This is a reducing power that can be due only to the reduced products formed by the reaction of carbon monoxide in the presence of palladous chloride and water. If iodine is present, palladium black does not form until the iodine is all consumed. This indicates that it is the palladium in solution which is the effective catalyst and not palladium black.

Additional evidence that palladium black is not the effective catalyst is shown by the reaction of vanadium solutions with carbon monoxide. Qualitative experiments were done using pervanadyl ion as the oxidizing agent. No formation of palladium black occurred as long as the yellow tint of the pervanadyl ion remained. When the reduction to vanadyl ion was complete, palladium black precipitated at once and no further reduction occurred. The absence of further reduction of vanadyl to vanadic ion also indicates the probable absence of adsorbed hydrogen on the surface of the palladium black. These experiments also indicate that the mechanism of the action of the palladium salt as a catalyst does not involve free hydrogen on the surface of palladium black.

Similar evidence that palladium black is not the effective catalyst is seen in the work of Shepherd[8] and co-workers who have used the catalytic effect of palladium in the detection and estimation of carbon monoxide in gases. Shepherd uses palladium sulfate to catalyze the formation of molybdenum blue by reduction of complex silicomolybdates with carbon monoxide. The green to dark blue colors formed on the surface of the silica gel supporting the active reagents are clear, which indicates that the formation of palladium black cannot be appreciable.

This evidence supports the statements that dissolved palladium, probably palladous chloride, is the effective catalyst and that palladium black is not essential for the catalysis. Adsorbed hydrogen is therefore not involved in the reaction. The absence of hydrogen from the mechanism is also indicated by the fact that the rate over the *p*H range 0–*ca.* 6.4 is constant. While this evidence is not conclusive as to the over-all mechanism, it points to the probable existence of a two-valent palladium couple constantly undergoing reduction and oxidation.

Summary

1. The reaction $CO + I_2 + H_2O = CO_2 + 2HI$ in acid solution has been found to be strongly catalyzed by palladous chloride.
2. Measurements of relative rates of the reaction show the rate to be essentially constant over *p*H range 0 to *ca.* 6.
3. The absence of formic acid and of adsorbed or free hydrogen is indicated.
4. The palladium catalyst has been shown to be effective in the dissolved state and not as palladium black.

COLUMBUS 10, OHIO RECEIVED DECEMBER 2, 1948

(8) Martin Shepherd, *Anal. Chem.*, **19**, 77–81 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

The Ultraviolet Absorption Spectra of Substituted Bitolyls

BY LUCY W. PICKETT,[*] MARIAN GROTH, SUSAN DUCKWORTH AND JANICE CUNLIFFE

The effect of steric hindrance on the ultraviolet absorption spectra of biphenyls has been studied by a number of investigators, some of whom are cited here.[1,2,3,4,5,6] It has been generally recognized that an increase in the intensity of absorption may be correlated with the approach to coplanarity of the benzene rings and hence to the extent that resonance structures involving both rings are possible. The present study of a group of bitolyls, namely, 6,6′-dinitro-2,2′-bitolyl, 5,5′-dinitro-2,2′-bitolyl, 6,6′-diamino-2,2′-bitolyl (I), 5,5′-diamino-2,2′-bitolyl (II), 4,4′-diamino-2,2′-bitolyl (III), 4,4′-diamino-3,3′-bitolyl (IV), as well as the hydrochlorides of the last four compounds is of interest in this connection. Kuhn and Rometsch[7] have reported measurements of the absorption, rotation dispersion and circular dichroism of I. The absorption curves for 4,4′-dinitro-2,2′-bitolyl and 4,4′-dinitro-3,3′-bitolyl have been determined.[6]

Experimental

Preparation of Compounds.—These compounds have all been reported in the literature[8] so that details are given only where procedures differed from those published.

6,6′-Dinitro-2,2′-bitolyl.—This was prepared by Ullmann synthesis from 2-iodo-3-nitrotoluene and purified by repeated crystallization from absolute alcohol; m. p. 110.8–111.3° (cor.).

