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A new role for organometallic reactions in organic synthesis in industry

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Abstract - Organometallic compounds are coming to play a significant role as catalysts and reagents for the synthesis of organic compounds in high technology industry. Some examples involving C-C bond formation include alkylation of chloronaphthoquinones and halobenzenes, a titanium-mediated cyclization of diynes, and a simultaneous alkylation and ring closure of hexenedioates to give cyclopentanone derivatives. Transition metal imides provide convenient reagents for C-N bond formation in a new synthesis of allylic amines.

INTRODUCTION

Many recent articles suggest that the chemical industry has matured. Traditional industrial chemicals and polymer intermediates have become commodities. The wave of the future is said to be specialty chemicals - small volume, high value materials for the new "high tech" industries. In this article, we discuss how this change in emphasis affects industrial organometallic chemistry and how our research is responding to the trend.

Even though the industrial use of soluble catalysts is as old as that of heterogeneous catalysts, the main flowering of homogeneous catalysts has occurred since 1950 when major advances began to occur in the organometallic chemistry of the transition metals. The major characteristics of homogeneous catalysis that enabled it to carve a niche for itself in process technology are mild reaction conditions and high product selectivity. This selectivity has opened a major role in production of polymer intermediates for which product purity is a dominant requirement. For example, production of intermediates for polyamides, polyesters and polyurethanes employs homogeneous catalysis very extensively. Overall, about 25 major industrial processes use soluble catalysts (ref. 1).

As the general knowledge of organometallic chemistry has increased, the sophistication of homogeneous catalysis has grown dramatically (ref. 2). This trend climaxed in the early 1970's with the commercialization of four processes (Table 1), each of which was to have substantial economic impact. These new processes, which were based on a substantial understanding of organometallic chemistry, displaced less sophisticated, but well-established processes for major industrial chemicals. In each instance, the initial commercial plant has

TABLE 1. Major homogeneous catalytic processes based on organometallic chemistry

Product	Company/Date	Chemistry
Acetic Acid	Monsanto (1970)	$CH_3OH + CO \xrightarrow{[Rh(CO)_2I_2]^-} CH_3COOH$
Adiponitrile	Du Pont (1971)	 $+ 2\,HCN \xrightarrow{Ni[P(OAr)_3]_4} NC(CH_2)_4CN$
Aldehydes	Union Carbide, Celanese (1976)	$RCH{=}CH_2 \xrightarrow[RhH(CO)(PAr_3)_3]{CO/H_2} RCH_2CH_2CHO$
α-Olefins	Shell (1977)	$nCH_2{=}CH_2 \xrightarrow{Ni(chel)_2} H_2C{=}CH(C_2H_4)_{(n-1)}H$
		chel = chelating ligand such as $Ph_2PCH_2COO^-$

been supplemented by two or more additional plants based on similar process technology. Each of these four processes is likely to maintain its dominance for the remainder of the century.

In the mid-1970's, the development of homogeneous catalysis underwent a major change. Few process innovations comparable to those of the early 1970's are emerging. Instead, the character of industrial research seems to be changing. Three factors for change are as follows:

- Maturity of the chemical industry. Few new large volume products are appearing. In contrast to the 1950's, when new polymers were announced almost yearly, there have been few new polymers requiring new intermediates. In addition, the processes for existing products are highly developed and are unlikely to change except in response to changes in feedstocks.

- New feedstocks. The "oil shocks" of 1973 and 1979 have provided a major incentive to seek new raw materials for the production of organic chemicals. A conspicuous example is the Tennessee Eastman plant for production of acetic anhydride from coal-based synthesis gas (CO/H_2). This plant, which began operation in 1983, is the major exception to the dearth of new homogeneous catalytic technology in recent years (ref. 3).

