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RADIOCHEMICAL ASSAY OF SOME GROUP I ORGANOMETAL DERIVATIVES USING TRITIATED PROPANOL

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SUMMARY

Hydrolysis of representative organometals of Group I by hydroxyl-tritiated n-propanol was investigated extensively as a method of analysis for these reactive substances. Using liquid scintillation counting as the radio-assay technique, a procedure was developed which permits determination of those organometals yielding hydrolysis products with boiling points above room temperature. The isotopic procedure is applicable widely to alkali metal-substituted hydrocarbons in presence of common sample impurities, including residual free metals. The method is similarly applicable to many of the radical anions formed in the electron transfer reaction of the metals with aromatic hydrocarbons in active ethers.

The radiochemical method was used as a reference technique to study the applicability of conventional titrimetric procedures to certain organometals of Group I, and particularly to metal-aromatic hydrocarbon complexes in tetrahydrofuran. The oxidimetric vanadium pentoxide method, as well as the disulfide cleavage method, yielded accurate results for freshly-prepared solutions of sodium naphthalene complex. Both titrimetric methods, however, failed with aged solutions, due to the presence of sodium hydride and other degradation products.

INTRODUCTION

Usefulness of many of the organometals derived from lithium, sodium, and potassium as initiators of anionic polymerization has greatly increased the importance in recent years of specific and sensitive analytical techniques for their characterization. Much of the impetus for these quantitative investigations stems from the fact that accurate and precise methods of initiator assay are desirable for the preparation of polymers having reasonably predictable number-average molecular weights. Of the organometals in question, those presently of greatest significance in polymer chemistry are alkyllithium compounds, radical anions formed in the electron transfer reaction between alkali metals and aromatic hydrocarbons, and oligomeric dianions derived from α-methylstyrene and 1,1-diphenylethylene.

A variety of essentially titrimetric methods have been proposed for assay of the more widely used organoalkali compounds. Thus, butyllithium has been determined using a modified double titration method[1], oxidimetrically[2], thermometrically[3], by high frequency titration[4], and through its reaction with *p*-tolyl disulfide[5], as well as by direct titration with an alcohol, using a visual indicator[6]. Radical anions and alkali metal-substituted alkylaryl hydrocarbons have been estimated by treatment with an excess of an alkyl halide and subsequent determination of the halide ion [7-10], by titration with an alcohol[11] or a standard solution of benzoic acid[12], and by measurement of base formed on hydrolysis[13]. Applicability of the methods for organolithium and effect of sample impurities are discussed in some detail in the respective papers. In the work dealing with the use of methyl iodide for determining the sodium–naphthalene complex[7], the effect of sodium hydride, an impurity in aged preparations of the complex[14], was not investigated. Interference of sodium hydride with all of the proposed titrimetric procedures for radical anions, however, makes an analytical technique desirable which is specific for these reactive intermediates.

This report describes a radiochemical method of analysis for alkali metal-aromatic hydrocarbon complexes which is applicable as well to many alkali metal-substituted aromatic and alkyl hydrocarbons. The solution of organometal is added to an excess of hydroxyl-tritiated n-propanol in dry toluene. Residual labile tritium is removed by washing the toluene solution of tritiated hydrolysis product with water. An aliquot of the dried solution is then taken for determination of combined tritium activity by liquid scintillation counting. The method permits determination of many organometal complexes and compounds of the elements of Group I without interference from hydrides, oxides, or alkoxides of the metals. Since the free metals do not interfere, the technique is useful for estimating quantitatively the extent of reaction in metallation of the α-carbon of alkylaryl hydrocarbons by metallic potassium[15].

EXPERIMENTAL

Preparation and radioassay of tritiated n-propanol

Reagent grade n-propanol was dried over Linde 4A molecular sieves and distilled. To 100 ml of distillate was added 0.5 λ of tritiated water of specific activity 1 curie per gram (New England Nuclear Corp.). An aliquot of 25 ml of this preparation was diluted to 100 ml with the purified n-propanol to provide a reagent having a specific activity of approximately 0.1 μCi/millimole.

