Journal of Organometallic Chemistry, 90 (1975) 123–131

THE OXIDATION REACTIONS OF ORGANOLITHIUM-*N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE COMPLEXES

HAJIME YASUDA, MICHAEL WALCZAK, WENDELL RHINE and GALEN STUCKY*
School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801 (U.S.A.)

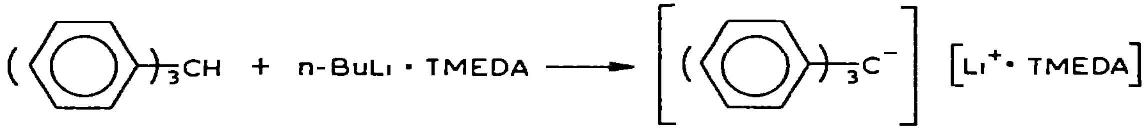
(Received January 24th, 1974; in revised form November 22nd, 1974)

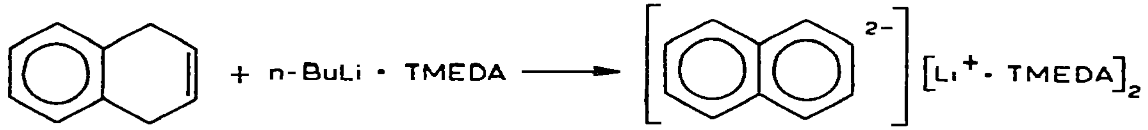
Summary

The reactions of polycyclic hydrocarbon lithium-TMEDA complexes with several transition metal halides and oxides and molecular oxygen have been investigated. Monoanions yielded the symmetric coupling product while dianions were oxidized to aromatic molecules. The stoichiometry for each reagent/anion combination was also determined.

Introduction

Recently there have been several reports concerning the generation of unsaturated delocalized hydrocarbon carbanions using n-butyllithium-*N,N,N',N'*-tetramethylethylenediamine (TMEDA) [1-5]. Typical examples of formation of monoanions and dianions are shown below. The kinetics and mechanism of formation [6] of the acenaphthylene dianion from acenaphthene and n-butyllithium-tetrahydrofuran, a reagent expected to behave similarly to n-butyllithium-TMEDA, have been investigated in detail. Harvey and coworkers [3] have found that the dianions of several polycyclic hydrocarbons are useful





intermediates in the dehydrogenation of dihydro precursors to aromatic molecules. The dianions, formed using n-butyllithium-TMEDA, were oxidized to the aromatic product using metal salts. While lead(II) chloride, copper(II) bromide and iodide, mercury(II) chloride and nickel(II) acetylacetonate all served as oxidizing agents, cadmium chloride was the preferred salt, as it gave cleaner products and higher yields than the other salts.

As part of a program which we have recently initiated to investigate the reactions between transition metal and main group element organometallic complexes, we wish to report some additional observations concerning the reactions of mono- and di-anionic polycyclic hydrocarbon lithium-TMEDA compounds with transition metal halides and oxides, and oxygen. We have found several new oxidizing agents suitable in the second step of the reaction process proposed by Harvey [3]. In addition, we find that these reagents cause coupling of the monoanion, R^-, giving the symmetrical product R—R.

Experimental

Benzene and n-hexane were refluxed over Na metal and distilled in an argon stream. TMEDA was dried over molecular sieves and distilled. n-Butyllithium in n-hexane was obtained from the Foote Mineral Company. Nickel, cupric and cobalt chloride were made by heating the hydrated metal halide at 130° for 20 h in a vacuum (0.5 torr). Other metal halides, such as zinc, magnesium, calcium, and cadmium chloride were dried in a vacuum (100°/0.5 torr) for 12 h. Metal oxides, except mercuric oxide, were dried at 150° under a reduced pressure (0.5 torr). Mercuric oxide was dried at 100° in a vacuum for 10 h. Diphenylmethane was dried over calcium hydride and purified by distillation. Triphenylmethane, bibenzyl, fluorene, acenaphthene and 9,10-dihydroanthracene were obtained from the Aldrich Chemical Company. The 9,10-dihydrophenanthrene was obtained from Columbia Organic Chemical Company and recrystallized three times in n-hexane at −20°. All the dehydrogenated aromatic hydrocarbons were confirmed by the comparison of their NMR and IR spectra and melting points with those of authentic samples.

