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α,β-ACETYLENIC DITHIO AND THIONO ESTERS[1]

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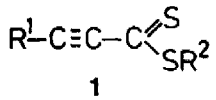
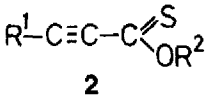
Summary: The α,β-acetylenic dithio and thiono esters 1 and 2 have been prepared by thiolysis of the iminium salts 7, by a palladium(II) catalyzed condensation of the acetylenes 3 with the thiocarbonyl chlorides 8 or 9, and by a thiocarbonylation of the magnesium acetylides 13 with the thionocarbonyl chloride 14.

α,β-Olefinic dithio and thiono esters were first prepared some 10 years ago[2]. Meanwhile their synthesis and chemical properties have been studied by several research groups[2]. To the best of our knowledge α,β-acetylenic dithio esters 1 and thiono esters 2 are completely unknown. We would like to report our first observations of their preparation, stability and reactivity.



1

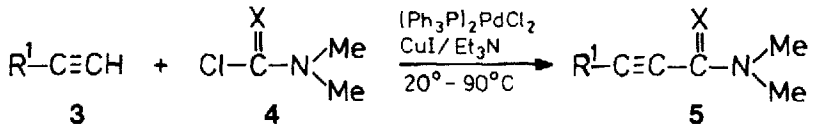
1	R^1	R^2
a	mesityl	Me
b	Ph	Me
c	β-naphthyl	Me
d	tert-butyl	Me



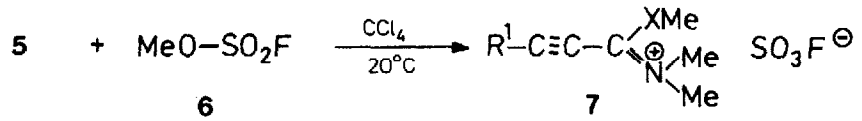
2

2	R^1	R^2
a	Ph	Me
b	tert-butyl	Me
c	n-butyl	Me
d	p-tolyl-S	Me
e	Ph	Ph
f	n-butyl	Ph

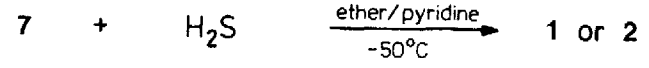
Starting with acetylenes 3 and carbamoyl or thiocarbamoyl chlorides 4 the acetylenic amides (5, X = O) or thioamides (5, X = S) are obtained in a condensation catalyzed by a palladium(II) complex in triethylamine as a solvent[3]. Alkylation of 5 by methyl fluorosulfonate 6 leads to the iminium salts 7, which can be converted into the dithio esters 1 or thiono esters 2 by hydrogen sulfide. This reaction requires temperatures at -50°C to -60°C in order to avoid the addition of H_2S to the triple bond[4]. The structures 1 and 2 are supported by elemental analysis, mass spectrometry and spectroscopic data[5].



3 **4** **5**

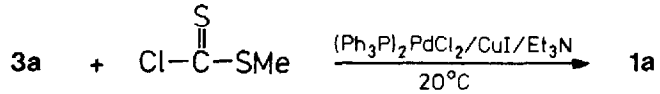


5 **6** **7**

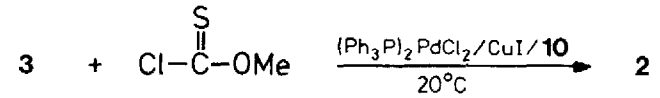


	mp/bp (°C)	yield (%)
1a	40-41	91
2a	46-47	65
2b	50 / 0.5 Torr	78
2c	90 / 0.1 Torr	80

The dithio ester 1a has also been obtained in a straight forward procedure by the palladium(II) catalyzed condensation of acetylene 3a with the dithiocarbonyl chloride 8 in triethylamine[6]. This approach, however, gives markedly lower yields in the preparation of the α,ß-acetylenic thiono esters 2. As triethylamine reacts vigorously with the thionocarbonyl chloride 9 a more hindered tertiary amine such as 1,2,2,6,6-pentamethyl piperidine (10, 1 equivalent) in CH_2Cl_2 is required. Ethyl diisopropyl amine as base and solvent proved to be less effective. In some cases, e.g. 2a, 2c, potassium carbonate in THF has been used with good results.