The hydroxyl-tritiated n-propanol was assayed in a mixed solvent scintillator prepared by combining 1470 ml of toluene, 210 ml of methanol, 315 ml of anhydrous ethanol, 10.5 g of 2,5-diphenyloxazole (PPO), and 0.63 g of 1,4-bis-2-(4-methyl-5-phenyloxazolyl)benzene (Dimethyl-POPOP). A weighed aliquot of ca. 200 λ of the n-propanol-^{3}H was diluted to 100 ml with the mixed solvent scintillator and six 15-ml aliquots were transferred to 20-ml liquid scintillation counting vials. Radioactivity in the vials was counted in the spectrometer after one hour at 3°. A radioassay of the n-propanol was made each day it was used for analysis of organometals.

Ratio of specific activity of tritium in the mixed solvent scintillator, used for assay of the isotope in labile form, to that in toluene scintillator, used for assay of the sample solutions containing the isotope in non-labile form, was obtained with acetanilide-^{3}H. Specific activity of the propanol-^{3}H determined in the mixed solvent scintillator medium was converted to the corresponding specific activity in the toluene scintillator solution using this ratio.

Preparation of alkali metal complexes and compounds for analysis

All complexes of alkali metals and aromatic hydrocarbons were prepared in tetrahydrofuran (THF) distilled in an argon atmosphere from a mixture of naphthalene and excess sodium. Naphthalene was purified by vacuum sublimation; other aromatic hydrocarbons, of the highest available purity, were used as received. The aromatic hydrocarbon, THF, and excess alkali metal were added in a current of argon to a 500-ml, 3-neck, round bottom flask, equipped with a stirrer. Sodium metal, cut in the atmosphere to intentionally introduce sodium hydroxide or under dry heptane to suppress alkali formation, was used in most of the preparations. After a reaction period of 6-8 hours at -5 to $-10°$ or at 20 to 25°, the solution of the complex was transferred to a dried and argon-flushed pint bottle fitted with a toluene-extracted butyl rubber gasket under a perforated metal cap. The solutions were stored approximately 16 h at $-23°$ and analyzed after reaching room temperature.

Divalent anions were prepared from 1,1-diphenylethylene, as received, and from vacuum-distilled α-methylstyrene using the above procedure with excess sodium.

Toluene and 2-methylnaphthalene were metallated on the methyl carbon using potassium metal, with sodium oxide and barium oxide, respectively, as hydrogen acceptors[15]. Aliquots for analysis were taken from the vigorously-stirred suspensions.

Cyclohexyllithium in toluene and cyclopentyllithium in cyclohexane were assayed as received from Foote Mineral Co. 1,2-Dilithio-1,2-diphenylethane was prepared by treating *trans*-stilbene with excess lithium in THF. Solutions of dilithium–polyisoprene adducts in benzene/dimethyl ether[16] (DiLi-1) were analyzed as received from Lithium Corp. of America.

Radiochemical method of analysis

Fifty ml of reagent-grade toluene, dried over calcium hydride and distilled in an argon atmosphere, was transferred to a dried, argon-filled, 250-ml separatory funnel equipped with a Teflon stopcock. A quantity of tritiated n-propanol sufficient to provide an excess of 100–200% over that required for hydrolysis of the sample was then added. A weighed specimen of 2 to 20 ml of organometal solution was slowly added from a hypodermic syringe fitted with a stopcock and 15-cm 18-gauge needle. A larger needle was necessary with the preparations metallated in the presence of the oxides of sodium and barium. The funnel was swirled carefully as the sample was added. After addition of 50 ml of toluene, the organic phase was washed with 100 ml of water containing a slight excess of hydrochloric acid, then with water, and finally with saturated sodium chloride solution. The toluene solution was transferred to a 250-ml Erlenmeyer flask and dried by slow addition of freshly ground calcium hydride. After standing overnight, the supernatant phase was transferred to a 250-ml volumetric flask, the Erlenmeyer flask was rinsed with toluene and the solid was separated by centrifuging. The sample solution was diluted to volume with dry, distilled toluene.