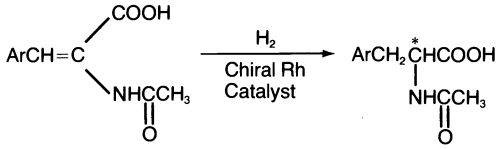
- High technology industry. The burgeoning electronics industry is an intensive user of chemicals. The volumes are small, but for many applications, such as high resolution photoresists for integrated circuits, high prices can be tolerated. Similarly, major advances in pharmaceuticals, medical diagnostics and agricultural chemicals have created similar opportunities. Extremely selective process technology is needed to make very complex organic molecules with precise biological functions. Homogeneous catalysis, which can display enzyme-like selectivity, is well adapted to meet these needs.

The remainder of this article will deal with this third point, namely, how the chemical industry is responding to the opportunity in fine chemicals. As shown in Fig. 1, there have been a number of developments in which homogeneous catalysis has been used to good effect in the synthesis of fine chemicals. For example, in Monsanto's synthesis of *l*-DOPA, which is used in treatment of Parkinson's disease, a rhodium catalyst with an optically active ligand catalyzes hydrogenation of a C=C bond to produce a specific optical isomer with enantioselectivity exceeding 90% (ref. 4).

Pharmaceuticals

Example: Monsanto's *l*-DOPA synthesis (commercialized 1971)

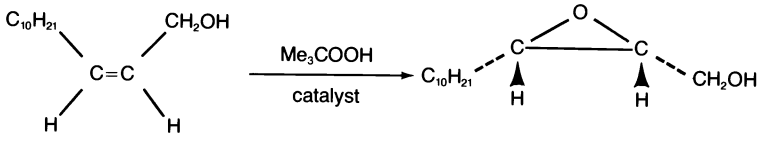
Key step:
Asymmetric hydrogenation



Agricultural chemicals

Example: Synthesis of Disparlure, a gypsy moth attractant

Key step:
Epoxidation



Flavors and fragrances

Example: SCM's synthesis of terpene alcohols (1982) (ref. 6).

Key step:
Isomerization of
an allylic alcohol

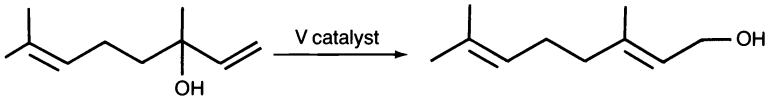
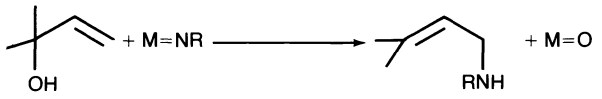


Fig. 1. Illustrations of the use of homogeneous catalysis in the synthesis of organic chemicals.

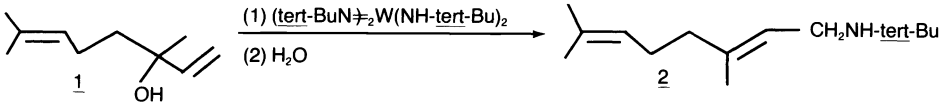
In keeping with this trend, some of Du Pont's organometallic research is now aimed at synthesis of specialty organic chemicals. The following examples suggest that organometallic methods may provide preferred syntheses of potentially important organic compounds. In the first example, an organometallic compound is used as a reagent rather than as a catalyst. For high value-in-use materials such as pharmaceuticals, an organometallic reagent may sometimes be used stoichiometrically if it provides sufficient process simplification.

ALLYLIC AMINE SYNTHESIS

This example involves the conversion of an allylic alcohol to an isomeric allylic amine.

