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Vicarious Nucleophilic Substitution of Pyridines and 1,2,3-Triazines *via* Their Dicyanomethylide Derivatives

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Vicarious nucleophilic substitution using chloromethyl phenyl sulfone was applied to pyridinium and 1,2,3-triazinium dicyanomethylides to afford corresponding 4-substituted pyridinium and 5-substituted triazinium dicyanomethylides, respectively. They were readily transformed to 4-phenylsulfonylmethylpyridines and 5-phenylsulfonylmethyltriazines by radical reaction.

Keywords pyridinium dicyanomethylide; 1,2,3-triazinium 2-dicyanomethylide; vicarious nucleophilic substitution; chloromethyl phenyl sulfone; molecular orbital calculations; MNDO method

Vicarious nucleophilic substitution (VNS),[1] which has been developed by Makosza *et al.*, has afforded a versatile methodology for the nucleophilic substitution of nitroarenes. Its peculiarity is that the nucleophile itself has a leaving group, such as chlorine, so that the oxidation of the intermediary dihydroadduct is avoided. A nitrosubstituent is essential for the reaction of benzene, pyridine,[2] pyrrole,[3] thiophene[4] *etc.*, and only 1,2,4-triazines[5] and pteridines[6] are sufficiently electron-deficient to undergo VNS in the absence of activating substituents.

During our study of heteroaromatic compounds with activating groups,[7] it was revealed that the dicyanomethylene group on nitrogen in azaaromatics functioned as an electron-withdrawing group to make nucleophilic reaction more feasible.[8] The results prompted us to investigate other nucleophilic reactions of azinium dicyanomethylides, and it was revealed that pyridinium and 1,2,3-triazinium dicyanomethylides react under VNS condition to afford γ-substituted dicyanomethylides and successive radical reaction removes the dicyanomethylene group to give the corresponding pyridine and triazine derivatives. The regioselectivity of the reaction was investigated using semi-empirical molecular orbital calculations. These results are presented in this paper.

VNS Reaction of 1,2,3-Triazinium 2-Dicyanomethylides (2)[9] 1,2,3-Triazines (**1**) are highly π-deficient owing to the presence of three adjacent nitrogen atoms in the ring system, and the ring is fairly unstable because of the tendency for N_2 elimination.[10] We made several attempts to synthesize substituted triazines *via* nucleophilic reaction,[11] but attack at the C-4 position proceeded predominantly to result in ring-opening accompanied by N_2 elimination,[12] and direct VNS reaction to the triazine ring caused ring opening to form a complex mixture of products.

Therefore the other triazine derivatives were subjected to VNS reaction and 1,2,3-triazinium dicyanomethylides (**2**), which were prepared from 1,2,3-triazines with tetracyanoethylene oxide (TCNEO), were found to form 5-substituted derivatives **3** on treatment with chloromethyl phenyl sulfone and sodium hydride or potassium *tert*-butoxide (Chart 1 and Table I). The compounds **3** thus obtained were transformed to the corresponding 5-phenylsulfonylmethyl-1,2,3-triazines (**4**) under reflux in the presence of ammonium persulfate in isopropanol solution (Chart 2).[13] Various alcohols were investigated as the solvent, and when methanol or ethanol was adopted as the solvent, the yields were low because of the nucleophilic attack of the solvent molecule on the C-4 position of **4**

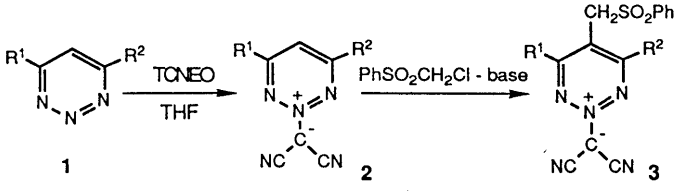

Chart 1

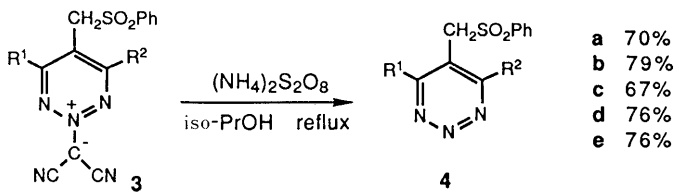

Chart 2

TABLE I. Yields (%) of 5-Phenylsulfonylmethyltriazinium Dicyanomethylides (**3**)

Entry	R^1	R^2	Yield of **2**	Conditions	Yield of **3**
1	Me	Me	86	*tert*-BuOK–DMSO	65
2	Me	Et	82	*tert*-BuOK–DMSO	42
3	Me	Ph	80	NaH–THF/DMSO	54
4	Et	Et	97	*tert*-BuOK–DMSO	55
5	Ph	Ph	82	NaH–THF/DMSO	84

TABLE II. Isolated Yields (%) of Compounds **6**, **7**, and **8**

Entry	R	**6**	**7**	**8**
a	H	90	76	quant.
b	Me	88	81	quant.
c	Et	87	92	95
d	Bu	quant.	83	86
e	OMe	94	86	98
f	OEt	89	87	97

