Tetrahedron Letters No.31, pp. 3491-3494, 1968. Pergamon Press. Printed in Great Britain.

REACTION OF STABLE SULFOXONIUM YLIDES WITH SULFENES*1

Junya Ide and Yasuo Yura

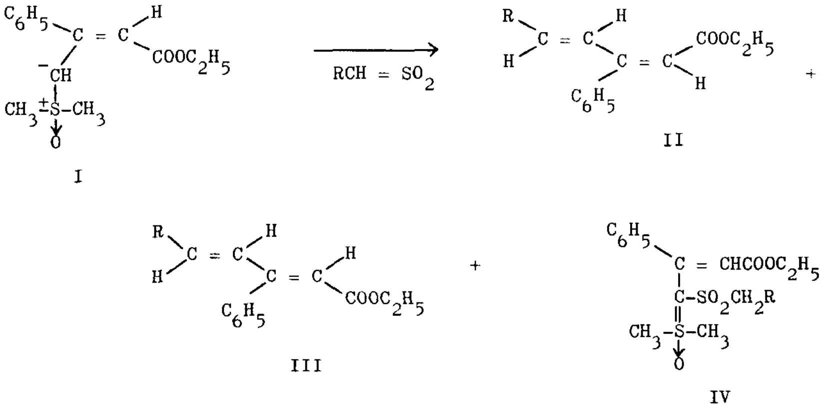
Central Research Laboratories, Sankyo Co., Ltd.

2-58, 1-chome, Hiromachi, Shinagawa-ku, Tokyo, Japan

(Received in Japan 28 March 1968; received in UK for publication 29 April 1968)

The appearance of a recent report (1) on the reaction of sulfonium ylides with methane sulfonylchloride derivatives has prompted us to report in a preliminary form our results on a highly stereospecific synthesis of butadiene derivatives by reaction of stable sulfoxonium ylides (2) with sulfenes.

Treatment of sulfoxonium ylide (I)(2a.b.3) with benzylsulfonylchloride in the presence of triethylamine in THF at 4-6° afforded ethyl trans,trans-3,5-diphenyl-2.4-pentadienoate (II, R=C_6H_5)(63% yield); bp 150-155°/0.0005 mmHg (bath temp.), IR spectrum $\left[\nu_{\max}^{\text{Liquid}}\ \text{cm}^{-1}\right.$: 1709, 1176, 1041, 1027, 990, 980, 873, 775, 757, 706, $\left.696\right]$; UV spectrum $\left[\lambda_{\max}^{\text{EtOH}}\ \text{m}\mu(\varepsilon)\right.$: 230(12,300), 260(9,900), $\left.316(26,800)\right]$, trans,cis-isomer (III, R=C_6H_5)(2.3% yield) and C-sulfonylated product (IV, R=C_6H_5)(1.3% yield), mp 157-158°, IR spectrum $\left[\nu_{\max}^{\text{Nujol}}\ \text{cm}^{-1}\right.$: 1709, 1468, 1383, 1297, 1170, 1111, $\left.1042\right]$, UV spectrum $\left[\lambda_{\max}^{\text{EtOH}}\ \text{m}\mu(\varepsilon)\right.$: 264(11,500), $\left.364(2,550)\right]$. These NMR spectra are shown in Table I and III.



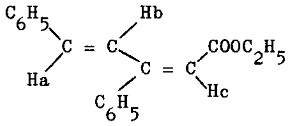
I II III IV

---

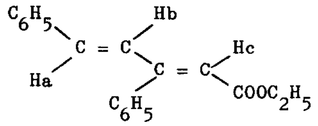
*1 This paper forms part V of a series entitled "Sulfoxonium Ylide Chemistry." For previous papers, See Ref. 2.

