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Syntheses and Reactions of Functional Polymers. LIV. Syntheses and Polymerizations of *O*-Substituted-*N*-hydroxymaleimides

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The reverse Diels-Alder reaction of *N*-substituted maleimide adducts of furan is a useful method for the preparation of *N*-substituted maleimides which can not be obtained by the direct dehydration of maleamic acids owing to the formation of the corresponding isomaleimides. *O*-Benzyl, *O*-acetyl, *O*-benzoyl, *O*-benzenesulfonyl, and *O*-methyl-*N*-hydroxymaleimide adducts of furan decompose at 140—190°C to produce the corresponding maleimides. The homo- and co-polymerization with styrene of these maleimides were carried out and monomer reactivity ratios and *Q-e* values for these maleimides were determined. The copolymer obtained were converted to the copolymer of *N*-hydroxymaleimide and styrene.

We reported the preparation of polymers having the *N*-hydroxyimide structure in the chain and activation of carboxylic acid group by use of those polymers.[1,2] Syntheses of several *N*-substituted maleimides were investigated for the preparation of such polymers.[3] However, the dehydrocyclizations of *N*-substituted maleamic acids afforded only isomaleimides instead of maleimides. Several attepmpts to convert isomaleimides to maleimides were unsuccessful except for a special case.

In this paper, we report a new method to obtain *N*-substituted maleimides effectively *via* the Diels-Alder adducts. The homo- and co-polymerization with styrene of these maleimides were carried out and the polymers obtained were hydrolyzed to give the corresponding *N*-hydroxyimide structure.

1) M. Akiyama, M. Narita, and M. Okawara, *J. Polymer Sci., Part A-1*, **7**, 1299 (1969).

2) M. Akiyama, Y. Yanagisawa, and M. Okawara, *ibid., A-5*, **7**, 1905 (1969).

3) M. Narita, M. Akiyama, and M. Okawara, This Bulletin, **44**, 437 (1971).

Results and Discussion

Preparation of O-*Substituted*-N-*hydroxymaleimide Adducts of Furan.* Dehydration of *N*-substituted maleamic acids produces the corresponding maleimides or isoimides depending on the nature of the maleamic acids and the conditions for dehydration.[4,5] On the other hand, it is well known that dehydration of *N*-substituted saturated amic acids produce only the corresponding imides except for *N*-substituted camphoramic acids.[5] The reverse Diels-Alder reaction is known to be a useful method for the preparation of maleimides. Maleic anhydride adducts of anthracene and cyclopolyenes give imides by treatment with amines since the dehydration of the *N*-substituted saturated amic acids produce only the corresponding imides. When these imides are pyrolized at 200—500°C, maleimides are

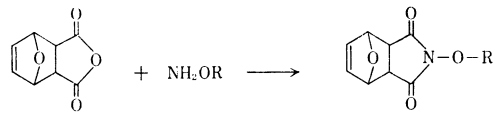
4) E. Hedaya, R. L. Hinman, and S. Theodoropulos, *J. Org. Chem.*, **31**, 1311, 1317 (1967).

5) W. R. Roderick and P. L. Bhatia, *ibid.*, **28**, 2018 (1963).

obtained.[6] Thus, the reverse Diels-Alder reaction is thought to be a very useful method for the preparation of *N*-substituted maleimides which can not be obtained by direct dehydration of maleamic acids owing to the formation of the corresponding isomaleimides.

The maleic anhydride adduct of furan, which is obtained easily in quantitative yield by the reaction of furan with maleic anhydride at room temperature, decomposes at lower temperature (*ca.* 125°C) than maleic anhydride adducts of anthracene and cyclopolyenes. We therefore prepared *N*-substituted maleimide adducts of furan by the reaction of the maleic anhydride adduct of furan with amines and decomposed them to synthesize *N*-substituted maleimides.

