form) ion exchange column. The eluant was collected and concentrated in vacuo. The residue was treated with methanolic ammonia for 48 h at room temperature. The solution was evaporated in vacuo, and the product was isolated by paper chromatography (2-propanol–concentrated ammonia–water (7:1:2 v/v). Yields were 84–89% as determined spectrophotometrically. Characterization of the deprotected oligonucleotides are collected Table II.

Registry No. **1a**, 78456-41-4; **1b**, 78479-39-7; **1c**, 78456-42-5; **1d**, 78456-43-6; **2a**, 78512-47-7; **2b**, 78512-48-8; **2c**, 78456-44-7; **2d**, 78456-45-8; **3**, 78513-23-2; **4**, 78512-49-9; **5**, 70007-96-4; **6**, 78456-46-9; **7**, 78456-47-0; 2-cyanoethyl phosphate, 2212-88-6; bis(dimethylthiocarbamoyl) disulfide, 137-26-8; 5′-*O*-(methoxytrityl)thymidine, 42926-80-7; 5′-*O*-(methoxytrityl)-N^4-anisoyldeoxycytidine, 57361-91-8; 5′-*O*-(methoxytrityl)-N^6-benzoyldeoxyadenosine, 24816-13-5; 5′-*O*-(methoxytrityl)-N^2-isobutyryldeoxyguanosine, 59321-92-5; 3′-*O*-benzoylthymidine, 17331-53-2; N^6-benzoyldeoxyadenosin-3′-yl 2-cyanoethyl phosphate, 78456-48-1; *d*-Tp, 2642-43-5; *d*-Cp, 6220-63-9; *d*-Ap, 15731-72-3; *d*-Gp, 6220-62-8; *d*-TpTp, 2476-56-4; *d*-TpTpTp, 4712-59-8.

Nonclassical Heteropentalenes Containing the Selenodiazole, Thiatriazole, and Selenotriazole Ring Systems[1]

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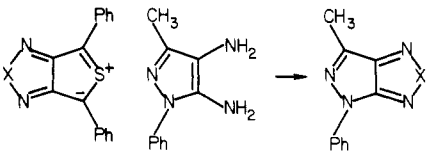
Heteropentalenes containing a "nonclassical" thiophene nucleus have been found to undergo a variety of cycloaddition reactions,[2] often leading to unexpected products.[3] The most interesting cycloaddition properties exist in those systems containing only one heteroatom in each of the two fused rings, additional heteroatoms resulting in increased stability and reduced chemical reactivity. Incorporation of a nitrogen atom at the ring junction of the bicyclic system also has a pronounced effect on the stability and properties of the resultant systems. In this publication evidence is presented to substantiate further the above generalizations.

Diphenylthieno[3,4-*c*][1,2,5]thiadiazole (1, X = S) undergoes[4] cycloaddition with electron-deficient dipolarophiles across the thiocarbonyl ylide dipole only. No reaction was observed at the N^-—S^+=N dipole. In this instance extrusion of sulfur occurs with formation of the corresponding benzothiadiazoles.[3,4] The corresponding diphenylthieno[3,4-*c*][1,2,5]oxadiazole (1, X = O) also undergoes reaction with acetylenic dipolarophiles across the thiocarbonyl ylide but in this system, in addition to the benzooxadiazole, an isoxazolyl dihydrothiophene derivative is formed by fission of the oxadiazole ring. An intermediate nitrile oxide then undergoes additional reaction with another molecule of the acetylene.[3] In contrast, the corresponding 4,6-diphenyl-2-methylthieno[3,4-*c*]-[1,2,3]triazole (1, X = NCH_3) did not undergo[5] cycloaddition with a variety of electron-deficient dipolarophiles. The 1,2,5-thiadiazolo[3,4-*c*]thiadiazole prepared[6] from 3,4-diamino-1,2,5-thiadiazole and sulfur monochloride in DMF proved to be a relatively stable ring system whose bond lengths indicated that it should be considered an heteroaromatic compound. It did not undergo cycloaddition with a variety of electron-deficient dipolarophiles.

We have found that reaction of 4,5-diamino-1-phenyl-3-methylpyrazole dihydrochloride (2) with sulfur monochloride readily afforded 6-methyl-4-phenylpyrazolo[3,4-*c*][1,2,5]thiadiazole (3, X = S). The structure of 3 (X =

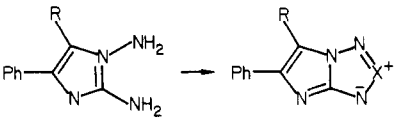


1 2 3

S) followed from its analytical and spectral data which are listed in Table I. No evidence of cycloadditions with dipolarophiles was found for 3 (X = S).