6,6′-Diamino-2,2′-bitolyl.—The compound just described was reduced by stannous chloride in glacial acetic acid.[9] By the following slightly modified procedure a better yield was obtained: 4 g. of the nitro compound was suspended in 12 ml. of glacial acetic acid and to this was added 40 g. of stannous chloride in 100 ml. of concentrated hydrochloric acid. The mixture was stirred for two hours,

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[*] Harvard University, Lalor Fellow, 1938.

(1) Pickett, Walter and France, THIS JOURNAL, **58**, 2296 (1936).

(2) O'Shaughnessy and Rodebush, *ibid.*, **62**, 2906 (1940).

(3) Williamson and Rodebush, *ibid.*, **63**, 3018 (1941).

(4) Pestemer and Mayer-Pitsch, *Monatsh.*, **70**, 104 (1937).

(5) Jones, THIS JOURNAL, **63**, 1658 (1941).

(6) Sherwood and Calvin, *ibid.*, **64**, 1350 (1942).

(7) Kuhn and Rometsch, *Helv. Chim. Acta*, **27**, 1080, 1346 (1944).

(8) Fanta, *Chem. Revs.*, **38**, 139 (1946).

(9) Kenner and Stubbings, *J. Chem. Soc.*, **119**, 600 (1921).

allowed to stand overnight, treated with a slight excess of 20% sodium hydroxide and extracted with ether. The white crystalline product was purified by repeated crystallization from absolute alcohol; m. p. 135–135.5° (cor.).

5,5′-Dinitro-2,2′-bitolyl.—Preparation of this by coupling the 2-iodo-4-nitrotoluene by means of copper bronze gave low yields as has been reported.[8] The method used by Sherwood and Calvin[6] for the preparation of 2,2′-dimethyl-4,4′-dinitrobiphenyl was used. Recrystallization from alcohol gave a product whose physical properties agreed with that from the first method. The crude yield was however much higher and the purification more easily accomplished; m. p. 181.4–181.9° (cor.).

5,5′-Diamino-2,2′-bitolyl.—This was prepared in similar fashion to the isomer above. The reduction seemed to be complete in one hundred fifty minutes but stirring was continued for one hour. Sodium hydroxide was then added until the tin compound dissolved and the amine was extracted with ether. After evaporation of the ether a glassy solid remained which was purified by dissolving in hot 25% hydrochloric acid. The hydrochloride which crystallized was filtered, dissolved in water and converted to the white crystalline amine by passing ammonia through the solution; m. p. 101–101.8° (cor.).

4,4′-Diamino-2,2′-bitolyl.—This was prepared by reduction of the corresponding nitro compound, kindly supplied by Dr. Calvin,[6] and was purified by conversion to the hydrochloride. The latter was recrystallized twice and changed to the free amine by passing ammonia through the aqueous solution. The white crystalline product melted at 105.5–106.5° (cor.).

4,4′-Diamino-3,3′-bitolyl.—The dihydrochloride of *o*-tolidine, obtained from Eastman Kodak Co., was crystallized repeatedly. The amine was formed by passing ammonia into an aqueous solution of the dihydrochloride; m. p. 129.2° (cor.).

Measurement of Ultraviolet Absorption Spectra.—Measurements were made with a Beckman spectrophotometer, Model DU, which had been tested with a solution of potassium acid phthalate. A solution containing one gram per liter in a 1.003-cm. cell had an optical density of 0.420 at 2640 Å. and 0.641 at 2810 Å., thus falling within the range of the instruments surveyed by Ewing and Parsons.[10] The temperature of the cell compartment was maintained at 25° in all measurements used in the calculation of ionization constants. The compound was weighed on a semimicro balance and dissolved in purified ethyl alcohol of tested transmission or in hydrochloric acid solution of known strength. At least two independent determinations were made in each case.

