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A Novel Diels-Alder Polymerization

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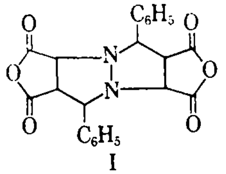
Synopsis

The double dienophiles *N,N'*-hexamethylene-bismaleimide and the *o*-, *m*-, and *p*-phenylene-bismaleimides were prepared and copolymerized with benzalazine by the Diels-Alder reaction. Melt polymerization afforded these polymers in high yields with inherent viscosities in the range 0.13 to 0.30 and softening temperatures from 238 to 325°. Solution polymerization gave no polymers and only starting materials were isolated. Benzalazine in this reaction behaves as a double diene and undergoes a 1,3-addition with the bismaleimides to form these polymers. That this 1,3-addition occurs in the polymer formation is further verified by the basic hydrolysis of the model compounds, 4,8-diphenyl-1,5-diazabicyclo[3.3.0]octane-2,3,6,7-tetracarboxylic acid bisanhydride (I) and 4,8-diphenyl-1,5-diazabicyclo[3.3.0]octane-2,3,6,7-bis-*n*-butylamide (II) and one of the polymers to give 4,8-diphenyl-1,5-diazabicyclo[3.3.0]octane-2,3,6,7-tetracarboxylic acid in each case.

I. INTRODUCTION

The 1,3-addition reaction of benzalazine with maleic anhydride to give 4,8-diphenyl-1,5-diazabicyclo[3.3.0] octane-2,3,6,7-tetracarboxylic acid bisanhydride (I) in low yield has been reported.[1,2] None of the normal Diels-Alder adduct resulting from 1,4-addition was formed.



I

In the reaction to form this adduct, benzalazine acts as a double diene and could therefore be expected to behave in a similar manner with a series of compounds such as the bismaleimides. It is evident however, that the particular example studied would not be suitable for polymerization reactions since the yields are far too low. It was necessary to find a system in which the adduct yield would be high enough to insure suitable yields of polymer and high molecular weight.

II. EXPERIMENTAL

Preparation of 4,8-Diphenyl-1,5-diazabicyclo[3.3.0]octane-2,3,6,7-bis-*n*-butylimide (II)

Benzalazine,[2] 1.86 g. (0.009 mole) and 2.998 g. (0.19 mole) of *n*-butylmaleimide[3] were mixed in the solid phase and heated to 200°C. The melt was maintained at this temperature for 10–15 min. and then allowed to cool to room temperature. The crude mixture was dissolved in acetone, the solution was decolorized with charcoal and then was cooled to 0°C. The precipitate was removed by filtration and air dried to afford 4.86 g. (100%) of II, m.p. 218–220°C.

ANAL. Calcd. for $C_{30}H_{34}N_4O_4$%; C, 70.000%; H, 6.60; N, 10.92%. Found: C, 70.21%; H, 6.36%; N, 11.00%.

When this reaction was attempted in a benzene solution, only starting materials were recovered.

Bismaleimides

All bismaleimides were prepared from the corresponding bismaleamic acids, as described,[4] except that the following modifications were adopted: A 50:1 molar ratio of acetic anhydride to bismaleamic acid and a heating time of 30 min. were employed to optimize the yield of bismaleimide. In this manner, hexamethylene- and the *o*-, *m*-, and *p*-phenylene-bismaleimides were obtained in 12, 7.5, 7.0, and 20% yields, respectively.

Polymerizations

All polymerizations were carried out by means of melt polymerization techniques. Solution polymerization did not afford polymers. The bismaleimide and benzalazine were intimately mixed, in the solid state, in 1:1 or 2:1 molar ratios, respectively. The mixtures were heated, under nitrogen, to 180–190°C., for 10–15 min., at which time the melt had either

TABLE I
Copolymerization of Benzalazine with Bismaleimides

Polymer	Mole ratio (maleimide to benzalazine)	Yield, %	M.p., °C.[a]	η_{inh}	Calculated[c]			Found		
					C, %	H, %	N, %	C, %	H, %	N, %
IVa	2:1	99	310 (s)[d] 315	0.195	69.79	4.08	11.63	69.15	4.34	11.60
	1:1	50		0.20						
IVb	2:1	89	450	0.13	69.79	4.08	11.63	69.02	4.47	11.77
IVc	2:1	85	325 (s)[d]	0.30	69.79	4.08	11.63	69.49	3.91	11.44
	1:1	59	360	0.30						
IVd	2:1	96	238 (s)[d] 315	0.24	68.93	5.58	11.49	68.32	5.51	11.57
	1:1	71		0.24						

[a] Capillary melting point.