1,2,5-Selenadiazoles are also readily available from 1,2-diamino compounds and selenium dioxide or selenium monochloride, this route being particularly suited to the synthesis of condensed aromatic systems.[8] Reaction of 2 with selenium dioxide readily gave 6-methyl-4-phenylpyrazolo[3,4-*c*][1,2,5]selenadiazole (3, X = Se) whose structure was established on the basis of its analytical and spectral data shown in Table I.

Applying similar reactions to appropriately substituted 1,2-diaminoimidazoles allows the introduction of a nitrogen atom at a ring junction position. Thus 1,2-diamino-4,5-diphenylimidazole[9] (4, R = Ph) was treated with thionyl chloride in hot pyridine solution and afforded 5,6-diphenylimidazolo[1,2-*c*]thiatriazole (5, X = S, R = Ph) as orange needles (68%). The structure of 5 (X = S, R =



4 5

Ph) was established on the basis of its analytical and spectral data. Its infrared spectrum was devoid of NH absorptions and its NMR spectrum consisted of a complex aromatic multiplet centered at δ 7.4. The molecular ion *m/e* 278 was the most abundant ion in the spectrum and an [M + 2] ion was consistent with the presence of one sulfur atom. 5-Phenylimidazolo[1,2-*c*]thiatriazole (5, X = S, R = H) was prepared in a similar manner from 1,2-diamino-4-phenylimidazole (4, R = H) and thionyl chloride/pyridine except that a reaction temperature of 0 °C was required. It was obtained after chromatography as yellow needles (40%), and it proved to be considerably less stable to heat than the diphenyl analogue. Its structure was consistent with its analytical and spectral data, the

(1) Abstracted in part from the Ph.D. Thesis (R.C., 1980) and the M.S. Thesis (R.J.D., 1978), Rensselaer Polytechnic Institute.

(2) For a summary of these reactions, see Cava, M. P.; Lakshmikantham, M. V. *Acc. Chem. Res.* **1975**, *8*, 139. Potts, K. T. "Special Topics in Heterocyclic Chemistry"; Weissberger, A., Taylor, E. C., Eds.; Wiley: New York, 1977; Chapter 6. Ramsden, C. A. *Tetrahedron* **1977**, *33*, 3203.

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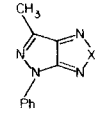
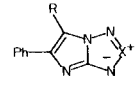
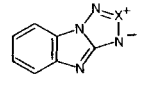
Table I. Some Polyazaheteropentalenes Containing Sulfur and Selenium Atoms

R	X	mp,[a] °C	% yield	crystal form	formula	analysis: calcd C	calcd H	calcd N	found C	found H	found N	M^{+}· (% rel int)	NMR data, δ ($CDCl_3$)	UV data (CH_3OH), nm (log ε)
Some Pyrazolo[3,4-*c*][1,2,5]thia- and selenadiazoles (3) 														
	S	45–47	36	colorless needles	$C_{10}H_8N_4S$	55.55	3.73	25.92	55.32	3.69	25.68	216 (100)	8.10–7.10 (m, 5, aromatic), 2.60 (s, 3, CH_3)	
	Se	98–100	52	yellow needles	$C_{10}H_8N_4Se$	45.64	3.06	21.29	45.87	3.02	21.39	263 (75)	7.50–7.20 (m, 5, aromatic), 2.62 (s, CH_3)	
Some Imidazolo[1,2-*c*]thia- and selenatriazoles (5) 														
Ph	S	145–146	68	orange needles	$C_{15}H_{10}N_4S$	64.74	3.62	20.13	64.51	3.71	20.03	278 (100)	7.4 (m, aromatic)	428 (3.87), 278 (4.17), 220 (4.33)
H	S	169–170	40	yellow needles	$C_9H_6N_4S$	53.44	2.99	27.71	53.75	3.06	27.51	202 (95)	8.27 (s, 1, C_6-H), 7.65 (m, 5, aromatic)	401 (4.02), 315 (4.05), 223 (4.16), 212 (4.16)
Ph	Se	206–206.5[b]	69	maroon needles	$C_{15}H_{10}N_4Se$	55.39	3.10	17.73	55.51	3.21	17.45	325 (13)	7.2–7.9 (m, aromatic)	472 (3.82), 337 (4.03), 279 (3.97), 233 (4.13)
H	Se	165–166	5	orange prisms	$C_9H_6N_4Se$	43.39	2.43	22.49	43.70	2.41	22.38	249 (43)	8.22 (s, 1, C-H), 8.05 (m, 2, aromatic), 7.37 (m, 3, aromatic)	442 (3.91), 345 (4.03), 263 (3.44), 229 (4.09)
Some Benzimidazolo[1,2-*c*]thia- and selenatriazoles (7) 														
	S	135	47	red needles	$C_7H_4N_4S$	47.72	2.29	31.80	47.55	2.23	31.77	176 (57)	8.2–7.2 (m, aromatic)	438 (3.96),,335 (3.91), 232 (4.28)
	Se	190–191	5	purple plates	$C_7H_4N_4Se$	37.68	1.81	25.12	37.81	1.81	24.76	223 (45)	8.3 (d, 2, C_6-H, C_7-H)[c] 7.6 (d, 2, C_5-H, C_8-H)	505 (3.30), 364 (4.33), 251 (4.46), 229 (4.30)

