THE DIENE SYNTHESIS WITH SULFUR-CONTAINING DERIVATIVES OF ACRYLIC ACIDS

V. S. Étlis, L. N. Grobov, and A. P. Sineokov

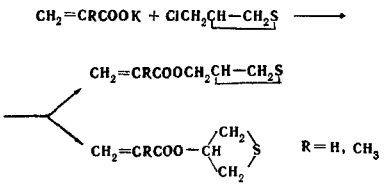
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 5, pp. 799–803, 1969

UDC 547.391.1+547.718

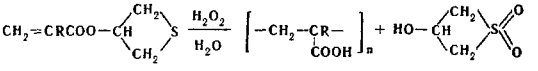
Reaction of aqueous solutions of salts of acrylic acids with thioepichlorohydrin affords thietyl acrylates, which on hydrolysis give 3-hydroxythietane, and on oxidation with hydrogen peroxide give 3-hydroxythietane 1,1-dioxide. The diene synthesis was carried out with these acrylates, and also with acryloyl and methacryloyl isothiocyanates.

Acrylic esters participate readily in the diene synthesis [1]. We have investigated the reaction of some sulfur-containing derivatives of acrylic acid (3-thietyl acrylates, which were previously unknown, and also acryloyl and methacryloyl isothiocyanates) with dienes.

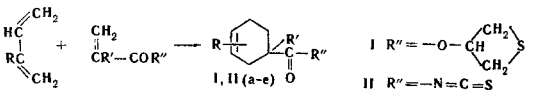
We synthesized 3-thietyl acrylates by reacting aqueous solutions of acrylate salts with thioepichlorohydrin. This reaction might be expected to give either thioglycidyl acrylates or, by analogy with acetate salts [2], thietyl acrylates:



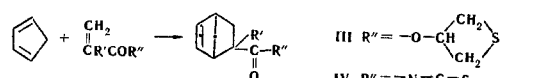
Thioglycidyl methacrylate had been obtained previously by reaction of thiourea with glycidyl methacrylate [3]. The structure of the acrylates which we have prepared has been confirmed by alkaline hydrolysis to 3-hydroxythietane. In addition, oxidation of the acrylates, and also of 3-hydroxythietane, with hydrogen peroxide gave 3-hydroxythietane 1,1-dioxide, thus confirming the presence of the thietane ring.



The diene synthesis was carried out with the synthesized dienophiles using butadiene, isoprene, chloroprene and cyclopentadiene as the dienes. In all cases, the corresponding adducts were obtained (either esters or acyl isothiocyanates):



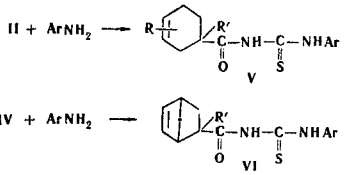
I a R = R′ = H; b R = H, R′ = CH$_3$; c R = CH$_3$, R′ = H; d R = R′ = CH$_3$;
II a R = R′ = H; b R = H, R′ = CH$_3$; c R = CH$_3$, R′ = H; d R = R′ = CH$_3$;
e R = Cl, R′ = H; f R = Cl, R′ = CH$_3$



III a R′ = H; b R′ = CH$_3$. IV a R′ = H; b R′ = CH$_3$

Acryloyl and methacryloyl isothiocyanates reacted with activated C=C bonds, but simultaneous formation of adducts of the isothiocyanate group, such as has recently been found for benzoyl isothiocyanate [4] was not observed.

The structure of the isothiocyanates obtained was confirmed by conversion to the corresponding thioureas:



V a R = R′ = H, Ar = C$_6$H$_5$; b R = H, R′ = CH$_3$, Ar = o-CH$_3$C$_6$H$_4$;
c R = CH$_3$, R′ = H, Ar = C$_6$H$_5$; d R = R′ = CH$_3$, Ar = o-CH$_3$C$_6$H$_4$;
e R = Cl, R′ = H, Ar = C$_6$H$_5$; f R = Cl, R′ = CH$_3$, Ar = o-CH$_3$C$_6$H$_4$.
VI a R′ = H, Ar = C$_6$H$_5$; b R′ = CH$_3$, Ar = o-CH$_3$C$_6$H$_4$

The IR spectra of the thioureas exhibit absorption bands due to the C=O group (1691–1708 cm^{-1}), C=C (1625–1650 cm^{-1}), and N—C (1530–1550 cm^{-1}), confirming the correctness of the proposed diene reaction scheme.