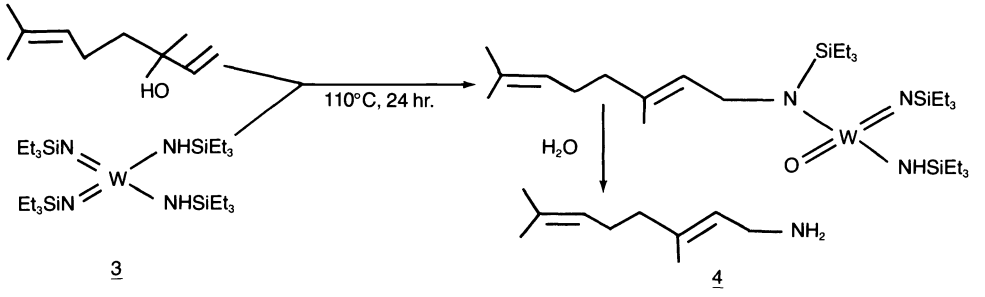


We recognized that this reaction, if achieved, would provide a simple way to introduce an amine function into a variety of organic molecules.
We began the study by screening the reaction of linalool with a series of transition metal imide complexes available from a previous study of M=N complexes (ref. 7). Surprisingly, the reaction occurs with several M=NR complexes and, with a tungsten imide, can give good yields of allylic amines (ref. 8).



When linalool (1) was heated with the tungsten imide in boiling toluene, the desired allylic amine 2 was formed in greater than 90% yield (after hydrolysis of the intermediate complex). A similar reaction of an imidovanadate, n-PrN=V(OSiR$_3$)$_3$, gave the corresponding allylic amine bearing a primary alkyl group in good yield. As noted above, the imido complexes are used as reagents rather than as catalysts, but the reaction provides a simple way to carry out a transformation that would require many steps by conventional organic methods. Similar reactions occur with other allylic alcohols and with some acetylenic carbinols.

This amination reaction would be even more useful to the synthesis chemist if it could be used to prepare allylic primary amines. Unfortunately, the unsubstituted metal imides with M=NH functions are not sufficiently tractable to be useful as reagents. The desired synthesis can be achieved, however, by an indirect route. The silylimide complex 3 serves as a reagent for synthesis of the desired primary amines. It reacts with linalool to form an allylic amine 4 just as does the tert-butylimido complex.

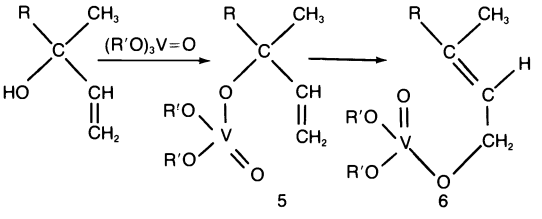


In this instance, however, hydrolysis of the initially formed tungsten complex cleaves both the W-N and Si-N bonds and gives the primary amine 4 in about 65% yield (ref. 8). This reaction extends the generality of the allylic amine synthesis to a wide range of desirable applications.

The mechanism of the allylic amination reaction has not been explored extensively, but, at least in a formal sense, it appears to parallel the commercial isomerization of linalool (ref. 6)

cited in Fig. 1. This parallelism is indicated in Fig. 2. The initial step in catalytic isomerization of linalool is formation of a vanadate ester (5) of the starting alcohol by ester exchange with a normal alkyl vanadate (Fig. 2, top). A series of bond shifts within the allylic vanadate ester gives an isomeric allylic vanadate 6. Hydrolysis or alcoholysis of this isomer yields the desired product, a primary allylic alcohol.

Catalytic Isomerization of an Allylic Alcohol



Proposed Allylic Amination Process

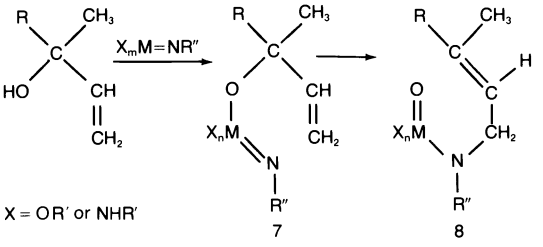


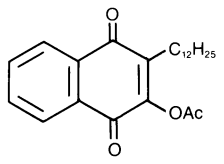
Fig. 2 Proposed mechanisms for catalytic isomerization of an allylic alcohol (left) and for allylic amination (right). R=$(CH_3)_2C{=}CHCH_2CH_2$

A key point in this mechanism is that the oxo oxygen of the vanadate ester forms the new C-O function in the rearranged ester. We believe that, in our process, the metal imide uses its M=N function similarly to make a C-N bond (Fig. 2, bottom). Esterification of an imido complex by the allylic alcohol gives the allyloxymetal imide 7. An isomerization analogous to that with the vanadate ester yields the alkylamido oxometal complex 8. Hydrolysis of the M-N bond gives the observed allylamine product.

