TABLE III

VELOCITY CONSTANTS FOR THE REACTION OF AMYLSODIUM WITH *as*-DIPHENYLETHYLENE AT 25°

	Without triethylamine				With one equivalent of triethylamine		
Time, hr.	0.167	0.333	0.5	0.667	0.0833	0.167	0.333
R[a]	0.157	0.150	0.155	0.156	0.144	0.153	0.157
O	.227	.227	.227	.227	.227	.227	.227
M	.0064	.0106	.209	.0300	.0164	.0279	.0640
D	.0012	.0048	.0124	.0200	.0052	.0145	.0242
M_s	.0027	.0045	.0045	.0055	.0027	.0045	.0064
k_1	.28	.28	.57	.65	1.4	1.2	1.5
k_2	10	12	15	11	36	28	10

[a] R = reagent = amylsodium; O = olefin = 1,1-diphenylethylene; M = monomeric adduct; D = dimeric adduct; M_s = substituted jonomeric adduct.

usually the case, proper allowance was made for the solubility of the solids in the solvent used. Some pertinent data are recorded in Table III. The graph in Fig. 1 shows the induction period.

Effect of Triethylamine.—Triethylamine (Eastman Kodak Co.) was distilled before use. The general procedure was the same as described above save for the addition of the amine. The effect of one equivalent of triethylamine on the respective velocities is shown in Table III. The effect of two and three equivalents is shown in Fig. 2. The period of the reaction was ten minutes. Triethylamine accelerates somewhat the addition of phenylsodium to diphenylethylene.

Summary

Amylsodium and phenylsodium cause styrene to polymerize. No addition products were isolated under conditions extremely favorable for such a result.

Amylsodium adds readily to 1,1-diphenylethylene. A mono- and di-adduct are formed. Some metalation of the mono product results.

Amyllithium is less reactive and amylpotassium is more reactive than amylsodium in the addition reaction.

Butylsodium and benzylsodium also add to the ethylene compound but phenylsodium scarcely reacts.

An induction period is present in the reaction between diphenylethylene and amylsodium.

The formation of the mono adduct is approximately independent of the quantity of the insoluble organoalkali metal reagent but is directly dependent on the concentration of the ethylene. The formation of the di-adduct is dependent on the concentration of the mono adduct and the ethylene.

Triethylamine accelerates the addition reaction.

CAMBRIDGE, MASS. RECEIVED APRIL 1, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polymerization. V. The Catalytic Polymerization of Butadiene by Phenylsodium and Amylpotassium

BY AVERY A. MORTON AND ROBERT L. LETSINGER

Previous work[1] in this Laboratory has shown that the polymerization of butadiene with amyl- and benzylsodium can be so carried out that intermediate products of low molecular weight are obtained; but that, curiously enough, the reaction with phenylsodium gives rubber with little, if any, such intermediates even though the conditions are exceptionally well suited for their isolation. The present examination of this reaction indicates (a) that phenylsodium and amylpotassium, the latter under special conditions, exert an action that is catalytic and unrelated to the stepwise addition process by which amylsodium operates, (b) that complex formation between phenylsodium and sodium chloride and between amylpotassium and potassium chloride may play a part in the catalytic process and (c) the effect that benzene or triethylamine exerts on the polymerization induced by amylsodium is not the same as is exerted on the polymerization induced by phenylsodium. Mercury has a deleterious effect on the catalytic activity of phenylsodium.

Phenylsodium.—If phenylsodium polymerizes butadiene by the stepwise addition mechanism shown by amylsodium, the rates of the initiation reaction, k_i, caused by these two sodium containing reagents will differ widely, but the rates of chain growth, k_n, will either be in the same relative order if the respective influences of the amyl and phenyl groups are continued or will be equal if these influences are nullified over the lengthened chain. Now the k_i value for amylsodium must be reasonably high because a sizable quantity of the first adduct and of higher adducts can be isolated without difficulty[1,2] when butadiene is added dropwise to a large excess of the reagent and the mixture is then carbonated. Moreover, the addition reaction of this reagent with diphenylethylene, a compound unusually well suited for a

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[1] Morton, Patterson, Donovan and Little, THIS JOURNAL, **68**, 93 (1946).