The curves were plotted in terms of the molecular extinction coefficient, ϵ, defined as d/cl where l is the cell length and d the optical density, c the molar concentration. In the case of equilibrium mixtures of the amine and its ions, the total concentration of these forms was used to give an apparent extinction coefficient.

Measurement of *p*H.—The *p*H determinations were made with a Beckman *p*H meter, Model G. The standards used for calibration included a 0.05 *m* solution of Bureau of Standards potassium acid phthalate[11] with a *p*H of 4.00. Titrations of the amines in alcohol–water mixtures with standard hydrochloric acid were carried out.

Discussion of Results

The absorption curves of the two dinitrobitolyls are shown in Fig. 1. The 5,5′-dinitrobitolyl has an absorption band which is appreciably more intense than that of the 6,6′-dinitrobitolyl. This is in accord with expectations since the steric hindrance in the latter compound must be very great because of the bulky nitro and methyl groups. Although methyl groups in the *o*-position as in 2,2′-bitolyl have been shown to cause effective interference,[2] Sherwood and Calvin[6] have noted that in the case of 2,2′-dimethyl-4,4′-dinitrobiphenyl their interaction was not sufficient to prevent resonance between the rings to any large extent. The more intense absorption of the 5,5′-dinitrobitolyl as compared with the 6,6′-isomer is consistent with the latter view.

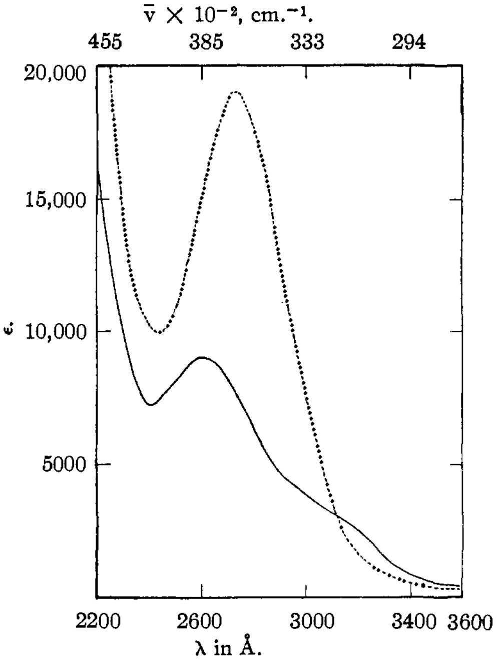

Fig. 1.—Absorption curves showing molecular extinction coefficients plotted against wave length of 6,6′-dinitro-2,2′-bitolyl (—), and 5,5′-dinitro-2,2′-bitolyl (- - - - -) in ethanol.

However, when the bitolyls are compared with the corresponding nitrotoluenes[6,12] the absorption bands are found to be similar in position but of lower intensity than would be expected. This is especially true of the 6,6′-dinitro-2,2′-bitolyl whose absorption maximum is only slightly higher than that of *m*-nitrotoluene rather than the twofold value which would be expected. This suggests that the effect of the steric hindrance is not alone to prevent coplanarity of the benzene rings but to block coplanarity of the nitro group with the ring to which it is attached.

The absorption curves of the four diaminobitolyls are shown in Fig. 2. While it was anti-

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(10) Ewing and Parsons, *Anal. Chem.*, **20**, 423 (1948).

(11) Hamer, Pinching and Acree, *J. Research Natl. Bur. Standards*, **36**, 48 (1946).

(12) Brown and Reagan, THIS JOURNAL, **69**, 1032 (1947).