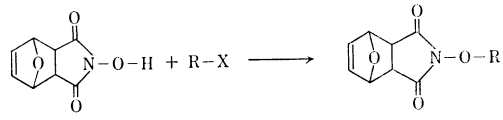
The maleic anhydride adduct of furan (3,6-endoxo-1,2,3,6-tetrahydrophthalic anhydride) reacted with *N*-benzyloxyamine produce *O*-benzyl-*N*-hydroxymaleimide adduct of furan (*O*-benzyl-*N*-hydroxy-3,6-endoxo-1,2,3,6-tetrahydrophthalimide) (I) in quantitative yield in benzene by heating. Similarly the *N*-hydroxymaleimide adduct of furan (II) was obtained by treatment of maleic anhydride adduct of furan with hydroxylamine in 64% yield in methanol as shown below.



R=$CH_2C_6H_5$, H I: R=$CH_2C_6H_5$
II: R=H

Scheme 1

The *N*-hydroxymaleimide adduct of furan (II) reacted with acetic anhydride, benzoyl chloride, benzenesulfonyl chloride and methyl iodide to produce the corresponding *O*-substituted-*N*-hydroxymaleimide adducts of furan (*O*-acetyl, *O*-benzoyl, *O*-benzenesulfonyl, and *O*-methyl-*N*-hydroxy-3,6-endoxo-1,2,3,6-tetrahydrophthalimide) as shown below.



III-VI

III: R=CH_3CO (X=$OCOCH_3$)
IV: R=C_6H_5CO (X=Cl)
V: R=$C_6H_5SO_2$ (X=Cl)
VI: R=CH_3 (X=I)

Scheme 2

The structures were confirmed by elemental analyses and infrared spectra. The results are summarized in Table 1 and Table 2. A characteristic feature of five membered ring imides is the presence of bands at *ca.* 1780 cm^{-1} (medium) and 1730 cm^{-1} (strong) in the infrared spectra. Infrared spectra of isoimides generally exhibit a strong absorption due to carbonyl group at 1780 cm^{-1} and a medium absorption due to imine linkage at 1670 cm^{-1}. All the compounds in Table 2 exhibit characteristic absorptions of imides.

We did not investigate the stereochemistry of the compounds. However it is well known that furan forms *exo* adducts exclusively with maleic anhydride[7] and maleimide.[8] From the results and the reaction condition, we presume that compounds (I—VI) are *exo* adducts.

Syntheses of O-*Substituted*-N-*hydroxymaleimides by Pyrolyses of Those Adducts of Furan.* We carried out the reverse Diels-Alder reaction of the *O*-substituted-*N*-hydroxymaleimide adducts of furan (preceding section). The compounds decompose at 140—190°C producing

Table 1. *N*-Substituted maleimide adducts of furan

Compd. Formula	Yield (%)	Mp (°C) (dec. temp.)	Anal. (Calcd) (%) C	H	N
I	95	115—116	66.88	4.58	5.16
$C_{15}H_{13}NO_4$		(~150)	(66.41)	(4.83)	(5.16)
II	64	187—188	53.39	3.75	7.96
$C_8H_7NO_4$		(~150)	(53.04)	(3.90)	(7.73)
III	97	137—138	54.20	4.02	6.34
$C_{10}H_9NO_5$		(~150)	(53.81)	(4.06)	(6.28)
IV	84	134.5—136	63.59	3.68	5.00
$C_{15}H_{11}NO_5$		(~150)	(63.16)	(3.89)	(4.91)
V	73	168—171	52.39	3.35	4.36
$C_{14}H_{11}NO_6S$[a]		(~150)	(52.33)	(3.45)	(4.36)
VI	40	139—140.5	55.85	4.63	7.22
$C_9H_9NO_4$		(~150)	(55.38)	(4.65)	(7.18)

a) S%, Found (Calcd): 9.94 (9.98).