[2] Morton, Brown and Magat, THIS JOURNAL, **68**, 161 (1946).

study of addition reactions, shows[3] a rate that is readily measured. Not so, however, is the case with phenylsodium. The k_i value, if any addition takes place, is so low as to be indeterminate because no trace of a first adduct with butadiene is present. Furthermore, its reaction with diphenylethylene cannot be observed during a period in which the corresponding one with amylsodium is over 70% complete, and is found to be only 5% complete[3] over a period more than nineteen times that long. If, therefore, the mechanisms of polymerization are similar and phenylsodium really does add to the diene, its k_i value probably does not exceed $^1/_{250}$ the k_i value for the amylsodium reaction. This initial slow rate should bring about an over-all lower conversion of diene to polymer, yet the experimental fact is that the amount of polymer formed by phenylsodium in a given time is as high, if not higher, than that produced by an equivalent amount of amylsodium (see Table I).

Another unique feature of the phenylsodium product is that the intrinsic viscosities of the polymers, though low, are approximately constant, irrespective of whether the conversion is 8 or 87%, or whether the diene/reagent ratio is 0.5 or 70. This fact contrasts sharply with the amylsodium products for which an increase in the diene/reagent ratio causes an increase in the intrinsic viscosity (see Table I). These observations suggest that phenylsodium and amylsodium cannot polymerize butadiene by the same mechanism and that the former exerts a catalytic action.

TABLE I

EFFECT OF CHANGE IN THE RATIO OF BUTADIENE TO ORGANOSODIUM REAGENT ON THE INTRINSIC VISCOSITY [η] OF THE PRODUCT

Butadiene, moles	RNa[a]	RNa, moles	Molal ratio diene to RNa	Vol. of pentane diluent	Conversion of diene, %	[η]	Recovered $PhCO_2H$, %
0.25	A	0.19	1.3	250	80	...[b]	
1.0	A	.083	12	300	84	0.071	
						1.07	
0.72	A	.007	100	60	89	2.7	
.11	P	.21	0.5	200	87	0.67	72
.21	P	.21	1.0	200	45	.74	79
.25	P	.21	1.2	200	60	.69	70
.28	P	.21	1.3	200	77	.74	68
.27	P	.05	5.0	200	23	.71	70
.35	P	.02	17.5	200	8	.69	
.70	P	.01	70[c]	60	75	.84	

[a] A = amylsodium. P = phenylsodium. [b] The molecular weights of these products were too low to be measured readily by the viscosity method. In the next experiment the two values were obtained on fractions obtained by alcohol precipitation from petroleum solution. [c] Reaction in pressure bottle.

Amylpotassium.—At 0° amylpotassium reacts with butadiene much as does amylsodium, except for the fact that more substitution occurs. At −30° this reagent induces a catalytic polymerization of the butadiene to a rubbery mass which has an intrinsic viscosity of 1.2. For the conditions, see Table II.

TABLE II

PRODUCTS OF THE REACTION OF AMYLPOTASSIUM WITH BUTADIENE AT DIFFERENT TEMPERATURES

Ratio[a] B/R	React. temp., °C.	Low polymer G	Rubber G
1.0	0	4.8	Trace
1.45	0	6.5	Trace
3.0	0	5.0[b]	0.8
1.2	−20 to −40		4.6
2.0	−25 to −30	0.3	5
2.5	−25 to −30	.54	4.6

[a] Molal ratio of butadiene to amylpotassium. [b] This product was a thick liquid.

The reaction is clearly of a different type at a lower temperature. Instead of a reduction in the total yield caused by a reaction about thirty degrees lower, the combined amount of all products was approximately as high as at 0°. Instead of a larger amount at 0° of the first stage of the addition reaction, the major product was the high polymer.

The different character of the reaction induced by amylpotassium at the two temperatures can be contrasted with the normal temperature effects found with amylsodium and phenylsodium. Amylsodium undergoes the addition reaction at 25° but at −25° the addition reaction is suppressed to the point where no reaction occurs. Phenylsodium at 25° causes a catalytic polymerization, but at −25° this polymerization process is suppressed. These two reagents show normal effects in that the reaction which progresses at the higher temperature occurs to a less degree at the lower temperature. The reversal of the usual rule in the case of amylpotassium accords with the idea of a change in the type of reaction.

