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THE FORMATION OF SOME STABLE SULFOXONIUM YLIDES FROM ACETYLENIC COMPOUNDS AND SOME FURTHER REACTIONS OF THESE STABLE YLIDES.

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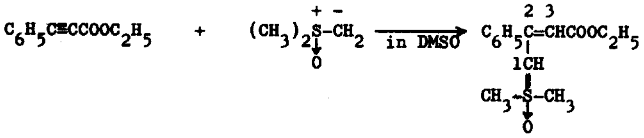
In the continuation and the extension of our studies on the chemistry of electrophilic reactions of acetylenic compounds (1, 2, 3, 4), we found the formation of some stable sulfoxonium ylides by the reactions of phenylpropiolate derivatives with dimethylsulfoxonium methylide (4, 5, 6, 7, 8). Moreover, we have encountered with some interesting behavior of the ylides derived from the acetylens. The appearance of a recent paper (9) on the formation of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (I) has prompted us to report in a preliminary form our results on these subjects. Some stable sulfoxonium ylides and the like have been found by E. J. Corey and his co-worker (10), H. König, H. Metzger and their co-workers (11, 12, 13, 14) and H. Nozak (15).

Reaction of ethyl phenylpropiolate with dimethylsulfoxonium methylide, which was prepared from trimethylsulfoxonium iodide and sodium hydride in dimethylsulfoxide, followed by treatment with water gave dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (I), m.p. 132-133°[*1] in 91% yield.

[*1] All melting points are uncorrected and satisfactory elemental analyses were obtained for all compounds reported here.



$$C_6H_5C\equiv CCOOC_2H_5 \quad + \quad (CH_3)_2\underset{\downarrow\atop O}{\overset{+}{S}}-\overset{-}{C}H_2 \xrightarrow{\text{in DMSO}} C_6H_5\overset{2}{C}(-\overset{1}{C}H=\underset{\downarrow\atop O}{S}(CH_3)_2)=\overset{3}{C}HCOOC_2H_5$$

I

The infrared spectrum showed absorptions at 1020 (-SO-) and 1667 cm^{-1} (α,β-unsaturated ester), and the ultraviolet spectrum showed absorption maxima at 230 (ℇ=8220), 270 (ℇ=6770) and 346 mμ (ℇ=15630). The n.m.r. spectrum[*2] exhibited the signals at 1.25 (3H, triplet) and 4.15 (2H, quartet) due to the ethyl ester, 7.45 (multiplet) assignable to the phenyl group, 2.95 as a singlet peak (six S-methyl protons), 4.77 (1H, singlet) assigned to the C-3 proton[*3] and 6.29 ppm (1H, slightly broader singlet) assigned to the C-1 proton. When one drop of deuterium oxide was added to a solution of I in deuterochloroform in a measurement of n.m.r. spectrum, there occurred remarkable decrease of the intensities of the peaks at 6.29 and 2.95 ppm. with more broadening, whereas none of the change was observed at the signal located at 4.77 ppm. On the basis of these data, the crystalline compound (I) was concluded to have a ylide type structure of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (I). Reactions of ethyl esters of some substituted phenylpropiolic acids with dimethylsulfoxonium methylide analogously gave the corresponding stable ylides (TABLE I). However, ethyl acetylenecarboxylate, dimethyl acetylenedicarboxylate, benzoylacetylene, p-tolylsulfonylphenylacetylene and 1,4-diphenyl-1,3-butadiyne also reacted with the methylide, in these cases the corresponding stable ylides were not isolated because of

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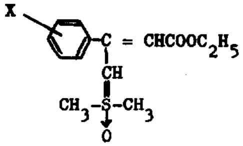
[*2] The n.m.r. spectra were measured using Varian A-60 spectrometer and the chemical shifts were expressed in ppm unit from the internal standard of tetramethylsilane in $CDCl_3$ solution.