Radioassays were made after pipeting three 5-ml aliquots of the sample solution into 20-ml counting vials and adding 10 ml of scintillator solution containing 7.5 g of PPO and 0.45 g of Dimethyl-POPOP in one liter of toluene. Radioactivity in the vials was counted in the liquid scintillation spectrometer after at least 1 h at 3°. Corrections for quenching effects relative to the toluene scintillator solution used for assay of the acetanilide-^{3}H were made using toluene-^{3}H as internal standard.

$$\text{Organometal content, meq/g} = \frac{50\,C}{S \cdot W} \text{ where,}$$

C = average radioactivity, in microcuries, corrected, in the vials,
S = specific activity, in microcuries/milliequivalent, of n-propanol-^{3}H in toluene scintillator,
W = weight of sample, g.

Titrimetric methods of analysis

The *p*-tolyl disulfide cleavage procedure was used as described[5] with the exception that 100-ml volumetric flasks were employed for the reactions and 15-ml aliquots were removed for amperometric titration. Sample weights were commonly taken to furnish 1.5 to 2 meq. of organometal, but did not exceed 10 g.

In the vanadium pentoxide method[2], dried toluene was used in place of heptane for all analyses. A reaction time of 15 min was employed.

Analyses using n-butyl bromide were performed by adding the sample solution to an excess of dry alkyl halide contained in a dried argon-flushed test tube fitted with a serum stopper. The bromide ion formed was determined by the method of Volhard.

Total base determinations were made by non-aqueous potentiometric titration. The organometal was hydrolyzed in a 1/1 isopropanol/ethylene glycol mixture, which was then titrated with a standard solution of hydrochloric acid prepared in the binary solvent.

Apparatus

A Packard Model 3303 Tri-Carb Liquid Scintillation Spectrometer was used for all radioassays.

RESULTS AND DISCUSSION

Use of tritiated hydrolytic agents in organometal chemistry

Hydrolysis of reactive organometals by compounds containing labile tritium has been shown to be a useful means for obtaining an insight into the mechanism of cleavage of metal–carbon bonds by such substances. These mechanistic studies involve measurement of the kinetic isotope effect of hydrogen in protolysis of the organometal when the latter is added to a large excess of proton donor. Extensive investigations[17–22] have been made of the hydrolysis of Grignard reagents by tritiated alcohols, phenols, water, and hydrochloric acid. The alcoholyses of tri-n-octylaluminum[23] and of the reaction products of triethylaluminum with 1-octene[24] have been studied in a similar manner. In addition, use of tritiated water for hydrolysis of the sodium–naphthalene complex in THF yielded evidence[25] in support of a mechanism previously proposed[26] for protonation of the radical anion.

Analytical use of the reactivity of certain organometal derivatives toward tritiated proton donors has heretofore been confined to determination of active centers in Ziegler and anionic polymerization. For experimental convenience, the methods employ addition of an excess of a labeled alcohol or acid to the polymer solution[27–30] or addition of a sample aliquot to an excess of alcohol in a hydrocarbon solvent[31]. Use of large excesses of labeled compounds in these techniques requires determination of the hydrogen kinetic isotope effect, which may be expressed as K_H/K_T, where K_H and K_T are the specific reaction rate constants in hydrolyses involving unlabeled species, respectively.

Magnitude of K_H/K_T depends, in general, on the strength of the organometal derivative as a proton acceptor relative to that of the substrate as a proton donor. Carbon–metal bonds in polyethylene prepared with titanium tetrachloride/alkylaluminum initiator, for example, reacted with tritiated methanol at 68° with an isotope effect of 3.7[27]. The polymeric carbanion of polybutadienyllithium is a much stronger base than carbon–metal bonds present in Ziegler polymerizations and reacts with lower aliphatic alcohols with a negligible isotope effect[31].

In the present method, use is made of this immediate and irreversible reaction of organic compounds and complexes of alkali metals with proton donors such as aliphatic alcohols for quantitative conversion of the derivatives to tritiated products. The reaction is conveniently performed by adding the organometal solution to a moderate excess of alcohol in a dry hydrocarbon. n-Propanol offers a reasonable compromise between volatility and ease of purification. Toluene is desirable as reaction medium because of its value as an efficient solvent in liquid scintillation counting. Composition of the mixed solvent scintillator solution employed in the present work for assay of the n-propanol-^{3}H is similar to that used previously for assay of substances containing labile tritium[32]. The high proportion of alcohols in this solution prevents significant loss of tritium activity by exchange with hydrogen of the glass containers.

