Tetrahedron Letters No. 22, pp 2075 - 2078.
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0040-4039/79/0522-2075$02.00/0

ISOPRENIC THIOVINYLCARBENES .2. INTERMOLECULAR REACTIONS WITH OLEFINS, DIENES AND ACETYLENES. DIRECT ACCESS TO CHRYSANTHEMIC ESTERS.

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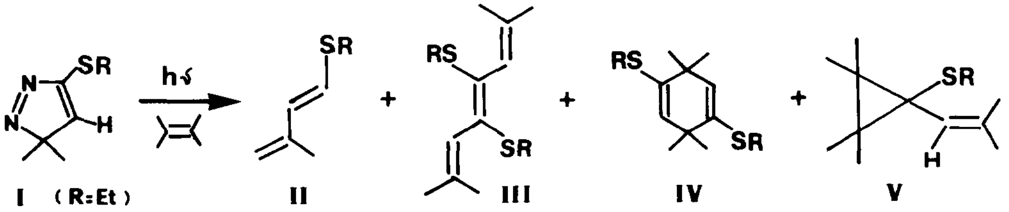
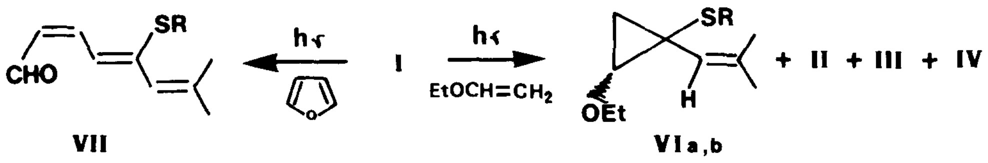
The isoprenic thiovinylcarbene formed by photolysis of gem-dimethyl-5-ethylthiopyrazolenine shows a surprisingly good intermolecular reactivity toward electrophilic olefins and acetylenes. A direct access to chrysanthemic esters is thus provided.

We have recently shown that the irradiation in allylic sulfides of gem-dimethyl-5-alkylthio and 5-arylthiopyrazolenines leads to rearranged diolefinic dithioaketals. Artemisia ketone could thus be synthetized in two steps from ethyl prenyl sulfide in 65% total yield (1). The easiest way to explain these results is to admit the transient existence of a vinylcarbene which reacts with the sulfide to an allylic sulfonium ylide. A [2,3] sigmatropic shift gives then the observed major products.

In this paper we are now describing the reactivity of these species toward multiple C-C bonds. The most striking fact is their far better intermolecular reactivity toward electrophilic as compared to nucleophilic double and triple bonds. The usually choosen nucleophilic olefins give indeed only poor yields of cyclopropanation products (V,VI) with this carbene, the main products being the same as those (II,III,IV) formed by photolysis (2) of pyrazolenine I in inert solvents (1).



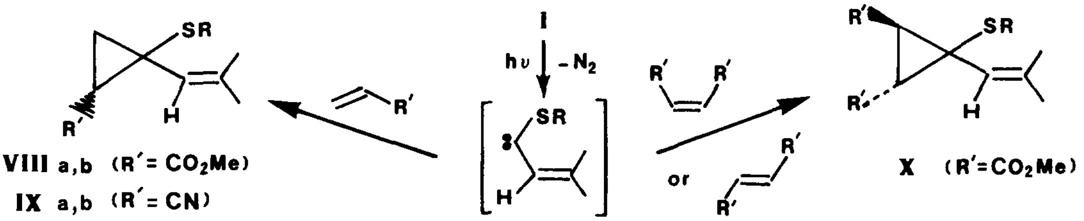


V : ∿ 20% present in the crude mixture (NMR); isolated (∿10%) and characterized (3) after transformation into the sulfone (MCPBA); NMR : cyclopropanic methyl singlets at 1,04ppm(6H) and 1,54ppm(6H); isobutenyl signals at 1,82ppm(3H,large s)1,84ppm(3H,large s)and 5,08ppm(1H,m)

