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THE ACYLATION OF ACETYLENES WITH β,γ-UNSATURATED ACID CHLORIDES A NEW SYNTHESIS OF 5,5-DISUBSTITUTED 2-CYCLOPENTENONES

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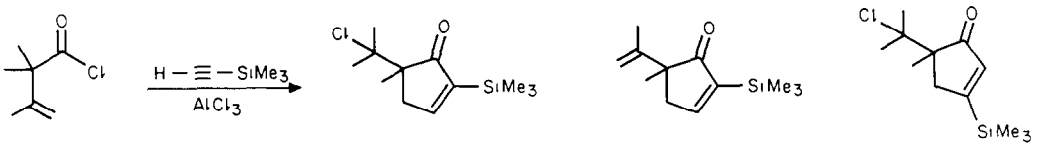
Abstract The acylation of acetylenes with α,α-disubstituted, β,γ-unsaturated acid chlorides was found to lead to 5,5-disubstituted 2-cyclopentenones by a novel intramolecular cyclization-rearrangement process.

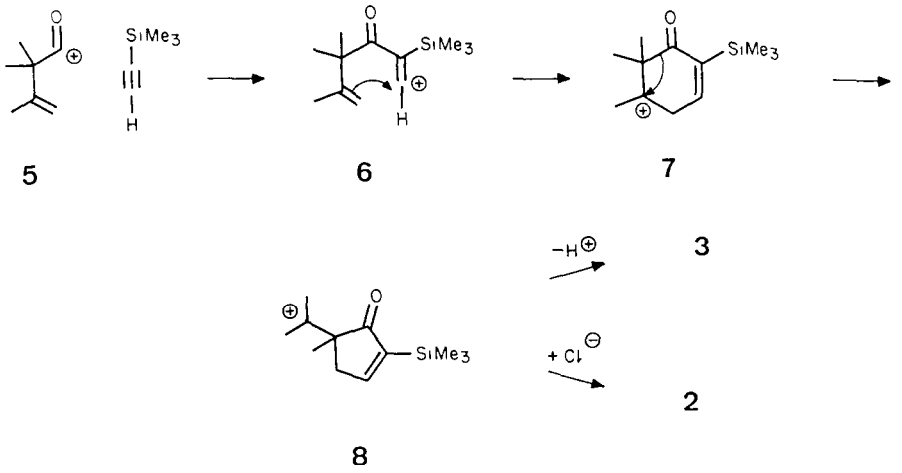
The acylation of trimethylsilyl substituted acetylenes with aliphatic and aromatic acid chlorides, activated by aluminum chloride, generally leads to α-acetylenic ketones by substitution of the trimethylsilyl group.[1,2] We have found that this reaction with 3,γ-unsaturated acid chlorides takes a different course, depending on the α-substitution of the acid chloride.

Upon addition of a mixture of 1[3] and trimethylsilylacetylene to aluminum chloride in dichloromethane at -70°C, followed by acid hydrolysis after warming up to -20°C, a mixture of 2, 3 and 4 was obtained[4,5], separable by column chromatography.



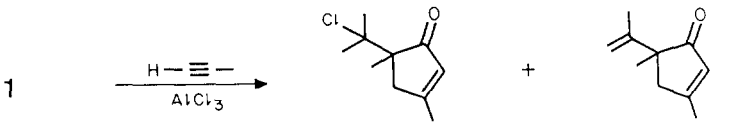
1 2 63% 3 13% 4 8%

The formation of 2 and 3 is rationalized by a process initiated by the electrophilic attack of the acyl cation 5 at the trimethylsilyl substituted acetylenic carbon to form the silicon stabilized vinyl cation 6. The intramolecular cyclization to 7, induced by the interaction of the cationic center and the β,γ-double bond in 6, is followed by a 1,2-acyl shift[6] to form 8, which is stabilized either by addition of a chloride ion yielding 2 or by loss of a proton yielding 3. The formation of 4 is explained by a related sequence initiated by the attack of 5 at the unsubstituted acetylenic carbon, so that the trimethylsilyl group is directed to C(3). This transformation represents a new variety of the behaviour of Lewis acid activated acyl halides towards alkynes.[7]



Compounds 5, 6, 7, 3, 8, 2

While the presence of an acetylenic trimethylsilyl group is essential for the the formation of α-acetylenic ketones[1], it is not a prerequisite for the transformation presented here, as shown by the reaction of 1 with propyne. The exclusive formation of the 3-methyl-2-cyclopentenones 9 and 10 can be attributed to the stabilizing effect of the acetylenic methyl group on the vinyl cation intermediate corresponding to 6.