Catalytic Activity and Complex Formation.—The phenylsodium, used in the polymerizations described above, was prepared from chlorobenzene and sodium. When phenylsodium is prepared from bromobenzene, the catalytic activity is largely lost, the conversion is far less and the intrinsic viscosity of the polymer is less than a third that found for the polymer made with the phenylsodium prepared from chlorobenzene. Carbonation shows, however, that the quantity of phenylsodium is the same irrespective of the phenyl halide used.

Similar results are obtained with the *p*-isopropylphenylsodium, prepared from the corresponding chloro- and bromo-*i*-propylbenzene (see Table III).

The activity of phenylsodium, prepared from bromobenzene, is raised by the addition of sodium chloride, particularly when that chloride is in the finely divided state obtained *in situ* by addition of amyl chloride to phenylsodium. Sodium methoxide and sodium hydroxide also cause the inactive phenylsodium (derived from bromoben-

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[3] Morton and Wohlers, THIS JOURNAL, **68**, 167 (1946).

Table III

Effect of Salts on the Polymerization of Butadiene by Phenylsodium and *p*-Isopropylphenylsodium

RCl used to prepare RNa	Salt formed from halide	Salt added to the reaction	Butadiene conversion, %	Polymer, n	Acid recovered, %
C_6H_5Cl	NaCl	None	60	0.69	70
C_6H_5Br	NaBr	None	22	.19	53
C_6H_5Br	NaBr	None	20	.21	57
C_6H_5Br	NaBr	NaCl[a]	22	.22	62
C_6H_5Br	NaBr	NaCl[b]	23	.36	65
C_6H_5Br	NaBr	NaCl[c]	73	.57	53
C_6H_5Br	NaBr	$NaOC_6H_5$	Trace	..	65
C_6H_5Br	NaBr	$NaOCH_3$	34	.49	61
C_6H_5Br	NaBr	NaOH	51	.52	50
i-$C_3H_7C_6H_4Cl$	NaCl	None	47	.26	56
i-$C_3H_7C_6H_4Br$	NaBr	None	8	Low	74

[a] One-third equivalent of ordinary dry sodium chloride, finely powdered. [b] One equivalent of sodium chloride as in [a]. [c] One-half equivalent of sodium chloride prepared *in situ* by the addition of the required quantity of amylchloride to the phenylsodium so that sodium chloride would form from the second stage of a Wurtz reaction.

zene) to become more active. Sodium phenoxide has no effect. Sodium bromide obviously has no action of its own in terminating the chain since it is present with sodium chloride, sodium methoxide, and sodium hydroxide when these agents are added in order to overcome the effect of the bromide.

These results show that the polymerizing activity is not dependent on phenylsodium alone and suggest that it may be caused by an association with other specific salts, such as sodium chloride, sodium methoxide or sodium hydroxide. A double salt, a simple form of which could be one with a complex anion $[C_6H_5NaX]^+Na$, where X is Cl, OCH_3 or OH seems likely. Such a complex differs from that which the organoalkali metal reagents form with tertiary amines, because the latter are strong electron donors and would form complex cations. So far the agents under discussion in this series appear to cause chain growth by a catalytic process or by a stepwise addition method, according as they may have a complex anion or a complex cation, but the converse does not necessarily follow that all such salts with complex anion or cation will thus affect a diene.

The catalytic activity of amylpotassium at −30° can be explained readily on the above basis and low temperatures would be favorable to the formation of complexes.

Effect of Benzene and Cumene.—The effect of benzene on the reaction of phenylsodium with butadiene could well be different from its effect on the reaction between amylsodium and the diene if the polymerization processes are different, although the manner in which a difference is manifested might not be known because the character of the catalytic process, by which phenylsodium causes polymerization, is not yet defined. If the stepwise addition with amylsodium obeyed the rules followed by this class of salts,[4] there would be no reason to expect that benzene would alter appreciably the nature of the reaction, because the organosodium salt formed by 1,2- or 1,4-addition has an allyl or more likely a diallyl sodium type of structure; and such compounds are less reactive toward acid–salt interchange[4,5] than is phenylsodium. Hence an appreciable amount of acid–salt interchange between benzene and the adduct is not expected.

