Preparation and Thermal Decomposition of Selected Pyrazolines

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Diazomethane has been added to a group of α, β-unsaturated esters and amides to form substituted pyrazolines and dipyrazolines. Several of these compounds have been decomposed thermally, and their alicyclic and olefinic decomposition products have been identified. For the identification of the olefin, a mixture of the cyclopropane and the olefin was treated with diazomethane, only the olefin reacted, and the mixture of the cyclopropane and the resulting pyrazoline could be separated by fractional distillation.

THE general procedure for the addition of diazomethane to the unsaturated compound was to dissolve the alkene in ether or dimethylformamide, cool the solution to 0° C. in an ice bath, and then distill an excess of an ethereal solution of diazomethane directly into the solution of the alkene. The diazomethane was prepared as needed using the procedure reported by Arndt (*1*). The reaction mixture was then placed in a refrigerator for periods varying from a few hours to several days. Excess ether and diazomethane were removed by distillation from a water bath held at 40° to 50° C. The last trace of ether was removed by means of a water aspirator. When dimethylformamide was used, the excess diazomethane and ether were removed at 40° to 60°, and then the dimethylformamide was removed at 72° to 74° under reduced pressure. The excess diazomethane was always absorbed in an ether solution of an α, β-unsaturated ester or of benzoic acid. If a solid separated from the reaction mixture while standing in the refrigerator, it was filtered before removing the excess ether and diazomethane. The physical constants of the pyrazolines are given in Table I.

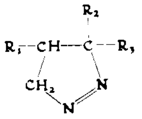
Seven substituted pyrazolines were decomposed by heating gradually at temperatures ranging from 80° to 170° C. for 2 to 4 hours. The substituted cyclopropane was identified as such, or as its hydrolysis product. The olefin was identified either as the dibromide or by adding diazomethane to it and identifying the pyrazoline so formed. Pertinent data are given in Table II.

Ethylene bis-(3-methyl-1-pyrazoline-3-carboxylate) when heated to 80° to 164° C. for 4 hours gave ethylene bis-(1-methylcyclopropane-1-carboxylate) and the mixed ethylene ester of 1-methylcyclopropane-1-carboxylic acid and tiglic acid, identified as the dibromide.

The physical constants of other new compounds are given in Table III.

Satisfactory analytical data for the compounds listed in Tables I and III have been obtained.

Table I. Substituted Pyrazolines

I


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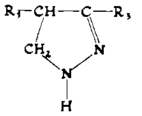

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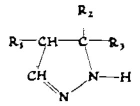

		Pyrazoline						
Alkene	Type	R_1	R_2	R_3	M.p., ° C.	B.p., ° C.	Mm.	n_D^{25}
$CH_2=C(CH_3)COOCH(CH_3)_2$	I	H	CH_3	$COOCH(CH_3)_2$	...	73–74	2	1.4422
$CH_2=C(CH_3)COOCH=CH_2$	I	H	CH_3	$COOCH=CH_2$	...	58–59	1	1.4660
$CH_2=C(CH_3)COOCH_2CH=CH_2$	I	H	CH_3	$COOCH_2CH=CH_2$	...	77–79	1.3	1.4645
$CH_3CH=C(CH_3)COOCH_3$	I	CH_3	CH_3	$COOCH_3$	...	45	0.07	1.4527
$CH_3CH=C(CH_3)COOCH=CH_2$	I	CH_3	CH_3	$COOCH=CH_2$	...	63–64	0.7	1.4640
$CH_3CH=C(CH_3)COOCH_2CH=CH_2$	I	CH_3	CH_3	$COOCH_2CH=CH_2$	...	84.5	0.10	1.4728
$CH_3CH=CHCOOCH=CH_2$	III	CH_3		$COOCH=CH_2$	58–59	107–108.5[a]	0.8	...
$CH_2=C(CH_2COOCH_3)COOCH_3$	I	H	CH_2COOCH_3	$COOCH_3$	...	...	...	1.4622
$C_2H_5OCH=C(COOC_2H_5)_2$	I	C_2H_5O	$COOC_2H_5$	$COOC_2H_5$	30–31	...	...	...
$C_2H_5OCH=C(COOC_2H_5)_2$	II	C_2H_5O	$COOC_2H_5$	$COOC_2H_5$	51.5–52.5	...	...	...
$C_6H_5CH=C(CH_2CH=CH_2)COOCH_3$	II	C_6H_5	$CH_2CH=CH_2$	$COOCH_3$	63.5–64	116	0.25	...
$C_6H_5CH=C(CH_2CH=CH_2)COOH$	II	C_6H_5	$CH_2CH=CH_2$	COOH	136–138	...	...	...
$CH_3CH=C(CH_3)CONH_2$	I	CH_3	CH_3	$CONH_2$	100–102	...	...	...
$[CH_2=C(CH_3)CONH]_2CH_2$	I	H	CH_3	$CONHCH_2NHCO$	156.5–158.5[a]	...	...	...
$[CH_2=C(CH_3)CONHCH_2]_2$	I	H	CH_3	$CONHCH_2CH_2NHCO$	149–150	...	...	...
$[CH_2=C(CH_3)COOCH_2]_2$	I	H	CH_3	$COOCH_2CH_2OCO$	...	...	...	1.4734