[*3] In the n.m.r. spectrum of ethyl trans-β-ethoxycinnamate, the signal of the vinylic proton appeared at 5.19 ppm.

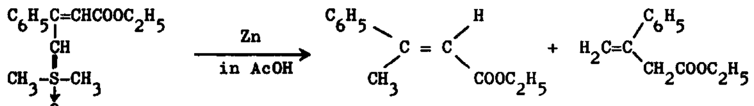
TABLE I



Substituent (X)	m.p. (C°)	Yield (%)	UV λ_{EtOH}^{max} mμ (ε)
H	132–133	91	230 (ε= 8220)
			270 (ε= 6770)
			346 (ε= 15630)
p-CH$_3$	120–121	86	237 (ε= 7930)
			256 (ε= 7590)
			346 (ε= 15690)
p-CH$_3$O	123–124	61.5	247 (ε= 7400)
			269 (ε= 8020)
			341 (ε= 18500)
o-Cl	130–131	71	344 (ε= 23650)
m-Cl	112–113	100	234 (ε= 8050) (shoulder)
			272 (ε= 6040)
			347 (ε= 17000)
p-Cl	133–134	87	240 (ε= 9980)
			277 (ε= 9510) (shoulder)
			347 (ε= 17830)

their instabilities. Phenylpropiolyl amide, diphenylacetylene and phenylacetylene failed to react with the methylide. When the reaction mixture of ethyl phenylpropiolate and dimethylsulfoxonium methylide in dimethylsulfoxide was treated with deuterium oxide, there found no deuterium at C-3 adjacent to the ester group, but the other seven protons at the carbon atoms adjacent to sulfur were completely exchanged with deuterium in the n.m.r. spectrum. Before the reaction mixture was treated with deuterium oxide, therefore, proton transfer might had occurred in an addition-intermediate. Although no decided mechanistic assumption is proposable, intermolecular proton transfer would operate in the formation of the ylide (I).

I was treated with zinc dust in acetic acid at 16-17° for six hours to afford a mixture of ethyl 3-phenyl-2-butenoate (II) and ethyl 3-phenyl-3-butenoate (III) in a ratio of 10:90 in 92% yield based on the n.m.r. and the gaschromatography.



I II III

10 : 90

The n.m.r. spectrum of II showed the signals at 1.22 (3H, triplet) and 6.20 (2H, quartet) due to the ethyl ester, a doublet at 8.54 (3H, J = 1.5 cps) for the methyl group, a triplet at 6.07 (1H, J = 1.5 cps) for the vinyl proton adjacent to ethoxycarbonyl group and multiplet phenyl protons centered at 7.70 ppm. The ultraviolet spectrum of II showed an absorption maximum at 265 mμ (ε=15,860) which tells the probable geometry, trans, for II (16)*4

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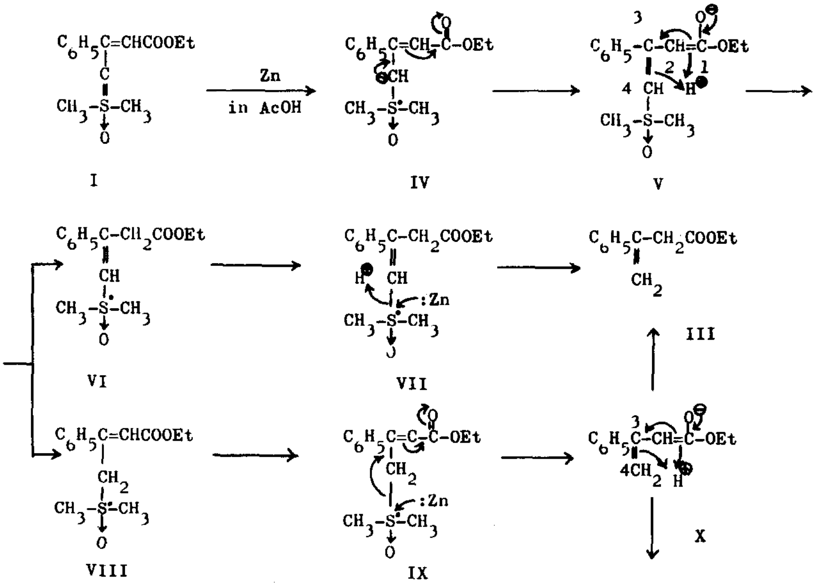
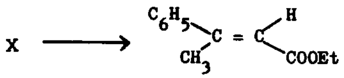
*4 The ultraviolet spectra of trans butyl 3-phenyl-2-butenoate, trans 3-phenyl-2-butenoic acid and cis 3-phenyl-2-butenoic acid show the absorption maxima at 269 (ε=16,000), 266 (ε=14,800) and 246 (ε=9,000), respectively.