VIa,VIb: ∿ 25% present in the crude mixture (NMR); two isomers isolated (13%) and separated on SiO_2 chromatoplate (6:1); NMR (major isomer): isobutenyl signals at 1,69ppm(3H,d) 1,79ppm(3H,d) and 5,31ppm(1H,m) J ≃ 1,5 Hz ; cyclopropanic protons as AMX spectrum (in C_6D_6 : J_{AM}= 7,0Hz ; J_{AX}= 6,5Hz ; J_{MX}= 4,5Hz).

We had seen that furan is an excellent carbene trap in our previous work on vinylcarbenes (4). Here we could not isolate a divinylcyclopropane which is the usual product formed from vinylcarbene addition to furan, but we did recognize the formation of the polyunsaturated aldehyde VII (δCHO = 10,15 ppm, J ≃ 7,5 Hz) which is probably formed directly from carbene and furan (< 25%).

With methyl acrylate or acrylonitrile as irradiation solvents the intermolecular reactivity becomes excellent. The cyclopropanation is now nearly quantitative (VIIIa and b, IXa and b) with the same high nitrogen evolution rate as for inert solvent irradiations. In the presence of dimethyl maleate or fumarate, only the trans cyclopropanic diester X is obtained still with the same high nitrogen evolution rate. The formation of the products II, III and IV is completely inhibited.

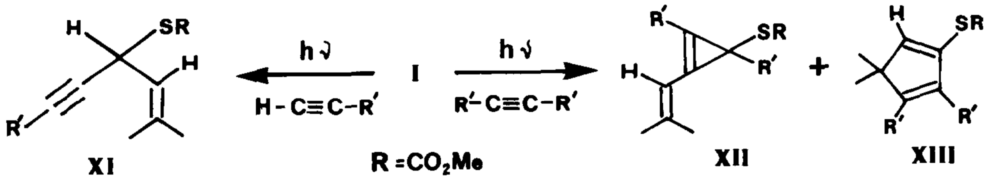


VIIIa, VIIIb : isolated as mixture in 90% yield ; separated by SiO$_2$ column chromatography in 45% and 27% yield respectively; IR : ν(C=O) 1745cm^{-1} ; NMR (major isomer) : isobutenyl signals at 1,71ppm(3H,d) 1,81ppm(3H,d) and 5,42ppm(1H,m) J ≃ 1,2Hz; cyclopropanic protons as AMX spectrum between 1,10 and 2,05ppm(3H).

IXa, IXb : 95% as mixture ; separated on florisil in 43% and 33% yield respectively; IR : ν(C≡N) 2250cm^{-1} ; NMR (major isomer) : isobutenyl signals at 1,72ppm(3H,d) 1,80ppm(3H,d) and 5,39ppm (1H,m) J ≃ 1,5Hz; cyclopropanic protons as AMX spectrum between 1,20 and 1,90ppm(3H).

X : isolated in 60% and 80% yield, respectively, from dimethyl maleate and dimethyl fumarate (5); F = 51°C; IR ν(C=O) 1720cm^{-1}; NMR : isobutenyl signals at 1,77ppm(3H,d) 1,85ppm(3H,d) and 5,27ppm(1H,m) J ≃ 1,5Hz; cyclopropanic protons at 2,60ppm and 2,72ppm (AB ∿ 6Hz).

The rate of the reaction between electrophilic acetylenes and our vinylcarbene is similar. The products are however more complex. Thus photolysis in methyl propiolate leads only to the acetylenic ester XI while in the presence of dimethyl butynedioate one obtains a mixture containing the two cyclic adducts XII and XIII (6).

