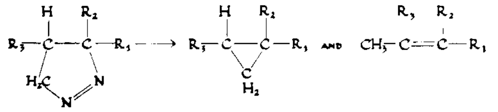
Table II. Thermal Decomposition of Selected Pyrazolines



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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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*).

Table I. Physical Properties of New Aryl Glycidyl Ethers

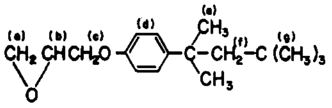
Glycidyl Ether	Boiling Point, °C./mm.	Melting Point,[a] °C.	Refractive Index (n_D^{25})		Analysis[b] % C	% H	% Cl
2,4,6-Trichlorophenyl	...	78–78.5	...	Found	42.87	2.80	41.95
				Calcd.	42.63	2.78	41.96
o-Isopropylphenyl	93/0.3	...	1.5149	Found	75.01	8.38	...
				Calcd.	74.96	8.39	...
p-Isopropylphenyl	93/0.2	...	1.5143	Found	74.80	8.39	...
				Calcd.	74.96	8.39	...
p-Octyl phenyl[c]	135/0.2	...	1.5102	Found	77.68	10.03	...
				Calcd.	77.81	9.99	...
p-Phenylphenyl	...	91–93	...	Found	79.37	6.12	...
				Calcd.	79.62	6.24	...
β-Naphthyl	180/0.2	64–66	...	Found	78.16	5.89	...
				Calcd.	77.98	6.04	...

[a] Melting points are uncorrected. [b] Galbraith Laboratories, Inc., Knoxville, Tenn. [c] 1,1,3,3-Tetramethylbutyl phenyl.

Table II. Spectral Data on Substituted Phenyl Glycidyl Ethers

Glycidyl Ether	IR Bands Characteristic of Glycidyl Ether Group, μ			NMR Chemical Shifts, τ[a]							Ref.
				a	b	c	d	e	f	g	
Phenyl	8.05	10.90	11.86	7.42	6.88	6.11	2.7–3.3	...	...	...	(*11*)
o-Tolyl	8.08	10.93	[b]	7.35	6.82	6.05	2.8–3.4	7.79	...	...	(*7*)
m-Tolyl	7.91	10.95	[b]	7.44	6.86	6.10	2.8–3.5	7.74	...	...	(*7*)
p-Tolyl	8.10	10.92	11.88	7.36	6.83	6.10	2.8–3.4	7.75	...	...	(*7*)
o-Isopropylphenyl	8.03	10.91	[b]	7.36	6.80	6.03	2.7–3.4	7.75	8.80	...	
p-Isopropylphenyl	8.05	10.95	[b]	7.41	6.87	6.10	2.8–3.3	7.25	8.82	...	
p-tert-Butyl phenyl	8.06	10.95	11.85	7.38	6.81	6.02	3.03	8.66	...	...	(*11*)
p-Octyl phenyl	8.05	10.92	11.90	7.39	6.85	6.05	2.7–3.4	8.68	8.30	9.28	
p-Phenylphenyl	8.01	10.92	[b]	7.25	6.68	5.93	2.3–3.1	...	...	...	
α-Naphthyl	8.06	10.92	11.89	7.42	6.82	6.06	1.6–3.5	...	...	...	(*10*)
β-Naphthyl	7.98	10.87	11.89	7.40	6.84	6.05	2.3–3.1	...	...	...	
o-Chlorophenyl	8.05	10.94	[b]	7.34	6.79	5.95	2.7–3.4	...	...	...	(*9*)
p-Chlorophenyl	8.10	10.95	11.85	7.39	6.84	6.08	2.8–3.4	...	...	...	(*9*)
2,4,6-Trichlorophenyl	8.05	10.98	[b]	7.35	6.77	5.93	2.72	...	...	...	

[a] Data obtained on Varian A60 using CCl_4 solvent. Hydrogens lettered in order of their distance from the primary carbon of oxirane—e.g.



[b] Band or bands present in this region, but assignment not made because of complexity of spectrum.

Nuclear magnetic resonance spectra of the known aryl glycidyl ethers—the phenyl, α-naphthyl, *p-tert*-butylphenyl, *o*-tolyl, *m*-tolyl, *o*-chlorophenyl, and *p*-chlorophenyl derivatives—were determined in CCl_4 solution with a Varian A60. Interpretation of the spectra indicated that the expected chemical shifts for the hydrogen atoms of the glycidyl group are 7.33–7.43 τ for the α-positions, 6.76–6.88 τ for the β-positions, and 5.98–6.11 τ for the γ-positions. The individual shifts for the two α-hydrogens were not determined, but the multiplets due to the α- and β-hydrogens were topologically quite similar for all of the compounds studied. As expected, the multiplets due to the γ-hydrogens reflected some minor changes in coupling constants with changes in the position and nature of the substituents on the benzene ring. The corresponding chemical shifts for the new compounds fall in the same ranges.

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