Syntheses of mono- and di-anions

TMEDA complexes of monoanions such as phenyl-(colorless), benzyl-(yellow), diphenylmethyl-(orange), triphenylmethyl-(dark red) or fluorenyllithium (yellow) were made by mixing 0.05 mol of benzene, toluene, diphenylmethane, triphenylmethane or fluorene with 0.06 mol of n-butyllithium and 0.06 mol of TMEDA at room temperature in 40 ml of n-hexane. After the n-hexane solution had been refluxed for 30 min, it was allowed to cool at room temperature to liberate the crystals. Phenyl- and benzyl-lithium-TMEDA complexes were cooled in an ice bath in order to induce crystallization. The needle crystals formed were isolated by filtration in an argon stream. Dianions such as anthracene (purple), acenaphthylene (black), stilbene (dark red) and bis(fluorenylidene) (red) were isolated as needle crystals by the reaction of 0.1 mol of 9,10-dihydroanthracene, acenaphthene, bibenzyl, and bifluorene with 0.2 mol of n-butyllithium and 0.22 mol of TMEDA in 200 ml of n-hexane. The solution was heated to reflux for 30 min and was allowed to stand at room temperature to induce crystallization. The phenanthrene dianion was used in situ without recrystallizing since pure crystals of this material were not obtained. Three mixtures of 9,10-dihydrophenanthrene, n-butyllithium and TMEDA in the ratio of 1/2/2, 1/4/4 and 1/2/10 were used in reactions which required the phenanthrene dianion.

Oxidation reactions by oxygen

The crystalline mono- (0.01 mol) or di-anion (0.005 mol) was dissolved in 50 ml of dry benzene in an argon stream in a 200 ml two-necked round-bottom flask. Molecular oxygen dried over phosphorus pentoxide was conducted into this flask with a gas tight hypodermic syringe. Upon adding 0.0025 mol of the oxygen, an exothermic reaction occurred and the solution became colorless. The solution was vigorously stirred for 12 h, 10 ml of water was added for hydrolysis and 100 ml of benzene to extract the hydrocarbon. The benzene soluble portion was filtered and evaporated to dryness. Tetraphenylethane, which formed as crystals, was separated from the recovered diphenylmethane by washing with n-hexane at 0° and filtering. *trans*-Stilbene obtained by the oxidation reaction was separated from bibenzyl by recrystallization from hexane. Anthracene was separated from 9,10-dihydroanthracene by sublimation. The peroxide of hexaphenylethane was separated by filtration after dissolving the triphenylmethane in ethyl acetate (25 ml for 1 g of oxidation product) at 0°. Bifluorene was purified by recrystallization from a mixture of n-hexane and toluene (3/1). Bis(fluorenylidine) was separated from bifluorene by dissolving the mixture in n-hexane (60 ml for 1 g of the mixture). The yellow colored n-hexane solution was cooled to −50° and red needle crystals of bis(fluorenylidine) were isolated. The percentage yield of oxidation product was determined by both gravimetric analysis and by NMR spectroscopy.

Oxidation reactions by metal salts or metal oxides

A benzene solution (50 ml) of the mono- (0.01 mol) or di-anion (0.005 mol) was added to the metal halide (0.005 mol) or metal oxide (0.005 mol) in an argon stream with vigorous stirring at room temperature. After stirring for 12 h, 10 ml of water was added for hydrolysis. The benzene soluble part was filtered and evaporated to dryness. The water insoluble black metal was washed three times with 100 ml of water. The cadmium metal which precipitated as a black powder was identified by dissolving it in hydrochloric acid with the evolution of hydrogen gas, evaporating the solution to dryness, dissolving the residual white solid in sulphuric acid, and subsequently converting it to yellow cadmium sulfide. The nickel metal which was obtained as a gray powder was identified by dissolving it in hydrochloric acid with the evolution of hydrogen gas, evaporating the solution to dryness, dissolving the green solid in dilute ammonia containing sodium fluoride, and finally forming the red nickel dimethylglyoxime.