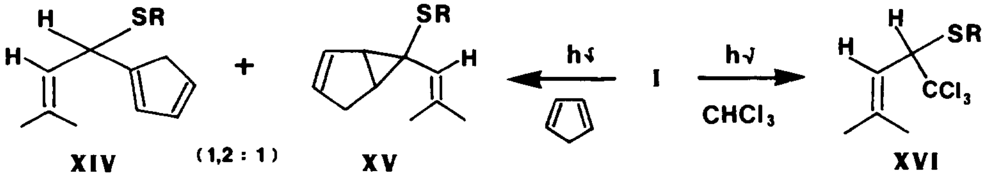


XI : isolated in 66% yield through SiO$_2$ filtration, but appears to be the sole constituent of the crude product (96%, NMR); IR: ν(C≡C) 2240cm^{-1}, ν(C=O) 1720cm^{-1}; NMR : isobutenyl signals at 1,69ppm(3H,d, J = 1,5Hz) 1,73ppm(3H,d, J = 1,5Hz) and 5,21ppm(1H,m, J = 1,5Hz and 9,5Hz) ; other single proton at 4,42ppm(d, J = 9,5Hz).

XII : isolated (6%) by SiO_2 chromatography; IR : 1835cm^{-1} (cyclopropene), ν(C=O) 1740 and 1725 cm^{-1}; NMR : isobutenyl signals at 2,06ppm(3H,large s) 2,13ppm(3H, large s) and 6,22ppm(1H,m) ; methylester singlets at 3,77 and 3,88ppm.
XIII : isolated (20%) by SiO_2 chromatography; UV (C_6H_{12}) : λ max = 229 nm (15000) and 245 nm (14200); NMR : methyl singlet at 1,36ppm(6H) ; methyl ester singlets at 3,81 and 3,92ppm ; vinylic proton as singlet at 6,28ppm.

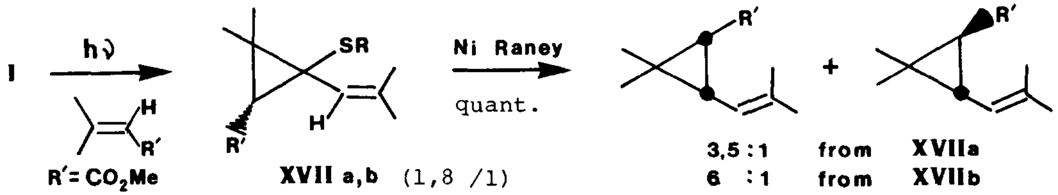
The origin of the products XI, XII and XIII is best explained by two step mechanisms, which are mandatory in the case of XII and likely for XI and XIII. However the possibility of a simple C-H insertion cannot be excluded for the formation of XI. The same is true for XIII where a direct [2+4] cycloaddition of the vinylcarbene as a 4 electron system could be invoked. These results are consistent either with the intermediacy of a very nucleophilic singlet vinylcarbene (Ylide form, proton abstraction and recombination, dipolar intermediates) or of a triplet carbene (see [1,4]H migration to diene II, direct observation of aldehyde VII, diradical intermediates) reacting both in a non concerted manner (Cf. trans diester X from maleate and fumarate).

The observation of enhanced reactivity toward cyclopentadiene - where the product of a formal C-H insertion XIV prevails over the divinylcyclopropane XV - and the exclusive formal insertion into the C-H bond of chloroform - XVI is isolated in 70% yield - are compatible with both of these hypotheses.



XIV, XV : formed quantitatively (NMR), isolated as mixture (1,2:1) in 75% yield; characterized after transformation into the sulfones (MCPBA) separated by SiO_2 HPLC :
XIV : NMR : isobutenyl signals at 1,79ppm(3H,d) 1,87ppm(3H,d) and 5,60ppm(1H,m (J ≃ 1,5Hz) d(J = 10,5Hz) cyclopentadienic protons at 3,19ppm(2H, large s) and 6,48-6,83ppm(3H,m) other single proton at 4,89ppm(d, J=10,5Hz); IR : ν(C=C) 1685cm^{-1},1710cm^{-1}
XV : (one isomer) NMR : isobutenyl and ethyl sulfonyl groups ; cyclopentenic protons at 2,24ppm (1H,d, J = 6,5Hz) 2,56ppm(1H,m) and 5,67 to 6,00ppm(2H,m).
XVI : isolated in 70% yield ; IR : ν(C-Cl) 770cm^{-1}; NMR : isobutenyl signals ; other single proton at 4,33ppm (d, J = 10Hz).