[a] All decomposed at melting point except *b*. [c] Me_2SO-d_6.

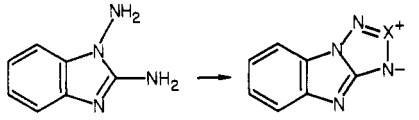
latter being very similar to those of the diphenyl compound. The imidazole ring proton in **5** (X = S, R = H) occurred as a singlet at δ 8.27, and in its mass spectrum, the molecular ion m/e 202 (95%) was not the most intense ion, that being m/e 116 corresponding to phenyl azirine. In the diphenyl analogue, the reverse was observed.

A tricyclic representative of this nonclassical heteropentalene system was also prepared from 1,2-diaminobenzimidazole[9b] (**6**) and thionyl chloride in pyridine. Benzimidazolo[1,2-*c*]thiatriazole (**7**, X = S) was obtained as red needles (47%), and the spectral data which established its structure are described in the Experimental Section. It is thought[10] that the above cyclizations involve an intermediate thionitroso oxide which undergoes cyclization to the cyclic *S*-oxide which, in turn, loses water to form the N=S$^+$—N$^-$ grouping. None of these ring-fused thiatriazole derivatives, and the selenium containing products described below, underwent cycloadditions with electron-deficient dipolarophiles under a wide variety of reaction conditions.

There are no reported examples of selenatriazoles, and the influence of a selenium atom on the properties of a nonclassical heteropentalene is of particular interest. Only one such selenium-containing heteropentalene has been described and it could only be isolated as its *N*-phenylmaleimide cycloadduct.[11]

Treatment of 1,2-diamino-4,5-diphenylimidazole (**4**, R = Ph) with 1 equiv of selenium dioxide in hot, absolute ethanol afforded 5,6-diphenylimidazo[1,2-*c*]selenatriazole (**5**, X = Se, R = Ph) as maroon needles (69%). As with the above sulfur-containing systems, the mass spectrum of **5** (X = Se, R = Ph) provided convincing evidence in support of the assigned structure with a molecular ion at m/e 325 (13) and a fragmentation pattern analogous to **5** (X = S, R = Ph).

1,2-Diamino-4-phenylimidazole (**4**, R = H) also reacted with selenium dioxide to give after chromatography, 5-phenylimidazolo[1,2-*c*]selenatriazole (**5**, X = Se; R = H) as orange prisms in very poor yield. The imidazole ring proton, present as a singlet at δ 8.17 and the molecular ion m/e 249 (43%) are consistent with the assigned structure. Benzimidazolo[1,2-*c*]selenatriazole (**7**, X = Se) was also obtained when **6** was treated with SeO_2 in absolute alcohol.



6 **7**

This heteropentalene was obtained as purple plates, again in poor yield. Spectral data on which the structural assignment is based are listed in the Experimental Section.

Attempts to prepare alkyl-substituted derivatives of **5** and **7** were unsuccessful due to our inability to prepare 1,2-diaminoalkylimidazoles by modification of the methods used to obtain[9a] aryl-substituted products. Reaction of the α-haloketones with benzalaminoguanidines in the initial step always resulted in the formation of intractable tars.