Results and discussion

Reactions of monoanions with oxygen

The results obtained for the *N,N,N',N'*-tetramethylethylenediamine (TMEDA) complexes of diphenylmethyl (I), triphenylmethyl (II), fluorenyl-

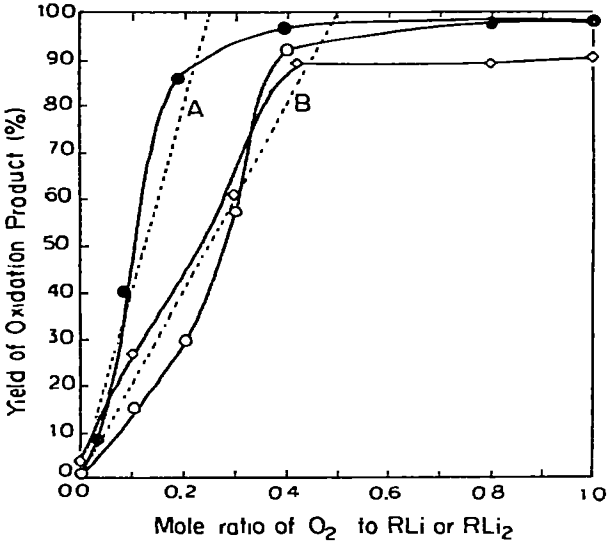


Fig. 1. Dependence of the yield of oxidation product from anthracene (○) and stilbene (◇) dianion or coupling product, tetraphenylethane, from diphenylmethyl monoanion (●) on the molar ratio of oxygen to organolithium employed. The slopes of dashed straight lines A and B were calculated from eqns. 1 and 2, respectively. The reaction was carried out at room temperature for 20 h in benzene.

lithium (III) as monoanions and stilbene (IV) and anthracene (V) as dianions are representative of those obtained for other mono- and di-anion systems and will be discussed in detail. The reaction of I with oxygen resulted in the formation of tetraphenylethane. For mole ratios of O_2 to RLi between 0.0 and 0.25, the yield of tetraphenylethane increased rapidly with increasing amounts of oxygen. A quantitative yield of tetraphenylethane was observed when more than 0.25 mole equivalents of oxygen were added to the solution of I (Fig. 1). With an excess of oxygen, the triphenylmethyl monoanion gave the peroxide of hexaphenylethane in a 40% yield instead of hexaphenylethane. This reaction is considered to proceed by the same mechanism as that for the diphenylmethyl monoanion; however, due to the well known autooxidation reaction of hexaphenylethane to give the peroxide and/or the greater stability of the peroxide intermediate of triphenylmethane relative to that of hexaphenylethane, the peroxide is the preferred product. The phenyllithium-TMEDA complex also gave a coupling compound, biphenyl, in 63% yield when the oxygen which was dried over calcium chloride was conducted slowly into the solution. If an excess amount of molecular oxygen was added rapidly into the solution, the yield of biphenyl was decreased to 28% as a result of the increase in the formation of phenoxide. The latter was evidenced by detection of phenol with GLPC after hydrolysis. Biphenyl did not result from phenylation of the solvent because a 63% yield of biphenyl was observed by using n-hexane in place of benzene as a solvent. The fluorenyl- and benzyl-lithium-TMEDA complexes gave only a small amount of the coupling compound, bifluorene (30%) or bibenzyl (5%), respectively, with an excess amount of oxygen or dried air. The data in Fig. 1, plotted as a function of the mole ratio of O_2 /lithium compounds against the yield of oxidation product, are consistent with the straight line obtained from eqn. 1:

$$4RLi + O_2 \rightarrow 2R{-}R + 2Li_2O \qquad (1)$$

Reactions of dianions with oxygen

The stilbene (IV) and anthracene (V) dianions gave *trans*-stilbene and anthracene, respectively, both in high yields. The presence of *cis*-stilbene was not detected by NMR. *trans*-Stilbene is thermodynamically preferred over the *cis* isomer, and it is of interest to note that the *trans* geometry exhibited by the planar stilbene dianion in the solid state [7] appears to be maintained in the final product. The yield of these dehydrogenated compounds increased rapidly up to approximately 0.5 mole equivalent of oxygen as shown in Fig. 1. The maximum yield was obtained for more than 0.5 mole equivalent of oxygen. From the dianion data in Fig. 1, the reaction of the dianion is reasonably explained by eqn. 2:

$$2RLi_2 + O_2 \rightarrow R{-}R + 2Li_2O \qquad (2)$$

Bisfluorenylidene dianions synthesized from bifluorene and n-butyllithium gave bisfluorenylidene in 30% yield upon the addition of an excess amount of oxygen.