The higher reactivity observed toward electrophilic derivatives could finally also be rationalized through the photodecomposition of a 1,3-dipolar cycloaddition product of an intermediate alkylthiodiazo derivative which is likely to be first formed during the photolysis of I (7). Such a diazo derivative is however probably rather unstable (8) and will rapidly loose nitrogen under our conditions. This is nevertheless not sufficient to exclude a rapid dipolar cycloaddition with electrophilic olefins and chiefly acetylenes. We prefer however the direct carbenic way, mainly on the ground of the very rapid rate of nitrogen evolution observed, without any rate change going from inert irradiation solvents like pentane to reacting electrophilic olefins. In the case of the acetylenic derivatives the nitrogen evolution rate does decrease but only after 50% conversion, the initial rate remaining the same. Whatever the effective mechanisms, it is definite that we are dealing with a vinylcarbene precursor which on photolysis in electrophilic olefins leads almost quantitatively to vinylcyclopropanes and not to intramolecular carbene stabilization products. This unexpected behaviour and the isoprenic structure of our vinylcarbene opens up a rapid access to chrysanthemic esters.The latter proceeds only with moderate yields but is nevertheless interesting, considering the preferred desulfurization to the <u>cis</u>-derivative from both isomeric adducts XVIIa and XVIIb :



XVIIa, XVIIb : separated by SiO_2 chromatography in 16% and 9% yield respectively. NMR (major isomer) : ethyl sulfide group ; isobutenyl signals at 1,78ppm (6H, large s) and 5,41ppm(1H,m) other cyclopropanic substituents at 1,17ppm(3H,s) 1,46ppm(3H,s) 1,68ppm(1H,s) and 3,71ppm(3H,s) NMR (minor isomer) : very similar with only small chemical shift differences.

Acknowledgments : This work was supported by the DGRST (ASCO n° 74-7-1449). We are also grateful for financial support from Roussel-Uclaf (to J.J. Lohmann).

REFERENCES AND NOTES

1) Part one : M.FRANCK-NEUMANN, J.J.LOHMANN Tetrahedron Letters <u>1978</u>, 3729

2) The photolysis conditions used are identical to those in reference (1).

3) All new compounds gave satisfactory microanalyses, mass,IR and NMR spectra ($CDCl_3$/TMS).

4) M. FRANCK-NEUMANN, C.BUCHECKER-DIETRICH, Tetrahedron <u>34</u>, 2797 (1978)
M. FRANCK-NEUMANN, J.J.LOHMANN Angew.Chem. <u>89</u>, 331 (1977) Int.Ed.Engl. <u>16</u>,323 (1977)

5) This is the only formed product in both cases.The difference in yield comes mainly from the greater difficulty of separation of X from dimethyl maleate than from fumarate.

6) This is only true when the photolysis is done in ether in the presence of one equivalent of dimethyl butynedioate. If the acetylenic diester is the irradiation solvent, the cyclopentadiene XIII formed, undergoes a rapid Diels-Alder addition leading to a norbornadiene tetraester (31%, F = 136°C).

7) G.L. CLOSS, W.A. BÖLL, H. HEYN et V.DEV, J.Am.Chem.Soc. <u>90</u>, 173 (1968)

8) D.M. LEMAL, E.H. BANITT Tetrahedron Lett. <u>1964</u>, 245.
U. SCHÖLLKOPF, E. WISCOTT, Ann., <u>694</u>, 44 (1966).

(Received in UK 29 March 1979)