Analogous sulfur and selenium heterocycles often show[12] many similarities in their electron spectra. This group of compounds provides a unique opportunity for evaluating the effect of replacing a sulfur atom with selenium, and these data are shown in Table I.

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(11) Gronowitz, S.; Konar, H. *J. Chem. Soc., Chem. Commun.* **1977**, 163.
(12) Sawicki, E.; Carr, A. *J. Org. Chem.* **1957**, *22*, 503. Sawicki, E. *Ibid.* **1954**, *19*, 1165. Sawicki, E. *J. Am. Chem. Soc.* **1955**, *77*, 957.

Experimental Section[13]

6-Methyl-4-phenylpyrazolo[3,4-*c*][1,2,5]thiadiazole (3, X = S). 4,5-Diamino-3-methyl-1-phenylpyrazole dihydrochloride (**2**; 0.52 g, 2 mmol) in DMF (10 mL) was cooled to 0 °C in an ice bath and treated dropwise with sulfur monochloride (800 μL, 0.01 mol). After the red-brown solution was stirred for 90 min, it was poured into ice–water (100 mL), the aqueous solution was extracted with Et_2O (4 × 50 mL), and the ether layer was dried (Na_2SO_4) and concentrated to a dark oil. Addition of a small volume of EtOH ultimately afforded grey needles which crystallized from ethanol as colorless needles: 0.15 g (36%), mp 45–47 °C (Table I).

6-Methyl-4-phenylpyrazolo[3,4-*c*][1,2,5]selenadiazole (3, X = Se). The diamino compound **2** (0.52 g, 2 mmol) in EtOH (5 mL) was treated with anhydrous NaOAc (0.32 g, 0.004 mol) followed by selenium dioxide (0.22 g, 0.002 mol). After stirring for 15 min the separated material was collected, dried, and recrystallized from EtOH, affording bright-yellow needles: 0.26 g (52%), mp 98–100 °C (Table I).

5,6-Diphenylimidazolo[1,2-*c*]thiatriazole (5, X = S, R = Ph). 1,2-Diamino-4,5-diphenylimidazole (**4**, R = Ph) (500 mg, 2 mmol) was stirred in pyridine (4 mL) and treated dropwise with thionyl chloride (250 μL). The resultant exothermic reaction mixture was heated at 125 °C for 15 min, after which additional thionyl chloride (30 μL) was added and heating continued for a further 30 min, this sequence being repeated once more. The reaction mixture was cooled in ice and poured into cold water (10 mL). The yellow solid that separated was collected, washed with cold water, and, after drying, recrystallized from benzene–petroleum ether (bp 60–80 °C), affording orange needles: 350 mg (68%), mp 145–146 °C (Table I).

5-Phenylimidazolo[1,2-*c*]thiatriazole (5, X = S, R = H). The diaminoimidazole (**4**, R = H; 500 mg, 2.8 mmol) was suspended in dry pyridine and treated dropwise with $SOCl_2$ (400 μL). After the reaction mixture was stirred for 30 min, it was poured into a 10% solution of acetic acid and ice. The yellow solid that separated was recrystallized from benzene–petroleum ether, final purification being effected by chromatography on alumina (benzene), affording yellow microneedles: 210 mg (40%), mp 169–170 °C dec (Table I).

Benzimidazolo[1,2-*c*]thiatriazole (7, X = S). 1,2-Diaminobenzimidazole (500 mg, 3.4 mmol) was suspended in dry pyridine (5 mL) and treated with $SOCl_2$ (250 μL). After the reaction mixture was heated at 100 °C for 15 min, two further additions of thionyl chloride (50 μL each) were made at 30-min intervals. After cooling, the reaction mixture was extracted with benzene and after evaporation of the solvent an orange brown residue was obtained. This crystallized from benzene–petroleum ether as red needles: 279 mg (47%), mp 135 °C dec (Table I).

5,6-Diphenylimidazolo[1,2-*c*]selenatriazole (5, X = Se, R = Ph). The diaminoimidazole **4** (R = Ph) (6.0 g, 23 mmol) was suspended in absolute ethanol and selenium dioxide was added. After the mixture was stirred for 20 min, heat was applied to afford a homogeneous solution. Evaporation to dryness followed by recrystallization of the residue from ethanol afforded maroon needles; 5.34 g (69%), mp 206–206.5 °C (Table I).

