

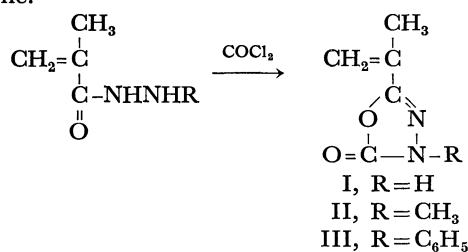
Syntheses and Reactions of Functional Polymers. LVII. Synthesis and Polymerization of Isopropenyl-1,3,4-oxadiazolin-5-ones

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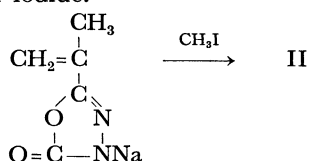
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It has been reported¹⁾ that 2-alkyl-1,3,4-oxadiazolin-5-ones are obtained by the reaction of hydrazides with phosgene, but the synthesis of 2-isopropenyl-1,3,4-oxadiazolin-5-ones is not known. We found that 2-isopropenyl-1,3,4-oxadiazolin-5-ones I-III were obtained easily by the reaction of corresponding hydrazides with phosgene.

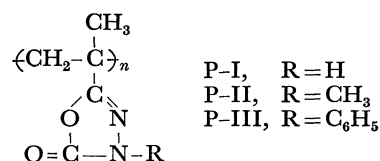


II was also obtained by the reaction of sodium salt of I with methyl iodide.



The structures of I-III were confirmed by IR spectrum and elementary analysis. The results are given in Table 1. IR spectra indicate three characteristic absorption bands.

Radical polymerization of I-III was carried out in bulk to give new type polymers containing oxadiazolone group in the side chain.



The results are shown in Table 2. The absorption attributable to double bond (C=C) in the polymers disappeared, and the absorption of C=N shifted to a higher wave number as compared with monomer due to the absence of conjugation with double bond (C=C). The polymers obtained were soluble in dipolar aprotic solvents such as dimethylformamide (DMF), dimethyl sulfoxide and methylpyrrolidone, but insoluble in common solvents such as water, alcohol and benzene.

TABLE 1. SYNTHESIS OF 2-ISOPROPENYL-1,3,4-OXADIAZOLIN-5-ONES

Compounds	Yield (%)	Melting point °C	C=C	IR (cm ⁻¹)		Elementary analysis (%)			
				C=N	C=O				
I	50	83—84	1640	1570	1770	Calcd	C	47.62,	H 4.80, N 22.22
						Found	C	47.27,	H 4.74, N 22.40
II	50	49—50	1637	1565	1775	Calcd	C	51.42,	H 5.75, N 19.99
						Found	C	50.90,	H 5.80, N 19.96
III	100	103—104	1635	1565	1765	Calcd	C	65.33,	H 4.98, N 13.86
						Found	C	65.54,	H 4.92, N 13.87

TABLE 2. POLYMERIZATION OF 2-ISOPROPENYL-1,3,4-OXADIAZOLIN-5-ONES

Compounds	Time (hr)	Temp. (°C)	Yield (%)	[η] ^{a)}	IR (cm ⁻¹)		Form of polymers
					C=N	C=O	
I	4	100	64.3	0.34	1600	1765	brown powder
II	4	100	47.0	0.22	1605	1780	white powder
III	3	110	54.3	0.20	1620	1785	white powder

Catalyst: azobisisobutyronitrile (AIBN) 3 mol% for monomers.

a) Measured at 30°C in DMF.

1) W. R. Sherman, *J. Org. Chem.*, **26**, 88 (1961).