Analysis of alkali metal-substituted hydrocarbons

Representative derivatives having alkyl hydrogen substituted by lithium, sodium, and potassium were assayed by the radiochemical and applicable titrimetric methods. The hydrolysis reaction $R^-M^+ + {}^3HOPr \rightarrow R^3H + MOPr$ limits usefulness of the present isotopic technique to those organometals which yield hydrocarbons of sufficiently low volatility to be quantitatively retained in the toluene solution during reaction and workup. Thus cyclopentyllithium, yielding a hydrocarbon of b.p. 49° was analyzed successfully, whereas analysis of n-butyllithium gave low results despite conditions designed to prevent volatilization of butane. Results for typical alkali metal-substituted hydrocarbons are given in Table 1.

In addition to wide applicability to the class of Group I organometal derivatives illustrated in Table 1, the radiochemical method possesses the additional advantage of being unaffected by free alkali metals often associated with organometallic compounds. Although the metal–alcohol reaction itself is not a source of error, protonation of alkali metal–aromatic hydrocarbon complexes liberates hydrocarbons which may, in the presence of free metal, form additional reactive species. The disulfide cleavage technique, which is perhaps the most generally applicable of the titrimetric methods, is subject to interference from residual lithium. A similar effect for metallic potassium was observed in the present study. Finely divided lithium metal is extensively used in synthetic work and may exist in the final preparations as a microscopic dispersion or as atomic clusters[5]. Dispersed potassium remaining unreacted in metallation of the α-carbon of alkylaryl hydrocarbons[15] is difficultly separable from insoluble organometal and excess of the oxides of sodium and barium. The present method permits direct determination of these potassium compounds, for

TABLE 1

ANALYSES OF ALKALI METAL-SUBSTITUTED HYDROCARBONS

Organometal derivative	Organometal content (meq/g)			Total base (meq/g)
	n-PrO^{3}H	p-[CH$_3$C$_6$H$_4$S]$_2$	V$_2$O$_5$	
Cyclopentyllithium	2.57 2.58 2.58	2.62 2.62	2.76	2.78
Cyclohexyllithium	0.402[a]	0.396 0.399	0.418 0.420	0.448
1,2-Dilithio-1,2-diphenylethane	0.885 0.886 0.896	0.876 0.876	0.871 0.868	0.949
Dilithium polyisoprene adduct (sample 1)	1.236 1.224 1.222	1.224 1.234	1.206 1.192	1.380
Dilithium polyisoprene adduct (sample 2)	1.122 1.129 1.121	1.116 1.110	1.094 1.115 1.116	1.216
Disodium 1,1-diphenylethylene dimer	0.459 0.455 0.460	0.461 0.463	0.459 0.456	0.510
Disodium α-methylstyrene tetramer	0.281 0.281	0.281 0.279	0.296 0.299	0.286
Benzylpotassium	0.179 0.174			
(2-Naphthylmethyl)potassium	0.318 0.306 0.312			

[a] Average of 4 analyses given in Table 2.

TABLE 2

EFFECT OF EXCESS n-PROPANOL-^{3}H ON ANALYSES FOR CYCLOHEXYLLITHIUM

Excess n-propanol (%)	Organolithium content (meq/g)
19	0.400
132	0.398
267	0.403
335	0.409

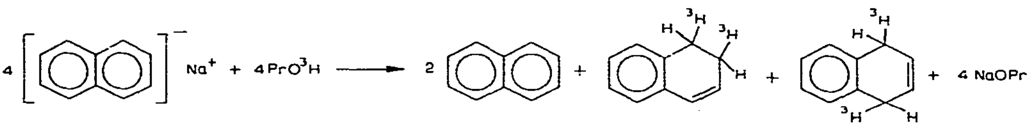
which carboxylation had previously been used. Tritium gas arising in reaction of alkali metals with the alcohol is removed from the toluene solution by hydrogen evolved on treatment of the wet solution with calcium hydride.

Limited data obtained with the vanadium pentoxide procedure[2] on disodium 1,1-diphenylethylene dimer and disodium α-methylstyrene tetramer suggest that the method is useful for determining certain organometallic derivatives of alkali metals other than lithium. Easily oxidized substances in the preparations may, however, lead to high values for organometal by reacting with the sulfatoceric acid used to titrate reduced vanadium.