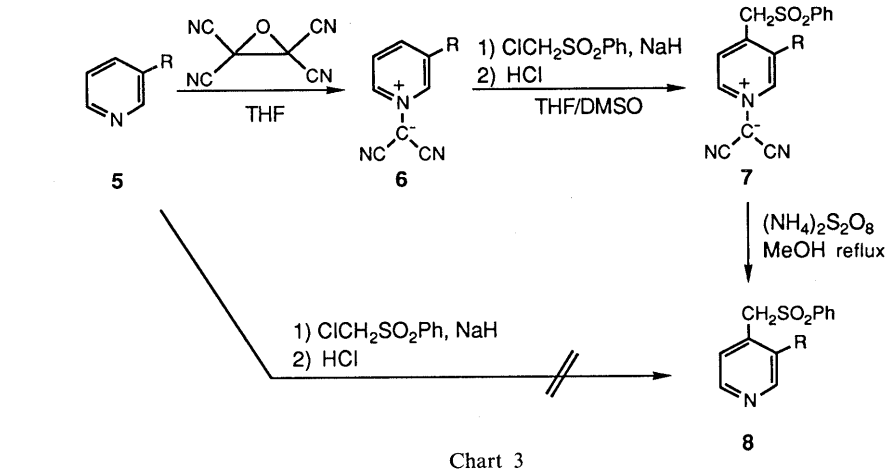

Chart 3

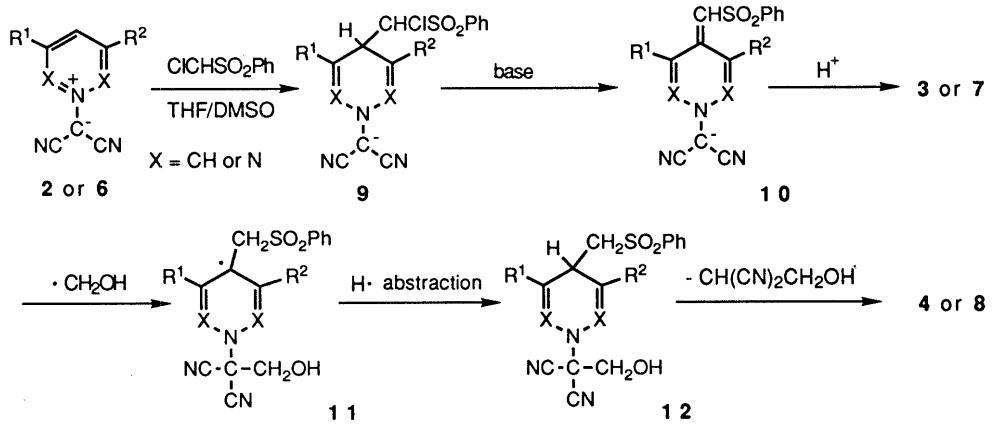

Chart 4

followed by ring opening.

VNS Reaction of Pyridinium Dicyanomethylides (6)[14] Next, the above method was applied to pyridines. Pyridine itself does not undergo VNS reaction, so the parent and 3-substituted pyridines (**5**) were derived to the corresponding *N*-dicyanomethylides (**6**) using TCNEO in tetrahydrofuran (THF). Pyridinium dicyanomethylide thus obtained was subjected to VNS reaction under similar conditions to afford only 4-substituted pyridinium dicyanomethylide (**7**) (Chart 3 and Table II), although general VNS has *o*,*p*-directivity.[1] Compound **7** was readily transformed to 4-substituted pyridines **8** under reflux in methanol with ammonium persulfate. In this case, any alcohol could be used because **8** is stable under reflux in alcohols.

Reaction Mechanism A possible reaction mechanism is shown in Chart 4. First, the azinium ring was attacked by the carbanion formed by treatment of chloromethyl phenyl sulfone with sodium hydride. Then the elimination of HCl occurred to afford **10**, followed by protonation to give **3** or **7**. The attack of the hydroxymethyl radical which was generated by the reaction of ammonium persulfate with methanol was considered to be directed to the dicyanomethylene carbon, and the resulting radical **11** would abstract hydrogen from the solvent, followed by 1,4-elimination to give **4** or **8**. In spite of having three reaction sites, pyridinium 1-dicyanomethylides also gave only 4-substituted products. Thus, we attempted to find the reason for this selectivity by using a semiempirical molecular orbital calculation (MNDO method).[15] The heats of formation (ΔH_f) of fully geometry-optimized reactants and reaction intermediates are shown in Chart 5. The calculations were carried out for the intermediates which were supposed to be formed *via* both α- and γ-attacks of the reactant. The energy level of intermediate **9a** was 4.7 kcal/mol lower than that of **9b**, and the total energy level of intermediate **10a** and HCl was 6.5 kcal/mol lower than that of **10b** and HCl. A protonated intermediate **9a** could be isolated, and when it was allowed to react with a base, 1,8-diazabicyclo[5.4.0]undec-7-ene, the starting material **6a** and product **8a** were obtained. This result suggests that the process of γ-attack on **6** is reversible, so the thermodynamic stability of **9** is thought to have a dominant effect on the selectivity. The difference between the rate of formation of **10** and that of **9** is likely to have a secondary effect on the selectivity. The LUMO energies of pyridine, pyridinium 1-dicyanomethylide, 1,2,3-triazine, and 1,2,3-triazinium 2-dicyanomethylide were also calculated by the MNDO method and were revealed to be 0.138, -1.300, -0.787, and -1.825 eV, respectively. Thus the dicyanomethylene group was proved to lower the LUMO energy level and to raise the electrophilic reactivity of the heteroaromatic ring. The phenylsulfonylmethyl group is known to be readily transformed to various substituents,[16] so the products **4** and **8** should be useful for the syntheses of other substituted 1,2,3-triazines and pyridines.[17]