This opinion is confirmed by experiments between amylsodium and benzene when the conditions are so adjusted as to avoid formation of phenylsodium by the metalation of benzene with amylsodium. One equivalent of amylsodium and two equivalents of butadiene are allowed to react together to form the usual mixture of mono-, di- and tri-addition products. One equivalent of benzene is then added, the mixture is stirred for thirty minutes, and eight more equivalents of butadiene are added. The final products are essentially the same as those obtained in the absence of benzene (see Table IV).

Table IV

Influence of Benzene on the Addition Polymerization of Butadiene Caused by Amylsodium

			Rubber fractions				
Equivalents of C_5H_6	$C_5H_{11}Na$, moles	C_4H_6, moles	Insoluble in ether, G	Sol. in ether but pptd. by acetone, G	[η]	Sol. in ether-acetone G	[η]
0	0.08	1.0	2.2	1.2	1.07	42.0	0.071
1.0	.08	1.0	2.6	1.5	1.0	43.0	.069

On the other hand, the addition of a like amount of benzene to the mixture in which phenylsodium is effecting the polymerization of butadiene causes a general lowering in the yield, a shift toward a higher percentage of an ether-soluble polymer and a marked reduction in the amount of ether-insoluble polymer; and the use of benzene as a solvent causes a large increase in the yields of ether-soluble polymer and the same decrease in the ether-insoluble polymer. The results are tabulated in Table V.

Table V

Influence of Benzene on the Polymerization of Butadiene by 0.21 Equivalent of Phenylsodium

Benzene, moles	Ether soluble polymer, G	%	Ether insoluble polymer, G	Benzoic acid recovered, %
0	6.0	74	2.1	70
0.21	5.0	86	0.8	74
2.1[a]	11.0	92	0.9	74

[a] Solvent.

Benzene has a marked effect on the intrinsic viscosity of the polymer produced by phenylsodium, whereas cumene has only a slight effect. The values for the polymers produced in pentane,

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(4) Morton, *Chem. Rev.*, **35**, 1 (1944).

(5) Morton and Brown, This Journal, **69**, 160 (1947); Morton, Brown, Letsinger, Magat and Holden, *ibid.*, **67**, 2224 (1945).

cumene, and benzene are 0.69, 0.62 and 0.16 respectively. Since the order is also the order of decrease in relative hydrocarbo acidities,[4] the inference might be made that chain termination is connected with acquisition of a proton from the solvent.

Effect of Triethylamine.—Triethylamine has already been shown[2] to accelerate the addition process of polymerization without altering appreciably the character of that process. Triethylamine has also been found to accelerate the addition of amylsodium or of phenylsodium to 1,1-diphenylethylene.[3] If the catalytic action of phenylsodium depends on the presence of a specific complex with sodium chloride the addition of triethylamine might break the complex by formation of another one with a complex cation. Such a process would eliminate the catalytic character of the polymerization reaction and convert it to one more like an addition process.

Experiment confirms this view. In three separate tests the main portion of the polymer, subsequent to carbonation, was an oil of such low molecular weight that a determination of the intrinsic viscosity was meaningless. The use of four equivalents of triethylamine produced a material which, after carbonation and esterification with diazomethane, was partially volatile in a molecular still. A portion which boiled at 250°/1 micron had a saponification equivalent of 475, indicative of the presence of considerable low molecular weight material. Other pertinent data are in the table below.

TABLE VI

EFFECT OF TRIETHYLAMINE ON POLYMERIZATION OF BUTADIENE INDUCED BY PHENYLSODIUM

Equiv. of Et_3N to PhNa		0.5	1	4
Polymer	Ether-sol. (S), g.	4.7	5.7	6.5
	Ether-insol. (I), g.	1.6	0.6	0.2
Ratio S/I		2.9	9.5	32.5
Benzoic acid, % recov.		69	68	66

These facts accord with the view that triethylamine largely, if not entirely, destroys the catalytic action of phenylsodium on butadiene and converts the process of polymerization into an addition one in which the k_i portion of the reaction is relatively low compared to that of butadiene with amylsodium.

