Ethyl *m*-[α-Pyridinium) acetyl]oxanilate Bromide (LXII).—Ethyl *m*-(bromoacetyl)oxanilate (LXI), 1.0 g., treated with pyridine by the procedure used for the acid, gave 1.21 g. (97%) of product, m.p. 170–172° dec. Recrystallization from absolute ethanol gave 1.1 g. (88%) of analytically pure product, m.p. 172–173° dec., $\lambda^{\text{Nujol}}_{\max(\mu)}$ 2.92, 3.12 (NH), 5.82 (C=O), 6.09, 6.67 ($C_5H_5N—^{\oplus}$). It moved in solvent G with R_f 0.64.

Anal. Calcd. for $C_{17}H_{17}BrN_2O_4$: C, 51.9; H, 4.36; Br, 20.3; N, 7.13. Found: C, 51.5; H, 4.15; Br, 20.1; N, 7.30.

Degradation of LXIV to *m*-Aminobenzoic Acid (LIII).—A mixture of 0.40 g. of LXIV in 10 ml. of 1 *N* sodium hydroxide solution was heated on a steam bath for 0.75 hr. The resultant solution was cooled in ice, acidified to pH 1 with hydrochloric acid, then evaporated to dryness. The residue was dissolved in 20 ml. of saturated sodium acetate solution and extracted with ethyl acetate (2 × 20 ml.). The extracts were combined, washed, dried, and evaporated to afford 0.10 g. (51%) of *m*-aminobenzoic acid as a light pink solid, m.p. 168–170°; m.p. 170–172° when mixed with authentic *m*-aminobenzoic acid of m.p. 172–173°. The infrared spectra and paper chromatographic behavior in several solvent systems were identical to those of the authentic *m*-aminobenzoic acid.

Degradation of Ethyl *m*-[α-(Pyridinium)acetyl]oxanilate Bromide (LXII) to *m*-Aminobenzoic Acid (LXIII).—A mixture of 0.50 g. of the ester LXII in 10 ml. of 1 *N* sodium hydroxide solution was heated for 5 hr. on a steam bath. The reaction was worked up as above to give 0.10 g. (59%) of product, m.p. 167–169°, which was established as *m*-aminobenzoic acid by mixed melting point and comparison of infrared spectrum and paper chromatographic behavior with those of an authentic sample.

Dibromination of Ethyl *m*-Acetyloxanilate (LVIII).—A mixture of 0.24 g. (1 mmole) of LVIII and 0.70 g. (2 mmoles) of tribromoacetophenone[32] was heated in an oil bath at 110° for 3 hr. The resulting amber oil was crystallized from absolute ethanol to give 0.26 g. (67%) of a dibromo derivative of ethyl *m*-acetyloxanilate, m.p. 104–105°; $\lambda^{\text{Nujol}}_{\max(\mu)}$ 3.05 (NH); 5.85, 5.92 (C=O); 6.45 (amide II). It moved in solvent F with R_f 0.46 (LVIII, R_f 0.52).

Anal. Calcd. for $C_{12}H_{11}Br_2NO_4$: C, 36.7; H, 3.82; Br, 40.1; N, 3.56. Found: C, 36.7; H, 3.82; Br, 40.1, N, 3.53.

On the basis of its preparation, this dibromo derivative is presumed to be ethyl *m*-(α,α-dibromoacetyl)oxanilate. However, this was not established.

Acknowledgment.—The authors are indebted to Dr. Peter Lim for interpretation of the infrared spectra and to his staff for the paper chromatography. They also wish to thank Mr. O. P. Crews and his staff for the large-scale preparation of certain intermediates.

Polymers. IV. Polymeric Diels-Alder Reactions[1,2]

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Received July 19, 1961

Polymeric Diels-Alder adducts were prepared from 2-vinyl-1,3-butadiene and *p*-benzoquinone, *m*-phenylenebismaleimide, ethylene diacrylate, and N,N′-methylenediacrylamide. The first two polymers were insoluble and melted above 500°. Diels-Alder polymers were also prepared from three derivatives of 2-hydroxy-1,3-butadiene, bis(2-butadienylmethyl) acetal, bis(2-butadienylmethyl) hexamethylenedicarbamate, and bis(2-butadienylmethyl) *m*-xylylenedicarbamate. Various combinations of these bifunctional dienes with *p*-benzoquinone, *p*-phenylenebismaleimide, and benzidinebismaleimide produced a series of polymers in yields varying from 53 to 99% with intrinsic viscosities from 0.05 to 0.28 and softening points from 74 to 194°.