This method for allylic amine synthesis dealt with a transition metal compound used as a reagent. The next two examples of our organometallic methodology also utilize an organometallic compound as a reagent, but both cases require a second metal compound as a catalyst to promote C-C bond formation.

SELECTIVE ALKYLATION OF NAPHTHOQUINONES

A wide variety of biologically active compounds are based on a 2-alkyl-3-hydroxynaphthoquinone structure. These compounds include vitamin K, various antimalarials and the proprietary miticide 9. The conventional organic syntheses of these compounds involve several steps, but relatively economical syntheses could be devised if one could achieve a selective monoalkylation of 2,3-dichloronaphthoquinone (10), which is commercially available as Phygon®.



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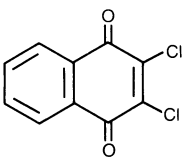
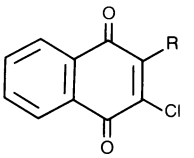


10

$C_6H_5CH_2PdCl(PPh_3)_2$

11



12 R = CH_3

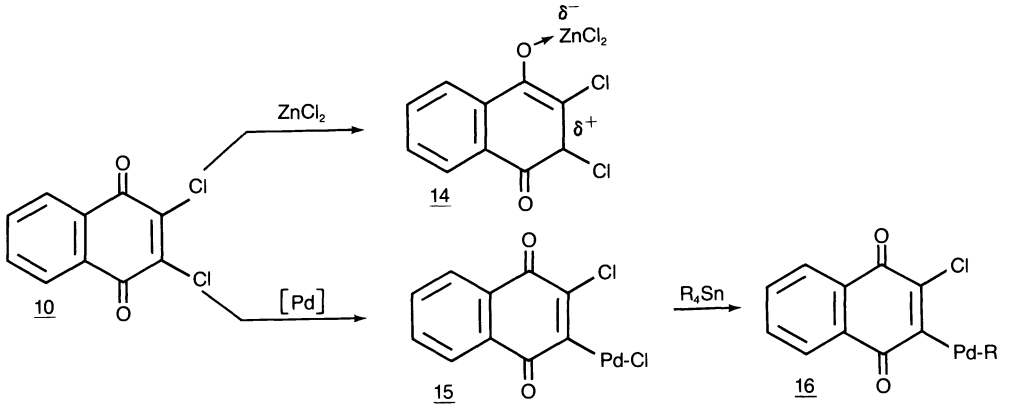
13 R = $C_{12}H_{25}$

Conventional alkylating agents such as Grignard reagents and alkyllithiums react with 10, but give very low yields of the desired 2-alkyl-3-chloronaphthoquinones. Dialkylation and reduction of the quinone are major complications. Mild alkylating agents such as tetraalkyltins do not react with the dichloro compound unassisted, but we found that the alkylation can be catalyzed. For example, the palladium complex 11 catalyzed the reaction of tetramethyltin with 10 to give the monomethyl derivative 12 in 88% yield (ref. 9). This reaction can be viewed as an analog of the Milstein-Stille synthesis of ketones by palladium-catalyzed alkylation of acyl chlorides with alkyltin reagents (ref 10). The analogy is quite close if one regards Phygon® as a vinylog of an acyl chloride.

This synthesis is efficient for the preparation of 12, a convenient precursor for preparation of vitamin K. However, it is less satisfactory for the synthesis of higher alkyl derivatives such as 13, needed for preparation of miticide 9. Reaction of the dichloro compound with tetradodecyltin gave only a 25% yield of 13, needed for preparation of miticide 9, even after a six-day reaction in boiling dioxane.