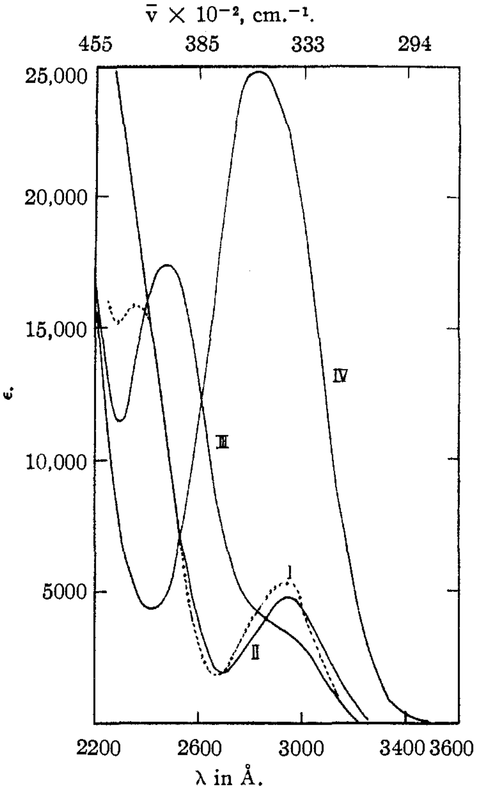

Fig. 2.—Absorption curves of diaminobitolyls I, II, III and IV in ethanol.

cipated that the 6,6'-diamino-2,2'-bitolyl (I) would have more steric hindrance than the others and hence be less absorptive, the small size of the amino group makes this difference of less importance than in the case of the larger nitro group. Counterbalancing this is the tendency of the amino group in the 6-position to increase the electron density of the ring-joining or co-annular bond[8] as the result of the displacement of the unshared electron pair of the nitrogen toward the biphenyl nucleus. Resonance considerations would indicate that the amino group in the 5-position would not contribute to the double bond character of the co-annular bond. Thus it seems reasonable that compounds I and II are similar in the absorption band near 2900 Å. because of the compensation of the two effects of steric hindrance and the electronic contribution of the amino group. In the case of *o*-tolidine (IV) there would be no steric hindrance to coplanarity of the rings and the amino groups are in a favorable position to contribute to the electron density of the co-annular bond. These factors correlate with the marked intensity of the absorption band at 2840 Å. By a similar argument, the 4,4'-isomer (III) would be expected to be intermediate between II and IV; while this is the case, there is a shift in position of the band which makes the interpretation less clear-cut than in the other cases.

In order to test further this explanation of spectral differences, the different diaminobitolyls were measured in hydrochloric acid solutions of a range of acidity in order to observe the effect

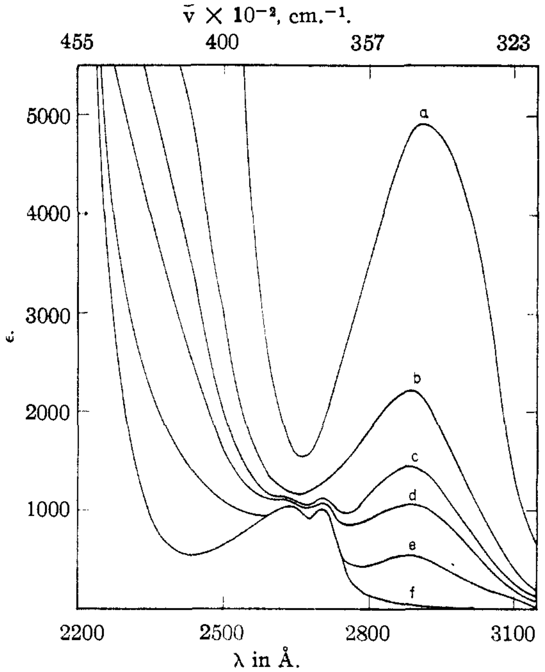

Fig. 3.—Absorption curves of 6,6'-diamino-2,2'-bitolyl in ethanol (a) and in excess hydrochloric acid: 0.001 *N* (b), 0.005 *N* (c), 0.01 *N* (d), 0.025 *N* (e), and 2 *N* (f).