[b] Inherent viscosities were obtained from a dimethylformamide solution of the polymer prepared by dissolving 0.25 g. of polymer in 100 ml. of dimethylformamide.

[c] For polymers IVa–IVc the analysis is based on 5 recurring units plus maleimido endgroups. For polymer IVd the analysis is based on 7 recurring units plus maleimido endgroups.

[d] Softening point.

resolidified or become a highly viscous mass. The crude polymer sample was washed thoroughly with chloroform and acetone to remove any unreacted monomer and then was dissolved in dimethylformamide. This solution was then stirred at room temperature with charcoal for 1 hr., the charcoal was removed by filtration, and the filtrate was poured into cold ether in order to precipitate the polymer. Two more reprecipitations afforded the polymers listed in Table I. The infrared spectra of the polymers and the infrared spectrum of the model compound (II) showed maxima (Nujol mull) at 1790, 1715, 1510, 1460, 1380, and 1187 cm.$^{-1}$. Polymerization with 1:1 molar amounts of monomer afforded lower conversion to polymer. Sublimation of benzalazine was evident in this reaction. When the reaction was run in solution, no polymer was formed.

Basic Hydrolysis

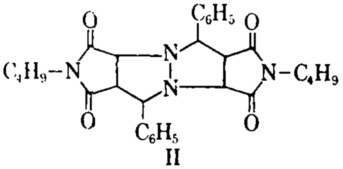
The basic hydrolysis of I, II, and IIIa were carried out under similar conditions. To the model compound or the polymer was added 25 ml. of 5–10% aqueous potassium hydroxide. The mixture was brought to the reflux temperature for 10 hr. and the resulting clear solution was cooled to room temperature, decolorized with charcoal, and then was acidified to precipitate the same tetra acid, 4,8-diphenyl-1,5-diazabicyclo-[3.3.0]-octane-2,3,6,7-tetracarboxylic acid (IV) in each case, m.p. 220–221°C. (reported,[2] 220–221°C.). The melting point of a mixture of these products was undepressed.

Molecular Weight of IIId

To a 0.1862 g. sample of IIId was added 20.80 g. of chloroform. The molecular weight of the solute was determined on a Mechrolab vapor pressure osmometer, Model 301A. The osmometer readings were interpolated by use of a standard calibration curve that gave the molecular weight of IIId of 3396.

III. RESULTS

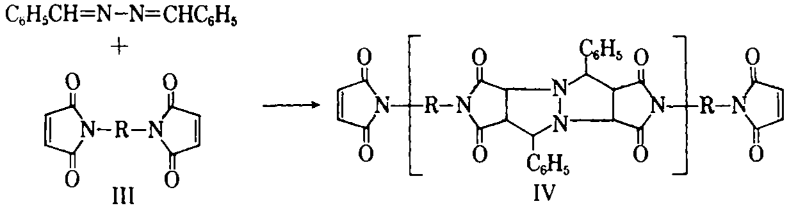
The reaction of benzalazine with *n*-butylmaleimide to give 4,8-diphenyl-1,5-diazabicyclo[3.3.0]octane-2,3,6,7-bis-*n*-butylimide (II)



II

in quantitative yield was undertaken to investigate the optimum reaction conditions for the polymerization of benzalazine with a series of bismaleimides and to obtain a model compound for such polymers.

When benzalazine was reacted with a series of bis maleimides (IIIa–IIId), polymers (IVa–IVd) with inherent viscosities in the range 0.13–0.30, are formed in high yield. The aromatic bismaleimide polymers all have softening and melting points over 300°C., while the *N*,*N*′-hexamethylene-bis maleimide polymer



III IV

[where R = (a) *o*-phenylene, (b) *m*-phenylene, (c) *p*-phenylene, and (d) *N*,*N*,-hexamethylene]

softens at 238°C. The higher softening temperatures of polymers obtained from aromatic bismaleimides is consistent with results obtained from a similar series of Diels-Alder polymers.[5-7]

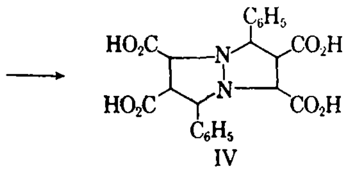
The molecular weight of the *N*,*N*′-hexamethylene-bismaleimide polymer (IVd) was shown to be 3400, as determined on a vapor pressure osmometer. This corresponds to seven recurring units, including endgroups.

