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Aminobutadienes. IV. Addition Reactions to 1-Phthalimido- and 2-Phthalimido-1,3-butadienes[1]

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1-Phthalimido-1,3-butadiene (I) and 2-phthalimido-1,3-butadiene (II) were chosen for study as typical imidobutadienes in order to clarify the role of such imido groups in determining the orientation of the addition reactions, and also the addition modes in their own polymerizations. The addition reactions of either I or II with bromine, hydrogen chloride, acrolein, acrylic acid and its methyl ester, maleic anhydride, and *p*-benzoquinone were shown to give the corresponding adducts. However, with crotonaldehyde, I and II each gave only the polymer. The ozonolysis studies have shown that all of the dibromides and monochlorides were 1,4-adducts, 1-chloro-1-phthalimido-2-butene (V) and 1-chloro-3-phthalimido-2-butene (XIII) respectively. No further hydrochlorination of V and XIII took place, even under more vigorous conditions. The major products obtained by the additions of acrolein, acrylic acid, and its methyl ester to I and II were shown to be 1-phthalimido-6-substituted-2-cyclohexene or 1-phthalimido-4-substituted-1-cyclohexene respectively.

Since studies of the chemistry of aminobutadiene and related compounds have been undertaken in our laboratory, eight new monomers of imidobutadienes have been prepared and found to easily polymerize either radically or, in some cases, cationically to form suitable high polymers.[3a-e] The monomers are 1-phthalimido-[4,5] and 1-succinimido-1,3-butadienes,[5] 2-phthalimido- and 2-succinimido-1,3-butadienes,[6] 2-phthalimidomethyl-1,3-butadiene,[7] 1-succinimido-2-methyl-1,3-butadiene,[8] 1-(2-oxopyrrolidino)-1,3-butadiene,[9] and 1-(*N*-methylanilino)-1,3-butadiene.[10]

Prior to a systematic investigation of the addition polymerization of these monomers, the electrophilic additions of bromine and hydrogen chloride to these monomers had been attempted in order to obtain basic knowledge about their chemical behaviors toward addition reactions. With the same intention, their Diels-Alder type additions were also studied, with acrolein, acrylic acid and its methyl ester, crotonaldehyde, crotonic acid, *p*-benzoquinone, and maleic anhydride as the dienophiles. The 1-phthalimido- and 2-phthalimido-1,3-butadienes (I and II) were chosen as typical imidobutadienes for the present paper.

The addition of an equimolar amount of bromine to each of the above imidobutadienes in carbon tetrachloride gave the corresponding dibromides, while an excess of bromine afforded the saturated tetrabromides. Usual ozonolysis study was undertaken to determine the positions of the bromine atoms and of the ethylenic linkages remaining in such dibromides; the I-dibromide was shown to be 1,4-dibromo-1-phthalimido-2-butene (III) (Fig. 3). In a similar manner, the dibromide of II was determined to be 1,4-dibromo-2-phthalimido-2-butene (XI), also resulting from a 1,4-addition to the butadiene chain.

The addition of hydrogen chloride to either I or II in a benzene solution at 5—10°C yielded the corresponding monochloride. The structure of these adducts were shown to be 1-chloro-1-phthalimido-2-butene (V) and 1-chloro-3-phthalimido-2-butene (XIII) respectively. No further hydrochlorination of V and XIII took place, even under more vigorous conditions.

These results lead us to conclude that, since an acid amide group, such as –NHCOR and –$NHSO_2R$,

1) A. Terada and K. Murata, Abstracts of the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

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3 a) A. Terada and K. Murata, Abstracts of the Meeting of the Chemical Society of Japan, Tokuyama, May, 1961; Paper V on aminobutadienes, *J. Polymer Sci., A-1*, in press. b) A. Terada and K. Murata, Abstracts of the Meeting of the Societies related to Chemistry, Tokyo, October, 1962. c) K. Murata and A. Terada, Paper VI, *J. Polymer Sci., A-1*, **4**, 2989 (1966). d) K. Murata and A. Terada, Paper VII, This Bulletin, **39**, 2494 (1966). e) K. Murata and A. Terada, Abstracts of the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

4) A. Terada, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **81**, 1773 (1960).