Table 2. Infrared data of *N*-substituted maleimide adducts of furan

Compd.	Characteristic absorption (cm^{-1}) imide	R[assignment]
I	1784(m)[a] 1728(s)[a]	3025(w)[a] [-C_6H_5]; several absorptions below 900 [-$CH_2C_6H_5$]
II	1785(m) 1725(s)	3470(m) (sh)[b], 3300(m) [-OH]
III	1782(s) 1745(s)	1805(m) [-CO-CH_3]; 1376(m) [CH_3-CO-]
IV	1775(s) 1742(s)	1800(m) [-CO-C_6H_5]; 1600(w), 1450(w) [-C_6H_5]
V	1791(m) 1747(s)	1580(w), 1450(m) [-C_6H_5]; 1392 (s) [ν_{as} SO_2]; 1182(s) [ν_s SO_2]
IV	1778(m) 1725(s)	2950(w); 1372(m) [-CH_3]

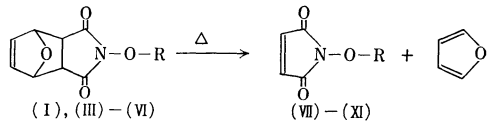
a) Absorption intensity: s=strong, m=medium, w=weak.
b) sh=shoulder.

6) E. J. Prill, U. S. 2524136; *Chem. Abstr.*, **45**, 1162 (1951).

7) H. Stockmann, *J. Org. Chem.*, **26**, 2025 (1961).

8) H. Kwart and I. Burchuk, *J. Amer. Chem. Soc.*, **74**, 3094 (1952).

the corresponding maleimides and furan except for the *N*-hydroxyimide (II) as shown below.



VII; R=$C_6H_5CH_2$, VIII; R=CH_3CO,
IX; R=C_6H_5CO, X; R=$C_6H_5SO_2$,
XI; R=CH_3

Scheme 3

The *N*-hydroxyimide (II) was decomposed at 190°C, but no *N*-hydroxymaleimide was obtained since it is probably unstable thermally. Confirmation of the structures of compounds (VII—XI) was achieved from elemental analyses, infrared and NMR spectra. Results are summarized in Tables 3, 4, and 5. The NMR spectra of compounds (VII—XI) were measured in deuteriochloroform solutions using tetramethylsilane as an internal reference. We stated that the NMR spectra of isomaleimides show two doublets due to unsymmetrical nature of olefinic hydrogen and maleimides have only one singlet due to the symmetrical nature of olefinic hydrogen[3]. The NMR data in Table 4 show only one singlet due to the symmetrical nature of olefinic hydrogen in every case and indicate the compounds to be maleimides. We described further that isomaleimides generally have two sharp bands in the infrared at *ca.* 1780 cm^{-1} (strong) and 1670 cm^{-1} (medium) which are associated with the anhydride-like carbonyl and imine bonds present in the isomaleimide ring and that maleimides have a characteristically broad carbonyl band in the infrared with maxima near 1720 cm^{-1}.[3] The infrared data in Table 5 show two bands at *ca.* 1780 cm^{-1} (medium) and 1740 cm^{-1} (strong) which are characteristic of five membered ring imides and indicate the compounds to be maleimides.

TABLE 3. *O*-SUBSTITUTED-*N*-HYDROXYMALEIMIDES

Compd. Formula	Yield (%)	Mp (°C) (bp)	Anal. (Calcd) (%) C	H	N
VII	93	89.5—91	65.08	4.09	6.85
$C_{11}H_9NO_3$			(65.02)	(4.46)	(6.89)
VIII	95	70.5—71.5	46.37	3.09	9.13
$C_6H_5NO_4$		(~140°C/ 25 mmHg)	(46.46)	(3.25)	(9.03)
IX	94	87—89	61.33	3.00	6.48
$C_{11}H_7NO_4$			(60.83)	(3.25)	(6.45)
X	90	108—109.5	47.35	2.71	5.46
$C_{10}H_7NO_5S$[a]			(47.43)	(2.79)	(5.53)
XI	80	109—111	47.50	3.75	11.23
$C_5H_5NO_3$		(~128°C/ 27 mmHg)	(47.25)	(3.97)	(11.02)

a) S%, Found (Calcd): 12.57 (12.66).