Survey of a broad range of organometallic alkylating agents gave mixed results. Dialkylzinc and trialkylaluminum reagents react very sluggishly with Phygon®, but mixed alkyl chloro reagents were much more reactive and gave good yields of the monoalkyl derivative 13. It soon became evident that Lewis acids such as $AlCl_3$ and $ZnCl_2$ promoted the initial alkylation of the dichloro compound. For example, tridodecylaluminum and 10 reacted to give the monododecyl product 13 in 82% yield in 10 min. at room temperature when a molar quantity of $ZnCl_2$ was added. In the absence of $ZnCl_2$, less than half that yield was obtained in a reaction conducted overnight. The Lewis acid-promoted alkylation was useful in preparing a broad range of 2-alkyl-3-chloronaphthoquinones (refs. 9, 11).

The activation of the dichloronaphthoquinone 10 by Lewis acids presumably involves complexation of the quinoid oxygen to the acidic metal salt to form a polarized structure such as 14. In such a complex the more remote C-Cl bond should be activated toward attack by a

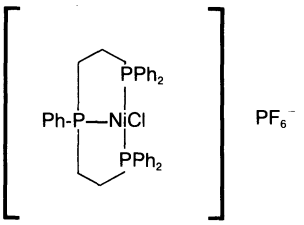


nucleophilic alkylating agent. In contrast, the palladium-catalyzed alkylation described earlier seems to involve an entirely different mechanism. It appears to be based on oxidative addition of a C-Cl bond of 10 to a low valent palladium species to form 15. Reaction of 15 with a tetraalkyltin gives 16 which can then effect C-C bond formation by reductive elimination of the quinoid and alkyl substituents from palladium. This mechanistic proposal parallels that suggested for the Milstein-Stille synthesis (ref. 10).

SELECTIVE ALKYLATION OF DICHLOROBENZENES

A problem analogous to that just discussed is the selective monoalkylation of dichlorobenzenes, a potentially useful route to several pharmaceutical and agrichemical intermediates. The major difference between the two systems is that a typical aryl-Cl bond is much less reactive than that in dichloronaphthoquinone.

Our initial approach to developing a selective monoalkylation of dichlorobenzenes was to explore alkylations catalyzed by nickel and palladium complexes. There is extensive literature on catalytic coupling of Grignard reagents with halobenzenes (refs. 12, 13), but the literature offers little encouragement to expect selective alkylation, except for a Pd-catalyzed alkylation of a dibromobenzene (ref. 14). By extensive scouting of the reaction of Grignard reagents with chlorobenzenes, we found that a cationic nickel complex 17 bearing a "triphos" ligand is exceptionally effective in promoting alkylation of chlorobenzene. With ethylmagnesium bromide, an 88% yield of ethylbenzene is obtained (ref. 15).



17

In contrast to many other nickel and palladium complexes, 17 is reasonably selective for monoalkylation of dialkylbenzenes when the experimental conditions are well chosen. For example, n-butylmagnesium chloride and m-dichlorobenzene react in boiling ether in the presence of 17 to give 68% of 1-n-butyl-3-chlorobenzene and 23% of 1,3-di-n-butylbenzene. As shown in Table 2, many other dichloroarenes give similar yields of monoalkylation products.

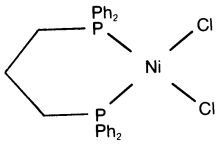
The examples in the table represent some of the more successful alkylations. Secondary alkyl, aryl and benzylic Grignard reagents give lower selectivities to monoalkylated products. Vinyl, allyl and tert-butyl Grignard reagents do not react with o-dichlorobenzene. The regioselectivity in alkylations of unsymmetrical dichlorobenzenes can be quite high as indicated by the reaction with 3,4-dichlorotoluene.

The selectivity for monoalkylation that is achieved with 17 as a catalyst is not attainable with all nickel complexes (ref. 16). For example, the neutral complex 18, obtained from a bidentate ligand, gives primarily dialkylation of o-dichlorobenzene (ref. 13).

