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Copolymerization of Cyclopentadiene and N-Phenylmaleimide*

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SUMMARY

The addition of cyclopentadiene containing a free radical catalyst having a half-life of less than two hrs at reaction temperature, to a solution of N-phenylmaleimide in chlorobenzene at 85°C, or the simultaneous addition of both solutions separately to a reaction tube preheated to 80-195°C, yields a saturated 1:2 cyclopentadiene-N-phenylmaleimide copolymer, identified by elemental analysis and ^{1}H-NMR spectroscopy, analogous to the formation of a saturated 1:2 copolymer in the reaction of cyclopentadiene with maleic anhydride under similar conditions.

INTRODUCTION

The uncatalyzed reactions of maleic anhydride (MAH) with cyclopentadiene (CPD) and with furan (F) yield the equimolar cyclic Diels-Alder adducts. However, in the presence of a free radical catalyst which has a short half-life at reaction temperature, diene-dienophile copolymerizations occur to yield a saturated 1:2 CPD-MAH copolymer (GAYLORD et al. 1976a,b) and an unsaturated 1:1 F-MAH copolymer (GAYLORD et al. 1972,1976b).

The uncatalyzed reaction of CPD with N-phenylmaleimide (NØMI) yields an equimolar cyclic Diels-Alder adduct. The results of an investigation of the radical catalyzed copolymerization of CPD and NØMI are reported herein.

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EXPERIMENTAL

Copolymerization reactions were carried out by the addition of a solution of the catalyst in CPD to a solution of NØMI in chlorobenzene (CB) or o-dichlorobenzene (DCB) or by the simultaneous addition of the separate solutions to a preheated reaction tube.

^{1}H-NMR spectra were obtained from $CDCl_3$ solutions of the CPD-NØMI copolymers with tetramethylsilane as internal standard, using a Varian 60 MHz NMR spectrometer.

RESULTS AND DISCUSSION

The addition of a solution of t-butyl peroxypivalate (tBPP) in CPD to a preheated solution of NØMI in CB at 85°C gave a chloroform-soluble, saturated 1:2 CPD-NØMI copolymer. The simultaneous addition of a solution of catalyst, i.e. tBPP, t-butyl peracetate (tBPA) or t-butyl hydroperoxide (tBHP-70), in CPD and a solution of NØMI in CB or DCB, to a reaction tube preheated to a temperature in the range of 80-195°C, where the selected catalyst had a half-life of less than 2 hrs, also resulted in the formation of a saturated 1:2 CPD-NØMI copolymer (Table I). The 1:2 structure of the copolymer was assigned on the basis of the elemental analysis and by calculating the ratio of aliphatic and aromatic hydrogens in the 60 MHz ^{1}H-NMR spectra.

TABLE I

COPOLYMERIZATION OF CPD AND NØMI

CPD mmoles	NØMI mmoles	Solvent	ml	Catalyst[a]	mmoles	Temp °C	Method[b]	Yield %
12.1	8.7	CB	4	tBPP	1.0	85	A	30.7[c]
10	10	CB	8	tBPP	1.0	90	B	19.9
12.1	8.7	CB	4	tBPA	0.7	155	B	50.3
10	10	DCB	9	tBHP-70	2.0	195	B	48.5[d]

[a] Catalysts: tBPP, 75% in mineral spirits; tBPA, 75% in benzene; tBHP-70, 70% tBHP and 30% di-t-butyl peroxide

[b] A = solution of catalyst in CPD added to preheated solution of NØMI; B = solution of catalyst in CPD and solvent solution of NØMI added simultaneously to pre-

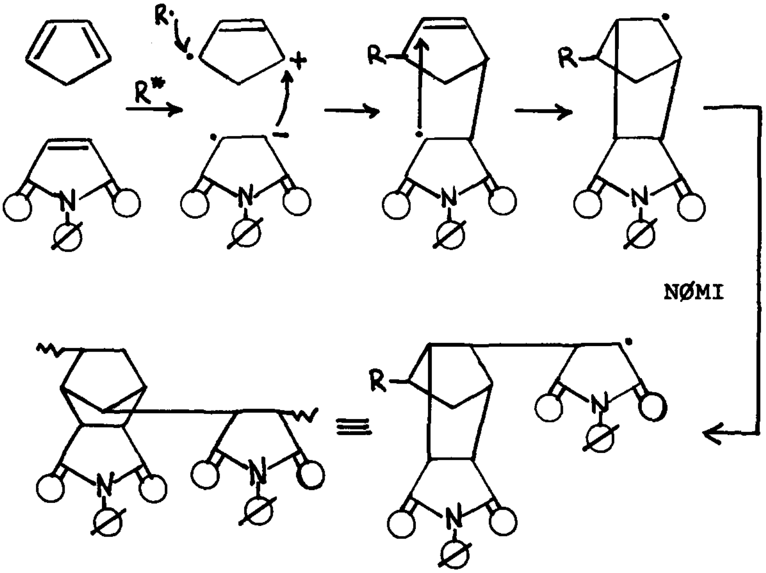
heated reaction tube

[c] Anal.: C,72.43; H,5.32; N,6.30. Calcd. for $C_{25}H_{20}O_4N_2$ (1:2 CPD-NØMI copolymer): C,72.82; H,4.85; N,6.80

[d] Anal.: C,71.55; H,4.98; N,6.17

The NMR spectra of the copolymers indicated the presence of catalyst moieties, i.e. t-butoxy groups. The molecular weight of the copolymer obtained at 90°C was 1374 (vapor pressure osmometry in $CHCl_3$) and that of the copolymer obtained at 195°C was 960.

Analogous to the mechanism proposed in the formation of the saturated 1:2 CPD-MAH copolymer under similar conditions (GAYLORD et al. 1976a), the saturated 1:2 CPD-NØMI copolymer presumably results from the cyclocopolymerization of the excited 1:1 CPD-NØMI donor-acceptor complex, followed by the addition of NØMI. The excitation of the CPD-NØMI complex, and possibly the NØMI, results from the rapid thermal decomposition of the catalyst (GAYLORD 1975).



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