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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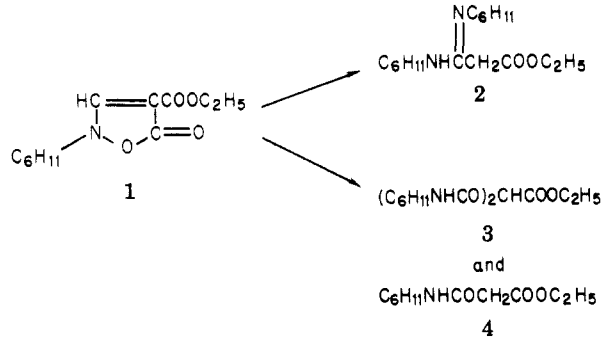
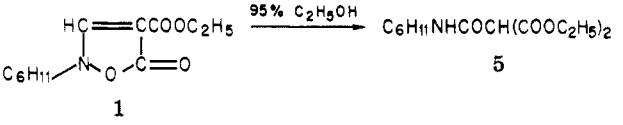
5(2*H*)-Isoxazolones which are not substituted in the 3-position undergo ring-opening reactions with nucleophiles.[1-7] Ulrich et al.[1] proposed that nucleophiles added to the 3-position carbon. Woodman et al.[2] found that the products of reaction with amines were diamides and not the amidines which 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.

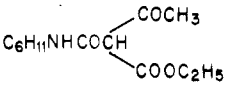


Woodman et al. provided no experimental conditions for the formation of diamides. In a later paper,[3] they report that an isoxazolone reacted with aqueous diethylamine to give products analogous to 3 and 4; the earlier work may also have utilized aqueous amines. Pepino et al.[4] report that diamides 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

(1) Ulrich, H.; Tilley, J. N.; Sayigh, A. A. *J. Org. Chem.* **1962**, *27*, 2160.
(2) Woodman, D. J.; Stonebraker, P. M. *Tetrahedron Lett.* **1970**, 4473.
(3) Woodman, D. J.; Stonebraker, P. M.; Weiler, L. *J. Am. Chem. Soc.* **1976**, *98*, 6036.
(4) Pepino, R.; Bossio, R.; Parrini, V.; Belgodere, E. *Gazz. Chim. Ital.* **1976**, *106*, 1135.
(5) Woodman, D. J.; Borman, C. H.; Tontapanish, N.; Stonebraker, P. M. *J. Org. Chem.* **1969**, *34*, 2981.
(6) Pepino, R.; Belgodere, E.; Bossio, R.; Parrini, V. *Chem. Ind. (Milano)* **1975**, *57*, 783.
(7) Woodman, D. J.; Campbell, W. H.; DeRose, E. F. *Heterocycles* **1977**, *7*, 247.
(8) Feuer, H.; Vincent, B. F. *J. Am. Chem. Soc.* **1962**, *84*, 3771.

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Table I. Ethanolysis of 1

concn of 1, M	alcohol	catalyst	time to disappearance of 1
9.1×10^{-4}	abs C_2H_5OH	none	no change
4×10^{-3}	95% C_2H_5OH	none	23 days
9.2×10^{-4}	abs C_2H_5OH	1 drop of $(C_2H_5)_3N$	43 h
5.3×10^{-2}	abs C_2H_5OH	2.2×10^{-1} M Na_2CO_3	3 h

Table II

run no.	pH	concn of 1, M	time to completion	% yield of 4
1	4.5	4×10^{-3}	no change	
2	6.6	9.2×10^{-4}	253 days	86
3	9.2	4×10^{-3}	65 days	95

and time were required for reaction in dry acetonitrile and 95:5 Me_2SO/H_2O. Amidine **2** was also obtained by refluxing **1** in dry dioxane with excess of cyclohexylamine.

(2) An NMR tube was charged with 72 mg (0.3 mmol) of **1**, 33 mg (0.3 mmol) of cyclohexylamine, and 1.25 mL of a mixture of 60:40 acetonitrile and water. On the basis of the NMR peak at 8.77 ppm, the isoxazolone had fully reacted within 75 min. The tube contents were extracted with 100 mL of ether. After drying over anhydrous magnesium sulfate, the ether was removed by distillation. The product was shown to be a 60:40 mixture of $(C_6H_{11}NHCO)_2CHCOOC_2H_5$ (**3**) and $C_6H_{11}NHCOCH_2COOC_2H_5$ (**4**) by NMR. The NMR spectrum was compared with those of samples of **3**[9] and **4**[10] synthesized via other routes. The enol H signal of **3** at 19.5 ppm is particularly distinctive.

Reaction of 1 with Ethanol. Dilute solutions of **1** as shown in Table I were allowed to stand at room temperature. Disappearance of isoxazolone was followed by changes in UV absorption. In runs 2 and 3, the product was shown by NMR to be $C_6H_{11}NHCOCH(COOC_2H_5)_2$ (**5**). In run 4, the product was isolated and recrystallized from ethanol/water to give a 78% yield of **5**, mp 74–75 °C (lit.[9] mp 75–76 °C). The structure was confirmed by NMR and IR.

