 Hz, CH_2), 7.83–8.33 (m, aromatics).

Anal. Calcd for $C_{11}H_9N_5$: C, 62.54; H, 4.29; N, 33.15. Found: C, 62.21; H, 4.36; N, 33.41.

1-Methyl-1,2,4-triazolium-4-dicyanomethylide (23a). The compound was prepared by method B with a reaction time of 72 h: yield 10%; mp 150–152 °C (from ethanol); IR (KBr) 2195 and 2140 (CN) cm^{-1}; NMR 3.98 (s, CH_3), 9.17 (s, H-3), 10.08 (s, H-5).

Anal. Calcd for C_6H_5N: C, 48.98; H, 3.40; N, 47.62. Found: C, 49.18; H, 3.45; N, 47.35.

1-Phenyl-1,2,4-triazolium-4-dicyanomethylide (24a). The compound was prepared by method B with a reaction time of 72 h: yield 19%; mp >260 °C (from ethanol); IR (KBr) 2190 and 2130 cm^{-1}; NMR 7.42–7.83 (m, aromatics) 9.42 (s, H-3), 10.82 (s, H-5).

Anal. Calcd for $C_{11}H_7N_5$: C, 63.14; H, 3.37; N, 33.47. Found: C, 62.86; H, 3.32; N, 33.80.

4-Phenyl-1,2,4-triazolium-1-dicyanomethylide (25a). The compound was prepared by method A: yield 74%; mp 228–230 °C (from ethanol); IR (KBr) 2200 and 2160 (CN) cm^{-1}; NMR 6.85–7.83 (m, Ph), 9.60 (s, H-3), 10.55 (s, H-5).

Anal. Calcd for $C_{11}H_7N_5$: C, 63.14; H, 3.37; N, 33.47. Found: C, 62.89; H, 3.38; N, 33.37.

Preparation of Quaternary Salts. The quaternary salts were prepared by known methods.

1,3-Dimethylbenzimidazolium Iodide (15b). The compound was prepared after the method of Auwers and Mauss.[24]

4-Phenyl-1-methyl-1,2,4-triazolium Iodide (25b). The compound was prepared as the 1-phenyl-3-methylimidazolium iodide.[20]

Registry No. 10, 109-06-8; **10a**, 83096-12-2; **11**, 91-22-5; **11a**, 69512-38-5; **12**, 930-36-9; **13**, 1739-84-0; **14**, 7164-98-9; **14a**, 83096-13-3; **14b**, 60311-34-4; **15**, 1632-83-3; **15a**, 83096-14-4; **15b**, 769-15-3; **16**, 7035-68-9; **16a**, 83096-15-5; **17**, 2876-08-6; **18**, 288-14-2; **19**, 78910-06-2; **19a**, 83096-16-6; **19b**, 45471-98-5; **20**, 95-16-9; **21**, 16584-05-7; **21a**, 83114-93-6; **22**, 16584-00-2; **23**, 6086-21-1; **23a**, 83096-17-7; **24**, 13423-60-4; **24a**, 83096-18-8; **25**, 16227-12-6; **25a**, 83096-19-9; **25b**, 67775-78-4; **26**, 16227-15-9; TCNEO, 3189-43-3.

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