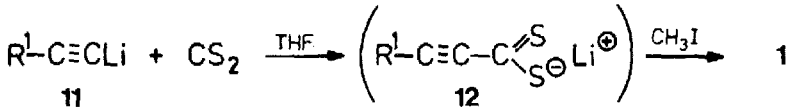


	yield (%)
1a	90
2a	61
2b	41
2c	32

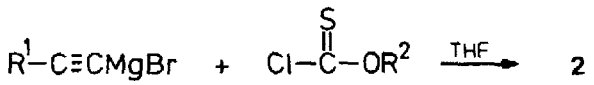


By treatment of lithium or magnesium acetylides with carbon disulfide salts of α,ß-acetylenic dithio acids should be formed. These salts turned out to be even more unstable than the corresponding α,ß-acetylenic dithio esters themselves leading readily to polymeric material. When the lithium salt 11 of mesityl acetylene (3a) was treated with carbon disulfide at 20°C and subsequently with methyl iodide, 1a could be isolated in about 50% yield. Evaporation of the solvent before methylation gave the salt 12 as a red powder. This was probably of polymeric nature as a dissolution in THF and methylation with methyl iodide did not yield the dithio ester 1a anymore.

The magnesium salts 13, obtained from 3 with ethyl magnesium bromide, react with the thionocarbonyl chlorides 14 to form the α,ß-acetylenic thiono esters 2a, and 2d-f[7].



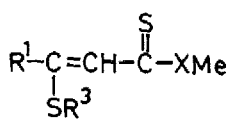
	mp (°C)	yield (%)
1a	40-41	50
2a	46-47	30
2d	32	50
2e	yellow oil[7]	35
2f	" " [7]	40



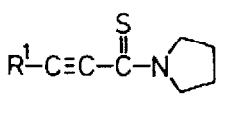
α,ß-Acetylenic dithio esters 1 are a rather unstable class of compounds, which decompose rapidly at room temperature to give mainly polymeric material. This process can be retarded by steric bulk of the substituent R^1. Thus the mesityl derivative 1a is perfectly stable at room temperature and can be stored for several months in the refrigerator. Other dithio esters such as 1b, 1c or 1d could be detected spectroscopically in solution at -50°C immediately after their preparation. A solution of 1b also endures room temperature for 1-2 hours.

In contrast to the α,ß-acetylenic dithio esters 1 the α,ß-acetylenic thiono esters 2 can be handled and stored at room temperature if R^2 is alkyl. No bulky groups are necessary to protect the triple bond, neither in the aromatic series (2, R^1 = aryl) nor in the aliphatic series (2, R^1 = alkyl). The O-phenyl thiono esters 2e-f, however, are markedly less stable than the O-alkyl derivatives 2a-d. They turn brown at room temperature and decompose within a few hours.

The triple bond in the α,ß-acetylenic thiono and dithio esters is readily attacked by sulfur nucleophiles, e.g. thiols, leading to the substituted acrylic thioesters 15. Secondary amines such as pyrrolidine yield the α,ß-acetylenic thioamides 16. Primary amines and gaseous ammonia react with the thio-



15 (X = S,O)



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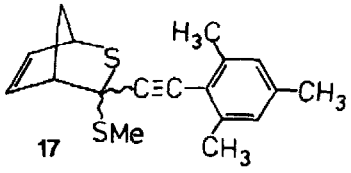

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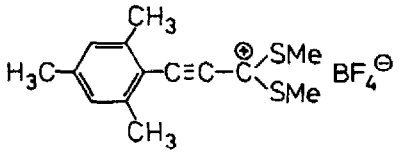

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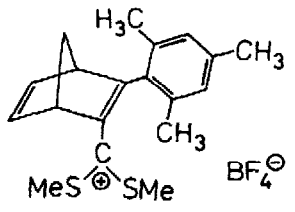

19

carbonyl group as well as with the triple bond resulting in a complex mixture of products. The thiocarbonyl group in 1a shows dienophilic properties, forming the Diels-Alder adduct 17 with cyclopentadiene as a mixture of the endo and exo isomer. Alkylation of 1a with oxonium salts lead to the highly reactive, but stable carbenium salt 18, which adds to cyclopentadiene with the triple bond to give the norbornene 19.