5) A. Terada and K. Murata, *ibid.*, **83**, 490 (1962).

6) A. Terada and S. Takahashi, *ibid.*, **83**, 485 (1962).

7) K. Murata and A. Terada, Paper IX, in preparation.

8) A. Terada and K. Murata, Abstracts of the Meeting on Olefins of the Chemical Society of Japan and the Society of Organic Synthetic Chemistry, Tokyo, November, 1964.

9) K. Murata and A. Terada, Paper VIII, This Bulletin, **40**, 414 (1967).

10) A. Terada, unpublished work.

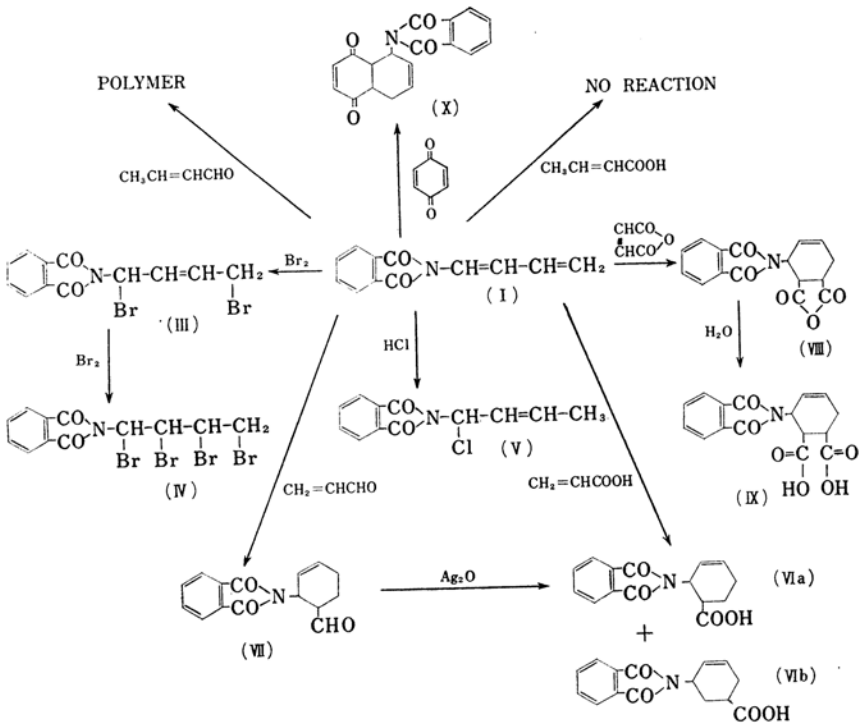
POLYMER
NO REACTION
CH₃CH=CHCHO
CH₃CH=CHCOOH
(X)
(I)
(III)
(IV)
(V)
(VIII)
(IX)
(VII)
(VIa)
(VIb)
Br₂
HCl
H₂O
Ag₂O
CH₂=CHCHO
CH₂=CHCOOH