In conclusion, VNS reactions of pyridinium and 1,2,3-triazinium dicyanomethylide were performed. The dicyanomethylene group, which was easily removed by

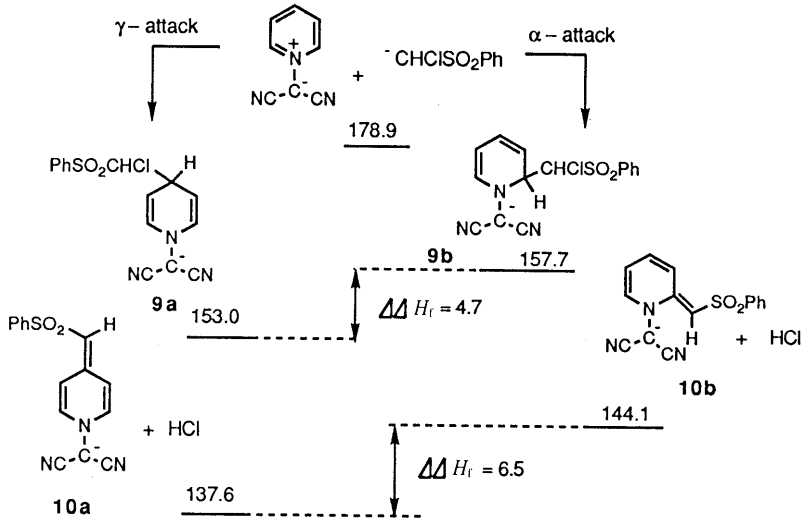

Chart 5. The Heats of Formation (ΔH_f) of Reactants and Reaction Intermediates (kcal/mol)

radical reaction in the subsequent process, made the heteroaromatic rings highly reactive to nucleophiles, and it also played a role in stabilization of the triazine rings. With respect to pyridine 2-dicyanomethylides, the VNS reaction was entirely regioselective to the γ-position, so this reaction system should provide a useful method for the introduction of substituents into the γ-position of the pyridine ring. The introduction of other substituents using this method is under investigation.

Experimental

All melting points were taken on a Yanaco micro melting point apparatus and are uncorrected. The nuclear magnetic resonance spectra were measured with JEOL JNM-FX100 and GX400 spectrometers using tetramethylsilane as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet.

The Reaction of 2 with Chloromethyl Phenyl Sulfone 1-Chloromethyl phenyl sulfone (2 mmol) and a base (potassium *tert*-butoxide or sodium hydride) (2.2 mmol) were allowed to react in dimethyl sulfoxide (DMSO) or THF (3 ml) for 30 min at room temperature. Then the solution was added to a DMSO solution (3 ml) of **2** (1 mmol) at room temperature and the mixture was allowed to stand for 10 min. The reaction was halted by the addition of 10% HCl (10 ml) and the mixture was extracted with ethyl acetate. The extract was dried over $MgSO_4$, and the solvent was evaporated off to leave the residue, which was chromatographed on alumina to afford **3**.

4,6-Dimethyl-5-phenylsulfonylmethyl-1,2,3-triazinium 2-Dicyanomethylide (3a) Yield 65%. Yellow needles from ethanol; mp 252—254 °C (dec.). *Anal.* Calcd for $C_{15}H_{13}N_5O_2S$: C, 55.03; H, 4.00; N, 21.40; S, 9.79. Found: C, 54.95; H, 3.90; N, 21.36; S, 9.49. ^{1}H-NMR (DMSO-d_6) δ: 2.27 (6H, s), 4.78 (2H, s), 7.48—7.91 (5H, m). ^{13}C-NMR (DMSO-d_6) δ: 19.47, 53.30, 74.00, 110.95, 113.44, 128.48, 129.78, 134.82, 138.31, 165.93. MS *m/z*: 327 (M^+), 186 ($M^+ - PhSO_2$).

