Tetrahedron Letters No. 33, pp 2923 - 2924, 1975. Pergamon Press. Printed in Great Britain.

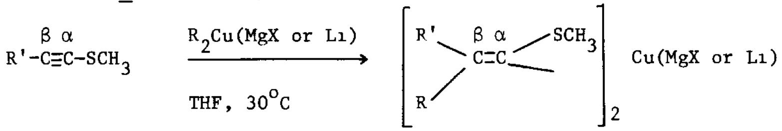
ANOMALOUS ALKYLATION OF ALKYLTHIOVINYLCOPPER(I) COMPOUNDS A STEREOSPECIFIC ROUTE TO *CIS*-CUMULENES

Hans Westmijze, John Meijer and P Vermeer x

(Laboratory of Organic Chemistry, Rijksuniversiteit Utrecht, The Netherlands)

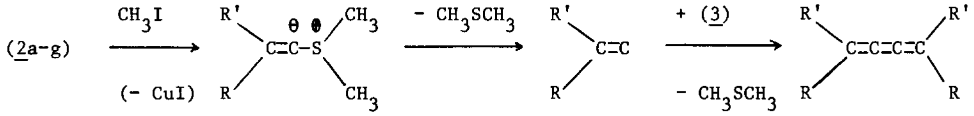
(Received in UK 20 June 1975; accepted for publication 7 July 1975)

As a part of our program concerning the preparation and reactions of heterosubstituted vinylcopper(I) compounds we are studying alkylations of the copper(I) reagents (2) A recent article of Normant *et al* [1] prompts us to report our preliminary results. As we have described before[2,3] species (2) can easily be prepared by a stereospecific *cis*- addition of R_2Cu(MgX or Li) to 1-alkynyl sulfides (1) in tetrahydrofuran (THF)



(1) (2)

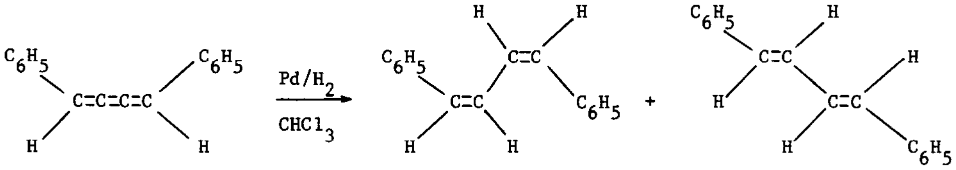
When solutions of (2) in THF are treated with excess of CH_3I at 0°C an exothermic reaction takes place under formation of the cumulenes (5) (yield 20-50%) and CH_3SCH_3 together with α-C methylated products of (2) and other unidentified compounds This result is different from that obtained for the alkylation of alkylthiovinyl lithium compounds in which only C- alkylation occurs[4] The formation of (5) is conceivable by assuming a primary methylation on the S- atom in (2) leading to the S- ylid (3), followed by loss of CH_3SCH_3 under formation of the alkylidene carbene (4) From a subsequent interaction of (4) with (3) compound (5) will be formed



(3a-g) (4a-g) (5a-g)

a: R'= C_6H_5, R= CH_3
b R'= C_6H_5, R= C_2H_5
c R'= C_6H_5, R= i-C_3H_7
d R'= C_6H_5, R= C_6H_5
e R'= H, R= C_6H_5
f R'= H, R= n-C_5H_{11}
g R'= H, R= *t*-C_4H_9

The cumulenes (5a-e) could easily be isolated as solid compounds by crystallization from pentane, whereas (5f-g) were purified by column- chromatography (Florisil/hexane) The structure of compounds (5a-g) was confirmed by ^{1}H-NMR, IR and UV analysis and it appeared that they were formed by our method in only one of the two possible geometries. Traces of I_2 caused a fast isomerization to a *cis/trans-* mixture as was shown by ^{1}H-NMR analysis. In order to establish the geometry of these compounds (5) we carried out a catalytic *cis-* hydrogenation of the inner double bond of the cumulenic system of (5e) with Pd/$CaCO_3$ in $CHCl_3$ leading to a mixture of two products, which could be separated by column- chromatography (Al_2O_3 W200-neutral/hexane). Identification by ^{1}H-NMR and UV showed the main component to be *cis,cis-* 1,3-butadiene (6) (m p. 70°C), whereas the UV- data of the minor one were identical to those reported for the *trans,trans-* -isomer (7)[5]. These results are in agreement with a *cis* - geometry for compounds (5a-g)



(5e) (6) (7)

Although several methods for the preparation of cumulenic systems are available this method is to our knowledge the first one dealing with a stereospecific synthesis for *cis* - cumulenes (for a recent method for the preparation of *trans* - cumulenes see ref 6)
Contrary to the methylation reactions allylation of compounds (2) with allylbromide afforded exclusively α-C allylated products (yield >90%). This result can be explained by a direct allylation on the α-C atom in (2), but a primary allylation on the S- atom (leading to $R'RC{=}C{=}S(CH_3)CH_2CH{=}CH_2$), followed by a [2.3]- sigmatropic rearrangement can not be excluded at the moment

1. J F Normant, A Alexakis, A Commerçon, G Cahiez and J Villieras, Compt Rend 279, C, 763 (1974)
2 P Vermeer, C de Graaf and J Meijer, Recl. Trav. Chim , 93, 24 (1974)
3. P Vermeer, J Meijer and Mrs C Eylander, *ibid*, 93, 240 (1974)
4 K Oshima, K Shimoji, H Takahashi, H. Yamamoto and H Nozaki, J. Amer Chem. Soc , 95, 2694 (1973)
5 J H Pinckard, B Wille and L Zechmeister, *ibid*, 70, 1938 (1948)
6 T Yoshida, R M Williams and E Negishi, *ibid*, 96, 3688 (1974)