5-Phenylimidazolo[1,2-*c*]selenatriazole (5, X = Se, R = H). The diaminoimidazole **4** (R = H; 1.0 g, 5 mmol) was suspended in absolute ethanol and SeO_2 (0.63 g, 5 mmol) was added. Stirring was continued until a homogeneous solution resulted and then the solvent was removed. The orange-brown solid was chromatographed on silica gel ($CHCl_3$) and, after recrystallization from chloroform, the product was obtained as orange prisms: 60 mg (5%), mp 165–166 °C (Table I).

Benzimidazolo[1,2-*c*]selenatriazole (7, X = Se) was obtained in the same way from 1,2-diaminobenzimidazole (500 mg, 3.4 mmol) and SeO_2 (360 mg, 3.4 mmol). After chromatography

(13) Spectral characterizations were carried out with the following instrumentation: IR, Perkin-Elmer Model 337 spectrophotometer; NMR, Varian T-60 spectrometer using Me_4Si as internal standard; mass spectra, Hitachi-Perkin Elmer RMU-6E mass spectrometer at 70 eV, using the direct insertion probe at about 120 °C. Evaporations were done under reduced pressure, using a Rotovap apparatus, and melting points were determined in capillaries. Analyses were by Instranal Laboratories, Inc., Rensselaer, NY, and Galbraith Laboratories, Inc., Knoxville, TN.

and recrystallization from $CHCl_3$, it was obtained as purple plates: 40 mg (5%), mp 190–191 °C (Table I).

Registry No. 2, 52943-88-1; 3 (X = S), 78515-08-9; 3 (X = Se), 78515-09-0; 4 (R = Ph), 19933-51-8; 4 (R = H), 15970-40-8; 5 (X = S; R = Ph), 78515-10-3; 5 (X = S; R = H), 78529-83-6; 5 (X = Se; R = Ph), 78515-11-4; 5 (X = Se; R = H), 78515-12-5; 6, 29540-87-2; 7 (X = S), 78515-13-6; 7 (X = Se), 78515-14-7.

Reactions of 4-Carbethoxy-2-cyclohexyl-5(2*H*)-isoxazolone

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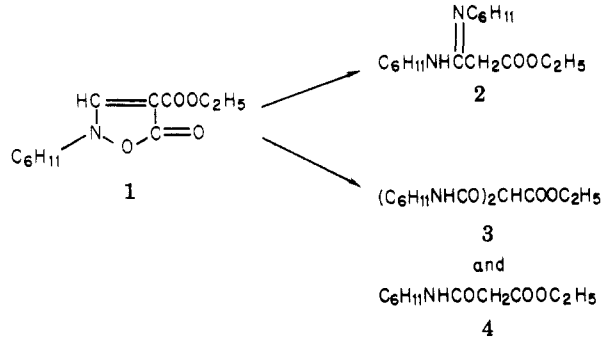
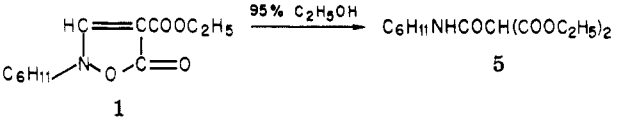
5(2*H*)-Isoxazolones which are not substituted in the 3-position undergo ring-opening reactions with nucleophiles.[1-7] Ulrich et al.[1] proposed that nucleophiles added to the 3-position carbon. Woodman et al.[2] found that the products of reaction with amines were diamides and not the amidines which would have resulted from addition to the 3-position. We find that either type of product can be obtained by reaction of cyclohexylamine with 4-carbethoxy-2-cyclohexyl-5(2*H*)-isoxazolone (1). Cyclohexylamine reacts slowly with 1 at room temperature in CCl_4, CH_3CN, or 95:5 Me_2SO/H_2O to form amidine 2. However, when 60:40 CH_3CN/H_2O was used as a solvent, a rapid reaction led to the formation of a mixture of diamide 3 and malonamate 4. The latter undoubtedly resulted from the base-catalyzed reaction of water with 1 accompanied by loss of CO_2.

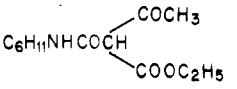


Woodman et al. provided no experimental conditions for the formation of diamides. In a later paper,[3] they report that an isoxazolone reacted with aqueous diethylamine to give products analogous to 3 and 4; the earlier work may also have utilized aqueous amines. Pepino et al.[4] report that diamides were formed with ammonia and a range of primary and secondary amines under either anhydrous or aqueous conditions but also fail to provide experimental conditions.

