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Alkali Metal Adducts of Aromatic Nitro Compounds—Reactions and Use in Polymerization of Vinyl Monomers

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ABSTRACT

The reaction of alkali metals with nitrobenzene and p-nitrotoluene in THF at various molar ratios was found to lead to the formation of radical ions, dianions, and alkali metal adducts of reduction derivatives of the nitro compounds such as azo- and azoxybenzene. The anionic polymerization of styrene, methyl methacrylate, methacrylonitrile, and acrylonitrile by these anions was investigated. All the initiators did not polymerize styrene while the least reactive radical-anion was found to polymerize acrylonitrile completely, methacrylonitrile to a small extent, but not methyl methacrylate.

The order of reactivity of those adducts toward organic halides was similar to that found in polymerization. Metallation of polynitrostyrene by lithium biphenyl solution led only to partial conversion of the nitro groups to radical-anions which were not reactive.

INTRODUCTION

The reaction of alkali metals with equivalent amounts of nitrobenzene in aprotic solvents such as tetrahydrofuran (THF) 1,2-dimethoxy ethane, and ether lead to the formation of the corresponding radical anion [1]. When an excess of alkali metal is used, the corresponding dianion is obtained [2]. The reactions between similar adducts of alkali metals and aromatic polycyclic hydrocarbons with alkyl and aryl halides have been extensively studied [3]. Reactions were quantitative and were recommended for determination of halogen in organic compounds [4]. On the other hand, less is known about the reaction of alkali metal adducts of aromatic nitro compounds with organic halides. The relative reactivities toward organic halides of sodium complexes of some aromatic nitro compounds as well as anils, imines, and hydrocarbons were determined [5]. It was found that the aromatic nitro compounds were the least reactive in this group.

It was our interest in the present work to investigate the extent of reaction of both radical anions and dianions of nitro aromatic compounds with several organic halides of different types and reactivity.

Alkali metal adducts of aromatic hydrocarbons are well known as initiators for anionic polymerization of vinyl monomers [6]. It was reported that electrochemically generated radical anions of nitrobenzene were able to polymerize acrylonitrile in DMF while such radicals were not reactive toward methyl methacrylate and styrene [7]. It was interesting to investigate the use of nitrobenzene radical anion and dianion prepared in the conventional way as initiators for anionic polymerization of vinyl monomers.

EXPERIMENTAL

Materials

THF (Frutarom) was dried as previously described [3] and was stored on CaH_2. Nitrobenzene, p-nitrotoluene, bromobenzene, benzyl chloride, α-bromonaphthalene, butyl bromide, propanol, biphenyl, methanol (B.D.H.), iodobenzene, fluorobenzene (Eastman Kodak), allyl bromide, allyl chloride (Hopkins and Williams), and 2,4-dinitrofluorobenzene (Fluka) were used.

Alkali Metal Adducts

Alkali metal adducts of nitrobenzene, p-nitrotoluene, and biphenyl were prepared by reaction of the compounds with the alkali metal in dry THF under inert atmosphere. The reactions were carried out in a closed flask equipped with a self-sealing rubber cap for the introduction of reagents by syringes. The reaction flask was flamed in vacuo and flushed with argon.

Titration of the Alkali Metal Adducts with Propanol

The adduct solution (5 ml) was injected, under vacuo, into a dry closed flask. Propanol (in molar excess) was added, followed after 30 min by 2,4-dinitrofluorobenzene. The unreacted propanol was determined quantitatively by GLC using toluene (0.2 ml) as internal reference.

Reaction of Sodium Adduct of Nitrobenzene with Mercury

The adduct solution (5 ml) was injected, under vacuo, into a dry closed flask containing purified mercury (5 ml). After 14 hr, THF (5 ml) was injected and the solution was analyzed by GLC using naphthalene (0.01 g) as internal reference.

Reaction of Alkali Metal Adducts and Halides

One equivalent of the halide was introduced, respectively, to two and six equivalents of alkali metal adduct, and the reaction mixture was left overnight. Methanol (2 ml) was added in the case of halobenzenes, and methanol-conc HCl (1:1) in the other cases. The reaction products were determined by GLC after addition of internal references.