EXPERIMENTAL

3-Thietyl acrylates. Acrylic or methacrylic acid in water was neutralized with potassium carbonate, and to the solution of the salt thus obtained was added the calculated amount of thioepichlorohydrin. The mixture was heated with stirring for 8 hr at 60° C in the presence of copper powder, hydroquinone, and Neozone D as inhibitors. When the reaction was complete, the lower layer was separated. The aqueous layer was extracted with ether, the ethereal extract combined with the lower layer and dried over calcined $MgSO_4$. The ether was distilled off, and the residue distilled in vacuo. The following acrylates were prepared:

3-Thietyl acrylate, bp 59.5° C (2 mm); d_4^{20} 1.1649, n_D^{20} 1.5115; yield 74%. Found, %: C 49.37, 49.60; H 5.37; 5.60; S 22.75, 22.33. M 148.0, 148.3; MR_D 37.06. Calculated for $C_6H_8O_2S$, %: C 50.00; H 5.55; S 22.22. M 144, MR_D 37.09.

3-Thietyl methacrylate, bp 70–73° (2 mm); d_4^{20} 1.1274, n_D^{20} 1.5050, yield 78.5%. Found, %: C 52.50, 53.00; H 6.22, 6.36; S 20.36, 20.43. M 160.0, 161.5; MR_D 41.54. Calculated for $C_7H_{10}O_2S$, %: C 53.16; S 20.25. M 158, MR_D 41.73.

3-Thietyl methacrylate was hydrolyzed by gradual addition to methanolic KOH, and heating the mixture on the water bath. The methanol was distilled off, the residue extracted with ether, and the ethereal extract dried over calcined $MgSO_4$. The ether was distilled off and the residue distilled in vacuo, giving the product, bp 75–76° C (6 mm), n_D^{20} 1.5412 (literature [5] values, bp 51–52° C (0.9 mm), n_D^{25} 1.5408).

The 3-hydroxythietane obtained was oxidized with hydrogen peroxide. This was effected by dropwise addition to a 30% solution of hydrogen peroxide warmed to 40° C. The excess peroxide was decomposed catalytically (Pt), and the solution evaporated until crystals separated. The crystals were twice recrystallized from alcohol, when they melted at 99–100° C (lit. [5], mp 101–102° C). A mixed mp with pure 3-hydroxythietane 1,1-dioxide gave no depression.

3-Thietyl acrylate was hydrolyzed similarly. In this case, in addition to 3-hydroxythietane 1,1-dioxide, acrylic acid polymer was also obtained.

Table 1

Constants and Analyses of the Esters Prepared

Compound	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	Molecular formula	Found					Calculated					Yield, based on reacted acrylate, %
					C, %	H, %	S, %	M	MR_D	C, %	H, %	S, %	M	MR_D	
Ia	124 (3)	1.5230	1.1428	$C_{10}H_{14}O_2S$	61.00 60.63	7.00 7.12	15.70 15.75	191 200	52.93	60.60	7.07	16.16	198	53.49	53.5
Ib	117—120 (5)	1.5157	1.1173	$C_{11}H_{16}O_2S$	61.88 61.94	7.38 7.59	14.98 15.06	212 207	57.28	62.26	7.55	15.09	212	58.14	42.5
Ic	132—133 (3)	1.5190	1.1136	$C_{11}H_{16}O_2S$	61.92 62.58	7.45 7.46	14.96 15.13	208 208	57.78	62.26	7.55	15.09	212	58.14	64.5
Id	127—129 (5)	1.5075	1.0800	$C_{12}H_{18}O_2S$	63.65 63.64	8.01 7.97	14.37 14.27	223 223	62.33	63.71	7.96	14.11	226	62.79	73.5
IIIa	123—125 (2)*	—	—	$C_{11}H_{14}O_2S$	62.55 63.01	6.42 6.70	15.40 15.20	207 213	—	62.86	6.67	15.24	210	—	88.0
IIIb	126—126,5 (2)	1.5242	1.1457	$C_{12}H_{16}O_2S$	64.57 64.27	7.13 7.15	14.07 15.13	224 222	59.84	64.29	7.14	14.29	224	60.61	88.0

*Mp 45 °C (from pentane)

Table 2

Constants and Analyses of the Isothiocyanates

Compound	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Molecular formula	Found N, %	Found M	Calculated N, %	Calculated M
IIa	96—98 (3)	1.5605	1.1413	48.15	47.59	C_8H_9NOS	8.21 8.27	165 167	8.38	167
IIb	93—96 (6)	1.5480	1.1074	51.90	52.24	$C_9H_{11}NOS$	7.75 7.70	180.5 178	7.73	181
IIc	95—97 (2)	1.5520	1.1073	52.23	52.24	$C_9H_{11}NOS$	7.60 7.65	180 178	7.73	181
IId	84—85 (2)	1.5412	1.0788	56.88	56.89	$C_{10}H_{13}NOS$	7.08 7.11	196 194	7.18	195
IIe	119—121 (1)	1.5770	1.2801	52.00	52.42	C_8H_8ClNOS	7.00 6.98	198 199	6.95	201.5
IIf	111—112 (1)	1.5640	1.2327	56.80	57.07	$C_9H_{10}ClNOS$	6.21 6.39	212 214	6.49	215.5
IVa	88—91 (2)	1.5680	1.1739	49.90	50.18	C_9H_9NOS	7.65 7.78	178 180	7.82	179
IVb	81 (1)	1.5570	1.1424	54.40	54.83	$C_{10}H_{11}NOS$	7.11 7.17	192 191	7.25	193