Effect of Mercury.—The deleterious influence of mercury in polymerization by phenylsodium was first suspected in an experiment in which phenylpotassium was prepared from diphenylmercury and potassium metal. No polymer was found, although the recovery of benzoic acid from the carbonated product was 44% of the theoretical amount possible. When the same experiment was carried out in benzene as a solvent instead of pentane, about 5.5 g. of rubbery polymer was obtained together with about 40% recovery of benzoic acid. Mercury (0.25 mole) was then added to phenylsodium and found to destroy its catalytic effect either in pentane or in a mixture of pentane and benzene. The effect is not surprising in view of the known tendency for sodium and mercury to displace each other in organoalkali metal compounds.

The authors are greatly indebted to the Research Corporation for financial support of this work.

Experiments

The Apparatus and Preparation of the Alkali Metal Reagents.—All reactions, unless otherwise specified, were carried out in the high-speed stirring apparatus regularly employed in these studies.[2] The reaction flask had the usual two creases in the side and the inverted cone bottom found so effective in this apparatus. The capacity before these alterations was 500 ml. The organosodium reagents were prepared by dropwise addition of the halide or other compound to two equivalents of sodium or potassium metal. The sodium metal was previously prepared in finely divided state by vigorously stirring in decane at about 110°. When cooled the metal settled slowly and was freed from decane by decantation and washing with pentane. The potassium sand was prepared similarly in decane. All operations, including preparation of the sand, were carried out in an atmosphere of nitrogen. The yields of organosodium reagents are given in Table VII.

Polymerizations.—The polymerizations were carried out in an atmosphere of nitrogen by dropwise addition of butadiene, over a period of approximately one hour, to 200 ml. of a pentane suspension of the organosodium reagent, prepared as described in above. The mixture was stirred for another hour and then carbonated by forcing the contents of the flask on solid carbon dioxide. When the carbon dioxide had largely evaporated, a little water was added carefully in order to remove the few small particles of sodium metal usually present, and then more water was added until a total of 200 ml. was used. Hydroquinone (0.4 g.) was added as a stabilizer. The pentane was removed by warming on a steam-bath. The polymer was then lifted from the aqueous layer, acidified with hydrochloric acid, and steam distilled in order to remove decane and benzoic acid. The rubbery mass was dried by distilling chloroform from it, and then freed from chloroform by reduced pressure.

For Table III the relative viscosities of the polymer (0.2 g. in 25 ml.) were determined in chloroform at 25°. In some cases, as illustrated in Table IV, the rubber was fractionated by dissolving as much as possible in ether, and then adding acetone to the ether solution. The rubber was thus divided into ether insoluble, ether-acetone insoluble and ether–acetone soluble. In other cases, the acetone precipitation was omitted.

The aqueous solution and suspension, left after removal of the viscous polymer, was acidified. The benzoic and similar acids were recovered by the usual processes of filtration, and extraction of the portion which remained dissolved. The weight of dried crude acid thus recovered is recorded in the columns of several of the tables. Usually the crude acid was of good quality that melted at 120° or better after a single crystallization. For cuminic acid a single crystallization was adequate to obtain a pure compound. If adducts of low molecular weight were present, they were converted to methyl esters and were fractionated, or were classified as oily polymers of low molecular weight.

Variations in the Polymerization Process.—The variations in the ratio of diene to organoalkali reagent are indicated clearly in the tables, together with other variations of temperature. All agents, such as sodium chloride, triethylamine and the like were added to the mixture before the addition of butadiene. The contents were then stirred thoroughly for about an hour in order to insure that the maximum amount of effect would be present during the subsequent polymerization.

TABLE VII

PREPARATION OF ALKALI METAL REAGENTS

Halide or other compound	G.	Mole	Solvent[a]	Metal	Addn. of RX to Na Temp., °C.	Addn. of RX to Na Time, min.	Stirring cond. after addn. Temp., °C.	Stirring cond. after addn. Time, min.	Yield of RNa, %
$C_5H_{11}Cl$	26.6	0.25	P	Na	−10	60	−10–25	60	75–80
$C_5H_{11}Cl$		.25	P	K[b]	−10–15	60	−10–0	25	3
C_6H_5Cl	28.2	.25	P	Na	25	60	25	120	86
C_6H_5Cl			B	Na	30[c]	60	30	240	74[d]
C_6H_5Cl			C	Na	30[c]	60	30	240	73[d]
C_6H_5Br			P	Na	15	60	25	240	53[d]
C_6H_5Cl			P	K	−20[e]	60	25	60	Trace
					+20	60	25	60	Trace
C_6H_5F			P	K	20	60	25	60	Trace
$(C_6H_5)Hg$	35.5	.10	P	K	20[f]	80	20–30	180	44[d]
$(C_6H_5)_2Hg$	35.5	.10	B	K	25	120	25	240	40[d]
p-$C_3H_7C_6H_4Cl$[g]	24	.22	P	Na	20	60	25	240	37[d]
p-$C_3H_7C_6H_4Br$		.22	P	Na	20–25	60	25	120	73?[d]