Polynitrostyrene

A modified procedure [9] was used. Polystyrene (10 g) was dissolved in fuming HNO_3 (100 g) and the solution was kept at -10°C. A nitration mixture composed of fuming HNO_3, conc H_2SO_4, and water (133:41:27) was added dropwise. After 2 hr at room temperature the polymer was precipitated by water, washed several times with hot water, triturated with boiling water for 0.5 hr, filtered, left overnight in water, and then filtered and dried at 120° in vacuo over P_2O_5. The polymer was purified by being extracted for 24 hr with THF in a Soxhlet apparatus: mp 235-239°, %N = 9.7.

Cross-linked Polynitrostyrene

The above nitration procedure was used in the nitration of cross-linked polystyrene (2% divinyl benzene). The polymer contained 9.9% N.

Reaction of Benzyl Chloride with the Lithium Adduct of Polynitrostyrene

Biphenyl lithium solution (0.67 N, 30 ml) was added to polynitrostyrene (2.32 g) in THF (40 ml). The extent of reaction was followed by acid titration of aliquots of the biphenyl lithium solution. Unreacted biphenyl lithium was removed by extraction with dry THF. Benzyl chloride (0.38 ml, 3.4 mmoles) was added, the reaction mixture left at room temperature for 20 hr, and the products were determined by GLC.

Determination of Reaction Products

The reaction products were determined by GLC using a Packard gas chromatograph Model 7300/7400. Nitrogen was used as carrier gas. Glass columns of 1.80 m and 0.25 in. tubing with solid support of chromosorb W/HMDS, 45/60 in the case of propanol and chromosorb P (60-80 mesh) in the other cases were used. Benzene, chlorobenzene, allyl bromide, and chloride were determined using 20% squalane as the liquid phase. Biphenyl, naphthalene, dibenzyl, bromobenzene, iodobenzene, α-bromonaphthalene, benzyl chloride, butyl bromide, nitrobenzene, azobenzene, and azoxybenzene were determined using 20% SE 30 as the liquid phase. Fluorobenzene was determined using 10% tricresyl phosphate as the liquid phase, and propanol by using 20% tricresyl phosphate as the liquid phase. Benzene, fluorobenzene, chlorobenzene, allyl bromide, allyl chloride, propanol and nitrobenzene were determined using toluene as the internal reference. Naphthalene, dibenzyl, and p-bromonaphthalene were determined using biphenyl as the internal reference. Biphenyl, bromobenzene, iodobenzene, azobenzene, and azoxybenzene were determined using naphthalene as the internal reference. Benzyl chloride and butyl bromide were determined using ethyl benzene as the internal reference.

Anionic Polymerization

The polymerizations were carried out at 0°C under anhydrous conditions, as described previously [8]. The polymerization was terminated after 0.5 hr by the addition of conc HCl (1 ml). The polymers were precipitated by methanol, filtered, and dried.

Molecular Weight Determination

Intrinsic viscosities were determined from one-point measurements of polymer solution viscosity (at $c = 0.1$ g/dl) using the equation $\eta = \eta_0 \exp[\eta]c$ [10]. The molecular weights were calculated from the Mark-Houwink equation:

$$[\eta] = KM^{\alpha}$$

For polymethyl methacrylate, $K = 0.70 \times 10^{-4}$, $\alpha = 0.720$, in toluene [11]; for polymethacrylonitrile, $K = 3.06 \times 10^{-3}$, $\alpha = 0.503$, in DMF [12]; and for polyacrylonitrile, $K = 2.33 \times 10^{-4}$, $\alpha = 0.740$, in DMF [13].

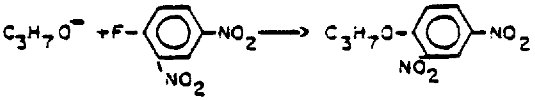
RESULTS AND DISCUSSION

Alkali metal adducts of nitrobenzene and p-nitrotoluene were prepared by reaction of lithium and sodium with aromatic nitro compounds in THF. The reaction was carried out using both equimolar amounts of the reactants and a molar excess of alkali metal.

Alkali metal adducts of aromatic compounds can be analyzed by acid titration after hydrolysis [14, 15], the amount of alkali hydroxide found being equivalent to the alkali metal in the adduct. When this analytical method was used for the determination of the alkali metal in the nitro adducts, high values were obtained. Thus when equimolar amounts of nitrobenzene and lithium were reacted, the amount of base titrated was twice as much as the original amount of lithium present in the reaction mixture. These high values may be understood from the report in the literature [16, 17] that radical anions or dianions of aromatic nitro compounds give aryl hydroxyl amine derivatives on hydrolysis. The presence of such bases will lead to high results when acid titration analysis is used.