Fig. 1

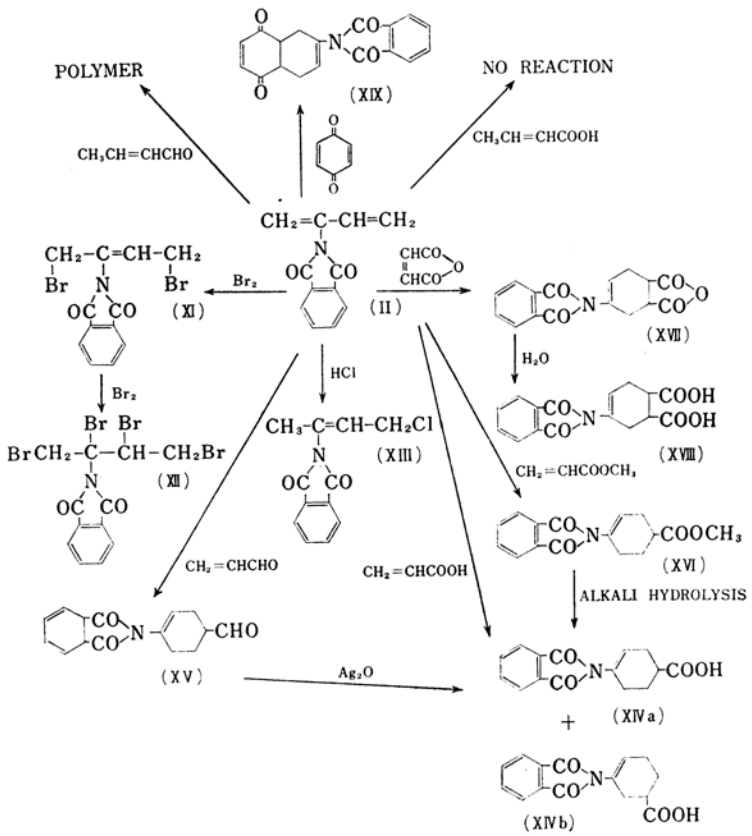
POLYMER
NO REACTION
CH₃CH=CHCHO
CH₃CH=CHCOOH
(XIX)
(II)
(XI)
(XII)
(XIII)
(XV)
(XVI)
(XVII)
(XVIII)
(XIVa)
(XIVb)
Br₂
HCl
H₂O
Ag₂O
CH₂=CHCHO
CH₂=CHCOOH
CH₂=CHCOOCH₃
ALKALI HYDROLYSIS

Fig. 2

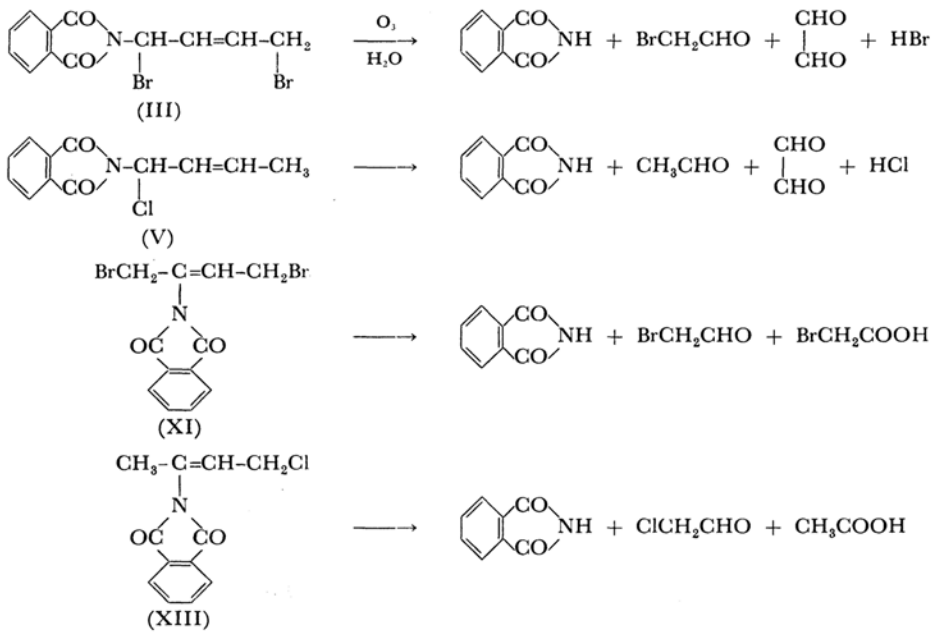

Fig. 3

Fig. 4

in a conjugated system is known to act as an electron-donating group,[11] the compounds I and II will generally be polarized by a phthalimido group, as is shown in Formulas XX and XXI (Fig. 4).
A cation attacks at the C-4 position of XX or at the C-1 position of XXI, and the remaining anion joins with another terminal carbon to form the 1,4-adducts.

With acrylic acid, both I and II react to give the corresponding Diels-Alder adducts. Generally speaking, two structural isomers are possible when the addition is carried out between both an unsymmetrical diene and an unsymmetrical dienophile, as in these cases. The acrylic acid adduct of I obtained had a narrow melting-point range, suggesting a single isomer. The structure of 2-phthalimido-1,2,5,6-tetrahydrobenzoic acid (VIa) seems more probable for this major isomer for the following reasons.[12] It has generally been suggested that such a Diels-Alder reaction is probably initiated by a coupling of the more anionoid end of the diene system with a cationoid carbon of the dienophile.[14] Thus, the adduct (VIa) would be produced predominantly rather than another isomer, 3-phthalimido-1,2,3,6-tetrahydrobenzoic acid (VIb). Acrolein with I also gave the corresponding aldehyde adduct, which could be converted into the above acid (VIa) by silver oxide oxidation.