4-Ethyl-6-methyl-5-phenylsulfonylmethyl-1,2,3-triazinium 2-Dicyanomethylide (3b) Yield 57%. Yellow needles from ethanol; mp 225 °C (dec.). *Anal.* Calcd for $C_{16}H_{15}N_5O_2S$: C, 56.35; H, 4.43; N, 20.54; S, 9.40. Found: C, 56.56; H, 4.47; N, 20.59; S, 8.95. ^{1}H-NMR (DMSO-d_6) δ 1.22 (3H, t, J=7 Hz), 2.37 (3H, s), 2.69 (2H, q, J=7 Hz), 4.22 (2H, s), 7.40—7.88 (5H, m). ^{13}C-NMR (DMSO-d_6) δ: 10.59, 19.80, 25.15, 52.98, 74.20, 110.53, 113.55, 113.63, 128.66, 129.92, 134.96, 138.51, 166.16, 169.18. MS *m/z*: 341 (M^+), 200 ($M^+ - PhSO_2$).

4-Methyl-6-phenyl-5-phenylsulfonylmethyl-1,2,3-triazinium 2-Dicyanomethylide (3c) Yield 54%. Yellow needles from ethanol; mp 259—261 °C (dec.) *Anal.* Calcd for $C_{20}H_{15}N_5O_2S$: C, 61.68; H, 3.88; N, 17.99; S, 8.23. Found: C, 61.49; H, 3.59; N, 18.08; S, 8.36. ^{1}H-NMR (DMSO-d_6) δ: 2.48 (3H, s), 4.81 (2H, s), 7.04—7.80 (10H, m). ^{13}C-NMR (DMSO-d_6) δ: 20.67, 53.48, 74.90, 109.83, 113.42, 113.49, 128.18, 128.66, 128.97, 129.92, 130.81, 131.68, 134.82, 138.05, 164.47, 167.88. MS *m/z*: 389 (M^+), 248 ($M^+ - PhSO_2$).

4,6-Diethyl-5-phenylsulfonylmethyl-1,2,3-triazinium 2-Dicyanomethylide (3d) Yield 55%. Yellow needles from ethanol; mp 237—240 °C (dec.). *Anal.* Calcd for $C_{17}H_{17}N_5O_2S$: C, 57.51; H, 4.83; N, 19.73; S, 9.03. Found: C, 57.77; H, 4.72; N, 19.86; S, 8.71. ^{1}H-NMR ($CDCl_3$) δ: 1.24 (6H, t, J=7 Hz), 2.71 (4H, q, J=7 Hz), 4.24 (2H, s), 7.44—7.88 (5H, m). ^{13}C-NMR (DMSO-d_6) δ: 10.65, 25.28, 52.48, 74.49, 109.95, 113.56, 128.66, 129.89, 134.92, 138.52, 169.25. MS *m/z*: 355 (M^+), 214 ($M^+ - PhSO_2$).

4,6-Diphenyl-5-phenylsulfonylmethyl-1,2,3-triazinium 2-Dicyanomethylide (3e) Yield 84%. Yellow needles from hexane–dichloromethane; mp 258—261 °C (dec.). *Anal.* Calcd for $C_{22}H_{17}N_5O_2S$: C, 66.57; H, 3.80; N, 15.53; S, 7.11. Found: C, 66.34; H, 3.69; N, 15.35; S, 6.79. ^{1}H-NMR ($CDCl_3$) δ: 4.62 (2H, s), 7.08—7.52 (15H, m). ^{13}C-NMR (DMSO-d_6) δ: 54.06, 75.98, 108.32, 113.22, 127.94, 129.09, 129.26, 129.87, 131.34, 132.36, 134.73, 137.90, 166.17. MS *m/z*: 451 (M^+), 310 ($M^+ - PhSO_2$).

The Transformation of 3 to 4 in the Presence of Ammonium Persulfate 5-Phenylsulfonylmethyl-1,2,3-triazinium 2-dicyanomethylide (**3**) (1 mmol) and ammonium persulfate (5 mmol) were suspended in isopropanol (10 ml), and the mixture was refluxed for 30 min. Then water was added, and the mixture was neutralized with sodium carbonate, and extracted with dichloromethane. The organic solution was dried over $MgSO_4$ and evaporated to give almost pure **4**.

4,6-Dimethyl-5-phenylsulfonylmethyl-1,2,3-triazine (4a) Yield 70%. Colorless needles from hexane–dichloromethane; mp 135—137 °C. *Anal.* Calcd for $C_{12}H_{13}N_3O_2S$: C, 54.73; H, 4.98; N, 15.96; S, 12.18. Found: C, 54.92; H, 4.96; N, 15.75; S, 11.90. ^{1}H-NMR ($CDCl_3$) δ: 2.52 (6H, s), 4.44 (2H, s), 7.36—7.92 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: 19.63, 54.88, 118.83, 128.19, 129.87, 134.92, 138.16, 159.62. FAB-MS *m/z*: 264 ($M+H$)$^+$.