TABLE I

NMR Spectra of II and III



II



III

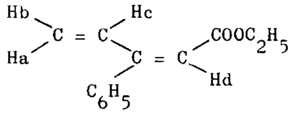
$R=C_6H_5$	CH_3	$O-CH_2Me$	Ha	Hb	Hc	Aromatic protons
II	8.68(t)	5.74(q)	3.37(q)	1.42(q)	4.17(q)	2.6 (m)
	J = 7 cps		Jab=16cps Jac=Jbc~1 cps			
III	8.94(t)	5.99(q)	3.62(q)	2.82(q)	3.89(q)	2.6 (m)
	J = 7 cps		Jab=16cps Jac=Jbc~1 cps			

The signals of the proton Hb in the trans,trans-isomer ($II, R=C_6H_5$) appear at an abnormally low field, which is ascribed to the anisotropic effect of carboethoxy group located on the same side of the diene system (4).

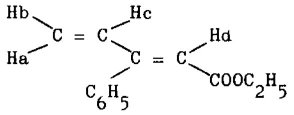
In the case of the reaction of methane sulfonylchloride with the ylide (I), the corresponding dienes, ethyl trans-3-phenyl-2,4-pentadienoate (II, R=H); bp 90-95°/0.03 mmHg (bath temp.)(54% yield), IR spectrum $\left[\nu_{max}^{Liquid}\ cm^{-1}\right.$: 1709, 1170, 1000, 934, 870, 775, 699$\left.\right]$, UV spectrum $\left[\lambda_{max}^{EtOH}\right.$ mμ(ε): 234(plateau)(9,160), 262(13,750)$\left.\right]$, the cis-isomer (III, R=H)(1.2% yield) and a C-sulfonylated product (IV, R=H), mp 155-156° (10.6% yield) were obtained. These NMR spectra were shown in Table II and III.

TABLE II

NMR Spectra of II and III (R=H)



II



III

R=H	CH_3	$O-CH_2-Me$	Ha	Hb	Hc	Hd	Aromatic protons
II	8.70(t)	5.76(q)	4.69(octet)	4.39(sextet)	2.02(octet)	4.16(quintet)	2.63(s)
	J=7 cps		Jab=Jbd=2 cps Jac=17 cps Jbc=11 cps Jad=Jcd~1 cps				
III	8.96(t)	5.99(q)	4.91(sextet)	4.53(sextet)	3.32(octet)	3.99(q)	2.6(m)
	J=7 cps		Jab=Jbd=Jad=Jcd~1 cps Jac=17 cps Jbc=10 cps				

TABLE III

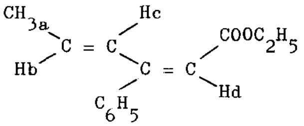
NMR Spectra of IV

IV R	CH_3	$O-CH_2-Me$	$CH_3-\overset{O}{\overset{\uparrow}{S}}-CH_3$	SO_2CH_3	$SO_2CH_2C_6H_5$	-C=CH-	Aromatic protons
C_6H_5	8.67(t) J=7 cps	5.75(q)	6.47(s)	-	5.87(s)	3.55(s)	2.4(m)
H	8.90(t) J=7 cps	5.96(q)	6.49(s)	7.10(s)	-	3.78(s)	2.6(s)

Similarly the reaction of the ylide (I) with ethane sulfonylchloride gave trans,trans-diene (II, R=CH_3); bp 100-105°/0.02 Hg (bath temp.)(40.8% yield), IR spectrum [ν_{max}^{Liquid} cm^{-1}: 1712, 1163, 980, 873, 775, 706], UV spectrum [λ_{max}^{EtOH} mμ(ε): 231(8,200), 274(17,240)].

