ADDITION OF ALKYLSULFENYL CHLORIDES TO CINNAMIC ACID AND SOME OF ITS DERIVATIVES

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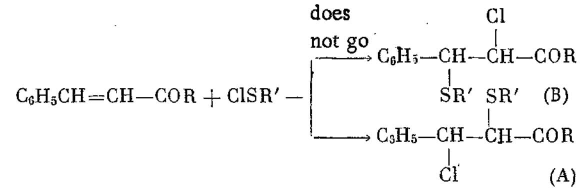
In the present paper was studied the addition of the methyl- and β-chloroethylsulfenyl chlorides to cinnamic acid and to its methyl and ethyl esters, the amide, anilide, and the acid chloride. It is known that alkylsulfenyl chlorides add to aliphatic α,β-unsaturated acids and their derivatives with the formation of a mixture of adducts, which change over to more stable isomers [1, 2]. The addition of alkylsulfenyl chlorides to cinnamic acid and its derivatives could also lead to adducts (A) and (B). However, the acid and its derivatives form only one stable isomer (A), which under the conditions, mentioned for the adducts of other α,β-unsaturated acids [1, 2], does not isomerize.



Alkylsulfenyl chlorides add smoothly to the esters, amide, and anilide of cinnamic acid in inert solvents, with the formation of the corresponding adducts. The acid chloride of cinnamic acid reacts more slowly with the sulfenyl chloride. Based on the NMR data, only 40% of the acid chloride reacted in one day. The addition of the sulfenyl chlorides to cinnamic acid could be accomplished only in glacial acetic acid. In order to avoid possible rapid isomerization, the addition of methylsulfenyl chloride to methyl cinnamate was run at −20°C in the presence of $CaCO_3$, but the presence of the second isomer was also not detected in this case. The formation of the sole isomer of the Markovnikov orientation was also mentioned earlier in the case of the addition of sulfenyl chlorides to styrene [1] and trans-1-phenyl-1,2-propene [3].

In order to prove the structure of the obtained compounds we took the NMR spectra of the specially synthesized model compounds: the acid chloride of α,β-dichloro-β-phenylpropionic acid and the methyl ester of α,β-dichloro-β-phenylpropionic acid, $C_6H_5CHClCHClCOCl$ $\delta_{\alpha\text{-CH}}$ 4.75, $\delta_{\beta\text{-CH}}$ 5.08 ppm; J 10.5 Hz and $C_6H_5CHClCHClCOOCH_3$, $\delta_{\alpha\text{-CH}}$ 4.48, $\delta_{\beta\text{-CH}}$ 5.07 ppm; J 10.7 Hz.* On the basis of these data, compounds (I)-(III), (VI)-(VIII), and (XI) were assigned the structure of (A). The characteristic chemical shifts are given in Table 1. The spectra of the compounds were taken on a Perkin–Elmer R-12 spectrometer (60 MHz), using 5% CCl_4 solutions and hexamethyldisiloxane as the internal standard.

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*From the data given in [4], for $C_6H_5CHClCHClCOOCH_3$ are given on the τ scale: $\tau_{\alpha\text{-CH}}$ 5.38, $\tau_{\beta\text{-CH}}$ 4.78 ppm; J 11.0 Hz.

TABLE 1

No.	Compound	$\delta_{\underset{\text{Cl}}{\text{CH}}}$, ppm	$\delta_{\underset{\text{S}}{\text{CH}}}$, ppm	J, Hz
I	$C_6H_5CHClCH(SCH_2CH_2Cl)COOH$	5,03	3,79	11,3
II	$C_6H_5CHClCH(SCH_2CH_2Cl)COOCH_3$	5,07	3,82	11,3
III	$C_6H_5CHClCH(SCH_2CH_2Cl)COOC_2H_5$	5,02	3,75	11,3
VI	$C_6H_5CHClCH(SCH_3)COOH$	5,05	3,69	11,3
VII	$C_6H_5CHClCH(SCH_3)COOCH_3$	5,05	3,64	11,2
VIII	$C_6H_5CHClCH(SCH_3)COOC_2H_5$	5,04	3,50	11,3
XI	$C_6H_5CHClCH(SCH_3)COCl$	4,98	3,96	11,1

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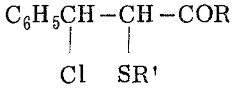
TABLE 2.