4-Ethyl-6-methyl-5-phenylsulfonylmethyl-1,2,3-triazine (4b) Yield 79%. Colorless needles from hexane–dichloromethane; mp 145—147 °C. *Anal.* Calcd for $C_{12}H_{15}N_3O_2S$: C, 56.36; H, 5.46; N, 15.17; S, 11.57. Found: C, 56.52; H, 5.46; N, 15.11; S, 11.16. ^{1}H-NMR ($CDCl_3$) δ:1.31 (3H, t, J=7 Hz), 2.52 (3H, s), 4.42 (2H, s), 7.36—7.75 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: 11.98, 19.75, 25.41, 54.13, 118.00, 128.09, 129.77, 134.84, 138.11, 159.61, 163.13. FAB-MS *m/z*: 278 ($M+H$)$^+$.

4-Methyl-6-phenyl-5-phenylsulfonylmethyl-1,2,3-triazine (4c) Yield 67%. Colorless needles from hexane–dichloromethane; mp 110—112 °C. *Anal.* Calcd for $C_{17}H_{15}N_3O_2S$: C, 62.82; H, 4.65; N, 12.93; S, 9.86. Found: C, 63.05; H, 4.63; N, 13.11; S, 9.49. ^{1}H-NMR ($CDCl_3$) δ: 2.84 (3H, s), 4.61 (2H, s), 6.80—7.56 (10H, m). ^{13}C-NMR ($CDCl_3$) δ: 20.76, 54.00, 117.56, 127.79, 128.69, 128.81, 129.47, 129.91, 133.10, 134.36, 137.69, 159.44, 161.17. FAB-MS *m/z*: 326 ($M+H$)$^+$.

4,6-Diethyl-5-phenylsulfonylmethyl-1,2,3-triazine (4d) Yield 76%. Colorless needles from hexane–dichloromethane; mp 137—138 °C. *Anal.* Calcd for $C_{14}H_{17}N_3O_2S$: C, 57.78; H, 5.89; N, 14.44; S, 11.02. Found: C, 57.84; H, 5.96; N, 14.55; S, 10.93. ^{1}H-NMR ($CDCl_3$) δ: 1.33 (6H, t, J=7 Hz), 2.83 (4H, q, J=7 Hz), 4.43 (2H, s), 7.35—7.80 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: 12.08, 25.63, 53.58, 117.17, 128.21, 129.81, 134.85, 138.16, 163.11. FAB-MS *m/z*: 292 ($M+H$)$^+$.

4,6-Diphenyl-5-phenylsulfonylmethyl-1,2,3-triazine (4e) Yield 76%. Colorless needles from hexane–dichloromethane; mp 190—193 °C. *Anal.* Calcd for $C_{22}H_{17}N_3O_2S$: C, 68.27; H, 4.43; N, 10.86; S, 8.28. Found: C,

68.42; H, 4.46; N, 10.86; S, 8.04. ^{1}H-NMR ($CDCl_3$) δ: 4.91 (2H, s), 6.95—7.60 (15H, m). ^{13}C-NMR ($CDCl_3$) δ:53.72, 115.93, 127.85, 128.99, 129.44, 129.50, 130.45, 134.00, 134.24, 137.72, 160.88. FAB-MS *m/z*: 388 $(M+H)^+$.

Synthesis of Pyridinium Dicyanomethylides (6) Pyridine (1 mmol) was added at 0 °C to a THF solution (10 ml) of tetracyanoethylene oxide (2 mmol), which was prepared according to the literature,[18] and the mixture was allowed to stand at 0 °C for 20 h. Then the solvent was evaporated off and the residue was chromatographed on alumina to give pyridinium dicyanomethylides (**6**). The spectral data of pyridinium 1-dicyanomethylide (**6a**) have already been reported.[18]

3-Methylpyridinium 1-Dicyanomethylide (6b) Yield 88%. Yellow needles from ethanol; mp 215—218 °C. *Anal.* Calcd for $C_9H_7N_3$: C, 68.77; H, 4.49; N, 26.74. Found: C, 68.68; H, 4.34; N, 26.71. ^{1}H-NMR (DMSO-d_6) δ: 2.41 (3H, s), 7.70—7.72 (2H, m), 8.37 (1H, s), 8.40 (1H, dd, J=4.0, 1.4 Hz). ^{13}C-NMR (DMSO-d_6) δ: 18.21, 58.17, 118.94, 127.53, 131.44, 133.05, 136.05, 138.82. MS *m/z*: 157 (M^+).

3-Ethylpyridinium 1-Dicyanomethylide (6c) Yield 87%. Yellow needles from ethanol; mp 159—161 °C. *Anal.* Calcd for $C_{10}H_9N_3$: C, 70.15; H, 5.30; N, 24.55. Found: C, 70.19; H, 5.25; N, 24.56. ^{1}H-NMR (DMSO-d_6) δ 1.21 (3H, t, J=7.5 Hz), 2.74 (2H, q, J=7.5 Hz), 7.74—7.77 (2H, m), 8.36 (1H, s), 8.40—8.43 (1H, m). ^{13}C-NMR (DMSO-d_6) δ: 14.63, 25.38, 58.35, 118.93, 127.77, 131.70, 132.45, 134.94, 144.42. MS *m/z*: 171 (M^+).