The acrylic acid adduct of II was obtained as a mixture of the two possible isomers; it showed a wide melting-point range, while the results of the elemental analyses agreed well with the calculated values. Since further purification by recrystallization was unsuccessful, repeated chromatographic separations and subsequent recrystallizations were carried out, finally giving one of the isomers, mp 188—188.5°C, as major product; this was assumed to be 4-phthalimido-1,2,5,6-tetrahydrobenzoic acid (XIVa). Also methyl acrylate with II gave the corresponding methyl ester (XVI) as the major product. The acrolein adduct of II was also converted into the above acid (XIVa) by silver oxide oxidation. Although complete structural deter-

11) E. R. Alexander, "Principles of Ionic Organic Reactions," Japanese transl., ed. by R. Goto, Nankodo Co., Tokyo (1957), p. 213.
12) A similar result has been obtained by Hünig and Kahanek in the case of 1-diethylamino-1,3-butadiene.[13]
13) S. Hünig and H. Kahanek, *Chem. Ber.*, **90**, 238 (1957).
14) H. L. Holmes, "The Diels-Alder Reaction, Ethylenic and Acetylenic Dienophiles," in "Organic Reactions," Vol. 4, ed. by R. Adams, John Wiley & Sons, New York (1948), p. 64.

minations for these isolated isomers, VIa, VII, XIVa and XV have not yet been made, by synthetic proof, for example, the above-mentioned assignments are reasonable.

The addition reactions of I and II to *p*-benzoquinone and to maleic anhydride readily gave the corresponding adducts in good yield, as Figs. 1 and 2 show.

The attempted additions of crotonaldehyde and of crotonic acid to these two imidobutadienes under the usual conditions of diene synthesis were unsuccessful. In the case of crotonaldehyde, both the imidobutadienes gave only their homopolymers, while with crotonic acid they showed no reaction at all.

Experimental

The Addition of Bromine to 1-Phthalimido-1,3-butadiene (I). To 0.75 g (3.8 mmol) of I in 10 m*l* of carbon tetrachloride, 1.5 g (9.4 mmol) of bromine in 30 m*l* of the same solvent was slowly added at room temperature. The solution was allowed to stand for 30 min and then washed successively with a saturated sodium sulfite solution, water, a dilute sodium bicarbonate solution, and water again, and finally dried over anhydrous sodium sulfate. After the removal of the solvent, the residue was recrystallized from benzene-petroleum benzine to give 1.20 g (61.5%) of the tetrabromide, melting at 138—140°C. This sample did not decolorize permanganate in acetone; it must, therefore, be 1-phthalimido-1,2,3,4-tetrabromobutane (IV).

Found: C, 28.16; H, 1.95; N, 2.23%. Calcd for $C_{12}H_9Br_4NO_2$: 27.78; H, 1.75; N, 2.57%.

ν_{max}^{Nujol} 1792, 1730 (C=O, phthalimido); 1613 (phenyl); 724 cm^{-1} (*o*-disubstituted benzene).

A similar procedure was used to prepare the dibromide using equal amounts of bromine and I; it gave a 83.3% yield of 1,4-dibromo-1-phthalimido-2-butene (III) as white crystals, mp 146.5—147.5°C (depressed on admixture with the tetrabromide).

Found: C, 40.19, 40.01; H, 2.53, 2.53; N, 3.77, 3.90%. Calcd for $C_{12}H_9Br_2NO_2$: C, 40.14; H, 2.53; N, 3.90%.

ν_{max}^{Nujol} 1799, 1739 (C=O, phthalimido); 1661 (C=C); 1618 (phenyl); 716 cm^{-1} (*o*-disubstituted benzene).