TABLE 2. Alkylation of dichloroarenes by ethylmagnesium bromide catalyzed by [NiCl(triphos)]PF_6

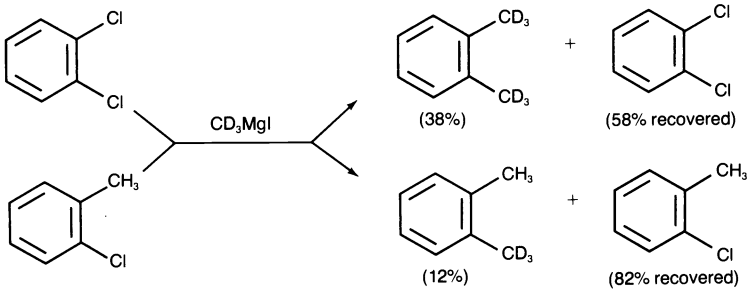
Arene	% yield of ethylation product	
	Mono	Di
o-dichlorobenzene	71	11
p-dichlorobenzene	75	9
2,6-dichloroanisole	60	14
3,4-dichlorotoluene	62*	17

*Exclusively 3-ethyl-4-chlorotoluene.

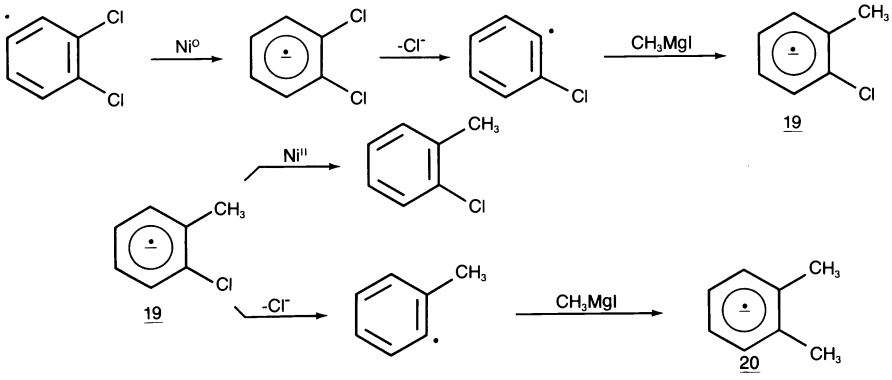


18

Reaction of equimolar CH_3MgI and o-dichlorobenzene in the presence of 18 gives 40% of o-xylene and only 4% of o-chlorotoluene. Free o-chlorotoluene does not seem to be an intermediate in the dialkylation. Reaction of an equimolar mixture of CD_3MgI, o-chlorotoluene and o-dichlorobenzene gave primarily o-xylene-d_6.



It is clear that there is a major difference between the catalytic activities of 17 and 18. These differences suggest a reaction mechanism in which the nickel catalyst, probably reduced to Ni(0) by the Grignard reagent, generates aromatic radical anions which are readily alkylated.

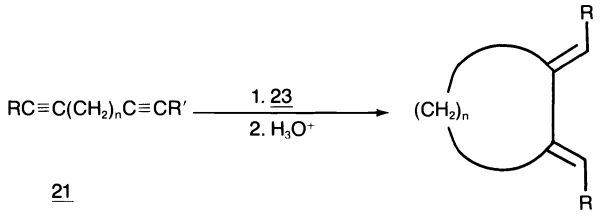


A key intermediate in this proposed sequence is the monoalkylated radical anion 19. If it reacts with a nickel(II) complex such as 17 more rapidly than it loses chloride ion, the monoalkylated product, o-chlorotoluene, is favored. On the other hand, complex 18, which may be less readily reduced than 17, may permit dialkylation of 19. The dialkylated radical anion 20 is eventually oxidized to give o-xylene.

The role of metal ion complexation to the arene has not been resolved and more conventional mechanisms based on oxidative addition and reductive elimination products cannot be totally excluded (ref. 16). Nevertheless, the sequence shown above is favored because the product distributions conform well with those predicted from spin densities calculated for radical anions.