3-Butylpyridinium 1-Dicyanomethylide (6d) Yield 99%. Yellow needles from ethanol; mp 106—108 °C. *Anal.* Calcd for $C_{12}H_{13}N_3$: C, 72.33; H, 6.57; N, 21.09. Found: C, 72.49; H, 6.47; N, 20.93. ^{1}H-NMR (DMSO-d_6) δ: 1.05 (3H, t, J=8.0 Hz), 1.24—1.89 (4H, m), 2.86 (2H, t, J=7.5 Hz), 7.78—7.81 (2H, m), 8.42—8.44 (2H, m). ^{13}C-NMR (DMSO-d_6) δ: 13.60, 21.54, 31.44, 32.06, 58.16, 118.59, 127.52, 131.46, 132.40, 134.95, 142.90. MS *m/z*: 199 (M^+).

3-Methoxypyridinium 1-Dicyanomethylide (6e) Yield 94%. Yellow needles from ethanol; mp 148—150 °C. *Anal.* Calcd for $C_9H_7N_3O$: C, 62.42; H, 4.07; N, 24.27. Found: C, 62.13; H, 3.91; N, 24.00. ^{1}H-NMR ($CDCl_3$) δ: 3.94 (3H, s), 7.04 (1H, dd, J=9.0, 1.0 Hz), 7.40 (1H, t, J=9.0 Hz), 8.02—8.05 (2H, m). ^{13}C-NMR (DMSO-d_6) δ: 56.77, 58.84, 118.29, 120.27, 121.06, 126.57, 128.25, 157.93. MS *m/z*: 173 (M^+).

3-Ethoxypyridinium 1-Dicyanomethylide (6f) Yield 89%. Yellow needles from ethanol; mp 156—157 °C. *Anal.* Calcd for $C_{10}H_9N_3O$: C, 64.16; H, 4.85; N, 22.45. Found: C, 64.38; H, 4.85; N, 22.72. ^{1}H-NMR ($CDCl_3$) δ: 1.48 (3H, t, J=8.0 Hz), 4.12 (2H, q, J=8.0 Hz), 6.99 (1H, dd, J=10, 1.0 Hz), 7.36 (1H, t, J=10 Hz), 8.01—8.04 (2H, m). ^{13}C-NMR (DMSO-d_6) δ: 14.13, 58.82, 65.27, 118.28, 120.53, 121.25, 126.43, 126.67, 128.30, 157.20. MS *m/z*: 187 (M^+).

The Reaction of Pyridinium Dicyanomethylides (6) with Chloromethyl Phenyl Sulfone in the Presence of a Base A DMSO solution (3 ml) of **6** (0.5 mmol) was added at 0 °C to a THF solution (3 ml) of chloromethyl phenyl sulfone (1.0 mmol) and sodium hydride (60%, 1.6 mmol), which had been preincubated for 30 min at room temperature, and the mixture was allowed to stand at 0 °C for 1 h. Then aqueous HCl (10 ml) was added, and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with water, dried over $MgSO_4$, and evaporated off to leave the residue, which was chromatographed on alumina to afford 4-phenylsulfonylmethylpyridinium dicyanomethylides (**7**).

4-Phenylsulfonylmethylpyridinium 1-Dicyanomethylide (7a) Yield 76%. Pale yellow granules from hexane–dichloromethane; mp 253—255 °C (dec.). *Anal.* Calcd for $C_{15}H_{11}N_3O_2S$: C, 60.66; H, 3.73; N, 14.15. Found: C, 60.92; H, 3.49; N, 13.85. ^{1}H-NMR (DMSO-d_6) δ: 4.97 (2H, s), 7.54 (1H, d, J=7.0 Hz), 7.62—7.67 (2H, m), 7.76—7.79 (3H, m), 8.52 (1H, d, J=7.0 Hz). ^{13}C-NMR (DMSO-d_6) δ: 58.68, 58.91, 118.04, 128.15, 129.43, 129.54, 132.84, 134.38, 135.46, 137.83. MS *m/z*: 297 (M^+).

3-Methyl-4-phenylsulfonylmethylpyridinium 1-Dicyanomethylide (7b) Yield 81%. Pale yellow needles from hexane–dichloromethane; mp 253—256 °C (dec.). *Anal.* Calcd for $C_{16}H_{13}N_3O_2S$: C, 61.79; H, 4.21; N, 13.51. Found: C, 61.77; H, 4.03; N, 13.70. ^{1}H-NMR (DMSO-d_6) δ: 2.17 (3H, s), 4.94 (2H, s), 7.47 (1H, d, J=6.6 Hz), 7.63—7.67 (2H, m), 7.77—7.82 (3H, m), 8.32 (1H, s), 8.42 (1H, d, J=6.6 Hz). ^{13}C-NMR (DMSO-d_6) δ: 16.03, 56.96, 58.40, 118.17, 128.23, 129.54, 130.10, 130.66, 132.61, 134.51, 134.57, 138.16, 138.87. MS *m/z*: 311 (M^+).