As indicated by the results for cyclohexyllithium in Table 2, the amount of excess labeled n-propanol within the range of 19 to 335 % had no significant effect on organometal content. An excess of 100–200 % is convenient, since it furnishes adequate reagent for analysis of solutions of unknown strength, while lessening the effect of adventitious moisture in the toluene used as reaction medium.

Analysis of freshly-prepared alkali metal-aromatic hydrocarbon complexes

Since the first reports[33,34] of the use of the reaction product of naphthalene and sodium in active ether solvents as an initiator for the preparation of "living polymers", the radical anions formed in electron transfer processes of this type have become increasingly significant in polymer chemistry. An important aspect of the use of these initiators is accurate determination of the concentration of the complex. Hydrolysis of the naphthalene radical anion by addition to excess hydroxyl-tritiated n-propanol yields a mixture of naphthalene and tritiated dihydronaphthalene:



Although the above equation defines the stoichiometric equivalence between radical anion and alcohol, the relative amounts of dihydronaphthalene isomers formed in hydrolysis may be affected significantly by the conditions used. No attempt was made in this work to determine the isomeric composition of the dihydronaphthalene, however, since it is without effect on results for radical anion concentration. Complexes of alkali metals with other aromatic hydrocarbons undergo protonation in a manner similar to that of the naphthalene adduct to yield partially reduced derivatives of the hydrocarbons.

Analytical results for freshly prepared THF solutions of radical anions derived from several aromatic hydrocarbons by both radiochemical and titrimetric techniques are given in Table 3. The counterion is sodium except where indicated otherwise.

Two of the preparations in Table 3 were also analyzed by adding aliquots to an excess of dried butyl bromide and determining bromide ion argentimetrically. Thus the sodium–naphthalene complex having a radical anion concentration of 0.555 meq/g by tritiation gave 0.564, 0.576, and 0.527 meq/g and the sodium– biphenyl complex yielded 0.138, 0.142, and 0.143 meq/g when analyzed by this method. The procedure is essentially the reverse of the sodium–naphthalene and –biphenyl methods for organic halogen[35–37] and has been used for assay of several anionic polymerization initiators[7–10].

The results indicate that all of the analytical methods evaluated are useful for determining the monovalent radical anion derived from naphthalene in freshly-prepared THF solutions, even though these solutions may exhibit a significant difference between metal–naphthalene complex concentration and total base. Metal hydroxides

TABLE 3

ANALYSIS OF FRESHLY PREPARED ALKALI METAL AROMATIC HYDROCARBON COMPLEXES IN THF

Aromatic hydrocarbon	Radical anion concentration (meq/g)			Total base (meq/g)
	n-PrO^{3}H	p-$[CH_3C_6H_4S]_2$	V_2O_5	
Naphthalene[a]	0.556 0.554	0.559	0.564	0.609
Napthalene	0.441 0.444	0.439 0.439	0.452 0.451	0.525
Napthalene	0.613 0.617	0.619 0.613	0.638 0.635	0.689
Naphthalene[b]	0.250 0.254	0.259 0.260	0.255 0.256	0.273
Naphthalene[c]	0.386 0.386	0.387	0.380	0.423
Phenanthrene	0.695 0.691	0.720 0.700	0.748 0.760	0.797
Anthracene[d]	0.782 0.775	0.776	No endpoint	0.808
Anthracene[e]	0.469 0.468	0.474 0.474	No endpoint	0.500
Biphenyl	0.137 0.136	0.141 0.139	0.128 0.137	0.170
1.4-Dihydronaphthalene	0.019 0.020	0.021	0.028	0.023

[a] Prepared at −5° to −10°; all other preparations were at room temperature. [b] Counterion is potassium. [c] Counterion is lithium. [d] Prepared using sodium, anthracene ratio of 3.8/1. [e] Prepared using sodium, anthracene ratio of 1.3/1.

introduced under the preparative conditions used constitute the principal impurity. In addition, protonation of the radical anion as it is formed by trace amounts of water or other substances containing active hydrogen yields dihydronaphthalenes, which react with both alkali metals[38] and the naphthalene radical anion[39]. Oxygen in the presence of excess metal increases total base as well. The present work is the first known application of the vanadium pentoxide method to analysis of the electron transfer complexes of naphthalene with alkali metals.