CYCLIZATION OF DIYNES

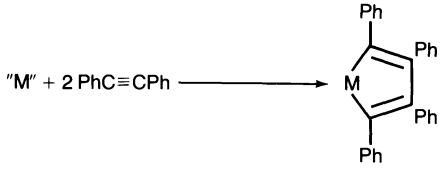
Another application of organometallic methods is the synthesis of conjugated exocyclic dienes 22 by reductive cyclization of alkadiynes 21. The key to success in this development was discovery of a titanium reagent 23 that coordinates the diyne and reduces it to form a new intramolecular C-C bond.



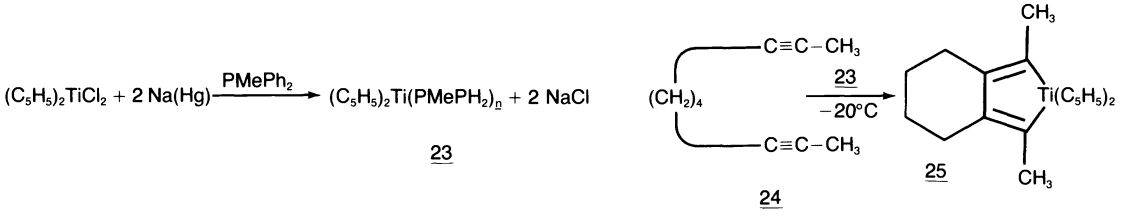
21 22

The exocyclic dienes 22 have exclusively the E, E structure and are reactive with many conventional dienophiles in the Diels-Alder reaction (ref. 17).

The development of this diyne cyclization is built on the known reductive dimerization of diphenylacetylene with a variety of transition metal reagents "M".



In such reactions in the literature, "M" can be diverse species such as "C_5H_5Co", "$(C_5H_5)_2Ti$" or "$(C_5Me_5)_2Cr$", which are generated from higher coordinate precursors (ref. 18). Scouting of a wide variety of possible reagent combinations uncovered a particularly effective mixture comprising $(C_5H_5)_2TiCl_2$, methyldiphenylphosphine and sodium amalgam. Presumably, these reactants form a phosphine-coordinated titanocene 23.

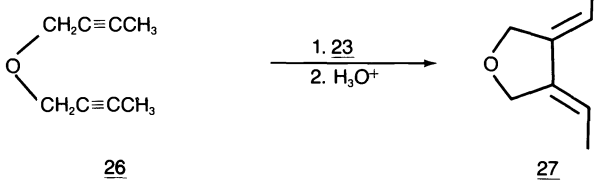


23 24 25

A plausible explanation of the cyclization reaction is that an alkadiyne molecule such as 2,8-decadiyne (24) can displace the phosphine ligands from 23 to form a titanacycle 25.

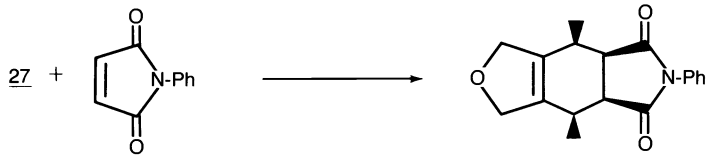
Hydrolysis of the reaction intermediate, presumably 25, gives an 80% yield of the exocyclic diene, (E, E)-1,2-diethylidenecyclohexane (22, R = CH_3, n = 4). Hydrolysis with deuterium oxide gives the same product with deuteriums in the two vinylic positions, as expected for deuterolysis of the C-Ti bonds in 25.

The scope of this cyclization is fairly broad. Internal diynes with three or four bridging methylene groups (21, n = 3 or 4) form the relatively unstrained cyclopentane and cyclohexane derivatives in good yield. The reaction is less efficient when strained rings are formed; the cycloheptane derived from 21 (n = 5) is produced in only 27% yield. The cyclooctane analog does not form. A wide variety of terminal alkyl and aryl groups (R and R' in 21) can be tolerated, but terminal alkadiynes (R = R' = H) do not work. The reaction works nicely with ether-containing diynes such as the dibutynyl ether 26.