In contrast to the behavior of the 1,4-dihydro ring systems, dianions such as acenaphthylene or phenanthrene, formed from 1,2-dihydro hydrocarbons, behaved in a somewhat different manner. The crystalline acenaphthylene dianion gave a red polymeric compound in 70% yield and acenaphthene was recovered in a 30% yield upon hydrolysis after reacting with an excess of oxygen in benzene. The polymeric compound was insoluble in hexane and had a variable melting point (145-165°). It could not be distilled by heating at 230° under a vacuum (0.5 torr). The isolation of phenanthrene dianion was attempted by reacting 9,10-dihydrophenanthrene and TMEDA with n-butyllithium in the mole ratio of 1/2/2, 1/4/2 and 1/4/4, but the metallation reaction did not proceed in every instance and starting materials rather than phenanthrene were recovered in 93% yield. However, when a large excess of TMEDA (10 mol/mol n-butyllithium) was used and the solution was heated to reflux for 1 h, phenanthrene was formed in 92% yield without adding any oxygen [3]. The use of 5 mol equivalent of TMEDA to n-butyllithium resulted in the formation of phenanthrene in 43% yield.

A simple adaptation of the above procedures can be used for the very convenient synthesis of coupled compounds from the monoanions or the dehydrogenated compounds from dianions. An open tube containing calcium chloride is attached to the reaction vessel, and the reaction mixture is stirred for 12 h at room temperature. Upon hydrolysis, diphenyl, tetraphenylethane, *trans*-stilbene, anthracene and bifluorene can be obtained in the same yields as if dry molecular oxygen is used.

Reactions with metal salts

Anhydrous nickel, cobalt, cupric and mercuric chlorides were found to be excellent oxidizing agents, not only for the oxidation of the dianion, but also for the formation of a coupled product from the monoanion. The efficien-

TABLE 1

PERCENTAGE YIELD FROM OXIDATION REACTIONS USING METAL HALIDES[a,b]

	Ph_2CH^-	Stilbene $^{2-}$	Anthracene $^{2-}$
$CoCl_2$	73	90	90
$NiCl_2$	98	91	64
$CuCl_2$	95	91	95
$ZnCl_2$	53	92	82
$CdCl_2$	98	90	96
$HgCl_2$	97	90	92
$CaCl_2$	2	3	2
$MgCl_2$	1	2	1

[a] The data represent the percentage yield of oxidation product (tetraphenylethane, *trans*-stilbene and anthracene) from corresponding mono- and di-anion. [b] Metal halide (0.01 mol) was reacted with mono- (0.02 mol) and di-anion (0.01 mol) at 25° for 20 h in benzene.

cy of these metal halides (Table 1) is almost the same as that found for cadmium chloride. In addition, the utility of cadmium chloride was further extended, as it was found also to be an efficient coupling agent for the monoanions. Zinc chloride was not as effective for the oxidation of the monoanion, but worked well for dianions. As shown in Fig. 2, a 1/2 molar ratio of cadmium or nickel chloride to I was necessary to obtain tetraphenylethane in a quantitative yield. The maximum yield of anthracene was obtained when equimolar amounts of the metal halide were reacted with V. As these plots follow a straight line and are independent of reaction time, these reactions are explicable in terms of eqns. 3 and 4:

$$2RLi + MX_2 \rightarrow R{-}R + M + 2LiX \qquad (3)$$

$$RLi_2 + MX_2 \rightarrow R + M + 2LiX \qquad (4)$$

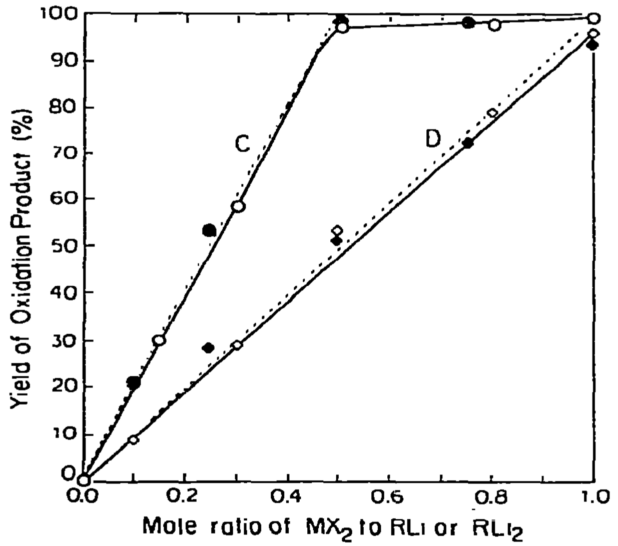


Fig. 2. Dependence of the yield of oxidation or coupling product on the molar ratio of metal halide to organolithium employed. Oxidation of diphenylmethyl monoanion by $CdCl_2$ (○) and $NiCl_2$ (●), and that of anthracene dianion by $CdCl_2$ (◇) and $NiCl_2$ (◆). Dashed straight lines C and D represent the slope calculated from eqns. 3 and 4, respectively. The reaction was carried out at 25° for 12 h in benzene.