Theoretically, any reaction that proceeds in high yields can be somehow adapted for use in a polymerization reaction. Although the Diels-Alder reaction has been used extensively in organic chemistry and very often gives very high yields, very little work has been carried out to adapt this interesting reaction to the production of polymers. One of the few reactions that has been studied is the self-condensation of cyclopentadiene.[5] In this reaction the double bond remaining after the reaction of the diene in a Diels-Alder reaction becomes the dienophile for the next condensation step. However, since this double bond is a poor dienophile, very vigorous conditions are required and the reaction proceeds to give only tetramers, pentamers, and hexamers.

A simpler procedure appeared to be the preparation of a bi- or polyfunctional diene which could be made to react with a polyfunctional dienophile. While a number of bifunctional dienophiles, such as benzoquinone and the bismaleimides, are available, reactive bifunctional dienes are not readily available. This scarcity stems from the fact that a simple diene, such as butadiene, is bifunctional with respect to many reactions but in the Diels-Alder reaction it is only monofunctional. Therefore, in order for a compound to be bifunctional with respect to the Diels-Alder reaction, it must contain two diene systems. The simplest compound containing two diene systems is 2-vinylbutadiene (I).

Since the pyrolysis of esters had been shown in

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[1] Previous paper in this series, *J. Org. Chem.*, **25**, 1800 (1960).

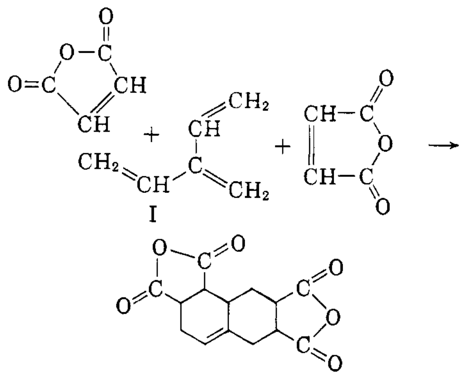
[2] Presented in part before the Division of Polymer Chemistry at the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954, and in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

[3] Office of Naval Research Fellow, 1953–1954.

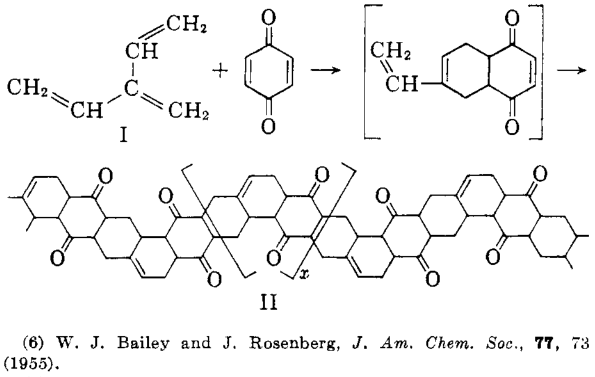
[4] Office of Naval Research Fellow, 1956–1957; National Science Foundation Predoctoral Fellow, 1957–1959.

[5] H. Staudinger and H. A. Bruson, *Ann.*, **447**, 97 (1926); K. Alder and G. Stein, *ibid.*, **496**, 204 (1932); K. Alder and G. Stein, *Ber.*, **67**, 613 (1934).

our laboratory to be an excellent method for the synthesis of polyfunctional compounds,[6] this method was used successfully for the preparation of 2-vinylbutadiene (I) from 1,5-diacetoxy-3-acetoxymethylpentane.[7] 2-Vinylbutadiene (I) was shown to be, indeed, bifunctional in the Diels-Alder reaction by the condensation with two moles of maleic anhydride to produce $\Delta^{4(9)}$-octalin-1,2,6,7-tetracarboxylic anhydride. The bifunctional character results from the fact that 2-vinylbutadiene possesses a cross-conjugated system.