TABLE 4. DETAILS OF THE NMR SPECTRA

Compd.	Chemical shift (δ)	Multiplicity[a]	Number of protons	Assignment
VII[1]	5.06	S	2	methylenic H
	6.53	S	2	olefinic H
	7.25—7.55	M	5	aromatic H
VIII	2.32	S	3	CH_3CO-
	6.75	S	2	olefinic H
IX	6.82	S	2	olefinic H
	7.40—8.25	M	5	aromatic H
X	6.86	S	2	olefinic H
	7.60—8.25	M	5	aromatic H
XI	3.93	S	3	CH_3-O-
	6.62	S	2	olefinic H

a) S=singlet, M=multiplet.

TABLE 5. INFRARED DATA OF *O*-SUBSTITUTED-*N*-HYDROXYMALEIMIDES

Compd.	Characteristic absorption (cm^{-1}) imide	R[assignment]
VII	1780(w)[a] (sh)[b]	1500(w), 1455(w) [-C_6H_5];
	1725(s)[a]	1480(w) [-CH_2-]; several
	1710(s) (sh)	absorptions below 900
		[-CH_2-C_6H_5]
VIII	1780(m)[a]	1814(s) [-CO-CH_3];
	1741(s)	1380(m) [CH_3-CO-]
IX	1770(s)	1600(w), 1580(w), [-C_6H_5]
	1742(s)	
X	1780(m) (sh)	1580(w), 1450(m) [-C_6H_5];
	1742(s)	1390(s) [ν_{as} SO_2];
		1196(s) [ν_s SO_2]
XI	1775(m) (sh)	2970(w) [CH_3-];
	1740(s)	1386(m) [CH_3-]
	1720(s) (sh)	

a) Absorption intensity: s=strong, m=medium, w=weak.
b) sh=shoulder.

Polymerization of O-*Substituted*-N-*hydroxymaleimides.* It is known that the radical homopolymerization of 1,2-disubstituted ethylenes proceeds only with great difficulty. The polymerization of maleic anhydride and maleimide was reported recently.[9]

Homopolymerization of the maleimides obtained above was carried out in dioxane with azobisisobutyronitrile (AIBN) at 70°C. The results are summarized in Table 6. The inherent viscosities observed were low, but the infrared absorption band at 810—830 cm^{-1} which can be associated with out-of-plane deformations of hydrogen of the -CH=CH- link disappeared completely in the products. The copolymerization of those maleimides (M_2) with styrene (M_1) were conducted in dioxane by use of AIBN as an initiator at low temperature (35°C) to suppress the rapid polymerization. Typical results (VIII-styrene) are shown in Table 7.

9) R. M. Joshi, *Makromol. Chem.*, **53**, 33 (1962); P. O. Tawney, R. H. Snyder, R. P. Conger, K. A. Leibbrand, and C. H. Stiteler *J. Org. Chem.*, **26**, 15 (1961).

Table 6. Homopolymerization of maleimides[a)]

Compd. (g) Formula	Yield (g)	Mp (°C)	$\eta_{acetone}^{30°C}$ (0.5 g/dl)	Anal. (Calcd) (%) C	H	N
VII (2.03) $C_{11}H_9NO_3$	1.82	190—205	0.055	63.83 (65.02)	4.26 (4.46)	6.75 (6.89)
VIII (1.98) $C_6H_5NO_4$	1.25	229—241	0.015	45.73 (46.46)	3.48 (3.25)	8.18 (9.03)
IX (1.09) $C_{11}H_7NO_4$	0.89	231—239	0.020	59.68 (60.83)	3.13 (3.25)	6.14 (6.45)
X (1.27) $C_{10}H_7NO_5S$	0.74	189—193	0.029	(47.43)	(2.79)	(5.53)
XI (1.27) $C_5H_5NO_3$	0.65	253—266	0.023	45.38 (47.25)	4.35 (3.97)	9.91 (11.02)

a) Polymerization conditions; 70°C, 10 hr in 5 ml of dioxane, 0.082 g of AIBN as initiator, in sealed tube.