Both cadmium and nickel metal were obtained as water insoluble black powders in quantitative yields. Magnesium and calcium chloride were not effective as oxidizing agents.

Bifluorene can be obtained in high yields by using metal halides, although it was obtained in only 30% yields with oxygen. The reaction between nickel (0.01 mol), cobalt (0.01 mol), or mercuric chloride (0.01 mol) and fluorenyllithium (0.005 mol) resulted in the formation of bifluorene in 62, 75 and 81% yields respectively. Cupric chloride (0.01 mol) and cadmium chloride (0.01 mol) gave bifluorene in 28 and 32% yields upon reaction with the fluorenyl monoanion. Zinc, calcium and magnesium chloride did not give bifluorene and fluorene was recovered quantitatively upon hydrolysis. Both oxygen and metal halides, such as nickel, cadmium, zinc, and cobalt chloride were not effective in converting the benzyl monoanion to bibenzyl, and all gave a 5% yield. The results with the 1,2-dianions are not yet clear. Although the acenaphthylene dianion gave mainly polymeric material upon oxidation with oxygen, $NiCl_2$ was effective in oxidizing the dianion to give acenaphthylene in approximately 70% yield at room temperature. Reaction between cadmium chloride and isolated acenaphthene dianion in benzene resulted in the formation of polymeric product, but cadmium chloride was effective as an oxidizing reagent only in the presence of an excess amount of TMEDA and at higher reaction temperature as reported by Harvey [3]. When an excess amount of TMEDA (50 mole equivalent of the dianion or metal halide) was added and the solution was heated to reflux for 1 h, the oxidation reaction proceeded smoothly to give 97% yield of acenaphthylene. Thus, 1,2-dianions needed an excess amount of TMEDA and a high reaction temperature for oxidation, whereas the oxidation of 1,4-dianions and monoanions could be obtained with $CdCl_2$ at room temperature by using a minimum amount of TMEDA. This fact suggests that the 1,2-dianions are more stable than 1,4-dianions and monoanions with respect to the oxidation reaction.

Metal oxides also were examined as potential oxidizing agents. The results of the oxidation of a mono- or di-anion by two molar equivalent amounts of metal oxide are given in Table 2. Cadmium, mercuric and cupric oxides were found to be excellent oxidizing agents. Zinc oxide would not react with these anions, although zinc chloride did oxidize these anions. The correlation between

TABLE 2

PERCENTAGE YIELD OF TETRAPHENYLETHANE AND *trans*-STILBENE FROM OXIDATION REACTIONS. OF DIPHENYLMETHYL MONOANION AND STILBENE DIANION USING METAL OXIDES [a]

Oxide	Ph_2CH^-	Stilbene $^{2-}$
CoO	25	95
NiO	8	96
CuO	98	92
ZnO	5	6
CdO	95	98
HgO	95	92

[a] Crystalline diphenylmethyl- and stilbene-lithium compounds (0.01 mol) were reacted with dispersed metal oxide (0.01 mol) in benzene at 25° for 20 h.

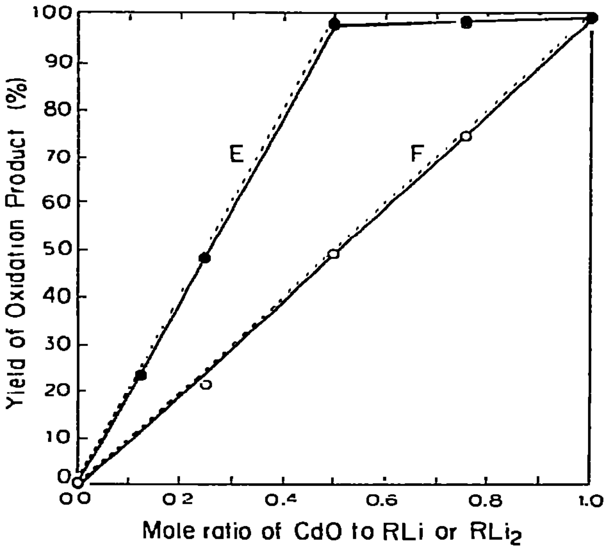


Fig. 3. Dependence of the yield of oxidation or coupling product on the molar ratio of cadmium oxide to diphenylmethyl monoanion (●) and stilbene dianion (○). Dashed lines E and F were calculated from eqns. 5 and 6, respectively. The reaction was carried out at 25° for 24 h.