The presence of water was also found to affect the reaction of 1 with ethanol. A dilute solution of 1 in absolute ethanol showed no reaction after 64 h at room temperature. However, 95% ethanol reacted slowly to yield 5. Pepino et al.[6] report that isoxazolones react with "moist" alcohols to give analogues of 5. Again no experimental details were given. Woodman et al.[5] had previously obtained analogous products with strong base catalysts. We find that absolute ethanol reacts with 1 to give 5 when catalyzed by triethylamine or sodium carbonate.



It had previously been shown that isoxazolones react with water in the presence of strong bases to yield decarboxylated amides analogous to 4.[5] We find that 1 reacts slowly in THF/H_2O at room temperature (pH 6.6) to give 4. Reaction is somewhat more rapid at pH 9.2 but THF/H_2O solutions of 1 are stable for months at pH 4.5 at room temperature. Parallel to a previous report,[5] it was found that 1 reacts with triethylamine acetate to form the aceto derivative 6. No reaction was observed with acetic acid.



Experimental Section

A Perkin-Elmer 137 infrared spectrophotometer, 90-MHz Varian EM-390 ^1H NMR spectrophotometer, and Cary 14 spectrophotometer were used in spectra determinations. Microanalysis were performed by Chemalytics, Inc., Tempe, AZ, or Galbraith Laboratories, Inc., Knoxville, TN.

4-Carbethoxy-2-cyclohexyl-5(2*H*)-isoxazolone (1). *N*-Cyclohexylhydroxylamine hydrochloride was synthesized by the procedure of Feuer and Vincent.[8] Ulrich's procedure[1] for synthesizing other 4-carbethoxy-5(2*H*)-isoxazolones was adapted for the synthesis of 1. A dry 25-mL flask was charged with 5.05 g (0.033 mol) of *N*-cyclohexylhydroxylamine hydrochloride, 7.21 g (0.033 mol) of diethyl ethoxymethylenemalonate, and 1.8 g (0.017 mol) of anhydrous Na_2CO_3 which had been freshly heated at 120 °C for several hours. The reaction mixture was stirred at room temperature for 20 h and then extracted with five 20-mL portions of benzene. After the insoluble NaCl was filtered off, the benzene was distilled off under vacuum. After the mixture stood for several days, crystals precipitated from the residual oil. The crystals were separated by filtration. Yield of crude product was 3.0 g (38%). White crystals, mp 73–74 °C, were obtained by recrystallization from benzene–petroleum ether: ^1H NMR (CCl_4) δ 1.0–2.3 (t at 1.23 superimposed on complex multiplet, 13 H), 3.87–4.33 (q on broad hump, 3 H), 8.77 (s, 1 H); IR (Nujol) 1757, 1697, 1514, 1222, 1156 cm^{-1}; UV λ_{max} 274 (ϵ 17900) and 222 nm (9500). Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.23; H, 7.16; N, 5.85. Found: C, 60.36; H, 6.98; N, 5.70.

Reaction of 1 with Cyclohexylamine. (1) An NMR tube was charged with 478 mg (2 mmol) of 1, 218 mg (2 mmol) of freshly distilled cyclohexylamine, and 1.5 mL of CCl_4 and stored at room temperature. Disappearance of 1 was followed by the NMR peak at 8.77 ppm. Disappearance was complete after 6 days. CCl_4 was removed by distillation. The residue was recrystallized from *n*-hexane 3 times to yield 375 mg (60.5%) of the half ethyl ester half *N,N'*-dicyclohexylamidine of malonic acid 2. The white crystals melted at 144.5–146 °C: ^1H NMR (CCl_4) δ 1.0–2.2 (t at 1.16 on a complex multiplet, 23 H), 3.16 (br m, 2 H), 3.73 (s, 2 H), 3.93 (q, 2 H), 8.6 (br, 1 H); IR (Nujol) 3278, 1613, 1587, 1550, 1400, 1333, 1176, 1145 cm^{-1}. Anal. Calcd for $C_{17}H_{30}N_2O_2$: C, 69.35; H, 10.27; N, 9.51. Found: C, 69.64; H, 9.88; N, 9.37. Equivalent weight by HCl titration: calcd 294, found 308. Similar results

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