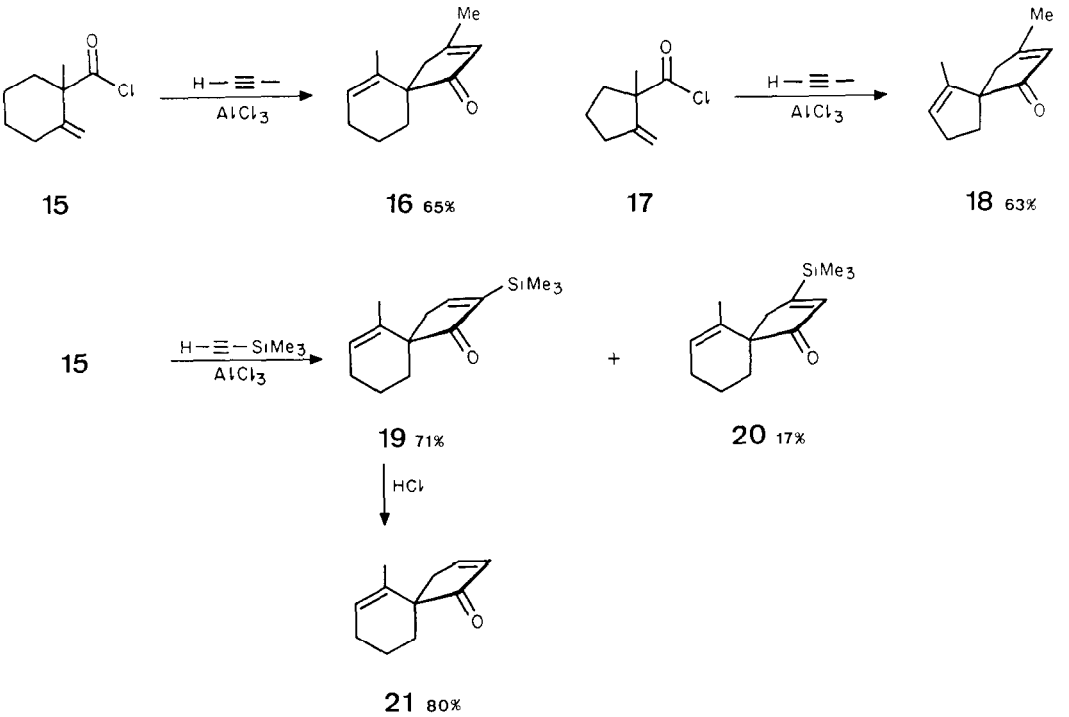


1 → 9 53% + 10 11%

With α,3-unsaturated acid chlorides bearing α-hydrogens however, the ring contraction does not occur, as demonstrated by the reaction of 11[8] and 13[9] with propyne and 2-butyne, respectively, leading to the phenols 12 and 14 after hydrolysis. In these cases, the stabilization takes place at the six membered ring stage corresponding to the intermediate 7.

11 → 12 69%; 13 → 14 39%

The transformation of α,α-disubstituted, 3,γ-unsaturated acid chlorides to 2-cyclopentenones can be applied to the synthesis of spiro compounds. The acylation of propyne with the carbocyclic acid chlorides 15 and 17[3] led exclusively to the spirodienones 16 and 18 respectively, without formation of chloro compounds. Although the corresponding spiro compounds with β-unsubstituted cyclopentenone moieties are not directly accessible by reaction with acetylene itself, these derivatives were obtained through the trimethylsilyl substituted intermediates, as shown by the reaction of 15 with trimethylsilylacetylene to 19 and 20. Subsequent deprotosilylation of 19 with hydrogen chloride in chloroform[10] afforded 21.



In view of the functional versatility of the 2-cyclopentenone moiety, these results may provide an easy entry into certain cyclopentanoids, including spiro systems.

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2. We applied this procedure to a number of aliphatic and alicyclic acid chlorides in connection with our investigation of the α-alkynone cyclization, a thermal process transforming α-acetylenic ketones to 2-cyclopentenones· M. Karpf & A.S Dreiding, Helv. Chim. Acta 1979, 62, 852, M. Karpf, J. Huguet & A.S, Dreiding, Helv. Chim. Acta 1982, 65, 13.