the amount of cadmium oxide used and the yield of the oxidation product is shown in Fig. 3. Both the diphenylmethyl monoanion and the stilbene dianions were oxidized completely (Fig. 3).

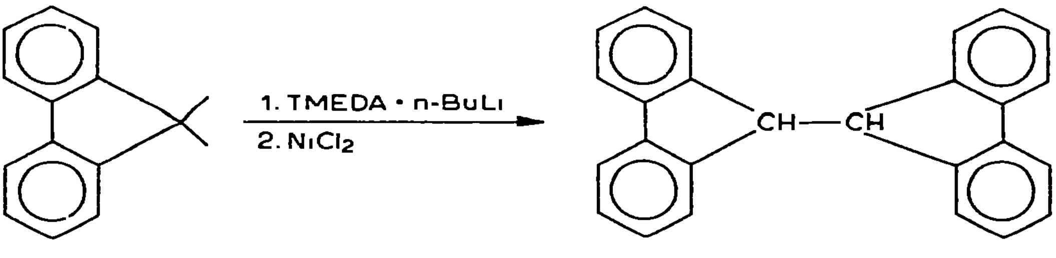
The reactions of the mono- and di-anion are, therefore, reasonably explained by equations 5 and 6, respectively:

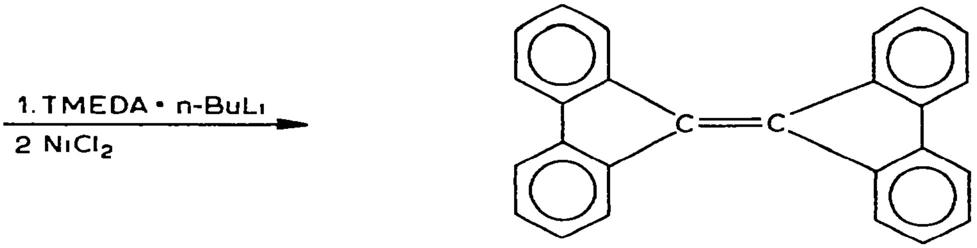
$$2RLi + MO \rightarrow R{-}R + M + Li_2O \quad (5)$$

$$RLi_2 + MO \rightarrow R + Li_2O + M \quad (6)$$

Cadmium or nickel metal was obtained from this reaction as a black precipitate, and the amount was proportional to the amount of added metal oxide. By using cadmium oxide, the yield of *trans*-stilbene was increased to 98% from the 90% obtained by using molecular oxygen or metal halide.

A number of aromatic alkyl mono- and di-anions are readily converted to the coupled product and the dehydrogenated compound respectively. The reaction in which bisfluorenylidene was obtained from fluorene was carried out and is given as a typical example:





Acknowledgement

The authors wish to express their gratitude to Professor R.G. Harvey of the University of Chicago for his comments. The support of the National Science Foundation under Grants NSF DMR 7203026 and NSF MPS 742300 is gratefully acknowledged.

References

1 A.W. Langer, Jr., Trans. N.Y. Acad. Sci., 27 (1965) 741.
2 J.J. Brooks, Ph.D. Dissertation, University of Illinois, Oct., 1971; J.J. Brooks, W. Rhine and G.D. Stucky, J. Amer. Chem. Soc., 94 (1972) 1346.
3 R.G. Harvey, L. Nazareno and H. Cho, J. Amer. Chem. Soc., 95 (1973) 2376; R.G. Harvey and H. Cho, J. Amer. Chem. Soc., 96 (1974) 2434.
4 G. Stucky, Advances in Chemistry Ser., 130 (1973) 56.
5 C.G. Screttas and J.F. Eastham, J. Amer. Chem. Soc., 87 (1965) 3276.
6 L.D. Kershner, J.M. Gadis and H.H. Freedman, J. Amer. Chem. Soc., 94 (1972) 985.
7 M. Walczak and G. Stucky, unpublished observations.