3-Ethyl-4-phenylsulfonylmethylpyridinium 1-Dicyanomethylide (7c) Yield 92%. Yellow needles from ethanol; mp 217—220 °C (dec.). *Anal.* Calcd for $C_{17}H_{15}N_3O_2S$: C, 62.82; H, 4.65; N, 12.93. Found: C, 63.02; H, 4.44; N, 12.88. ^{1}H-NMR (DMSO-d_6) δ: 1.06 (3H, t, J=7.5 Hz), 2.59 (2H, q, J=7.5 Hz), 4.93 (2H, s), 7.54 (1H, d, J=6.6 Hz), 7.63—7.68 (2H, m), 7.77—7.84 (3H, m), 8.25 (1H, d, J=1.5 Hz), 8.44 (1H, dd, J=6.6, 1.5 Hz). ^{13}C-NMR (DMSO-d_6) δ: 13.86, 22.33, 56.33, 58.65, 118.17, 128.25, 129.50, 130.35, 130.62, 131.90, 133.75, 134.47, 138.16, 143.83. MS *m/z*: 325 (M^+).

3-Butyl-4-phenylsulfonylmethylpyridinium 1-Dicyanomethylide (7d) Yield 83%. Yellow needles from ethanol; mp 152—153 °C. *Anal.* Calcd for $C_{19}H_{19}N_3O_2S$: C, 64.64; H, 5.43; N, 11.91. Found: C, 64.39; H, 5.24; N, 11.97. ^{1}H-NMR (DMSO-d_6) δ: 0.86 (3H, t, J=7.1 Hz), 1.24—1.38 (4H, m), 2.50 (2H, t, J=7.3 Hz), 4.91 (2H, s), 7.56 (1H, d, J=6.6 Hz), 7.63—7.68 (2H, m), 7.77—7.83 (3H, m), 8.25 (1H, d, J=1.4 Hz), 8.44 (1H, dd, J=6.6, 1.4 Hz), ^{13}C-NMR (DMSO-d_6) δ: 13.57, 21.80, 28.65, 31.46, 56.42, 58.67, 118.08, 128.24, 129.48, 130.38, 130.51, 132.08, 133.75, 134.44, 138.13, 142.57. MS *m/z*: 289 (M^+ −C(CN)$_2$).

3-Methoxy-4-phenylsulfonylmethylpyridinium 1-Dicyanomethylide (7e) Yield 86%. Yellow needles from ethanol; mp 242—244 °C (dec.). *Anal.* Calcd for $C_{16}H_{13}N_3O_3S$: C, 58.76; H, 4.01; N, 12.85. Found: C, 58.94; H, 3.82; N, 12.87. ^{1}H-NMR (DMSO-d_6) δ: 3.55 (3H, s), 4.78 (2H, s), 7.60—7.64 (3H, m), 7.72—7.78 (3H, m), 7.87 (1H, d, J=1.4 Hz), 8.31 (1H, dd, J=6.6, 1.4 Hz). ^{13}C-NMR (DMSO-d_6) δ: 54.25, 56.71, 59.59, 117.66, 118.04, 124.15, 126.44, 128.16, 129.28, 129.93, 134.26, 138.35, 155.55. MS *m/z*: 327 (M^+).

3-Ethoxy-4-phenylsulfonylmethylpyridinium 1-Dicyanomethylide (7f) Yield 87%. Orange needles from ethanol; mp 212—214 °C (dec.). *Anal.* Calcd for $C_{17}H_{15}N_3O_3S$: C, 59.87; H, 4.43; N, 12.33. Found: C, 59.83; H, 4.34; N, 12.51. ^{1}H-NMR (DMSO-d_6) δ: 1.04 (3H, t, J=7.0 Hz), 3.79 (2H, q, J=7.0 Hz), 4.77 (2H, s), 7.60—7.78 (6H, m), 7.82 (1H, d, J=1.4 Hz), 8.31 (1H, dd, J=6.6, 1.4 Hz). ^{13}C-NMR (DMSO-d_6) δ: 13.68, 54.22, 59.59, 65.33, 117.90, 118.08, 124.18, 126.37, 128.19, 129.31, 129.98, 134.27, 138.43, 154.76. MS *m/z*: 341 (M^+).

The Synthesis of 4-Phenylsulfonylmethylpyridines (8) Compound **7** (0.5 mmol) and ammonium persulfate (1 mmol) were suspended in methanol (20 ml), and the mixture was heated under reflux until the yellow color of **7** had entirely disappeared (approximately 1 h). Then water was added, the solvent was neutralized with Na_2CO_3, and the mixture was extracted with dichloromethane. The organic layer was dried over $MgSO_4$ and evaporated to leave the residue, which was almost pure **8**.