Aryl hydroxylamines [18] in basic media are converted to the corresponding azo and azoxy derivatives, which are not titrated by acid. That is why different results were obtained when the acid titration was carried out at different time intervals after hydrolysis. Thus the normality of a hydrolysis mixture of lithium nitrobenzene adduct dropped from 0.84 to 0.56 $\underline{N}$ when the hydrolysis mixture was allowed to stand for 5 hr; the expected normality based on total consumption of the lithium present was 0.46.

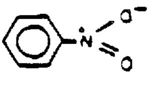
Direct titration with propanol was used for the analysis of alkali metal adducts of aromatic compounds [19], the disappearance of the color of the alkali metal adduct indicating the end point. In our case this end point could not be detected because the reaction mixture remained intensely colored so that we had to introduce modifications to permit the analysis of alkali metal adducts of aromatic nitro compounds by this method. Now, in the reaction of propanol with the alkali metal adduct of nitrobenzene, the propanol is converted to the corresponding alkoxide derivative. The amount of alkoxide formed is equivalent to the amount of alkali metal in the adduct. By using a known excess of propanol, unreacted alcohol can be determined by GLC and from this the alkali metal present in the adduct can be calculated. In order to prevent hydrolysis of propoxide to the alcohol during analysis, which would lead to low results, it was etherified immediately by reaction with 2,4-dinitrofluorobenzene:



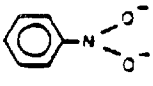
Addition of the 2,4-dinitrofluorobenzene was essential to obtain reproducible results. This method of analysis was checked by the determination of alkali metal in lithium biphenyl adduct. A 1.20 N solution of lithium biphenyl in THF (the normality determined by acid titration) was analyzed by this method and the normality found was 1.18 N.

The determination of the ratio of alkali metal/nitro group by this method is reported in Table 1. The results show that the amount of alkali metal found in the adduct is in agreement with that initially present in the reaction mixture.

We studied the formation of alkali metal adducts of nitrobenzene and p-nitrotoluene, using molar ratios of alkali metal/nitro compound = 1 or 2 and higher. The reaction of equimolar amounts of alkali metal and nitrobenzene was reported to yield anion radicals, I, and that with two equivalents of alkali metal to yield dianions, II,



I



II

We found that when a molar excess of lithium was used the molar ratio between reacted lithium, as determined by propanol titration, and the nitrobenzene exceeded 3. Since electron transfer to the dianion, II, does not seem possible, the results indicate that other reactions in which lithium metal is being consumed are taking place. Nitrobenzene via its alkali metal adduct may be converted by reaction with excess of lithium present to azo and azoxybenzene, which in turn can form adducts with lithium [20].

Thus more lithium will be consumed and analyzed. In fact, azobenzene and azoxybenzene were actually found in the reaction mixture on treatment with metallic mercury, as exemplified below. This treatment in the case of sodium benzophenone dianion was shown to decompose the adduct into its components [21].

When a solution in which the ratio of reacted sodium to nitrobenzene was 2.55 was added to mercury and later analyzed by GLC, it was found that 5% of the nitrobenzene present initially was converted to azobenzene and another 20% to azoxybenzene. When an adduct solution in which this molar ratio was 1.4 was subjected to the same treatment, it was found that 1% of the nitrobenzene present initially was converted to azobenzene and another 25% to azoxybenzene. This shows that such products can be formed even before all the nitrobenzene is converted to its dianion derivative.

Ion-radicals of Polynitrostyrene

It was interesting to investigate the ability of the nitrobenzene group substituted on a vinyl polymer backbone to form radical-anions. Polynitrostyrene was prepared by nitration of both soluble polystyrene and insoluble polystyrene (cross-linked with 2% divinylbenzene).