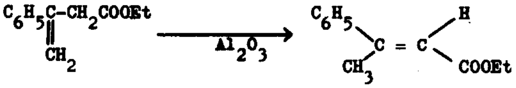
The n.m.r. spectrum of III showed the triplet peak at 1.15 and the quartet at 4.05 due to the ethyl ester group and a ABX_2 pattern(H_A, 5.46 (vinylic proton), H_B, 5.18 (vinylic proton), H_{X2}, 3.40 (terminal methylene), J_{AB} = 1.2 cps, J_{BX} = 0 (nearly), J_{AX2} = 1.2 cps.) . The ultraviolet spectrum of III showed an absorption maximum at 243 mμ (ε=10600) and the infrared spectrum showed a terminal methylene group at 909 cm^{-1}. One could assume that the reduction of the sulfoxonium ylide (I) with zinc dust in acetic acid would proceed through an anion radical which would have been produced by the transfer of the electrons from the metal surface to the carbon C-1 adjacent to the sulfur atom (17, 18). There has been only one example for the reduction of the sulfoxonium ylide with zinc dust in acetic acid (19). The reduction, however, of 2,3-dimethylbenzyl dimethyl ammonium salt with sodium amalgam to give 1,2,3-trimethylbenzene (20) has been believed to proceed <u>via</u> the formation of an anion radical followed by elimination of a stable anion (21).





II

Protonations of plausible reaction intermediates (V) and (X) would occur preferentially at C-2 according to the Ingold's theory[*5] (22). Ringold and Malhotra (23) reported the protonation of the potassium enolate of cholest-4-en-3-one in aqueous acetic acid led to the β,γ-unsaturated ketone (Δ^5-3-one) in high yield[*6] demonstrating preferential C-4 protonation of the anion (24). Treatment of III with alumina by column chromatography reverted to the stable isomer (II).



III II

Treatment of the ylide (I) with triethylamine in benzene afforded 3-ethoxycarbonyl-2-phenyl-1,3-batadiene (XI) in 85% yield which could not be distilled even under reduced pressure (0.1 mm Hg), owing to the unstable nature for polymerization. However, the butadiene could be purified by

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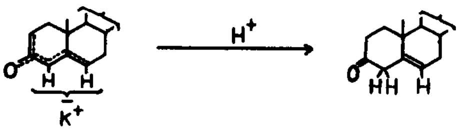
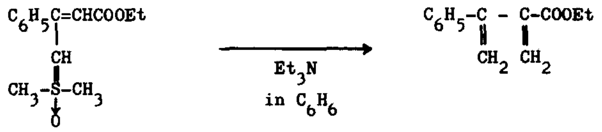
[*5] Weak acids lead to the kinetically-controlled product by proton attack at the central position of the enolate anion and strong acids or equilibrating conditions give the product of thermodynamic control by attack of the proton at the terminal position.