Table 7. Copolymerization of *N*-acetoxymaleimide (M_2) with styrene (M_1)[a)]

Initial mixture M_1 mol%	Initial mixture M_2 mol%	Polymerization time(min)	Conversion %	Analysis N, %	Polymer composition M_1 mol%	Polymer composition M_2 mol%
95	5	135	5.5	4.40	61.1	38.9
90	10	105	5.9	4.67	58.2	41.8
80	20	120	9.9	4.84	56.3	43.7
70	30	30	9.2	5.01	54.5	45.5
50	50	30	9.3	5.26	51.7	48.3
30	70	30	10.3	5.16	52.8	47.2
20	80	30	14.3	5.27	51.5	48.5
10	90	30	10.1	5.40	50.1	49.9
5	95	50	8.9	5.46	49.4	50.6

a) Polymerization conditions; 35°C in dioxane, monomer mixture 1.0 mol/l, AIBN initiator 0.025 mol/l.

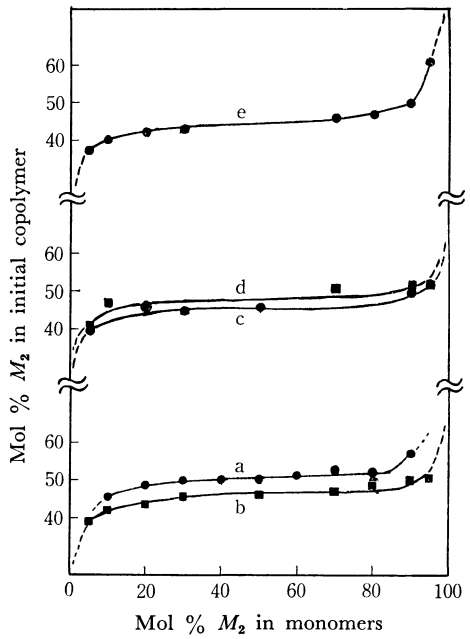


Fig. 1. Copolymerization diagram for *N*-substituted maleimides (M_2) and styrene (M_1).
a: VII, b: VIII, c: IX, d: X, e: XI

The polymerization curves were determined by inserting successive values of r_1 and r_2 in the following equation, until the best fit of the resulting curve with the experimental points was obtained.

$$\frac{m_1}{m_2} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1}$$

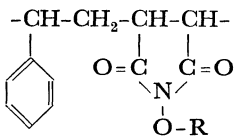
A marked tendency for alternation can be observed as shown in copolymerization diagram for *N*-substituted maleimides and styrene (Fig. I). The Q and e values for these maleimides were calculated by means of the equation of Alfrey-Price with the values of r_1 and r_2, and the results are shown in Table 8. The high Q value as well as a strong alternation tendency would be explained by the fomation of molecular complexes in the transition

Table 8. Monomer reactivity ratios and Q-e values of maleimides (M_2) [(M_1)=styrene]

M_2	r_1	r_2	Q_2	e_2
VII	0.02	0.03	5.65	1.93
VIII	0.02	0.01	4.85	2.12
IX	0.03	0.01	3.42	2.05
X	0.02	0.03	5.65	1.93
XI	0.02	0.02	5.32	2.00

state between styrene and maleimides as in the case of styrene and maleic anhydride. The formation of charge transfer complex was examined by measurement of UV spectrum in the N-actoexymaleimide-styrene system. However, neither the change of λ_{max} (290 mμ) of *N*-acetoxymaleimide nor an appearance of new absorption band due to the C-T complex formation was observed by the addition of styrene.