Polynitrostyrene of 9.7% N was used. The polymer was suspended in THF and the polyion-radical was prepared by electron transfer reaction with lithium biphenyl. Though excess of lithium biphenyl was used, only 39% of the nitro groups present reacted after 160 hr. Extent of reaction was determined from the decrease in lithium biphenyl concentration. When the polyradical anion was hydrolyzed in water and the filtrate was titrated with acid, it was found that 43% of the nitro groups were converted to radical ions. With the cross-linked polymer it was found that even after 17 days in lithium biphenyl solution only 7% of the nitro groups reacted. The decrease in the reactivity of the nitrobenzene group on the polymer should be attributed to limited accessibility to the polymer. The fact that the lower extent of reaction occurred with the cross-linked polymer supports this assumption.

It may be noted that the formation of azo- and azoxy-aryl derivatives during hydrolysis will lead to cross-linking, and thus a change in the solubility and the melting point of the polymer is expected. In fact, the polynitrostyrene radical ion lost its solubility in DMF after hydrolysis of its poly-anion radical and the regenerated polymer did not melt up to 360°.

TABLE 1. Alkali Metal Determination in Adducts of Nitro Aromatic Compounds[a]

[Alkali metal]/ [nitro compound]	Propanol Added (mmoles)	Propanol Unreacted[b] (mmoles)	Alkali metal in adduct[c] (mmoles)	[Alkali metal in adduct]/ [nitro compound]
Series A				
10.7	160	95	65	3.2
10.7	160	97	63	3.1
3.2	133	81	52	2.6
3.2	146	103	43	2.9
2.2	93	57	36	1.8
2.2	107	73	34	1.7
1.5	67	41	26	1.3
1.5	67	43	24	1.2
Series B				
10.7	160	102	58	2.9
10.7	160	106	54	2.7
2.2	120	79	41	2.0
2.2	120	83	37	1.8
1.2	67	48	19	1.0
1.2	67	47	20	1.0

Series C				
6.7	160	110	50	2.5
6.7	160	106	54	2.7
3.1	146	103	43	2.1
3.1	146	104	42	2.2
2.4	146	114	82	1.8
2.4	146	109	87	1.9
1.5	160	143	17	0.9
1.5	160	140	20	1.0

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[a] Experimental conditions: The nitro compound adducts were prepared by reacting the alkali metal with 50 ml solution of 0.4 M nitrobenzene in tetrahydrofuran. 5 ml of this solution was used for determining the alkali metal in the adduct by addition of propanol followed by 2,4-dinitrofluorobenzene. Series A, nitrobenzene reacted with Li. Series B, p-nitrotoluene reacted with lithium. Series C, nitrobenzene reacted with sodium.

[b] Determined by GLC.

[c] Calculated from the propanol titration.

Reactions of Lithium Adducts with Aryl and Alkyl Halides

The reaction of lithium adducts of nitrobenzene and p-nitrotoluene with alkyl and aryl halides was investigated using radical anions, dianions, and adduct solution in which the ratio of lithium to the nitro compound was higher than 2. It was shown that no reaction between nitrobenzene radical anion (molar ratio of lithium to nitrobenzene in solution = 0.8) and alkyl or aryl halides took place. The following halides were used: iodo-, bromo-, chloro-, and fluorobenzene; benzyl chloride; α-bromonaphthalene; allyl chloride; and butyl bromide. The dianion of nitrobenzene reacted only with the more reactive halides, benzyl chloride, allyl bromide, and butyl bromide; an excess of lithium adduct led to an increase in the extent of reaction (Table 2).

In this reaction several products are expected to be formed [22] such as the corresponding organometallic derivative of the alkyl halide, alkylation products of the alkali metal adduct and dimers, and disproportionation products derived from the alkyl halides. The relative proportions of these reactions were found to depend on the alkyl or halide (Table 2).

When a solution of lithium adducts of nitrobenzene and p-nitrotoluene in which the ratio of lithium in the adduct to the nitro compound was higher than 2 were reacted with the halides, it was found (Table 3) that all halides except chloro- and fluorobenzene reacted. The extent of reaction varied with the halide reactivity. When an excess of lithium adduct solution was used, an increase in reaction yield was observed. It is obvious that the higher reactivity of these adduct solutions as compared to those in which the molar ratio of Li to nitro compound = 2 (or less) should be attributed to the presence of other lithium compounds present in the reaction mixture such as lithium azo- and azoxybenzene derivatives, as mentioned before.