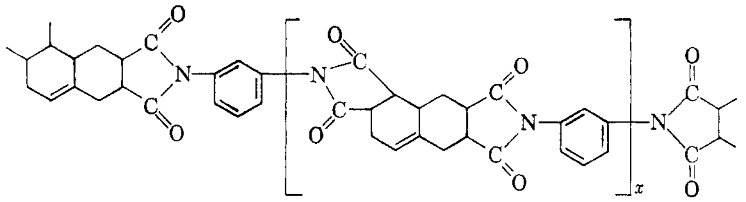

I

The polymerization of 2-vinylbutadiene (I) and benzoquinone was carried out by allowing them to react first at room temperature, presumably to form a 1:1 adduct, and then under reflux in a tetrachloroethane solution. The polymer IIa that precipitated softened at 340–400° and was essentially insoluble in all cold solvents, but soluble in very hot solvents. The fraction IIb that remained soluble in the chlorinated solvent softened at 170–200° and was shown to have a molecular weight of 440. It can be concluded that the more insoluble fraction IIa has a molecular weight greatly in excess of 440, possibly in the range of 2000. The polymer II is of special interest since it is a double stranded or ladder polymer.


I

II

When 2-vinylbutadiene (I) was allowed to react with N,N'-*m*-phenylenebismaleimide under refluxing acetone, precipitation occurred almost immediately to produce a white, essentially insoluble polymer III, which did not melt below 500°. Very similar polymers were prepared from the triene I and *p*-phenylenebismaleimide and benzidinebismaleimide. When 2-vinylbutadiene was heated with ethylene diacrylate, a colorless translucent glass resulted. Although the polymer was not completely soluble, most of the polymer could be extracted by acetone in a Soxhlet extractor. Even though a free radical inhibitor was present during the polymerization, the possibility of a small amount of a competing free radical polymerization cannot be excluded. A very similar polymer resulted from heating 2-vinylbutadiene and N,N'-methylenediacrylamide. When 2-vinylbutadiene was stored for several weeks, a mixture of cyclic dimers was formed. If this mixture of dimers was heated under reflux for 48 hr. in cyclohexane, a light yellow polymer, softening point 130–165°, precipitated. Presumably, this homopolymer of 2-vinylbutadiene is a polymeric Diels-Alder adduct.


III

In order to study Diels-Alder polymerizations more extensively a more general synthesis of bifunctional dienes was undertaken. One of the most interesting dienes for this study was 2-hydroxymethylbutadiene, not only because it was an active diene, but also because it possessed a functional group to form polyfunctional derivatives. The pyrolysis of esters made possible several syntheses of this interesting hydroxydiene.[8] Treatment of this diene alcohol with vinyl acetate in the presence of boron trifluoride gave bis(2-butadienylmethyl) acetal (IV) or with a diisocyanate gave bis(2-butadienylmethyl) hexamethylenedicarbamate (V) and bis(2-butadienylmethyl) *m*-xylylenedicarbamate (VI).

The reaction of the acetal IV with quinone gave a soluble glass VII, softening about 130–140°, while the product from IV and *p*-phenylenebismaleimide was a white crystalline powder VIII, which softened at 185–194° and was soluble in dimethylformamide.

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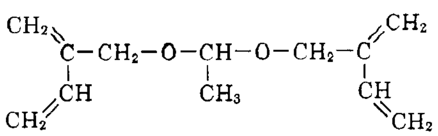
(6) W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

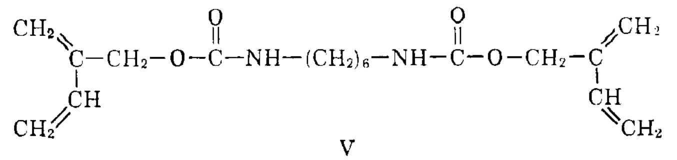
(7) W. J. Bailey and J. Economy, *ibid.*, **77**, 1133 (1955).

(8) W. J. Bailey, W. G. Carpenter, and M. E. Hermes, *J. Org. Chem.*, **27**, 1975 (1962).

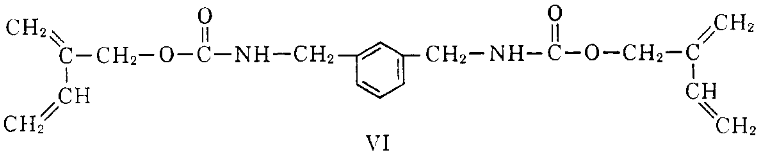
(9) W. J. Bailey and M. E. Hermes, *ibid.*, From page proofs of "Cyclic Dienes. XXII. Synthesis of Bisdienes from 2-Hydromethyl-1,3-butadiene."