The Ozonolysis of the I-Dibromide (III). A dilute ozone prepared from air was passed for 3 hr into a solution of 315 mg of III in 15 m*l* of chloroform cooled in an ice-salt bath. The removal of the solvent under reduced pressure at room temperature left the ozonide as a white, crystal-like material. To this, 40 m*l* of water was added, after which the temperature of the system was gradually raised to a boil; approximately 20 m*l* of water plus, the volatile products were thus distilled out.

This distillate showed bromide ions on the addition of a silver nitrate solution, and also 59 mg of a yellow precipitate on 2,4-dinitrophenylhydrazone formation. This hydrazone was separated into a hot ethanol extract and an insoluble material. The former gave a positive Beilstein test and was proved to be bromoacetaldehyde-2,4-dinitrophenylhydrazone after isolation. The latter, ethanol-insoluble part was crystallized from nitrobenzene to give a sample of glyoxal-bis-2,4-dinitrophenylhydrazone, melting at 304—307°C, which was identified by a mixed-melting-point test with an authentic sample.

The residue in the distillation flask separated 78 mg (60.5%) of phthalimide, melting at 228—231°C, which was identified by means of a mixed-melting-point determination.

The Addition of Bromine to 2-Phthalimido-1,3-butadiene (II). A procedure like that above gave the dibromide (XI), mp 127.5°C, as white crystals; it was identical with the dibromide previously obtained.[6]

The Ozonolysis of the II-Dibromide (XI). This procedure gave bromoacetaldehyde and phthalimide, proving the structure to be 1,4-dibromo-2-phthalimido-2-butene.

The Tetrabromide. This compound was given by the use of an excess of bromine; it was obtained as white crystals of 2-phthalimido-1,2,3,4-tetrabromobutane (XII) mp 115.5—116.5°C.

Found: C, 28.03, 28.09; H, 1.89, 1.86; N, 2.91, 2.79%. Calcd for $C_{12}H_9Br_4NO_2$: C, 27.78; H, 1.75; N, 2.57%.

1-Chloro-1-phthalimido-2-butene (V). Dry hydrogen chloride was rapidly introduced into a solution of 0.50 g (2.5 mmol) of I in 15 m*l* of benzene at 5°C for 1 hr. The solutin was then washed with water, a dilute sodium bicarbonate solution, and water again, and dried over anhydrous sodium sulfate. After the removal of the solvent and dilution with petroleum benzine, 0.55 g (93.5%) of crystals melting at 111—115°C were separated. Recrystallization from petroleum benzine raised the melting point to 114—115°C (depressed on admixture with the starting material, with a mp of 114.5—116°C).

Found: C, 61.13; H, 4.30; N, 5.62%. Calcd for $C_{12}H_{10}ClNO_2$: C, 61.16; H, 4.28; N, 5.94%.

ν_{max}^{Nujol} 1776, 1718 (C=O, phthalimido); 1658 (C=C); 1610 (phenyl); 715 cm^{-1} (*o*-disubstituted benzene).

No saturated adduct other than the above monochloride was obtained when the reaction was carried out under reflux.

Ozonolysis. This procedure was carried out using 350 mg of V. Working up as usual gave chroride ions, 163 mg (74.5%) of phthalimide and 192 mg of a 2,4-dinitrophenylhydrazone mixture. The paper chromatography of this hydrazone mixture according to the technique of Maruta and Suzuki[15] gave the results summarized in Table 1. Therefore, the monochloride must be 1-chloro-1-phthalimido-2-butene (V).

Table 1. R_f Values of 2,4-Dinitrophenylhydrazone

	R_f
Glyoxal	0.087
Acetaldehyde	0.52
Sample obtained here	0.087
and	0.53

1-Chloro-3-phthalimido-2-butene (XIII). This was obtained as above from II; it was also shown to be the II-monochloride (XIII) by the following analysis.

Found: C, 61.18; 4.47; N, 5.64%. Calcd for

15) S. Maruta and Y. Suzuki, *Kogyo Kagaku Zassh (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **64**, 2129 (1961).

$C_{12}H_{10}ClNO_2$: C, 61.16; H, 4.28; N, 5.94%.