The radiochemical and disulfide cleavage methods are applicable to the complexes of alkali metals with phenanthrene and anthracene, whereas the vanadium pentoxide technique is inapplicable, presumably because of oxidative side reactions in the titration with sulfatoceric acid.

All methods studied, including the tritiation technique, determine total metal–hydrocarbon complex concentration and therefore cannot be used to distinguish the product of the initial reaction of the metal and original hydrocarbon from secondary derivatives arising in the reaction of protonated species with excess metal. Dihydronaphthalenes for example, formed in hydrolysis of naphthalene radical anions, yield complexes with sodium[38]. Formation of these secondary complexes, however, may be prevented by excluding proton donors from the system.

As indicated in Table 4, amount of excess n-propanol within the range of 24 to 204% excess has no significant effect on observed radical anion concentration for a typical preparation of the sodium–naphthalene complex.

TABLE 4

EFFECT OF EXCESS n-PROPANOL-^{3}H ON ASSAY FOR SODIUM–NAPHTHALENE COMPLEX

Excess n-propanol (%)	Radical anion (meq/g)
24	0.536
86	0.548
145	0.545
204	0.548

Analysis of an aged sodium naphthalene complex

Instability of THF solutions of the sodium–naphthalene complex at room temperature has been observed by several investigators. Decomposition over a seven year period of a reagent prepared under high vacuum conditions produced dihydronaphthalene, sodium–dihydronaphthalene, and possibly other products[38]. Use of less rigorous preparative conditions evidently results in more rapid deterioration. A solution of the complex prepared under conditions which did not involve use of high vacuum techniques yielded hydrogen upon addition to water after standing overnight, although no gas evolution was observed with the fresh reagent[11]. The reactive decomposition product is sodium hydride[14].

The decrease in apparent radical anion concentration in a solution of sodium–naphthalene complex prepared at −5° to −10° was followed during a storage period of two weeks at room temperature using the radiochemical, disulfide cleavage, and vanadium pentoxide methods. The results of this study are summarized in Table 5.

TABLE 5

EFFECT OF AGING ON A SODIUM–NAPHTHALENE COMPLEX IN THF

Days at room temperature	Apparent radical anion concentration (meq/g)[a]		
	n-PrO^{3}H	p-[CH$_3$C$_6$H$_4$S]$_2$	V$_2$O$_5$
0	0.665	0.664	0.656
	0.659	0.655	0.672
4	0.522	0.537	0.582
	0.522		
14	0.418	0.482	0.498
	0.421		

[a] Total base, 0.736 meq/g.

The radiochemical and disulfide methods determine the total concentration of alkali metal–hydrocarbon adducts and thus include any sodium–dihydronaphthalene complex arising in the decomposition of the initial reaction product. The slower decrease in organometal content indicated by disulfide cleavage is attributable to reaction of sodium hydride, formed in deterioration of the sodium–naphthalene complex, with *p*-tolyl disulfide. Although addition of the freshly prepared solution to the n-propanol/toluene reagent liberated no hydrogen, vigorous gas evolution was observed during addition of the aged preparation. The amount of gas evolved increased with sample storage time, paralleling the previously reported reaction of aged solutions with water[11]. Cleavage of disulfide by sodium hydride was confirmed using a 1/1 dispersion of the compound in mineral oil. Lithium hydride, however, exhibited no reaction with the disulfide, in accordance with previous observations[5]. High results for radical anion concentration in the aged solution by the vanadium pentoxide method are due presumably to the presence of easily oxidized degradation products.

Applicability of the radiochemical technique

The isotopic method is widely applicable to solutions of the organometals of Group I which yield hydrolysis products sufficiently non-volatile to be retained for radioassay by liquid scintillation counting. The technique may be applied to solutions ranging in concentration from that of commercially available samples to the dilute preparations used as initiators of anionic polymerization. Alkali metal-substituted derivatives may be determined without interference from the alkoxides, hydroxides, or oxides of the metals, as well as in the presence of the free metals. In the case of metal–naphthalene complexes hydrolysis must be performed in absence of free metals to preclude further formation of complex by reaction of excess metal with naphthalene arising in hydrolysis. The highly specific nature of the radiochemical technique makes it useful for evaluating titrimetric methods, particularly with regard to the effect of sample impurities which are not organometal in character. An extreme degree of sensitivity may be attained through use of n-propanol of high specific activity.