IV



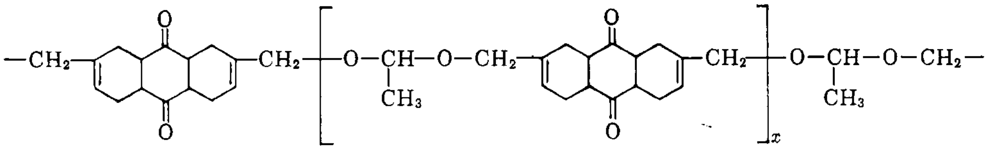
V



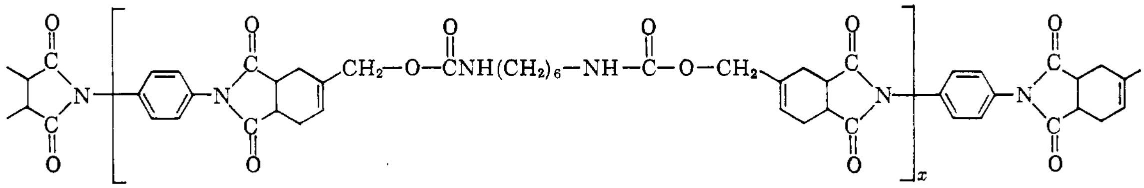
VI

A similar polymer IX from benzidinebismaleimide and IV softened at 170–174°.

When the hexamethylenedicarbamate V was treated with *p*-phenylenebismaleimide, the soluble polymer X, softening at 74–78°, was obtained. Similarly, compound V with benzidinebismaleimide gave the soluble polymer XI, softening at 133–137°.

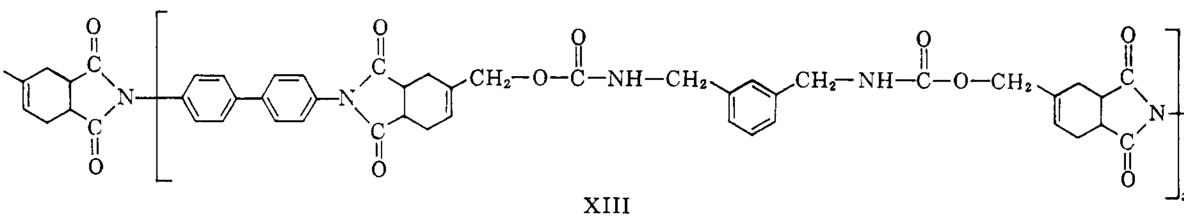


VII



X

Bis(2-butadienylmethyl) *m*-xylylenedicarbamate with *p*-phenylenebismaleimide and benzidinebismaleimide gave the soluble polymer XII, softening point 90–95°, and the soluble polymer XIII, softening point 145–150°, respectively.



XIII

These polymers, related to 2-hydroxymethylbutadiene, were produced in yields varying from 53 to 97% and with intrinsic viscosities varying from 0.05 to 0.28. Polymer XIII, for instance, was produced in a 72% yield after precipitation from a dimethylformamide solution with diethyl ether and possessed an intrinsic viscosity of 0.15.

The present work demonstrates the feasibility of polymerization through the Diels-Alder reaction. 2-Hydroxymethylbutadiene appears to be a particularly attractive monomer for this reaction, since bifunctional dienes with a large variety of groups connecting the two diene ends can be conveniently prepared.

Since our work originally was presented,[2] two other approaches to the preparation of Diels-Alder polymers have been published. A recent patent[10] describes the use of a cyclic diene which will eliminate a bridge group from a bicyclic Diels-Alder adduct to produce a new diene system which can react further. Thus 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer plus hexamethylenebismaleimide gave a Diels-Alder polymer plus carbon monoxide; similarly, *α*-pyrone and the bismaleimide gave a polymer plus carbon dioxide. A bifunctional diene, prepared by the alkylation of the anion of cyclopentadiene with a dihalide, was recently reported to give Diels-Alder polymers.[11] A recent attempt to make a Diels-Alder polymer from *p*-6-(1,2,3,4-tetrachlorofulvenyl)phenyl *p*-maleimidobenzoate was unsuccessful.[12]

(10) E. A. Kraiman, U. S. Patent 2,890,206 (June 9, 1959).

(11) J. K. Stille and L. Plummer, Abstracts of the 136th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1959, p. 3-T.