IV. DISCUSSION

In the Diels-Alder polymerization of benzalazine with a series of bismaleimides, benzalazine acts as a double diene. It is interesting to note however, that this addition cannot really be considered a true Diels-Alder reaction. It is instead of a 1,3-addition, of which there are few reported examples.

That a 1,3-addition occurs in the formation of these polymers was further verified by the basic hydrolysis of the model compounds I and II and the polymer IIIa to yield the same tetra acid (IV) in each case.

I, II, or IIIa



IV

Comparison of the infrared spectra of these polymers with the spectrum of the model compound shows similar characteristic maxima.

It is surprising that even pentamers were obtained when a 2:1 monomer unbalance was employed and that the polymers were isolated in such high conversion. Since a high excess of bismaleimide is present during the reaction, the endgroups are evidently maleimido groups. Termination of the polymer by benzalazine endgroups would necessitate a 1,4-addition of benzalazine to an exposed maleimido function; a reaction which is not observed with the model compound. When exactly stoichiometric quantities of the monomers were present, higher molecular weights were not obtained.

This may be due to the fact that some benzalazine sublimed during the reaction. Lower conversions were obtained from the 1:1 reactions.

Prolonged heating of the crude polymer samples over 200°C. apparently brought about the reverse Diels-Alder reaction, as indicated by the lowering of the polymer solution viscosity. This decrease in molecular weight was also observed when the crude polymer samples were dissolved in dimethylformamide and the solution was heated at the reflux temperature for 48 hr.

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Résumé

Les diénophiles *N,N'*-hexaméthylène-bis-maléimide et les *o*-, *m*-, et *p*-phénylè-ne-bis-maléimides sont préparés et copolymérisés avec la benzalazine par la réaction de Diels-Alder. La polymérisation à liétat fondu fournit ces polymères à hauts rendements avec des viscosités inhérentes se rangeant de 0.13 à 0.30 et des températures de ramollissement de 238° à 325°. La polymérisation en solution ne donne pas de polymères et on n'isola que les matériaux de départ. La benzalazine dans cette réaction se comporte comme un double diène et subit l'addition 1,3 avec les bis-maléimides pour former ces polymères. Pour vérifier cette 1,3-addition dans la formation du polymère, on effectue une hydrolyse basique des composants, du même genre, le 4,8-diphényl-1,5-diazabicyclo[3,3,0]octane-2,3,6,7-tétracarboxylique acide-bis-anhydride (I) et le 4,8-diphényl-1,5-diazabicyclo[3.3.0]-octane-2,3,6,7-bis-n-butylimide (II) et chacun des polymères donnent dans chaque cas l'acide-4,8-diphényl-1,5-diazabicyclo[3.3.0]-octane-2,3,6,7-tétracarboxylique.

Zusammenfasusng

Die doppelt dienophilen Substanzen *N,N'*-Hexamethylen-bismaleinimid und *o*-, *m*- und *p*-Phenylen-bis-maleinimid wurden dargestellt und mit Benzalazin durch eine Diels-Alder-Reaktion copolymerisiert. Die Polymeren wurden durch Polymerisation in Schmelze in hoher Ausbeute mit Viskositätszahlen von 0,13 bis 0,30 und Erweichungstemperaturen von 238° bis 325° erhalten. Lösungspolymerisation lieferte keine Polymeren; es konnete nur das Ausgangsmaterial isoliert werden. Benzalazin verhält sich bei deiser Reaktion als Doppel-Dien und bildet mit den Bis-maleinimiden Polymere durch 1,3-Addition. Das Auftreten einer 1,3-Addition bei der Polymerbildung wird weiters durch basische Hydrolyse der Modellverbindungen, 4,8-Diphenyl-1,5-diazabicyclo[3,3,0]octan-2,3,6,7-tetracarbonsäure-bis-anhydrid (I) und 4,8-Diphenyl-1,5-diazabicyclo[3,3,0]octan-2,3,6,7-bis-n-butylimid (II) und eines der Polymeren unter Bildung von 4,8-Diphenyl-1,5-diazabicyclo[3,3,0]octan-2,3,6,7-tetracarbonsäure in jedem Falle bestätigt.

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