ν_{max}^{Nujol} 1764, 1715 (C=O, phthalimido); 1667 (C=C); 1610 (phenyl); 715 cm^{-1} (*o*-substituted benzene).

Moreover, this hydrogen chloride addition could not afford any of the saturated adduct, even under more drastic conditions.

Ozonolysis. Working up as usual gave chloroacetaldehyde-2,4-dinitrophenylhydrazone[16] and phthalimide; this adduct was, therefore, confirmed to be 1-chloro-3-phthalimido-2-butene (XIII).

The Addition of Acrylic Acid to 1-Phthalimido-1,3-butadiene (I). A mixture of 0.40 g (2 mmol) of I and 0.43 g (6 mmol) of acrylic acid in 6 m*l* of benzene was refleuxed for 10 hr. After the removal of the benzene, dilution with petroleum benzine gave 0.15 g of crystals melting at 130—156°C. One recrystallization from water increased the melting point to 159—161°C, but further recrystallization from various solvents did not raise the melting point.

The following analysis indicated that this compound was 2-phthalimido-1,2,5,6-tetrahydrobenzoic acid (VIa), one of the two structural isomers.

Found: C, 66.60, 66.65; H, 4.84, 4.85; N, 5.01, 5.10%. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16%.

ν_{max}^{Nujol} 1779, 1721 (C=O, phthalimido); 1701 (C=O, acid); 1656 (C=C); 1613 (phenyl); 716 cm^{-1} (*o*-disubstituted benzene).

The Addition of Acrylic Acid to 2-Phthalimido-1,3-butadiene. This procedure gave an isomeric mixture of the adducts, mp 138—160°C. The attempted separation of this mixture into its components by repeated recrystallizations was unsuccessful, but the following analysis and a study of the infrared spectrum indicated suitable results.

Found: C, 66.24; H, 4.95; N, 4.95%. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16%.

ν_{max}^{Nujol} 1781, 1721 (C=O, phthalimido); 1710 (C=O, acid); 1665 (C=C); 1624 (phenyl); 716 cm^{-1} (*o*-disubstituted benzene).

Repeated chromatographic separation using silica gel[17] and recrystallizations finally gave 470 mg (76.6%) of 4-phthalimido-1,2,5,6-tetrahydrobenzoic acid (XIVa), mp 188—188.5°C.

Found: C, 66.12; H, 4.95%.

The Addition of Methyl Acrylate to 2-Phthalimido-1,3-butadiene (II). A mixture of 597 mg (2.99 mmol) of II, 1.00 g (11.6 mmol) of freshly-distilled methyl acrylate, and a small amount of hydroquinone in 10 m*l* of benzene was refluxed for 10 hr. The reaction mixture was then concentrated, diluted with methanol, and filtered to remove a precipitate, which might be a polymeric substance. After another concentration, 729 mg of the crude adduct was obtained. Chromatographic separation using 80 g of silica gel[17] gave a fraction, 457 mg of crystals, eluted by 50 m*l* of a petroleum benzine-benzene mixture (6: 4). Repeated recrystallizations from benzene-petroleum benzine and from petroleum benzine gave 219 mg of a pure sample, mp 155.5—156.5°C, methyl 4-phthalimido-1,2,5,6-tetrahydrobenzoate (XVI).

Found: N, 4.91%. Calcd for $C_{16}H_{15}NO_4$: N, 4.91%.

ν_{max}^{Nujol} 1758, 1707 (C=O, phthalimido); 1726 (C=O, ester); 1671 (C=C); 1188 (ester); 709 cm^{-1} (*o*-disubstituted benzene).

The Alkali Hydrolysis. A sample of 29 mg of the methyl ester obtained above was dissolved in 2 m*l* of acetone and mixed with 100 mg of sodium hydroxide in 6 m*l* of water. After 30 minutes' stirring at room temperature, the system was slightly acidified with dilute hydrochloric acid. Vacuum concentration gave 12 mg of crystals, mp 188—189°C, identical with the product obtained from the addition of II and acrylic acid.