(12) J. S. Meek and P. Argabright, *J. Org. Chem.*, **22**, 1708 (1957).

Experimental

Polymer II from 2-Vinylbutadiene and Benzoquinone.—After a solution of 0.40 g. (0.005 mole) of 2-vinylbutadiene (I) and 0.54 g. (0.005 mole) of benzoquinone in 15 ml. of chloroform was allowed to stand at room temperature for 4 days, it was heated under reflux for an additional 24 hr. After 20 ml. of tetrachloroethane had been added, most of the chloroform was removed by distillation. The residual solution was heated under reflux for 48 hr. to produce a brown precipitate. The polymer was removed by filtration and dried under vacuum to give 0.52 g. of a Diels-Alder polymer IIa, softening point 340–400°. Since this polymer IIa was appreciably soluble in solvents only at temperatures above 300°, no direct estimation of its molecular weight was feasible. However, when the filtrate was concentrated under reduced pressure, 0.43 g. of a brown polymer IIb, softening point 170–200°, was obtained. Since this material was soluble in camphor, a molecular weight determination by the Rast method gave a molecular weight of 440.

Polymer III from 2-Vinylbutadiene and N,N′-*m*-Phenylenebismaleimide.—To a solution of 0.30 g. (0.0038 mole) of 2-vinylbutadiene (I) in 5 ml. of acetone was added a solution of 1.00 g. (0.0038 mole) of N,N′-*m*-phenylenebismaleimide[13] in 15 ml. of acetone. After the solution was heated under reflux for 15 min. and cooled to room temperature, the mixture was filtered to yield 1.29 g. (99%) of a white Diels-Alder polymer III, which was essentially insoluble in all the cold solvents tested. Although polymer III began to skrink around 400°, no melting had occurred at 500°. Above 500°, decomposition was evident.

Very similar polymers were prepared from 2-vinylbutadiene and *p*-phenylenebismaleimide and benzidinebismaleimide.[14]

Polymer from 2-Vinylbutadiene and Ethylene Diacrylate.—A mixture of 0.235 g. (0.0029 mole) of 2-vinylbutadiene, 0.50 g. (0.0029 mole) of ethylene diacrylate, and 0.005 g. of hydroquinone was sealed in a 6-cm. test tube and allowed to stand for 5 days at room temperature. After the solution was heated on a steam bath for 24 hr., a water-white, transparent, glassy polymer was obtained. Although this polymer did not appear to be appreciably soluble in any solvent, it could be almost completely extracted by acetone in a Soxhlet extractor.

Polymer from 2-Vinylbutadiene and N,N′-Methylenediacrylamide.—After a solution of 0.50 g. (0.0033 mole) of N,N′-methylenediacrylamide and 0.262 g. (0.0033 mole) of 2-vinylbutadiene in 25 ml. of dimethylformamide had been allowed to stand at room temperature for 5 days, it was heated under reflux for 5 days. The dimethylformamide was removed from the clear solution by evaporation under reduced pressure to give a hard, glassy brown polymer which was almost completely insoluble in camphor but had an intrinsic viscosity in dimethylformamide of 0.05.

Homopolymer from 2-Vinylbutadiene.—When 1.0 g. of 2-vinylbutadiene (I) was kept at 0° for 2 weeks, a viscous liquid, n^{25}_{D} 1.4970, presumably a mixture of cyclic dimers, was obtained. This liquid was diluted with 50 ml. of cyclohexane, and the resulting solution was heated under reflux for 2 days. The reaction mixture was filtered to give 0.40 g. of a light yellow polymer, softening point 130–165°, that was insoluble in all cold solvents.

Polymer VII from Bis(2-butadienylmethyl) Acetal and Quinone.—To 0.23 g. (0.0021 mole) of quinone, purified by sublimation, was added 0.42 g. (0.0021 mole) of bis(2-butadienylmethyl) acetal[9] and a small amount of N-phenyl-β-naphthylamine to give a clear yellow solution. A tube containing this solution was sealed under nitrogen and heated at 100° for 1 hr. and then at 150° for 1.5 hr. At this temperature, the mixture was quite viscous but still flowed; however, when the polymer was cooled, it hardened to a brittle glass and 0.63 g. (97%) of the straw-colored polymer VII was obtained after the tube was broken open.

The Diels-Alder polymer VII was soluble in dimethylformamide and its intrinsic viscosity in this solvent at 50° was determined to be 0.28.