Reaction of 1 with Water. Solutions of **1** in 50:50 THF/H_2O were allowed to stand at room temperature. Disappearance of isoxazolone was followed by changes in UV spectra. In run 1 the pH was adjusted to 4.5 by addition of acetic acid and in run 3 the pH was ajusted to 9.2 by addition of NaOH solution. The pH of run 2 (solution of **1** in solvent mixture) was 6.6. Results are shown in Table II. The hydrolysis product, $C_6H_{11}NHCOCH_2COOC_2H_5$ (**4**) was recrystallized from *n*-hexane, mp 73–74 °C (lit.[10] mp 73–73.5 °C). The structure was confirmed by NMR.

Reaction of 1 with Acetic Acid. A solution of 1×10^{-3} mol of **1** and glacial acetic acid in 0.5 mL of CCl_4 showed no change in the NMR peak at δ 8.77 after standing 90 h at room temperature. However, the δ 8.77 NMR peak disappeared completely when a solution of 1×10^{-3} mol of each of **1**, glacial acetic acid, and triethylamine stood at room temperature for 195 h. Ethyl acetyl-*N*-cyclohexylmalonamate (**6**) was recovered by distilling off the CCl_4 and recrystallizing from *n*-hexane. The melting point was 44–46 °C (lit.[10] mp 47.2–48 °C). The structure was confirmed by NMR.

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Registry No. **1**, 78514-48-4; **2**, 78514-49-5; **3**, 65179-95-5; **4**, 71433-06-2; **5**, 65179-99-9; **6**, 73453-43-7; *N*-cyclohexylhydroxyamine·HCl, 25100-12-3; diethyl ethoxymethylenemalonate, 3377-21-7; cyclohexylamine, 108-91-8.

(9) Wicks, Z. W., Jr.; Kostyk, B. W. *J. Coat. Technol.* **1977**, *49*(634), 77.

(10) Wicks, Z. W., Jr.; Wu, K. J. *J. Org. Chem.* **1980**, *45*, 2446.

2,3,4,5-Tetraphenyliodolium Ion and an Isomer

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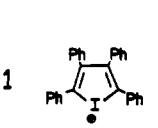
In 1972 Beringer and co-workers[1] reported a low-yield (2.5%) synthesis of the novel Hückel aromatic 2,3,4,5-tetraphenyliodolium ion (**1**), isolated as the chloride and iodide salts. These authors did not report conclusive evidence for the ionic nature of their compounds, nor did they investigate the chemical properties of the ion beyond the thermal decomposition of their salts in a mass spectrometer.

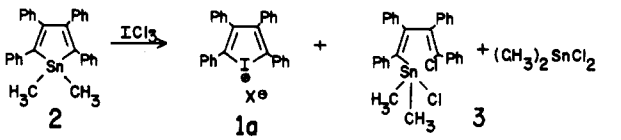


1 (a) Cl^-, ICl_2^- and/or ICl_4^-; (b) I^-; (c) $I^- \cdot H_2O$; (d) BPh_4^-; (e) $SbCl_6^-$

As early as 1969 we prepared a compound which we believed to be the monohydrate **1c**,[2] but after several successful preparations the method no longer yielded product. The melting behavior of our product differed markedly from that of the compound reported by the Beringer group, raising doubts that the basic structures were the same. Moreover, the ionic nature of both products was presumed mainly because one of the halogens exchanged very readily. The work of Doorakian et al.,[3] who reported facile vinylic halide exchange in the related mono and dihalides of 1,2,3,4-tetraphenyl-1,3-butadiene, casts doubt on the validity of this presumption. In this paper we present a modification of our original method which reliably produces either **1** or its hydrate **1b** in 12–18% yield, the ionic structure of **1** is confirmed, and some of its reactions are briefly investigated. In addition, an interesting isomer of **1** believed to be 5-ioda-1,2,3,4-tetraphenylbicyclo[2.1.0]pentenium hexachloroantimonate is reported.

Results and Discussion

Originally **1** was prepared by treatment of an ether slurry of 1,1-dimethyl-2,3,4,5-tetraphenylstannole[4] (**2**) with a solution of freshly prepared iodine trichloride[5] in ether at −68 °C. This yielded a yellow crystalline product with a



2 → (ICl₃) → **1a** + **3** + $(CH_3)_2SnCl_2$

melting point which varied from 79 to 104 °C in different preparations. The material was unstable, decomposing to a dark colored tar with the release of iodine vapor upon

(1) F. M. Beringer, P. Ganis, G. Avitabile, and H. Jaffe, *J. Org. Chem.*, **37**, 879 (1972).

(2) G. Buske and V. R. Sandel, Abstract, 6th Great Lakes Regional Meeting of the American Chemical Society, Houghton, MI, June 22–23, 1972.

(3) G. A. Doorakian, H. H. Freedman, R. F. Bryan, and H. P. Weber, *J. Am. Chem. Soc.*, **92**, 399 (1970).

(4) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternhas, and D. S. Lehman, *J. Am. Chem. Soc.*, **82**, 5099 (1960).

(5) H. Booth and W. Morris, *Inorg. Synth. 1*, 167 (1939).

0022-3263/81/1946-4069$01.25/0