The Addition of Acrolein to 1-Phthalimido-1,3-butadiene (I). A solution of 0.40 g (2 mmol) of I and 0.5 g (9 mmol) of freshly-distilled acrolein in 6 m*l* of benzene was allowed to react as usual. After the removal of the solvent, the resulting oil was diluted with petroleum benzine to precipitate the adduct. Recrystallizations from petroleum benzine yielded 0.34 g of an analytical sample as colorless crystals, mp 83—84°C, 2-phthalimido-1,2,5,6-tetrahydrobenzaldehyde (VII).

Found: C, 70.81, 70.75; H, 5.30, 5.27; N, 5.13, 5.52%. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49%.

ν_{max}^{Nujol} 1780 (C=O, phthalimido); 1735—1710 (broad, phthalimido and aldehyde carbonyls); 1663 (C=C); 1622 (phenyl); 720 cm^{-1} (*o*-disubstituted benzene).

The Oxidation of VII to the Corresponding Acid (VIa). The aladehyde VII obtained above (200 mg) was dissolved in 4 m*l* of ethanol and mixed with 400 mg of silver nitrate in 2 m*l* of water. To this mixture, 400 mg of potassium hydroxide in 4 m*l* of water was then added at room temperature. After 48 hours' stirring, the system was diluted with ethanol and filtered. After concentration, acidification with dilute hydrochloric acid, and subsequent concentration to dryness, the residue was extracted with hot benzene. A crude crystalline product was obtained on the removal of the solvent; this product gave 191 mg (89%) of an analytical sample of VIa, melting at 159—161°C, by recrystallization from water. No melting-point depression was a observed on admixture with an authentic sample of VIa.

The Addition of Acrolein to 2-Phthalimido-1,3-butadiene. This procedure was carried out as above. After the usual working-up, 0.53 g of the adduct, mp 78—92°C, was obtained. Recrystallization from petroleum benzine raised the melting point to 97—100°C.

Found: C, 71.89, 72.10; H, 6.17, 6.29%. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13%.

The Oxidation of XV to the Corresponding Acid (XIVa). This procedure was carried out as in the case of VII, using the aldehyde sample obtained above; it gave 15 mg of an analytical sample, mp 187—188°C. This was identical with XIVa.

The Addition of Maleic Anhydride to 1-Phthalimido-1,3-butadiene (I). A mixture of 1.00 g (5 mmol) of I and 0.50 g (5 mmol) of maleic anhydride in 10 m*l* of benzene was refluxed on a steam bath for 1 hr. When the solution was cooled to room temperature, some crystals precipitated. The extraction of the product with hot benzene and subsequent cooling gave 0.90 g (60%) of 3-phthalimido-1,2,3,6-tetrahydrophthalic anhydride (VIII), as white crystals, mp 161—163°C.

Found: C, 64.73; H, 4.09; N, 4.69%. Calcd for $C_{16}H_{11}NO_5$: C, 64.64; H, 3.71; N, 4.71%.

16) This was identified with the authentic sample obtained according to the method of J. Meisenheimer and W. Schmidt, *Ann.*, **475**, 182 (1929).

17) For chromatographic analysis, 100 mesh, Mallinckrodt Chemical Works, U.S.A.

ν_{max}^{Nujol} 1855, 1779 (C=O, five-membered-ring acid anhydride); 1724 (C=O, phthalimido); 1661 (C=C); 1623 (phenyl); 724 cm^{-1} (*o*-disubstituted benzene).

The crystallization of the benzene-insoluble residue from hot water gave white crystals, soluble in alkali but insoluble in acid, mp 206—208°C, 3-phthalimido-1,2,3,6-tetrahydrophthalic acid (IX). The hydration of VIII in boiling water gave IX.

Found: C, 60.60; H, 4.23; N, 4.31%. Calcd for $C_{16}H_{13}NO_6$: C, 60.95; H, 4.16; 4.44%.

ν_{max}^{Nujol} 3636 (OH, acid); 1770, 1712 (C=O, phthalimido); 1695 (C=O, acid); 1667 (C=C); 1613 (phenyl); 716 cm^{-1} (*o*-disubstituted benzene).

The Addition of Maleic Anhydride to 2-Phthalimido-1, 3-butadiene. This procedure was carried out as above. After working-up as usual, a 73% yield of 4-phthalimido-1, 2, 3, 6-tetrahydrophthalic anhydride (XVII), mp 178—179°C, was obtained.