[a] P = pentane. B = benzene. C = cumene; 200 ml. of solvent usually used. [b] 0.625 g. atom of potassium used in place of the usual 0.5 g. atom, although theoretical quantities were used in some of the runs not recorded in this table. [c] 45° at start of reaction. [d] The yield is determined at the end of the polymerization reaction. [e] +20 at the start of the reaction. [f] 30° at the start of the reaction. [g] This chloro compound appeared to contain some of the ortho isomer.

Summary

In the polymerization of butadiene, phenylsodium exerts a catalytic effect, which is distinct from the stepwise addition process imparted by amylsodium.

Amylpotassium at 0° causes an addition polymerization but at −30° causes a catalytic process.

Phenylsodium prepared from chlorobenzene and sodium makes a far better agent than phenylsodium from bromobenzene and sodium. A reagent prepared from *p*-chloroisopropylbenzene is also better than one from *p*-bromoisopropylbenzene. These facts accord with the view that a complex between the phenylsodium and sodium chloride is present.

Benzene has little influence on the addition polymerization induced by amylsodium but markedly affects the one caused by phenylsodium. Triethylamine accelerates addition polymerization by amylsodium but changes the character of the phenylsodium process from a catalytic process to a stepwise addition process.

Mercury has a deleterious effect on the polymerization caused by phenylsodium probably because of a destruction of the organoalkali metal reagent.

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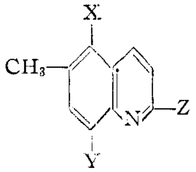
[CONTRIBUTION FROM THE ROSS CHEMICAL LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

Some Derivatives of 6-Methylquinoline

BY JULIUS D. CAPPS

The purpose of this investigation was to study certain previously unreported nitro, amino, substituted amino and arsonic acid derivatives of 6-methylquinoline. Conditions were worked out for the successful application of heretofore recorded reactions to the synthesis of compounds I through XIV.



(see Table I for compounds IX through XIV)

I Z = OH, X = NO_2, Y = H
II Z = Cl, X = NO_2, Y = H
III Z = OH, X = NH_2, Y = H
IV Z = Cl, X = NH_2, Y = H
V Z = Cl, X = H, Y = NH_2
VI Z = Cl, X = C_6H_5CONH—, Y = H
VII Z = Cl, X = H, Y = C_6H_5CONH—
VIII Z = Cl, X = H, Y = CH_3CONH—

An attempt to reduce nitro compound I with tin and hydrochloric acid, however, gave chiefly a chloroamine.

Experimental

6-Methylquinoline.—A combination of the procedure reported by Clarke and Davis[1] with that of Cohn[2] for synthesizing quinoline was used to convert *p*-toluidine into 6-methylquinoline needed in this investigation.

6-Methyl-5-nitroquinoline.—6-Methylquinoline (130 g.) was nitrated by the method of Bogert and Fisher[3] to give 170 g. (99.3% yield) of 6-methyl-5-nitroquinoline.

6-Methyl-5-aminoquinoline.—The directions of Noelting and Trautmann[4] sufficed to produce 6-methyl-5-aminoquinoline (30.0 g., 93.8% yield) from 6-methyl-5-nitroquinoline (38.0 g.).

2-Hydroxy-6-methyl-5-nitroquinoline (I).—Subjection of 6-methyl-5-nitroquinoline to the action of hypochlorite

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(1) H. T. Clarke and Anne W. Davis, "Organic Syntheses," Coll. Vol. 1, 2nd ed., 478 (1941).

(2) Essie W. Cohn, THIS JOURNAL, **52**, 3685 (1930).

(3) M. T. Bogert and H. L. Fisher, *ibid.*, **34**, 1570 (1912).

(4) E. Noelting and E. Trautmann, *Ber.*, **23**, 3657 (1890).