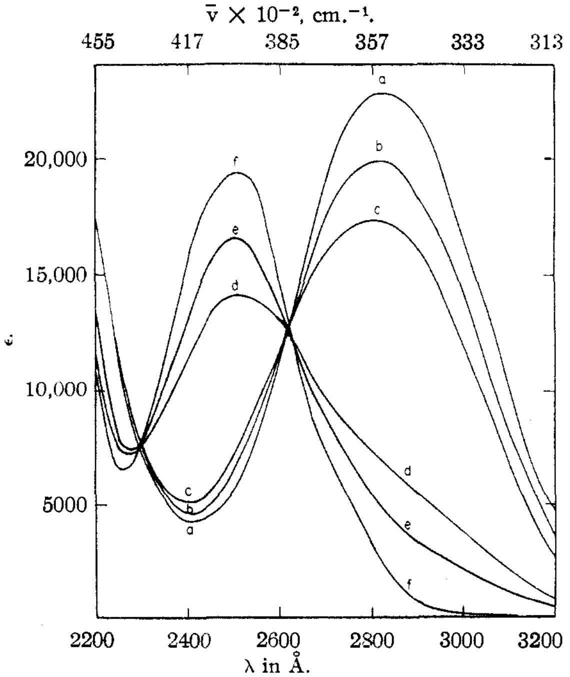

Fig. 4.—Absorption curves of *o*-tolidine (IV) in aqueous solutions of *p*H: 10.29 (a), 4.72 (b), 4.19 (c), 3.04 (d), 2.73 (e) and in 2 *N* hydrochloric acid (f).

of stabilizing the electron pair of the nitrogen so that it could no longer contribute to the resonance of the molecule. The changes of apparent extinction coefficient with *p*H for two of the four isomers (I) and (IV) are shown in Figs. 3 and 4. The 5,5′-diamino isomer (II) gave a set of curves very similar to those of I except that the intermediate curves were found at appreciably higher *p*H values. In all cases unless otherwise indicated the molar ratio of acid to amine was larger than two, since the conversion was incomplete at the stoichiometric point.

A number of conclusions may be drawn from the results. In all four cases the long wave length absorption band disappeared in the acid solution and a limiting curve was found which was not affected by further increases in hydrogen ion concentration. In the case of the three compounds with methyl groups in the 2,2′-positions, the limiting curve showed an absorption band at 2600–2700 Å. with a maximum extinction coefficient about 1000. This is similar to the absorption curve of 2,2′-bitolyl.[3] In like manner the acid solution of *o*-tolidine (IV) showed an intense absorption band at 2500 Å. comparable with that of 3,3′-bitolyl. These facts indicate that the substitution of charged NH_3^+ groups in a bitolyl molecule has but little effect on the absorption spectra of the latter.

The comparative base strength, measuring the ease of acquisition of the proton by the different isomers, could be determined from the results. It was necessary first to determine whether the singly charged or the doubly charged ion was responsible for the limiting curve in the acid solution. By analysis of the crystals of I obtained from 3 *N* hydrochloric acid it was shown that the doubly charged ion was present (Cl calcd. for $C_{14}N_2H_{16}\cdot 2HCl$, 24.86; found 24.72, 24.58). The intermediate absorption curves therefore represent equilibrium mixtures of doubly charged ions, singly charged ions and amine molecules.

Calculation of Ionization Constants.—Spectrophotometric methods have been used for the successful calculation of the two dissociation constants of *p*-hydroxybenzoic acid[13] where the two constants differ greatly and the intermediate ion may be identified. In the present studies the first and second ionization constants show but a small difference and it is impossible for a solution containing only the singly charged ion to exist. This fact together with the low solubility in water of these amines and their weakness as bases, make any method of determination of their ionization constants somewhat uncertain.

Three approaches to the problem were made. First potentiometric titration curves of each were made and the constants found from the *p*H at the points where the molar ratio of acid to amine was one-half and three halves, respectively (method A).