Anal. Calcd. for $(C_{18}H_{22}O_4)_x$: C, 71.52; H, 7.28. Found: C, 71.68; H, 7.05.

Polymer VIII from Bis(2-butadienylmethyl) Acetal and *p*-Phenylenebismaleimide.—To a 50-ml. flask fitted with condenser were added 0.24 g. (0.0012 mole) of bis(2-butadienylmethyl) acetal, 0.005 g. of N-phenyl-β-naphthylamine, 0.33 g. (0.0012 mole) of *p*-phenylenebismaleimide,[14] 15 ml. of dimethylformamide, and 30 ml. of acetone. After the solution was heated under reflux for 18 hr. at 70°, the acetone was removed by distillation *in vacuo*, and the resulting clear solution was poured into 300 ml. of ether. The precipitated polymer was cooled, centrifuged, and removed by filtration to give 0.43 g. (76%) of a white polymer VIII, softening at 185–194°. The intrinsic viscosity in dimethylformamide at 50° was 0.08.

Polymer IX from Bis(2-butadienylmethyl) Acetal and Benzidinebismaleimide.—To a solution of 0.165 g. (0.00085 mole) of the acetal in 25 ml. of acetone were added 0.005 g. of *N*-phenyl-β-naphthylamine, 0.292 g. (0.00085 mole) of benzidinebismaleimide, and 20 ml. of dimethylformamide. After the resulting solution was heated under reflux at 80° for 18 hr., the acetone was removed under reduced pressure, and the remaining solution was poured into 500 ml. of ether to precipitate the polymer. This mixture was centrifuged and the polymer was collected on a filter to yield 0.25 g. (55%) of a brick-red polymer IX, softening at 170–174° with an intrinsic viscosity of 0.19.

Polymer X from Bis(2-butadienylmethyl) Hexamethylenedicarbamate and *p*-Phenylenebismaleimide.—A mixture of 0.090 g. (0.00027 mole) of bis(2-butadienylmethyl) hexamethylenedicarbamate, 0.072 g. (0.00027 mole) of *p*-phenylenebismaleimide, and 0.005 g. of N-phenyl-β-naphthylamine was dissolved in 25 ml. of dimethylformamide contained in a 50-ml. flask fitted with a condenser. After the solution was heated at 75° for 22 hr., the cooled solution was filtered to remove a small amount of insoluble material. The filtrate was then poured into 200 ml. of water, and the precipitate was collected and dried to yield 0.10 g. (62%) of a tan polymer X, softening at 74–78°, with an intrinsic viscosity of 0.20.

Anal. Calcd. for $(C_{32}H_{36}N_4O_8)_x$: C, 63.57; H, 5.96. Found: C, 63.39; H, 5.72.

Polymer XI from Bis(2-butadienylmethyl) Hexamethylenedicarbamate and Benzidinebismaleimide.—After a solution of 1.00 g. (0.00298 mole) of bis(2-butadienylmethyl) hexamethylenedicarbamate and 1.02 g. (0.00298 mole) of benzidinebismaleimide in 40 ml. of dimethylformamide was heated at 105° for 24 hr., the cooled solution was poured into 2000 ml. of ether. After the mixture was cooled, the brown precipitate was removed by filtration to yield 1.08 g. (53%) of the polymer XI, which softened at 133–137° and had an intrinsic viscosity of 0.19.

Anal. Calcd. for $(C_{38}H_{40}N_4O_8)_x$: C, 67.06; H, 5.88. Found: C, 66.82; H, 5.61.

Polymer XII from Bis(2-butadienylmethyl) *m*-Xylylenedicarbamate and *p*-Phenylenebismaleimide.—After a solution of 0.13 g. (0.00037 mole) of bis(2-butadienylmethyl) *m*-xylenedicarbamate, 0.10 g. (0.00037 mole) of *p*-phenylenebismaleimide, and 0.005 g. of N-phenyl-β-naphthylamine in 20 ml. of dimethylformamide was heated at 100° for 24 hr., the cold polymer solution was poured slowly into a solution of 200 ml. of ether and 200 ml. of petroleum ether (b.p. 60–80°). The resulting precipitated material was collected on a filter and dried to yield 0.13 g. (56%) of tan polymer XII, softening at 90–95°, with an intrinsic viscosity of 0.05.