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References and Notes

1. Dithio and Thiono Esters, 48. Dithio and Thiono Esters, 47: K.Hartke and O.Kunze, Liebigs Ann.Chem. 1989, in print.

2. a) P.Gosselin, S.Masson and A.Thuillier, Tetrahedron Lett. 1978, 2715 and 1980, 2421. b) H.Westmijze, E.Kleijn, J.Meijir and P.Vermeer, Synthesis 1979, 432. c) R.Hoffmann and K.Hartke, Chem.Ber. 113, 919 (1980). d) S.Scheibye, S.O.Lawesson and C.Roemming, Acta Chem.Scand. B 35, 239 (1981). e) C.Davrinche, J.-D.Brion and P.Reynaud, Synth.Commun. 14, 1181 (1984). f) K.R.Lawson, A.Singleton and G.H.Whitham, J.Chem.Soc.Perkin Trans I, 1984, 859. g) K.Hartke, O.Kunze and W.Hoederath, Synthesis 1985, 2325. h) P.Metzner, T.N.Pham and J.Vialle, Tetrahedron 42, 2025 (1986).

3. This procedure has been described for α,β-acetylenic amides: Y.Tohda, K.Sonogashira and N.Hagihara, Synthesis 1977, 777. It works even better for the corresponding thioamides with yields between 80-100% obtained at room temperature.

4. A stirred mixture of dry ether (60ml) and pyridine (5ml) is saturated with H_2S at 0°C. After cooling to -50° till -60°C the salt 7 (10mmol) is added and a slow stream of H_2S continued for about 4 hours. The cold solution is rapidly filtered and shaken several times with dil. HCl and water. The dried organic layer is concentrated in vacuo and the residue is recrystallized from hexane (e.g. 1a, 2a) or distilled in the Kugelrohr (e.g. 2b-c).

5. 1a: MS(70eV): m/z(%) = 234 (34, M^+). ^{1}H-NMR(CCl_4): δ(ppm) = 6.8 (bs, 2H, aromat. H), 2.7 (s, 3H, SMe), 2.45 (s, 6H, 2'-, 6'-Me), 2.25 (s, 3H, 4'-Me). ^{13}C-NMR($CDCl_3$): δ(ppm) = 204 (C=S), 142 (C-2', -6'), 141 (C-4'), 128 (C-3', -5'), 118 (C-1'), 102 (C-3), 98 (C-2), 21.5 (4'-Me), 20.8 (2'-, 6'-Me), 19.4 (SMe). IR(KBr): 2170cm^{-1}(C≡C).
2a: MS(70eV): m/z(%) = 176 (77, M^+). ^{1}H-NMR(CCl_4): δ(ppm) = 7.6-7.2 (m, 5H, aromat. H), 4.1 (s, 3H, OMe). ^{13}C-NMR($CDCl_3$): δ(ppm) = 193 (C=S), 133 and 128 (C-2', -3', -5', -6'), 130 (C-4'), 120 (C-1'), 89.7 (C-3), 89.1 (C-2), 58 (OMe). IR(KBr): 2200cm^{-1} (C≡C).

6. Bis(triphenylphosphine)-palladium dichloride (20mg), copper(I) iodide (20mg) and triphenyl phosphine (26mg) are added to a stirred mixture of 3a (10mmol) and 8 (10mmol) in triethylamine (30ml). After 15 h at room temperature the reaction mixture is filtered and the filtrate evaporated in vacuo.

7. A solution of 14 (22mmol) in THF (30ml) is added in one portion to a stirred solution of the magnesium salt 13 (20mmol) in THF (50ml) at -30°C. After 30 min the reaction mixture is allowed to warm to room temperature within 2 h. A saturated aqueous solution of NH_4CL (50ml) is added and the mixture is extracted with diethyl ether. The organic phase is evaporated and the oily residues are chromatographed on silica gel with petrol ether. 2d crystallizes at -60°C from petrol ether, 2e-f decompose on distillation.

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