The second approach (method B) may be illustrated in the case of compound I. It was assumed that in solutions of sufficiently high acidity, the concentration of free amine was negligible. Since at a wave length of 2900 Å. the doubly charged ion has negligible absorption, the concentration of the singly charged ion could be evaluated as d/ϵ where d is the optical density of the solution in a 1-cm. cell and ϵ is the molecular extinction coefficient of this ion. A number of solutions of differing *p*H values were measured at this wave length and an expression for K_1 (acid) set up for each of the form.

$$K_1 = \frac{[NH_2Ar_2NH_3{}^+]aH^+}{[NH_3{}^+AR_2NH_3{}^+]} = \frac{d/\epsilon\ (aH^+)}{(C_0 - d/\epsilon)}$$

where K_1 is an apparent ionization constant defined in terms of the activity of the hydrogen ion (aH^+) and the molarity of the other substances,[13] and C_0 is the original concentration of amine in the solution.

By equating expressions for K_1, the molecular extinction coefficient for the singly charged ion could be found, and from this K_1 could be determined.

A method used by Stearns and Wheland[14] for finding the dissociation constant of 2,4-dinitroaniline in ethanol solution was adapted for the present work (method C). By combining expressions for the true and apparent extinction coefficients of the singly charged ion with that for K_1 an equation was obtained $1/\epsilon' = 1/\epsilon + aH/K_1\epsilon$. Hence by plotting the hydrogen ion activity against the reciprocal of the apparent extinction coefficient (ϵ') for different solutions, ϵ and K_1 were found from the intercept and slope of the straight line obtained.

The values obtained by the different methods are shown in Table I.

TABLE I

	pK_1 (acid)[a]			pK_2 (acid)
Method	A	B	C	A
6,6′-Diamino-2,2′-bitolyl	...[b]	2.2	2.1	3.7
4,4′-Diamino-3,3′-bitolyl	3.3	3.5	3.4	4.5
4,4′-Diamino-2,2′-bitolyl	3.7	...[c]	...[c]	4.9
5,5′-Diamino-2,2′-bitolyl	3.8	3.8	3.8	5.0

[a] pK_1 (acid) = $pK_w - pK_2$ (base). [b] Conversion to doubly charged ion incomplete. [c] No suitable wave length for measurement.

The results show that the 6,6′-isomer is markedly different from the other three compounds in that it is a weaker base and has a larger ratio of the two ionization constants. This seems reasonable in that the crowded conditions in that part of the molecule would be expected to interfere with the reaction with the first hydronium ion, and electrostatic forces would further interfere with the acquisition of the second proton. The increasing order of base strength of the other three compounds is compatible with steric effects and with the decreasing tendency of the electrons of the nitrogen to be displaced toward the biphenyl

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[13] Sager, Schooley, Carr and Acree, *J. Research Natl. Bur. Standards*, **35**, 521 (1945).

[14] Stearns and Wheland, THIS JOURNAL, **69**, 2025 (1947).

nucleus; and indicates that the greatest base strength is found when the amino groups are in the 5,5′-position rather than the 4,4′- and that the non-planar molecule has greater base strength than a corresponding planar molecule.

Acknowledgment.—The work was completed under contract with the Office of Naval Research. The authors also wish to acknowledge the help of Katherine Matthews and Constance O'Hara who did some of the exploratory work.

Summary

Ultraviolet absorption curves of two dinitrobitolyls and four diaminobitolyls have been determined in alcohol solution. The results give additional information regarding the effect of steric hindrance and position of the substituent group on the absorption of the molecule and are in accord with predicted effects.

The absorption curves of the four diaminobitolyls have been studied in hydrochloric acid solutions of different strengths. Ionization constants for the equilibria between amine, singly and doubly charged ions were calculated by potentiometric and spectrophotometric means.

SOUTH HADLEY, MASS. RECEIVED JUNE 15, 1949

[CONTRIBUTION NO. 94 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER CO.]