$C_6H_5\underset{Cl}{CH}-\underset{SR'}{CH}-COR$

Compound No.	R*	Mp, °C	Yield %	Found, %		Empirical formula	Calc., %	
				C	H		C	H
I	OH	82-84 (ether, petroleum ether)	65	47,29	4,20	$C_{11}H_{12}Cl_2O_2S$	47,33	4,33
II	OCH_3	68,5-70 (petroleum ether)	51	49,19	4,71	$C_{12}H_{14}Cl_2O_2S$	49,16	4,81
III	OC_2H_5	39-40 (petroleum ether)	94	50,97	5,40	$C_{13}H_{16}Cl_2O_2S$	50,83	5,24
IV	NH_2	114-114,5 (benzene)	72	47,87	4,66	$C_{11}H_{13}Cl_2NOS$	47,66	4,72
V	NHC_6H_5	121-123 (ether)	42	57,53	4,74	$C_{17}H_{17}Cl_2NOS$	57,62	4,83
VI	OH	114-115 (ether and petroleum ether)	44	51,70	4,65	$C_{10}H_{11}ClO_2S$	52,06	4,80
VII	OCH_3	84-86 (petroleum ether)	88	53,80	5,52	$C_{11}H_{13}ClO_2S$	54,00	5,36
VIII	OC_2H_5	70-72 (petroleum ether)	73	55,61	5,82	$C_{12}H_{15}ClO_2S$	55,71	5,84
IX	NH_2	136-138 (dioxane, petroleum ether)	70	52,41	5,16	$C_{10}H_{12}ClONS$	52,28	5,26
X	NHC_6H_5	144-145 (ether)	61	62,68	5,14	$C_{16}H_{16}ClONS$	62,85	5,27
XI	Cl	50-52° (petroleum ether)	23	47,66	4,17	$C_{10}H_{10}Cl_2OS$	48,20	4,17

* From (I) through (V), R = CH_2CH_2Cl;
from (VI) through (XI), R = CH_3.

EXPERIMENTAL METHOD

Addition of Sulfenyl Chlorides to Cinnamic Acid. To a solution of 0.02 mole of cinnamic acid in 50 ml of specially prepared glacial acetic acid* was added in drops a solution of 0.02 mole of the sulfenyl chloride in 15 ml of glacial acetic acid. The reaction mixture was allowed to stand overnight at room temperature. The glacial acetic acid was vacuum-distilled, and the residual oil crystallized when stored. The 3-phenyl-3-chloro-2-(β-chloroethylsulfenyl) propionic (I) and 3-phenyl-3-chloro-2-(methylsulfenyl)propionic (VI) acids were obtained. The constants and yields are given in Table 2.

Addition of Sulfenyl Chlorides to Cinnamic Acid Derivatives. The methyl and ethyl esters of cinnamic acid were dissolved in absolute ether, the amide and anilide were dissolved in absolute $CHCl_3$, and the acid chloride was dissolved in absolute CCl_4. To the solutions at room temperature was added in drops an equivalent amount of either β-chloroethylsulfenyl chloride or methylsulfenyl chloride, dissolved in the appropriate solvent. The reaction mixture was allowed to stand overnight. The solvent was distilled off, and the obtained compound was purified by recrystallization. The constants and yields of the obtained compounds are given in Table 2.

CONCLUSIONS

Alkylsulfenyl chlorides react with cinnamic acid and its derivatives to yield only one stable adduct, namely the α-alkylthio-β-chloro-β-phenylpropionic acid and its derivatives.

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*A mixture of 300 ml of glacial acetic acid and 30 ml of acetic anhydride was refluxed for 5 h, after which the acetic acid was distilled.