TABLE IV

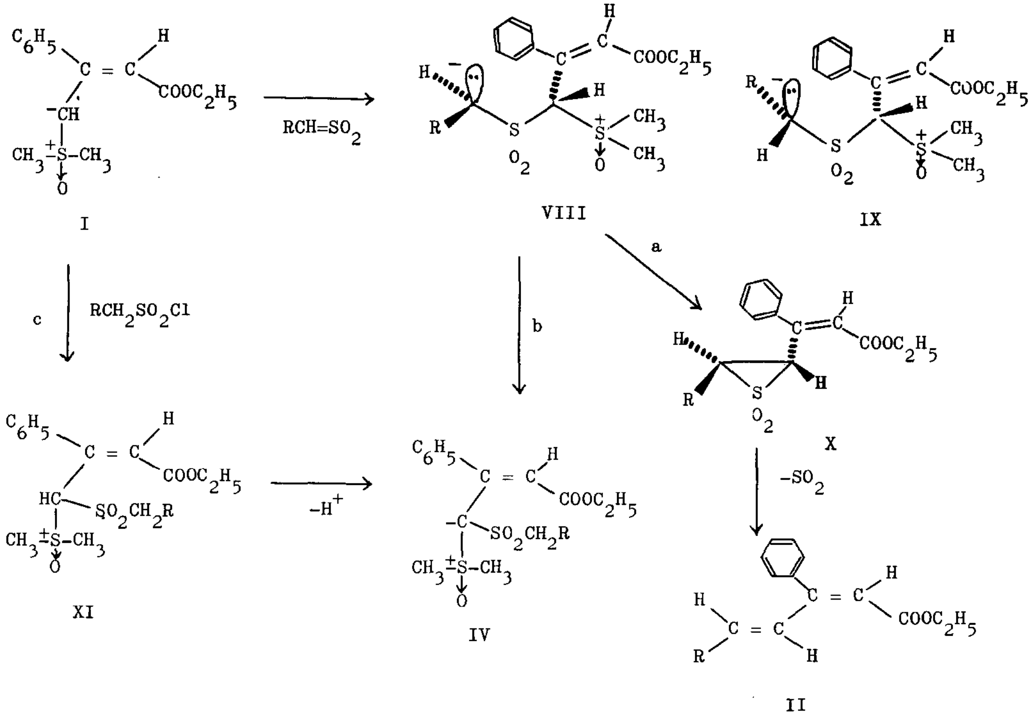
NMR Spectra of II



II

R=CH_3	CH_3	$O-CH_2-Me$	CH_{3a}	Hb	Hc	Hd	Aromatic protons
	8.69(t)	5.77(q)	8.13(octet)	4.14(octet)	2.24(octet)	4.32(q)	2.65(s)
			Jab=7cps Jac=2cps Jbc=16cps Jad=Jbd=Jcd$\sim$1 cps				

The highly stereospecific formation of double bond would proceed through a thermal cis-elimination (5) of sulfur dioxide from a trans-episulfone (X). The addition of the ylide-carbanion to sulfenes would form the transition states (VIII and IX). The large cinnamyl and R (R=CH_3, C_6H_5) groups interfere each other in IX but not in VIII. Thus the elimination of DMSO proceeding through transition state (VIII) takes place more readily than that proceeding through IX. The C-sulfonylated product would be formed either by proton transfer of VIII or IX (path b), or by a direct substitution of the sulfonylchloride with ylides followed by stabilization to a C-sulfonylated ylide (IV) (path c). We are currently extending this work to the reaction of other ylides with sulfenes in the hope of "a new type of Wittig reaction" with high stereospecificity.



References

1. H. Nozaki, M. Takaku and Y. Hayashi, Tetrahedron Letters, 1967, 2303.

2. a) J. Ide and Y. Kishida, Tetrahedron Letters, 1966, 1787; b) J. Ide and Y. Kishida, Chem. Pharm. Bull. (Tokyo), in press; c) J. Ide and Y. Kishida, Chem. Pharm. Bull. (Tokyo), in press; d) Y. Kishida and J. Ide, Chem. Pharm. Bull. (Tokyo), 15, 360 (1967); e) Y. Kishida, T. Hiraoka and J. Ide, Tetrahedron Letters, 1968, 1139.

3. C. Kaiser, B. M. Trost, J. Beeson and J. Weinstock, J. Org. Chem., 30, 3972 (1965).

4. L.M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, p124, Pergamon Press, London (1959).

5. a) N.P. Neureiter and F.G. Bordwell, J. Am. Chem. Soc., 85, 1209 (1963); b) N. Tokura, T. Nagai and S. Matsumura, J. Org. Chem., 31, 349 (1966); c) G. Opitz, Angew. Chem. (Internat. Edit.), 6, 107 (1967); d) N.P. Neureiter, J. Am. Chem. Soc., 88, 558 (1966).