Copolymerization. XIV.[1] Copolymerization by Non-radical Mechanisms

BY CHEVES WALLING,* EMORENE R. BRIGGS, WILLIAM CUMMINGS AND FRANK R. MAYO

Although the "copolymerization equation"[2] describing the composition of a copolymer in terms of feed composition and monomer reactivity ratios contains no assumption as to charge type of the active center involved, and although it was noted in the first paper on copolymerization from this laboratory that copolymer compositions may vary with polymerization mechanism,[2b] application of the equation to "ionic" or "polar" polymerizations has only recently been established by Alfrey and Wechsler[3] and by Florin.[4] The purpose of this paper is to report the results of a similar investigation carried out concurrently with early work on radical copolymerization in this laboratory.[2b,5] Because few monomers could be found sufficiently similar in reactivity in ionic polymerization to yield copolymers, the investigation was not carried very far; nevertheless, it showed copolymerization to be an elegant tool for distinguishing between mechanisms of polymerization by different catalysts, and permitted a consideration of some of the differences which distinguish carbonium ion, radical, and carbanion-type polymerizations.

Styrene–methyl methacrylate was the monomer pair chosen for preliminary work. Previous papers have shown that an equimolecular mixture of these substances, polymerized at 60° by a free radical mechanism using benzoyl peroxide as a catalyst, yields an initial copolymer containing 51 mole % styrene, and this composition is unchanged by the addition of good or poor solvents[2b,6,7] or by carrying out the reaction in emulsion,[8] and is only slightly affected by changes in temperature.[7] Strikingly different results are obtained when these monomers are copolymerized using "ionic" catalysts. On the one hand, stannic chloride or boron trifluoride etherate leads to an initial polymer consisting of almost pure polystyrene. On the other, metallic sodium or potassium produces initially over 99% pure polymethyl methacrylate (*cf.* Table I).

Stannic chloride and boron trifluoride etherate belong to the class of generalized acid or Friedel–Crafts-type catalysts which apparently, providing a proton source[9,10] or other suitable material[11] is available, give rise to polymerization through an active center of the carbonium ion type.[12,13] The composition of the styrene–methyl methacrylate product, in keeping with both the failure of acid catalysts to polymerize methyl methacrylate alone and the ready solvolysis of compounds such as the α-phenethyl halides,[14] supports the idea that a substituted benzyl carbonium ion is more stable and more easily formed than a carbonium ion with an α-carbomethoxy group.

The result with metallic sodium or potassium is even more interesting, since it helps to establish the mechanism of this type of polymerization, for which both radical[15] and carbanion[16] active cen-

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[*] Harvard College B.A. 1937.

[1] For the preceding paper in this series, see Walling, THIS JOURNAL, **71**, 1930 (1949).

[2] (a) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); (b) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944); (c) Wall, *ibid.*, **66**, 2050 (1944).

[3] Alfrey and Wechsler, *ibid.*, **70**, 4266 (1948).

[4] Florin, *ibid.*, **71**, 1867 (1949).

[5] Lewis, Mayo and Hulse, *ibid.*, **67**, 1701 (1945).

[6] Nozaki, *J. Polymer Sci.*, **1**, 445 (1946).

[7] Lewis, Walling, Cummings, Briggs and Mayo, THIS JOURNAL, **70**, 1519 (1948).

[8] Smith, *ibid.*, **68**, 2067 (1946).

[9] Evans, Holden, Plesch, Polanyi, Skinner and Weinberger, *Nature*, **157**, 102 (1946).

[10] Norrish and Russell, *ibid.*, **160**, 543 (1947).

[11] Pepper, *Trans. Faraday Soc.*, **45**, 397 (1949).

[12] Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

[13] Williams, *J. Chem. Soc.*, 775 (1940).

[14] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, Ch. V and VI.

[15] Bolland, *Proc. Roy. Soc.* (*London*), **A178**, 24 (1941).

[16] (a) Price, "Reactions at Carbon–Carbon Double Bonds,"