Conversion of Copolymers into N-*Hydroxymaleimide-Styrene Copolymer.* Treatment of the *N*-benzyloxyimide polymer (VII′) with hydrogen bromide in acetic acid,[3] gave debenzylated *N*-hydroxymaleimide type copolymer (XIII). The structure of polymer was confirmed by the agreement of infrared absorption peaks with those of the polymer obtained previously.[2] The *N*-acetoxyimide polymer (VIII′) was hydrolyzed into the hydroxymaleimide type copolymer (XIII) when the polymer in dioxane containing 6N hydrochloric acid was refluxed for ten hours. Treatment of the copolymer (VIII′), (IX′), and (X′) with water - triethylamine in dioxane gave also hydrolyzed polymer (XIII). However, the polymers obtained were combined with triethylamine tightly. Polymer (XIII) showed imide carbonyl absorption band at 1710 cm^{-1} in the infrared spectrum, while in the case of the polymer (XIII′) it shifted to 1710 and 1680 cm^{-1}. In order to confirm the interaction of triethylamine with the *N*-hydroxyimide group, the model reaction was carried out. Thus *N*-hydroxysuccinimide and triethylamine gave a 2:1 molecular compound, whose infrared specturm also showed two peaks at 1710 and 1680 cm^{-1}.



VII′: R=CH_2-C_6H_5
VIII′: R=$COCH_3$
IX′: R=COC_6H_5
X′: R=SO_2-C_6H_5
XIII: R=H

$$\text{VII}' \xrightarrow[CH_3COOH]{HBr} \text{XIII} \xleftarrow[\text{dioxane}]{6N\ HCl} \text{VIII}'$$

$$\text{VIII}', \text{IX}', \text{and X}' \xrightarrow[\text{dioxane}]{Et_3N\text{-}H_2O} \text{XIII}\cdot Et_3N\ (\text{XIII}')$$

Experimental

All melting and boiling points are uncorrected. Infrared spectra of the products were obtained as potassium bromide disks using a Hitachi Infrared Photometer Model EPI-S2. NMR spectra were obtained with a Japan Electron Optics C-100 spectrometer in deuteriochloroform solution with tetramethylsilane as an internal standard. Solvents used for reactions were purified by the usual method.

Preparation of N-*Benzyloxymaleimide Adduct of Furan (I).* Maleic anhydride adduct of furan (4.15 g) was dissolved in 100 m*l* of benzene and 3.08 g of *N*-benzyloxyamine was added. The mixture was refluxed for 3 hr and then concentrated to *ca.* 15 m*l* and cooled. The white crystals (6.33 g) were filtered off and washed with ethanol, yield 95%. They are recrystallized from ethanol, mp 115—116°C (dec. 150°C).

Preparation of N-*Hydroxymaleimide Adduct of Furan (II).* Maleic anhydride (300 g) was added to a solution of 210 g of furan in 400 m*l* of benzene and the mixture was kept overnight at room temperature with stirring. The mixture became a lump. The lump was added little by little by cooling with ice-cold water and stirring to a solution of 102 g of hydroxylamine in 1.5 *l* of methanol prepared by Lashua's procedure.[10] When heat evolution from the reaction mixture ceased, the mixture was kept for 7 hr at room temperature. Benzene and methanol were then distilled off and 700 m*l* of ethanol was added to the residue. The mixture was refluxed for 3 hr and cooled by ice-cold water. The white crystals were filtered off and washed with ethanol, yield 270 g, mp 187—188°C (dec.). After concentration of the mother liquor, an additional 78 g of the product was obtained to give a total yield of 64%.

Preparation of N-*Acetoxymaleimide Adduct of Furan (III).* *N*-Hydroxymaleimide adduct of furan (II) (7.0 g) was suspended in 20 m*l* of acetic anhydride and kept at 80—90°C for 3 hr when all the compounds dissolved in the solution gradually. After the reaction was over, it was cooled with ice-cold water and the product was filtered under suction and washed thoroughly with benzene, yield 5.0 g, mp 135—136°C (dec.). After concentration of the mother liquor, an additional 2.4 g of the product was obtained to give a total yield of 97%. It was recrystallized from benzene, mp 137—138°C (dec.).