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(13) The authors are grateful to Dr. Eugene Kraiman, formerly of the Union Carbide Plastics Co., Bound Brook, New Jersey, for a generous sample of this maleimide.

(14) The authors are grateful to Dr. John S. Meek, Department of Chemistry, University of Colorado, Boulder, Colorado, for samples of these two bismaleimides.

Polymer XIII from Bis(2-butadienylmethyl) *m*-Xylylenedicarbamate and Benzidinebismaleimide.—A solution of 0.31 g. (0.00090 mole) of benzidinebismaleimide, 0.32 g. (0.00090 mole) of bis(2-butadienylmethyl) *m*-xylylenedicarbamate and 0.005 g. of *N*-phenyl-β-naphthylamine in 25 ml. of dimethylformamide was heated at 100° for 24 hr. After addition of the polymer solution to 700 ml. of ether, the precipitated polymer was removed by filtration and dried to yield 0.45 g. (72%) of the tan powdery polymer XIII, softening at 145–150°, with an intrinsic viscosity of 0.15.

Notes

Elimination Reactions of α-Halogenated Ketones. VIII.[1a] Efficiency of Chloride Ion and Perchlorate Ion in the Promotion of Dehydrobromination of 2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone in Solvent Acetonitrile

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It has been shown in a previous communication[2] that addition of tetraethylammonium bromide to an acetonitrile solution of 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) leads to a facile second-order elimination reaction, yielding only the endocyclic α,β-unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II). Concurrent substitution would merely regenerate the bromotetralone I, and it was not established as to whether bromide ion exchange accompanied the elimination reaction. It has been found that an identical elimination reaction is promoted by the addition of chloride ions as tetraethylammonium chloride.

At 25.0° the chloride ion-promoted elimination reaction is 26 times faster than for that promoted by an identical concentration of bromide ions. At 37.0° the reaction yielded 100% olefin formation as measured by acid production and a 99% yield of the endocyclic α,β-unsaturated ketone II was isolated. No evidence for any accompanying 2-benzyl-2-chloro-4,4-dimethyl-1-tetralone (III) was obtained.

Throughout each individual run the integrated second-order rate coefficients, first order with respect to bromotetralone I and first order with respect to tetraethylammonium chloride were constant during the initial stages of reaction and it appears that each hydrogen ion eliminated removes from the reaction mixture one kinetically active chloride ion, presumably as undissociated hydrochloric acid. Since the bromide ions liberated are less reactive than chloride ions by a factor of 26, only during the later stages of each run would interference by bromide ions be discernible. The formation of hydrochloric acid rather than hydrobromic acid is consistent with the excess of chloride ions over bromide ions present during the initial stages of reaction and with the known stronger acidity of hydrobromic acid over hydrochloric acid in solvent acetonitrile.[3]

The majority of the runs were followed by determination of the acidity developed within the solution but in one instance a run was followed by determination of the increase in halide ion concentration. It was found that at a given temperature the initial second-order rate coefficients were identical, independent of whether the reaction was followed by determination of the development of acidity or the development of halide ion.

The constant value obtained for the initial second-order rate coefficient over a wide range of reactant concentrations (Table I), clearly shows that reaction cannot involve a rapid substitution of chloride for bromide followed by elimination either from the chlorotetralone III or from an equilibrium mixture of bromotetralone I and chlorotetralone III.

The frequency factor of $10^{11.4}$ l. mole^{-1} sec.$^{-1}$ is greater than for that for bromide ion-promoted elimination[2] of $10^{10.9}$ l. mole^{-1} sec.$^{-1}$ and the activation energy of 18.5 kcal./mole is lower than for bromide ion-promoted elimination of 19.7 kcal./mole. It can be seen that both frequency factor and activation energy considerations favor at a given temperature a higher rate for chloride ion-promoted elimination relative to that of bromide ion-promoted elimination.

An attempt to determine the relative rates of bromide ion- and chloride ion-promoted elimination in 87% aqueous ethanol failed; solvolysis of

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[1] (a) For paper VII in this series see D. N. Kevill, P. H. Hess, P. W. Foster, and N. H. Cromwell, *J. Am. Chem. Soc.*, **84**, 983 (1962); (b) To whom corresponding concerning this article should be addressed.

[2] D. N. Kevill and N. H. Cromwell, *J. Am. Chem. Soc.*, **83**, 3812 (1961).

[3] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *ibid.*, **83**, 3927 (1961).