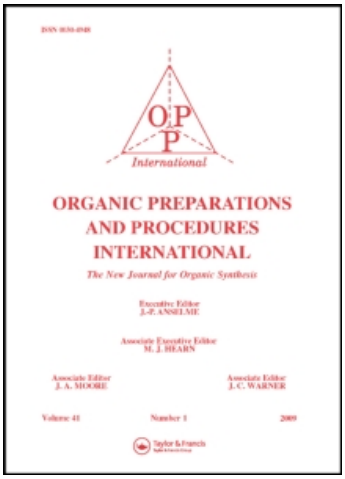

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TETRACHLOROCYCLOPROPENE, A HIGHLY REACTIVE REAGENT FOR 4 (1*H*)-PYRIDINONE SYNTHESIS

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Hydrolysis of V with hot 10% NaOH aq. soln. for a short period of time gave IV in good yield.

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4. A 5% solution of an authentic sample of β-hydroxypyridine in d_6-DMSO was used for assigned identification.

TETRACHLOROCYCLOPROPENE, A HIGHLY REACTIVE REAGENT FOR 4(1H)-PYRIDINONE SYNTHESIS

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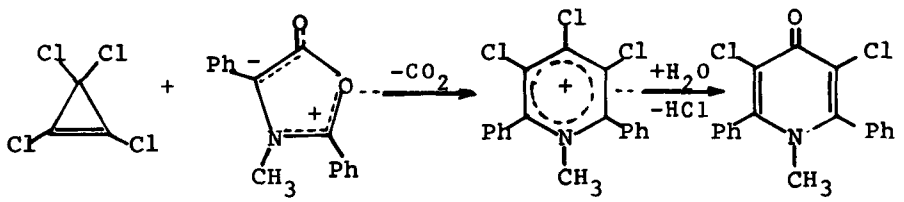
The 1,3-dipolar cycloaddition of cyclopropenes and cyclopropenones with various mesoionic five-membered heterocycles affords 1,4-dihydropyridines and 4(1H)-pyridinones with substitution patterns which are fixed by the choice of reactants.[1] Substituents at C_3, C_4 and C_5 of the pyridinyl product derive

from the cyclopropenoid reactant while the dipole donates the C_2, C_6 and N_1. The use of a 3,3-dichlorocyclopropene with a heterocyclic betaine produces a 4(1H)-pyridinone, a product which is more commonly derived from a cyclopropenone.

The reaction mixture from tetrachlorocyclopropene (I) with 2,4-diphenyl-3-methyloxazolium 5-oxide[2] (II) yields IV [3,5-dichloro-2,6-diphenyl-1-methyl-4(1H)-pyridinone]. The intermediate 4-chloropyridinium salt III evidently underwent hydrolysis[3,4] to IV under the mild conditions used for reaction and work-up.



I II III IV

The 4(1H)-pyridinone IV exhibits ultraviolet, infrared and mass spectral patterns which correlate with 1-methyl-;[5] 2,6-diphenyl-1-methyl-;[6] 1-methyl-2,3,5,6-tetraphenyl-[7] and 3,5-dichloro-1-methyl-substituted 4(1H)-pyridinones.[8] 2(1H)-Pyridinones isomeric with IV exhibit dissimilar spectra.[9]

Tetrachlorocyclopropene offers the preparative advantage of facile reaction with betaines. Comparison of new results with those in the literature allows one to set reactivities with Münchnone (II) in the order tetrachlorocyclopropene > diphenylcyclopropenethione[7b] > diphenylcyclopropenone[7a-b,10,11] > 1,2,3-triphenylcyclopropene.[12] Cyclopropene I is extraordinarily reactive in other $_4\pi + _2\pi$ cycloadditions such as in 1,3-dipolar cycloadditions with diazomethanes[13,14] and azides,[14]

and in Diels-Alder[15-17] reactions. The special reactivity of I in some situations has been attributed[16,17] to favorable orbital interactions and to the existence of its charge-separated form (i.e., trichlorocyclopropenium chloride).

EXPERIMENTAL

Apparatus used for mp (uncorr.), IR, UV and MS measurements were, respectively, a Kofler hotstage microscope, a Perkin Elmer model 237B grating infrared spectrometer, a Cary 11 Recording Spectrophotometer and an AEI-MS9 operated at 70 eV with an accelerating voltage of 8 kV and a source temperature of 300 or 345°. The plc plate (silica gel, Merck F-254; 2.0 mm) was activated one hr at 100° immediately prior to use.

Reaction of Tetrachlorocyclopropene with II.- Compound I (3.06 mmol) was added dropwise over 4 min. to II (3.18 mmol) in 7.2 mL benzene. Within 3 min., carbon dioxide was swept with nitrogen into a barium hydroxide solution. The white solid (0.49 g), which appeared after 16 min., was collected and gave a pH response (to moist pH paper) of 1-2. Of the initially used I, 41% was shown (by glc) to be present in the filtrate.

The white organic solid (from above) was recrystallized from dimethylformamide to yield neutral prisms (41% recovery), mp. 312.6-316.3°; UV (C_2H_5OH): λ_{max} 231 (O.D. 0.349), 282 (O.D. 0.173) and 288 (sh, O.D. 0.155) nm; IR (Nujol): ν_{max} 1615, 1593, 1584, 1570, 1563, 1529, 1521 and 1511 cm^{-1}; MS: (m/e > 101) 333 (M^+, R.I. 12), 332, 331 (M^+, 100), 305 (M-CO), 304 (M-HCN), 303 (M-CO), 302 (M-HCN), 301 (M-CO), 296, 295, 230, 151 1/2 (M-CO), 150 1/2 (M-CO), 118, 115 1/2, 115, 114, 113 and 103 (PhCN). This product was stirred in water 1.75 hr (62% recovery) and sublimed (bath temperature of 153° and pressure of 0.09 mm Hg) to afford a solid, mp. 314.0-315.0°.

Anal. Found: m/e 329.0404 (by high resolution mass spectrometry). Electrostatic effects precluded measurement of the sample by combustion analysis.

Preparative layer chromatography (eluant, ethyl acetate) of the evaporated filtrate (from the reaction mixture) yielded, following work up of key regions from the plc plate, 0.166 g additional IV, 0.121 g of N-benzoyl-N-methylphenylglycine,[2] and 0.055 g of a white solid, [18] mp. 226° (with resolidification and subsequent decomp.); UV (C_2H_5OH): λ_{max} 247 (O.D. 0.817), 280 (sh, O.D. 0.142) and 287 (sh, O.D. 0.115) nm; IR ($CHCl_3$): ν_{max} 3073, 2975, 1690, 1668, 1654, 1648, 1637, 1599 and 1578 cm^{-1}; MS: (m/e > 101) 446 (M^+, R.I. 34), 445 (100), 141, 139, 129, 128, 125, 123, 119, 118, 117, 115, 111, 109, 108, 107, 106, 105, 104 and 103.

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