[*6]



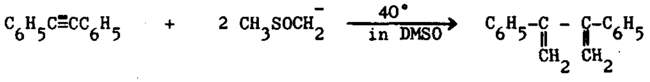
alumina column chromatography (Woelm, neutral, grade II, eluting with n-hexane: benzene=3:1). The infrared spectrum showed absorption bands at 900 (terminal methylene), 1613 (conjugated double bond with ester) and 1733 cm^{-1} (α,β-unsaturated ester) and an absorption maximum in the ultraviolet spectrum appeared at 240 mμ (ε=9620). The n.m.r. spectrum showed the signals at 1.06 (triplet) and 4.10 (quartet) due to the ethyl ester and two sets of AB type pattern at 5.39 and 5.49 (2H, J_{AB}=1.1 cps) and at 5.78 and 6.30 ppm (2H, J_{AB}= 2.0 cps) for two characteristic terminal methylene groups.



$$C_6H_5C(=CH-\overset{O}{\underset{}{S}}(CH_3)_2)CH COOEt \xrightarrow[\text{in } C_6H_6]{Et_3N} C_6H_5-C(=CH_2)-C(=CH_2)-COOEt$$

I XI

In an earlier paper, one of the authors has described the formation of 2,3-diphenyl-1,3-butadiene (XII) by the reaction of diphenylacetylene with dimethylsulfinyl carbanion (25). The AB type patterns of the n.m.r. spectrum of XII are very similar to those of XI.

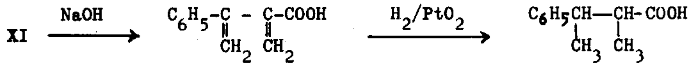


$$C_6H_5C{\equiv}CC_6H_5 \quad + \quad 2\ CH_3SOCH_2^- \xrightarrow[\text{in DMSO}]{40^\circ} C_6H_5-\underset{CH_2}{\underset{\|}{C}}-\underset{CH_2}{\underset{\|}{C}}-C_6H_5$$

XII

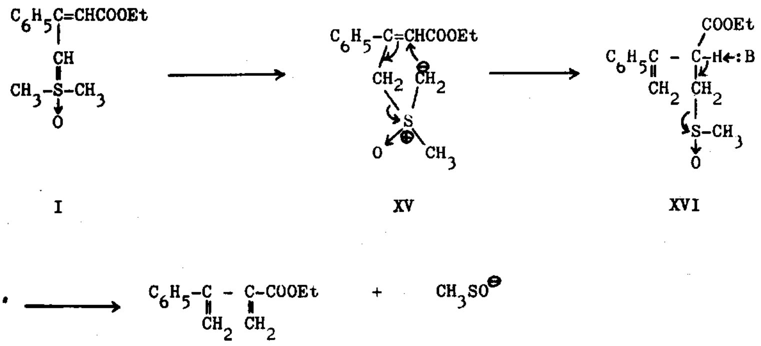
XI was hydrolysed in sodium hydroxide solution to give the corresponding acid (XIII), m.p. 106-107°. The absorption maximum in the ultraviolet spectrum appeared at 240 mμ (ε=12,390). The n.m.r. spectrum showed a pair of AB type patterns at 5.38 and 5.52 (2H, J_{AB}=1.3 cps), and 5.88 and 6.44 (2H, J_{AB}=1.7 cps) assignable to two characteristic terminal methylene groups and a slightly broadening singlet at 10.22 ppm for the proton of a carboxylic acid. The acid (XIII) was catalytically hydrogenated in the presence of platinum to give 2-

methyl-3-phenylbutyric acid (XIV), m.p. 132-133° (26, 27) uptaking two moles of hydrogen.



XI → XIII → XIV

A mechanistic assumption for the formation of the butadiene derivative (XII) from the ylide (I) would be expressed as follows:


I XV XVI

XII

Since it has been very difficult to obtain the butadiene derivatives having the substituents of phenyl and carboxylate at the 2 and 3 positions, this method is quite useful for the preparation. The investigation of the chemical behavior of these butadiens is now undergoing.

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