Anionic Polymerization Initiated by Lithium Adducts of Nitrobenzene

It was interesting to investigate the three types of lithium adducts of nitrobenzene in solution to find their effectiveness as initiators for anionic polymerization. Styrene, methyl methacrylate, methacrylonitrile, and acrylonitrile, which vary considerably in their reactivity as monomers, were used. The order of reactivity of the initiators (Table 4) was: adducts in which the ratio of lithium to nitrobenzene was higher than 2 > dianion of nitrobenzene > radical-anion. All three initiators did not polymerize styrene while the least reactive radical-anion was found to polymerize acrylonitrile completely, methacrylonitrile to a small extent, but not methyl methacrylate.

TABLE 2. Reaction of Lithium Nitrobenzene and p-Nitrotoluene Adducts with Organic Halides[a]

Nitro compound	Halide	(mmoles)	Lithium adduct (mmoles)	Reacted halide[b] (%)
Nitrobenzene	Benzyl chloride	2.0	4.0	12.0
Nitrobenzene	Benzyl chloride	2.0	12.0	40.0
Nitrobenzene	Allyl chloride	2.0	4.0	60.0
Nitrobenzene	Allyl chloride	2.0	12.0	86.0
Nitrobenzene	Butyl bromide	2.1	4.3	33.0
Nitrobenzene	Butyl bromide	2.1	12.9	60.0
p-Nitrotoluene	Butyl bromide	2.0	4.1	28.0
p-Nitrotoluene	Butyl bromide	2.0	12.3	52.0

[a] The lithium adducts used had a molar ratio of lithium to nitro compound of 2:1 and were prepared from 0.4 M nitro compound solution in THF. The organic halides were injected into the adduct solution.

[b] Determined by GLC using ethyl benzene as internal reference for benzyl chloride and butyl bromide, and toluene for allyl bromide.

TABLE 3. Reaction of Lithium Nitro Adducts ($[Li]/[-NO_2] > 2$) With Halides[a]

Halide	(mmoles)	Lithium adduct		Reacted halide	
		Mmoles	$[Li]/[-NO_2]$[b]	%	Li-derivative (%)[c]
Series A					
Iodobenzene	3.2	6.4	3.2	14.0	14.0
Iodobenzene	3.2	18.8	3.2	40.0	37.0
α-Bromonaphthalene	3.1	6.5	3.1	12.0	3.5
α-Bromonaphthalene	3.1	19.5	3.1	22.0	11.6
Benzyl chloride	3.2	6.4	3.2	81.0[d]	0.0
Benzyl chloride	3.2	19.2	3.2	87.0[e]	0.0
Allyl bromide	3.0	6.4	3.0	100.0	-
Allyl bromide	3.0	19.2	3.0	100.0	-
Allyl chloride	3.1	6.3	3.1	57.0	-
Allyl chloride	3.1	18.9	3.1	89.0	-
Butyl bromide	2.7	5.3	2.7	56.0	-
Butyl bromide	2.7	15.9	2.7	89.0	-
Series B					
Bromo benzene	2.6	5.1	2.6	4.5	3.2
Bromo benzene	2.6	15.4	2.6	12.5	9.3
Iodo benzene	2.6	5.1	2.6	14.5	11.2
Iodo benzene	2.6	15.6	2.6	38.4	38.4

α-Bromonaphthalene	2.5	4.9	2.5	23.5	1.6
α-Bromonaphthalene	2.5	14.7	2.5	20.0	3.2
Benzyl chloride	2.4	5.0	2.4	62.0	-
Benzyl chloride	2.4	15.0	2.4	96.0	-
Allyl chloride	2.5	5.0	2.5	60.0	-
Allyl chloride	2.5	15.0	2.5	100.0	-
Butyl bromide	2.4	4.9	2.4	34.0	-
Butyl bromide	2.4	14.7	2.4	78.0	-

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[a] The halide was injected into the adduct solution (5 ml). Series A, nitrobenzene adducts. Series B, p-nitrotoluene adducts.

[b] Determined by titration with propanol and 2,4-dinitrofluorobenzene.

[c] Percent of alkyl or aryl-Li formed from initial halide introduced.

[d] Dibenzyl 1.2% was found.

[e] Dibenzyl 2.9% was found.