Preparation of N-*Benzoyloxymaleimide Adduct of Furan (IV).* *N*-Hydroxymaleimide adduct of furan (II) (54.6 g) and 48 g of benzoyl chloride were dissolved in 200 m*l* of *N,N*-dimethylformamide. Pyridine (27 g) was added dropwise to this solution with stirring and by cooling with ice-cold water. The mixture was stirred for 7 hr at 0—20°C and then poured into 1 *l* of water. The precipitate was filtered off and washed with water. Recrystallization from benzene gave 68 g of the product, mp 134.5—136°C. After concentration of the mother liquor, an additional 4 g of the product was obtained to give a total yield of 84%.

Preparation of N-*Benzenesulfonyloxymaleimide Adduct of Furan (V).* *N*-Hydroxymaleimide adduct of furan (II) (36.4 g), 40 g of benzenesulfonyl chloride, and 18 g of pyridine were dissolved in 400 m*l* of benzene. The mixture was refluxed for 3 hr and then cooled. The crystals were filtered off and washed thoroughly with water. Recrystallization from acetone gave 29 g of the product, mp 171—173°C (dec.). After concentration of the mother liquor, an additional 17.5 g of the product was obtained to give a total yield of 73%.

Preparation of N-*Methoxymaleimide Adduct of Furan (VI).* *N*-Hydroxymaleimide adduct of furan (II) (18.2 g) and 56 g of methyl iodide were dissolved in 100 m*l* of *N,N*-dimethylformamide (free from water). Granulated barium oxide (45 g) was added to this solution and allowed to stand for 15 hr at room temperature. The precipitates of barium oxide and barium iodide were filtered off and the filtrate was concentrated under reduced pressure. The viscous residue was poured into 300 m*l* of water. The precipitate was filtered off and washed with water, yield 7.8 g, mp 138—140°C (dec.). It was recrystallized from ethanol, mp 139—140.5°C (dec.).

Synthesis of N-*Benzyloxymaleimide (VII).* The *N*-benzyloxyimide (I) (2.0 g) was heated in an oil bath at 170—180°C under a gentle stream of air. The solid slowly melted with vigorous furan evolution. After 1 hr, the yellowish liquid was cooled. Recrystallization from *n*-hexane gave 1.4 g (95% yield) of the product, mp 88—90°C. A second recrystallization from *n*-hexane gave light yellow crystals, mp 89.5—91°C (lit,[3] 89.5—91).

Synthesis of N-*Acetoxymaleimide (VIII).* The *N*-acetoxyimide (III) (36g) was pyrolized in an oil bath at 180—190°C under reduced pressure (25 mmHg). The solid slowly melted

10) S. C. Lashua, U. S. 3202689 (1965); *Chem. Abstr.*, **64**, 599d (1966).

with vigorus furan evolution and *N*-acetoxymaleimide was distilled at ~140°C (25 mmHg), yield 23.8 g (95 %), mp 68—71°C. Recrystallization of crude product from carbon tetrachloride furnished white crystals, mp 70.5—71.5°C.

Synthesis of N-*Benzoyloxymaleimide (IX).* The *N*-benzoyloxyimide (IV) (20 g) was dissolved in 70 m*l* of nitrobenzene and heated in an oil bath at 170—175°C for 1 hr under a gentle stream of air. Nitrobenzene was then distilled off under reduced pressure. The residue was recrystallized from carbon tetrachloride to give 14.3 g of the product, yield 95%, mp 85—88°C. A second recrystallization from *n*-hexane - carbon tetrachloride using charcoal gave white crystals, mp 87—89°C.