[a] Decomposed.

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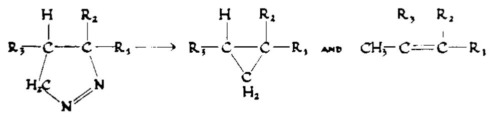
Table II. Thermal Decomposition of Selected Pyrazolines



R	R	R	Temp., ° C.	Time, hours	Identification of Cyclopropane	Identification of Olefin
$COOCH_3$	CH_3	H	90–120	2	As acid	Dibromide and CH_2N_2 adduct
$COOCH=CH_3$	CH_3	H	83–140	4	As ester	CH_2N_2 adduct
$COOCH_2CH=CH_2$	CH_3	H	118–170	3:5	As ester	CH_2N_2 adduct
$CONH_2$	CH_3	H	90–152	3	As amide	
CN	CH_3	H	100–140	3.5	As nitrile	
$COOC_2H_5$	$COOC_2H_5$	OC_2H_5	80–160	4	As ester	

Table III. Miscellaneous New Compounds

Compound	M.P., ° C.	B.P., ° C. (mm.)	n_D^{25}
α-Allylcinnamic acid	94–95		
Methyl α-allylcinnamate		80.5–81.5(0.15)	1.5504
N,N'-Ethylene bis-α-methacrylamide	170–171		
N,N'-Ethylene bis-α-methacrylamide tetrabromide	150–151		
2-Methacrylamidoethyl methacrylate		111–112(0.2)	1.4843
Dimethyl tetramethylfulgenate	76–77		
Vinyl 1-methylcyclopropane-1-carboxylate		132–133(760)	1.4381
Allyl 1-methylcyclopropane-1-carboxylate		147–149(760)	1.4368
Ethylene bis-(1-methylcyclopropane-1-carboxylate)		64–64(0.02)	1.4539
Ethylene (1-methylcyclopropane-1-carboxylate)-(2,3-Dibromo-2-methylbutanoate	41–43		

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LITERATURE CITED

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Aryl Glycidyl Ethers

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Three new aryl glycidyl ethers, the 2,4,6-trichlorophenyl, o-isopropyl, and p-isopropyl glycidyl ethers, have been synthesized. Physical properties, including infrared and nuclear magnetic resonance spectrophotometric data, have been determined on these and related aryl glycidyl ethers.

A SERIES of aryl glycidyl ethers was prepared by reaction of the appropriate phenol with potassium hydroxide an excess of epichlorohydrin without isolation of the intermediate chlorohydrin (*5*). Fractional distillation, recrystallization, and sublimation were used to obtain high purity monomers from the crude reaction products. The 2,4,6-trichloro, *o*-isopropyl, and *p*-isopropyl derivatives are new compounds with pertinent physical properties given in Table I. The *p*-octyl and the *p*-phenyl derivatives have been mentioned in the patent literature previously (*1, 3, 4*) but have not been adequately characterized.

β-Naphthyl glycidyl ether had been characterized at an early date (*6*), but the authors have been unable to reproduce the melting point of 81° C. reported in Beilstein (*2*) and cited subsequently in the literature (*10*). In this laboratory, the epoxide, prepared and purified by the literature method, melted at 64–65° C.; exhaustive purification did not change it.

Infrared spectral data, obtained on neat samples of the liquid derivatives and on Nujol mulls of the solid ones by use of a Beckman IR-5 spectrophotometer, are given in Table II. The position of the characteristic 8-, and 11-, and 12-μ bands is given, except that in the case of the *o*-tolyl, *m*-tolyl, *o*-isopropyl, *p*-phenylphenyl, *o*-chlorophenyl, and 2,4,6-trichlorophenyl derivatives, assignment of a definite wavelength in the 12-μ region is precluded by the presence of the characteristic aromatic out-of-plane C—H deformation bands in addition to the expected epoxide band. The remainder of the spectra (2–15 μ) was consistent with the postulated structures (*8*).