TABLE 4. Polymerization of Vinyl Monomers by Lithium Nitrobenzene Adducts[a]

Monomer	(moles/liter)	$\frac{[\text{Lithium}]}{[\text{nitrobenzene}]}$[b]	Nitrobenzene adduct[c] (mole/liter)	Yield (%)	$[\eta]$ (dl/g)	Molecular weight[d]
Methyl methacrylate	0.93	3.2	0.074	100	1.44	938,000
Methacrylonitrile	1.19	3.2	0.095	100	0.45	20,100
Acrylonitrile	1.51	3.2	0.121	100	0.29	12,890
Methyl methacrylate	0.93	2.6	0.074	11	1.14	828,000
Methacrylonitrile	1.19	2.6	0.095	100	0.63	49,700
Acrylonitrile	1.51	2.6	0.121	100	0.29	12,890
Methyl methacrylate	0.93	1.9	0.074	18	1.20	749,000
Methacrylonitrile	1.19	1.9	0.095	54	0.45	20,100
Acrylonitrile	1.51	1.9	0.121	100	0.29	12,890
Methyl methacrylate	0.93	1.0	0.074	0	-	-
Methacrylonitrile	1.19	1.0	0.095	13	0.25	6,150
Acrylonitrile	1.51	1.0	0.121	100	0.45	23,710

[a] Polymerization was carried out by adding the adduct solution to the monomer (5 ml) solution in THF (45 ml). Polymerization was carried out for 0.5 hr at 0°.

[b] Molar ratio in the adduct.

[c] Concentration of the lithium in the adduct solution.

[d] Calculated from the intrinsic viscosities.

The higher reactivity of adducts in which the ratio of Li to nitrobenzene was more than 2 may be attributed to the presence, in relatively high concentrations, of such active anionic species as Li-azobenzene and Li-azoxybenzene, which were shown to be present in the adduct solutions.

Differences in reactivity between monosodium and disodium benzophenone, as initiators of anionic polymerization of vinyl monomers, were previously reported [23].

REFERENCES

[1] T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend, and S. I. Weissman, J. Phys. Chem., 57, 504 (1953).

[2] V. O. Luckashevich, J. Gen. Chem. USSR, 11, 1007 (1941); Chem. Abstr., 40, 1150 (1946).

[3] G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, Principles of Organometallic Chemistry, Methuen, London, 1968, p. 55.

[4] F. L. Benton and W. H. Hamill, Anal. Chem., 20, 269 (1948).

[5] A. Mathias and E. Warhurst, Trans. Faraday Soc., 58, 942 (1962).

[6] M. Szwarc, Carbanions, Living Polymers, and Electron Transfer Processes, Wiley (Interscience), New York, 1968, p. 16.

[7] G. Mengoli, G. Farnia, and E. Vianello, Eur. Polym. J., 5, 61 (1969).

[8] A. Zilkha and Y. Avny, J. Polym. Sci., A1, 549 (1963).

[9] H. Zenftman, J. Chem. Soc., 1950, 982.

[10] D. K. Thomas and T. A. J. Thomas, J. Appl. Polym. Sci., 3, 129 (1960).

[11] S. N. Chinai, J. D. Matlack, A. L. Resnick, and R. J. Samuels, J. Polym. Sci., 17, 391 (1955).

[12] C. G. Overberger, E. M. Pearce, and N. Mayes, Ibid., 34, 109 (1959).

[13] R. L. Cleland and W. H. Stockmayer, Ibid., 17, 473 (1955).

[14] N. P. Scott, J. F. Walker, and V. L. Hansley, J. Amer. Chem. Soc., 58, 2442 (1936).

[15] N. P. Keevil and H. E. Bent, Ibid., 60, 193 (1938).

[16] V. O. Lukaschevich, Justus Liebigs Ann. Chem., 521, 198 (1936).

[17] B. Kastening, Electrochim. Acta, 9, 241 (1964).

[18] E. H. Rodd, Chemistry of Carbon Compounds, Vol. IIIA, Elsevier, Amsterdam, 1954, p. 132.

[19] F. M. Brower and H. W. McCormic, J. Polym. Sci., A1, 1749 (1963).

[20] M. V. George, P. B. Talukdar, C. W. Gerow, and H. Gilman, J. Amer. Chem. Soc., 82, 4562 (1960).

[21] W. E. Bachmann, Ibid., 55, 1179 (1933).

[22] J. F. Garst, Polym. Preprints, 11, 8 (1970).
[23] A. Zilkha, P. Neta, and M. Frankel, Bull. Res. Council Israel, 9A, 187 (1960).

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