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THE PREPARATION OF N-TRICHLOROACETAMIDO-1,2-DIENES

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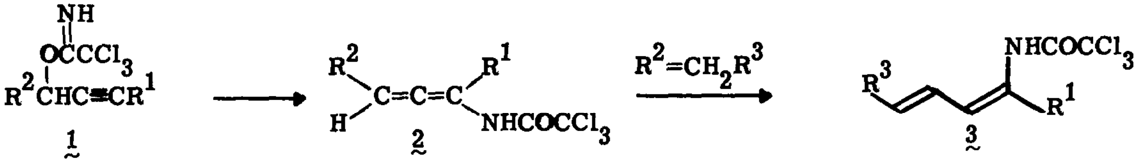
Although a variety of heteroatom-substituted allenes have been prepared, N-acylamino-1,2-dienes are virtually unknown.[2] The preparation of 1,2-propadienyl-2-pyrrolidinone by base catalyzed rearrangement of 1-(2-propynyl)-2-pyrrolidinone[3] is, to our knowledge, the only reported synthesis of an N-allenamide. We recently proposed[4] that trichloroacetamido-1,2-dienes (2) were intermediates in the thermal conversion of propargylic trichloroacetimidates to 1-trichloroacetamido-1,3-dienes (3), eq 1. In this letter we report that a variety of N-allenamides 2 may be isolated from the thermal rearrangement of imidates 1.



(1)

Thermolysis of imidates 1a-1e[5] in refluxing xylenes (0.1M, containing 1% 4-tert-butylcatechol) for 1-4 hr afforded, after silica gel chromatography and recrystallization, the pure allenamides 2a-2e in isolsted yields of 10-20% (see Table). Purification of 2 was attended with substantial losses and the crude yields (^{1}H-NMR or HPLC analysis) were significantly (ca. 2 times) higher. Trichloroacetamido-1,2-dienes 2 [6,7] showed characteristic[8] C=C stretching absorptions in the infrared spectrum (CCl_4) at 1965-1975 cm^{-1}, and the expected[9] low field absorptions for the central vinylic carbon in the ^{13}C-NMR spectrum ($CDCl_3$) at 193-203 ppm. Heating allene 2d in refluxing xylene resulted in its conversion (at a rate 2-3 times slower than its formation from 1d) in high yield to 2,2,2-trichloro-N-[(1Z, 3E)-1,3-pentadienyl] acetamide (3, R^1= H, R^3=CH_3).[4]

Although [3,3]-sigmatropic rearrangement of imidates 1 affords N-trichloroacetamido-1,2-dienes 2 in low isolated yield, the procedure is experimentally simple and represents the only general synthetic route to allenamides of this type.

Table. Synthesis of Trichloroacetamido-1,2-Dienes

Trichloroacetamido-1,2-diene	R^1	R^2	mp, °C	Time, hr	Isolated Yield, %
2a	H	H	70-71	4.5	11
2b	H	$(CH_3)_3C$	90-91	1	19
2c	$(CH_3)_3C$	$(CH_3)_3C$	59-60	3	14
2d	H	CH_3CH_2	69-70	1.1	16
2e	H	$(CH_3)_2CH$	63-65.5	1.8	18

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References and Notes

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3. W.B. Dickinson and P.C. Lang, Tetrahedron Lett., 3035 (1967).
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5. Prepared in high yield by base catalyzed condensation of the corresponding propargylic alcohol with trichloroacetonitrile: L. Overman, J. Am. Chem. Soc., **98**, 2901 (1976).
6. Allenes **2a**-**2c** gave correct combustion analyses, and allenes **2d** and **2e** exhibited high resolution mass spectrum consistent with their composition.
7. 2,2,2-Trichloro-N-(1,2-propadienyl) acetamide (**2a**): IR (CCl_4, 0.5 M) 3440 (NH), 1965 (C=C=C), and 1720 (C=O) cm^{-1}; ^1H-NMR (CCl_4, δ) 7.9 (broad s, NH), 6.86 (dt, J=6.3, and 11Hz, =CHN), 5.44 (d, J=6.3 Hz, $=CH_2$); ^{13}C-NMR ($CDCl_3$, δ) 202.7 (C=C=C), 159.0(C=O), 94.0 (=CHN), 92.0 (CCl_3), 87.3 ($=CH_2$); Anal. Calcd for $C_5H_4Cl_3NO$: C, 29.96; H, 2.01; N, 6.99. Found: C, 30.12; H, 2.04; N, 6.96.
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