Synthesis of N-*Benzenesulfonyloxymaleimide (X).* The *N*-benzenesulfonyloxyimide (V) (13 g) was heated in an oil bath at 190—195°C under a gentle stream of air. The solid solwly melted with vigorous furan evolution. After 20—30 min, the liquid was cooled and combined with 50 m*l* of acetone and allowed to stand in a refrigerator overnight. Crystals (V) were filtered off and the filtrate was concentrated and the residue was recrystallized from carbon tetrachloride-chloroform to give 9 g of the product, yield 90%, mp 107—109°C. Further recrystallization from carbon tetrachloride-chloroform gave white crystals, mp 108—109.5°C.

Synthesis of N-*Methoxymaleimide (XI).* The *N*-methoxyimide (VI) (18 g) was pyrolyzed in an oil bath at 180—185°C under reduced pressure (27 mmHg). The solid slowly melted with vigorous furan evolution and *N*-methoxymaleimide was distilled at 128°C/27 mmHg, yield 80%, mp 102—108°C. Recrystallization from carbon tetrachloride - *n*-hexane using charcoal gave light yellow crystals, mp 108—110°C.

Homopolymerization of O-*Substituted*-N-*hydroxymaleimides.* Homopolymerization of maleimides (VII, VIII, IX, X, and XI) was performed in 5 m*l* of dioxane with 0.082 g of AIBN as an initiator at 70°C. The amounts of monomers used are described in Table 6. The polymerization tubes were sealed off in a vacuum. After 10 hr, the polymer solution was poured into ether and the polymer obtained was purified by dissolving twice in dioxane and precipitating in ether.

Copolymerization of O-*Substituted*-N-*hydroxymaleimides.* Copolymerization of maleimides (VII, VIII, IX, X, and XI) with styrene was perfomred in dioxane with AIBN as an initiator. The total amount of monomers was 1.0 mol/*l* and the amount of initiator was 0.025 mol/*l*. The polymerization tubes were sealed off in a vacuum and heated in a thermostated bath at 35°C, till a yield of approximately 10% of polymer was obtained. The polymer solution was then poured into ether, and the polymer was purified by reprecipitation from dioxane to ether. The polymer composition was determined by nitrogen analysis. The measurement of UV spectrum of *N*-acetoxymaleimide (VIII) was carried out for the ethylene chloride solution (2.5—10^{-3} mol/*l*) in the absence or presence of a large excess of styrene with a Hitachi Spectrophotometer EPS-3T.

Conversion of Copolymers into N-*Hydroxymaleimide-Styrene Copolymer.* Treatment of the *N*-benzyloxymaleimide type copolymer (VII′) with hydrogen bromide in acetic acid was performed as mentioned previously.[3] The *N*-acetoxyimide polymer (VIII′) (15.0 g) was dissolved in 250 m*l* of dioxane containing 50 m*l* of 6N hydrochloric acid and refluxed for 10 hr. The polymer solution was poured into 1 *l* of water and the polymer obtained (XIII) was purified by dissolving twice in dioxane and precipitating in ether. Yield 11.7 g.

The *N*-acetoxymaleimide polymer (VIII′) (0.3 g) was hydrolyzed in 10 m*l* of dimethylformamide containing 1 m*l* portions of water and triethylamine at room temperature for 7 hr. The polymer solution was poured into ether and 0.2 g of polymer (XIII′) was obtained. Hydrolysis of polymer IX′ and X′ was carried out in the same procedure.

Molecular Compound of N-*Hydroxysuccinimide with Triethylamine.* To a solution of *N*-hydroxysuccinimide (1.16 g) in 10 m*l* of tetrahydrofuran, was added 2.02 g of triethylamine. The precipitate appeared instantly, and the reaction mixture was kept at room temperature for 30 min. The precipitate was filtered and washed with tetrahydrofuran, yield 1.97 g, mp 112—113°C. From elemental analyses, the product was found to consist of 2 moles hydroxysuccinimide and 1 mole triethylamine.

Found: C, 50.99; H, 7.62; N, 12.70%. Calcd for $2C_4H_5NO_3C_6H_{15}N(C_{14}H_{25}N_2O_3)$: C, 50.74; H, 7.61; N, 12.68%.