Table 3

Melting Points and Analyses of the Thioureas

Compound	Mp, °C (from alcohol)	Molecular formula	Found C, %	Found H, %	Found S, %	Found M	Calculated C, %	Calculated H, %	Calculated S, %	Calculated M
Va	138	$C_{14}H_{16}N_2OS$	64.51 64.21	6.14 6.00	12.29 12.02	259 260	64.60	6.15	12.31	260
Vb	66	$C_{16}H_{20}N_2OS$	66.57 66.32	6.81 7.08	10.87 10.89	292 290	66.70	6.94	11.12	288
Vc	132	$C_{15}H_{18}N_2OS$	66.00 65.97	6.78 6.80	11.92 11.69	274 273	65.70	6.56	11.68	274
Vd	67	$C_{17}H_{22}N_2OS$	67.58 67.50	7.23 7.15	10.64 10.12	304 301	67.50	7.29	10.60	302
Ve	137	$C_{14}H_{15}ClN_2OS$	56.71 56.67	5.16 5.25	10.82 10.95	293.5 292	57.05	5.09	10.87	294.5
Vf	106	$C_{16}H_{19}ClN_2OS$	59.32 59.34	5.92 5.92	9.88 10.00	316.4 318	59.60	5.89	9.93	322.5
VIa	126	$C_{15}H_{16}N_2OS$	66.17 65.92	5.78 5.88	11.48 11.60	269 271	66.20	5.88	11.78	172
VIb	128	$C_{17}H_{20}N_2OS$	68.06 68.22	6.47 6.61	10.61 10.20	304 301	68.00	6.66	10.67	300

Diene synthesis with 3-thietyl acrylates. Equimolecular proportions of the reactants in benzene (50%) were heated at 150° C in sealed ampuls for 5–10 hr. Benzene and unreacted diene were distilled off on the water bath, and the residue distilled in vacuo. The reaction of 3-thietyl acrylate with cyclopentadiene was effected under milder conditions. Even at room temperature, on keeping the ampul for 5 days, the yield of adduct amounted to 68.5% based on reacted material. This reaction also proceeded without pressure, by heating the reactants in benzene solution in a flask under reflux on the water bath for 9–10 hr. The yield in this case amounted to 88%.

The constants and analyses of the adducts are given in Table 1.

The diene synthesis with acryloyl and methacryloyl isothiocyanates. The dienes (butadiene, isoprene, chloroprene) and the dienophiles (acryloyl and methacryloyl isothiocyanates, obtained from the corresponding acid chlorides and a suspension of potassium or lead thiocyanate in benzene, dioxane, or acetone, by previously described methods [6,7]) were heated in 1 : 1 molar proportions in benzene solution (50%), in presence of a catalytic amount of hydroquinone in ampuls at 90–95° C for 2–10 hr. In the case of cyclopentadiene, the reaction was carried out at room temperature for 12 hr. Fractionation gave 60–70% of the corresponding isothiocyanates (Table 2).

Preparation of thioureas. To a solution of 0.02 mole of the isothiocyanate in 50 ml of ether was added dropwise with stirring during 15 min a solution of 0.02 mole of the arylamine in 50 ml of ether at 20–25° C. After 15 min, colorless crystals of the thiourea had separated from the ethereal solution. Yield 95–98%. Melting points and analyses are given in Table 3.

The authors thank M. E. Sergeeva and M. I. Mironova for the IR spectra and the elemental analyses.

REFERENCES

1. P. Batsulik, The Chemistry of Monomers (Russian translation), IL, Moscow, 1, 454, 1960.

2. E. P. Adams, K. N. Ayad, F. P. Doyle, D. O. Holland, W. H. Hunter, J. H. Nayler, and A. Queen, J. Chem. Soc., 2665, 1960.

3. F. E. Rogers, J. Polym. Sci., A3, 2701, 1965.

4. B. A. Arbuzov and I. N. Zobova, DAN, 167, 815, 1966.

5. D. C. Dittmer and M. E. Chrisfy, J. Org. Chem., 26, 1324, 1961.

6. V. V. Alderman and D. D. Coffman, U. S. patent no. 2327985, 1943; C. A., 38, 818, 1944.

7. Farbenfabriken Bager Akt.-Ges., British patent no. 800807, 1958, C. A., 53, 5134, 1959.

5 April 1967

State Associated Scientific-Research Institute for Chloroorganic Compounds and Acrylates, Dzerzhinsk