Found: C, 64.54; H, 3.67; N, 4.73%. Calcd for $C_{16}H_{11}NO_5$: C, 64.65; H, 3.73; N, 4.71%.

ν_{max}^{Nujol} 1850, 1786 (C=O, five-membered-ring acid anhydride); 1773, 1722 (C=O, phthalimido); 1667 (C=C); 1613 (phenyl); 716 cm^{-1} (*o*-disubstituted benzene).

The hydrated sample, 4-phthalimido-1,2,3,6-tetrahydrophthalic acid (XVIII), mp 220.5—222°C, was prepared as usual.

Found: C, 61.10; H, 4.48; N, 4.42%. Calcd for $C_{16}H_{13}NO_6$: C, 60.95; H, 4.16; N, 4.44%.

ν_{max}^{Nujol} 3534 (OH, acid); 1779 (C=O, phthalimido); 1733—1681 (carbonyls of acid and phthalimido); 1667 (C=C); 1618 (phenyl); 715 cm^{-1} (*o*-disubstitusted benzene).

The Addition of *p*-Benzoquinone to 1-Phthalimido-1,3-butadiene (I). A mixture of 0.80 g (4 mmol) of I and 0.43 g (4 mmol) of *p*-benzoquinone in 10 m*l* of benzene was refluxed for 1 hr. After concentration to a half of the original volume, the remaining solution was diluted with petroleum benzine to precipitate the adduct. Crystallization from benzene-petroleum benzine gave 5-phthalimido-5,8,9,10-tetrahydro-1,4-naphthoquinone (X), mp 154—155°C, as white crystals.

Found: C, 70.50; H, 4.40; N, 4.43%. Calcd for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.26; N, 4.56%.

ν_{max}^{Nujol} 1776, 1718 (C=O, phthalimido); 1689 (C=O, *p*-quinone); 1613 (phenyl); 722 cm^{-1} (*o*-disubstituted benzene).

The Addition of *p*-Benzoquinone to 2-Phthalimido-1,3-butadiene. The procedure shown above gave 6-phthalimido-5, 8, 9, 10-tetrahydro-1, 4-naphthoquinone (XIX), mp 187—190°C, as white crystals.

Found: C, 70.82; H, 4.25; N, 4.61%. Calcd for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.26; N, 4.56%.

ν_{max}^{Nujol} 1770, 1718 (C=O, phthalimido); 1689 (C=O, *p*-quinone); 1613 (phenyl); 717 cm^{-1} (*o*-disubstituted benzene).

The Reaction of Crotonaldehyde with 1-Phthalimido-1,3-butadiene (I). A mixture of 0.37 g (2 mmol) of I and 0.40 g (6 mmol) of freshly-distilled crotonaldehyde in 10 m*l* of benzene was refluxed for 7 hr. After concentration and then dilution with petroleum benzine, 0.37 g of a polymeric substance was precipitated. The polymer was purified by fractional prepicitation from the *sym*-tetrachloroethane solution into methanol; subsequent nitrogen analysis showed that the polymer was mainly poly-1-phthalimido-1,3-butadiene, perhaps contaminated with crotonaldehyde resin.

Found: N, 6.11, 6.28%. Calcd for $C_{12}H_9NO_2$: N, 7.01%.

With 2-Phthalimido-1,3-butadiene. The above procedure resulted only in the formation of the II-polymer.

The Reaction of Crotonic Acid with 1-Phthalimido-1,3-butadiene (I). A mixture of 0.40 g (2 mmol) of I and 0.30 g (4 mmol) of crotonic acid in 10 m*l* of benzene was refluxed for 10 hr. After the removal of the solvent, the remaining oil was diluted with petroleum benzine to give crystals. Recrystallization from methanol yielded 0.27 g (67.5%) of I, melting at 114—115°C; it did not depress the melting point of an authentic sample on admixture.

From the mother liquor, another sample of I was recovered, but no other product, such as I-polymer, could be isolated. Therefore, it may be concluded that no reaction occurred under such reaction conditions.

With 2-Phthalimido-1,3-butadiene. Results such as those above were obtained.

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