3. The compounds 1, 15 and 17 were obtained from the appropriate β-keto esters by Wittig condensation ($Ph_3P{=}CH_2$/THF/RT according to the procedure described by H. Schmidbaur, H. Stuhler & W. Vornberger, Chem. Ber. 1972, 105, 1084 and M. Rey, Ph. D. Thesis, University of Sheffield, 1975), followed by saponification of the resulting β,γ-unsaturated esters (KOH/MeOH/H_2O) and conversion of the acids into the acid chlorides($SOCl_2$/reflux/1 hr) in overall yields of 50 to 80%.

4. Satisfactory elemental analyses were obtained for all new compounds.

5. The data of 2, 3 and 4 serve to illustrate the spectral characteristics of the 2-cyclopentenones described here

2 mp. 79°C, UV (EtOH) λ_{max} 226 nm (ε 7400), IR ($CHCl_3$): ν 1690s, 1585s cm^{-1}, ^{1}H-NMR (200 MHz, $CDCl_3$) δ_H 7.73 (t, J = 2.6 Hz, 1 H, H-C(3)), 3.17 (dd, J = 20.0 & 2.6 Hz, 1 H, H-C(4)), 2.48 (dd, J = 20.0 & 2.6 Hz, 1 H, H-C(4)), 1.74 (s, 3 H, H_3C-CCl), 1.47 (s, 3 H, H_3C-CCl), 1.26 (s, 3 H, H_3C-C(5), 0.17 (s, 9 H, 3 H_3C-Si) ppm, ^{13}C-NMR (20 MHz, $CDCl_3$): δ_C 212.6 (s, C(1)), 169.4 (d, (C(3)), 146.0 (s, C(2)), 74.7 (s, CCl), 55.1 (s, C(5)), 45.4 (t, C(4)), 28.7 and 28.4 (each q, 2 CH_3-CCl), 21.4 (q, CH_3-C(5)), -2.0 ppm (q, C-Si) ppm.

3 mp. 46°C; UV (EtOH) λ_{max} 223 nm (ε 8000), IR ($CHCl_3$)· ν 1690s, 1645m, 1580s cm^{-1}, ^{1}H-NMR (200 MHz, $CDCl_3$)· δ_H 7.73 (t, J = 2.6 Hz, 1 H, H-C(3)), 4.93-4.85 (m, 2 H, H_2C=), 2.85 (dd, J = 19.6 & 2.6 Hz, 1 H, H-C(4)), 2.49 (dd, J = 19.6 & 2.6 Hz, 1 H, H-C(4)), 1.58 (dd, J = 1.3 & 0.7 Hz, 3 H, H_3C-C=), 1.21 (s, 3 H, H_3C-C(5)), 0.18 (s, 9 H, 3 H_3C-Si) ppm, ^{13}C-NMR (20 MHz, $CDCl_3$) δ_C 214.6 (s, C(1)), 169.1 (d, (C(3)), 145.9 and 145.7 (each s, C(2) and quart. C of isopropenyl), 111.1 (t, CH_2=), 52.5 (s, C(5)), 45.4 (t, C(4)), 22.1 and 19.3 (each q, CH_3-C(5) and CH_3-C=), -2.2 ppm (q, C-Si) ppm.

4: mp. 35°C, UV (EtOH) λ_{max} 233 nm (ε 13100), IR (film) ν 1690s, 1575s cm^{-1}, ^{1}H-NMR (200 MHz, $CDCl_3$) δ_H 6.25 (t, J = 2.0 Hz, 1 H, H-C(2)), 3.22 (dd, J = 19.4 & 2.1 Hz, 1 H, H-C(4)), 2.48 (dd, J = 19.4 & 1.9 Hz, 1 H, H-C(4)), 1.74 (s, 3 H, H_3C-CCl), 1.46 (s, 3 H, H_3C-CCl), 1.26 (s, 3 H, H_3C-C(5)), 0.22 (s, 9 H, 3 H_3C-Si) ppm; ^{13}C-NMR (20 MHz, $CDCl_3$) δ_C 210.4 (s, C(1)), 181.7 (s, (C(3)), 139.9 (d, C(2)), 75.0 (s, CCl), 54.8 (s, C(5)), 47.0 (t, C(4)), 28.7 and 28.5 (each q, 2 CH_3-CCl), 21.7 (q, CH_3-C(5)), -2.5 ppm (q, C-Si) ppm.

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