4-Phenylsulfonylmethylpyridine (8a) Quantitative yield. Colorless needles from hexane–dichloromethane; mp 205—207 °C. *Anal.* Calcd for $C_{12}H_{11}NO_2S$: C, 61.85; H, 4.76; N, 6.01. Found: C, 61.66; H, 4.59; N, 6.16. ^{1}H-NMR ($CDCl_3$) δ: 4.24 (2H, s), 6.93 (2H, d, J=5.0 Hz), 7.22—7.65 (5H, m), 8.39 (2H, d, J=5.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 61.81, 125.38, 128.47, 129.13, 134.15, 136.94, 137.38, 150.01. MS *m/z* 233 (M^+).

3-Methyl-4-phenylsulfonylmethylpyridine (8b) Quantitative yield. Colorless granules from hexane–dichloromethane; mp 137—139 °C. *Anal.* Calcd for $C_{13}H_{13}NO_2S$: C, 63.21; H, 5.31; N, 5.67. Found: C, 62.97; H, 5.26; N, 5.63. ^{1}H-NMR ($CDCl_3$) δ: 2.08 (3H, s), 4.29 (2H, s), 6.85 (1H, d, J=5.0 Hz), 7.25—7.68 (5H, m), 8.22 (1H, d, J=5.0 Hz), 8.26 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 15.98, 59.04, 125.66, 128.53, 129.19, 133.30, 134.19, 135.30, 137.83, 147.48, 151.47. MS *m/z*: 247 (M^+).

3-Ethyl-4-phenylsulfonylmethylpyridine (8c) Yield 95%. Colorless flakes from hexane–dichloromethane; mp 85—86 °C. *Anal.* Calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36. Found: C, 64.24; H, 5.78; N, 5.34. ^{1}H-NMR ($CDCl_3$) δ: 1.11 (3H, t, J=7.5 Hz), 2.46 (2H, q, J=7.5 Hz), 4.38 (2H, s), 6.99 (1H, d, J=4.8 Hz), 7.47—7.52 (2H, m), 7.63—7.70 (3H, m), 8.36 (1H, d, J=4.8 Hz), 8.43 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 14.65, 22.66, 58.36, 125.73, 128.50, 129.14, 134.13, 134.51, 137.79, 138.78, 147.26, 150.48. MS *m/z*: 261 (M^+).

3-Butyl-4-phenylsulfonylmethylpyridine (8d) Yield 86%. Colorless needles from hexane–dichloromethane; mp 70—71 °C. *Anal.* Calcd for $C_{16}H_{19}NO_2S$: C, 66.40; H, 6.62; N, 4.84. Found: C, 66.36; H, 6.62; N, 4.87. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, t, J=7.3 Hz), 1.24—1.41 (4H, m), 2.37 (2H, t, J=7.9 Hz), 4.36 (2H, s), 7.03 (1H, d, J=4.8 Hz), 7.45—7.50 (2H, m), 7.61—7.66 (3H, m), 8.34 (1H, d, J=4.8 Hz), 8.38 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 13.70, 22.40, 29.20, 32.53, 58.42, 125.94, 128.50, 129.19, 134.20, 135.32, 137.76, 137.90, 146.67, 150.47. MS *m/z*: 289 (M^+).

3-Methoxy-4-phenylsulfonylmethylpyridine (8e) Yield 98%. Colorless flakes from hexane–dichloromethane; mp 92—93 °C. *Anal.* Calcd for $C_{13}H_{13}NO_3S$: C, 59.30; H, 4.98; N, 5.32. Found: C, 59.55; H, 4.78; N, 5.36. ^{1}H-NMR ($CDCl_3$) δ: 3.50 (3H, s), 7.27 (1H, d, J=4.8 Hz), 7.56—7.72 (5H, m), 8.21 (1H, d, J=4.8 Hz), 8.25 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 52.58, 54.02, 123.75, 124.44, 126.13, 127.01, 131.36, 131.98, 136.42, 139.46, 151.44. MS *m/z*: 263 (M^+).

3-Ethoxy-4-phenylsulfonylmethylpyridine (8f) Yield 97%. Colorless plates from hexane–dichloromethane; mp 88—89 °C. *Anal.* Calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05. Found: C, 60.84; H, 5.35; N, 5.22. ^{1}H-NMR ($CDCl_3$) δ: 1.09 (3H, t, J=7.0 Hz), 3.77 (2H, q, J=7.0 Hz), 7.35 (1H, d, J=4.7 Hz), 7.55—7.72 (5H, m), 8.23 (1H, d, J=4.7 Hz), 8.25

(1H, s). ^{13}C-NMR ($CDCl_3$) δ: 14.16, 54.41, 64.21, 126.30, 126.62, 128.06, 129.00, 133.40, 133.97, 138.35, 140.74, 152.86. MS *m/z*: 277 (M^+).

Molecular Orbital Calculations The calculations were carried out using the MNDO[15] procedure with the standard parameters, as implemented in the MOPAC[19] program.

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