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REFERENCES

1 H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, 2 (1964) 447.
2 P. F. Collins, C. W. Kamienski, D. L. Esmay and R. B. Ellestad, *Anal. Chem.*, 33 (1961) 468.
3 W. L. Everson, *Anal. Chem.*, 36 (1964) 854.
4 S. C. Watson and J. F. Eastham, *Anal. Chem.*, 39 (1967) 171.
5 C. A. Uraneck, J. E. Burleigh and J. W. Cleary, *Anal. Chem.*, 40 (1968) 327.
6 S. C. Watson and J. F. Eastman, *J. Organometal. Chem.*, 9 (1967) 165.
7 C. Stretch and G. Allen, *Proc. Chem. Soc.*, (1959) 399.
8 F. Wenger, *Makromol. Chem.*, 36 (1960) 200.
9 G. Allen, G. Gee and C. Stretch, *J. Polym. Sci.*, 48 (1960) 189.

10 S.-P. S. Yen, *Makromol. Chem.*, 81 (1965) 152.
11 F. M. Brower and H. W. McCormick, *J. Polym. Sci., Part A*, 1 (1963) 1749.
12 D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, 51 (1955) 1375.
13 M. Baer, *J. Polym. Sci., Part A*, 1 (1963) 2171.
14 M. Szwarc, *Advan. Polym. Sci.*, 2 (1960) 275.
15 C. E. Claff, Jr., and A. A. Morton, *J. Org. Chem.*, 20 (1955) 981.
16 C. W. Kamienski, A. C. Diesing and R. C. B. Morrison (Lithium Corporation of America), *U.S. Pat.* 3,388,178 (1968).
17 L. O. Assarsson, *Acta Chem. Scand.*, 9 (1955) 1399.
18 L. O. Assarsson, *Acta Chem. Scand.*, 10 (1956) 1509.
19 L. O. Assarsson, *Acta Chem. Scand.*, 11 (1957) 1283.
20 L. O. Assarsson, *Acta Chem. Scand.*, 12 (1958) 1545.
21 L. O. Assarsson, *Acta Chem. Scand.*, 12 (1958) 1547.
22 L. O. Assarsson, *Ark. Kemi*, 20 (1963) 259.
23 E. Kohn and J. M. Gill, *J. Organometal. Chem.*, 7 (1967) 359.
24 E. Perry and H. O. Ory, *J. Org. Chem.*, 25 (1960) 1685.
25 S. Bank and W. D. Closson, *Tetrahedron Lett.*, 19 (1965) 1349.
26 D. E. Paul, D. Lipkin and S. I. Weissman, *J. Amer. Chem. Soc.*, 78 (1956) 116.
27 C. F. Feldman and E. Perry, *J. Polym. Sci.*, 46 (1960) 217.
28 E. Kohn, H. J. L. Schuurmans, J. V. Cavender and R. A. Mendelson, *J. Polym. Sci.*, 58 (1962) 681.
29 G. Bier, W. Hoffmann, C. Lehmann and G. Seydel, *Makromol. Chem.*, 58 (1962) 1.
30 D. L. Glusker, E. Stiles and B. Yonkoski, *J. Polym. Sci.*, 49 (1961) 297.
31 D. R. Campbell and W. C. Warner, *Anal. Chem.*, 37 (1965) 276.
32 J. A. Giles, *Anal. Chem.*, 32 (1960) 1716.
33 M. Szwarc, M. Levy and R. Milkovich, *J. Amer. Chem., Soc.*, 78 (1956) 2656.
34 M. Szwarc, *Nature*, 178 (1956) 1168.
35 B. Pecherer, C. M. Gambrill and G. W. Wilcox, *Anal. Chem.*, 22 (1950) 311.
36 F. L. Benton and W. H. Hamill, *Anal. Chem.*, 20 (1948) 269.
37 L. M. Liggett, *Anal. Chem.*, 26 (1954) 748.
38 M. Ladacki, *J. Appl. Polym. Sci.*, 9 (1965) 1561.
39 N. D. Scott and J. F. Walker, *Ind. Eng. Chem.*, 32 (1940) 312.