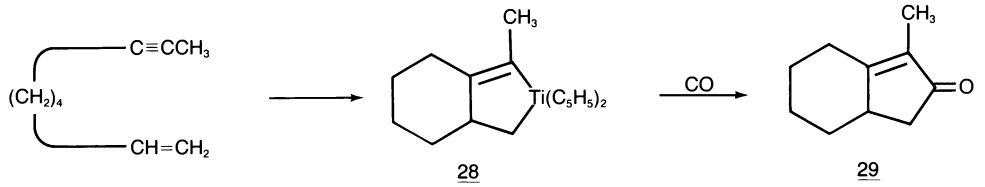


26 27

The exocyclic dienes produced by reductive cyclization work well in Diels-Alder reactions with dienophiles that bear electron withdrawing substituents. For example, the cyclic ether 27 reacts cleanly with N-phenylmaleimide.



The titanacycle 25 and its presumed analog 28, derived from 1,7-nonenyne, show interesting reactions with electrophiles other than proton. The titanacycle 28 reacts with either CO or CO_2 to produce the ketone 29 in about 40% yield.

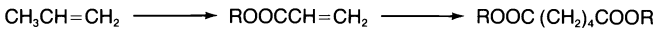


28 29

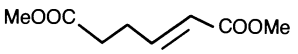
We are studying other reactions of the intermediate titanocycles in order to broaden the utility of the reductive cyclization reaction.

CYCLOPENTANONES VIA CYCLIZATION

The final example of our work on organometallic methods for organic synthesis differs from the previous four in that the original research was aimed at a propylene-based route to adipic acid



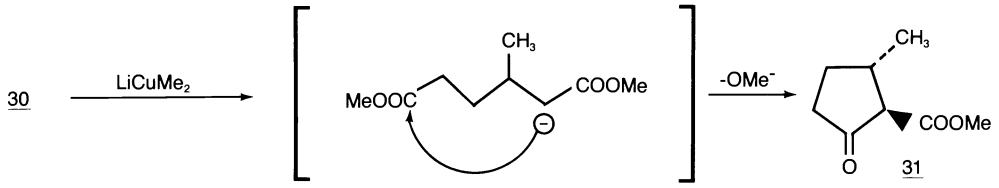
derivatives. The dimerization of methyl acrylate was explored. In contrast to previous work on dimerization of acrylate esters (ref. 19), high yields of a single isomer were obtained with a cationic palladium catalyst (refs. 20, 21). When methyl acrylate was treated with a mixture of $[Pd(NCMe)_4](BF_4)_2$ and $LiBF_4$ at 40°C, a 93% yield of dimers was obtained. The distilled product was 93-96% of dimethyl (E)-2-hexenedioate (30).



30

The significance of this finding was uncertain in terms of a new commercial synthesis of adipic acid, but the structure of the product suggested that it might be a useful intermediate in synthesis of substituted cyclopentanones. Since the 2,3-disubstituted cyclopentane structure is fundamental to the prostaglandins and other important biologically active compounds, we decided to pursue this possibility.

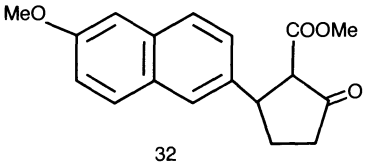
The key discovery was that conjugate addition of a nucleophile to the C=C bond of 30 generated an anion that spontaneously cyclized to form a five-membered ring. For example, addition of a methyl group from lithium dimethylcuprate initiates the following sequence.



31

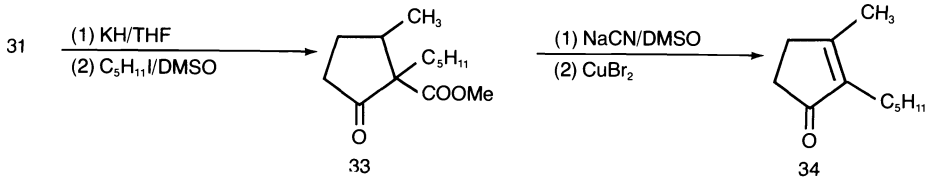
This particular reaction to form 31 proceeds in 76% yield when carried out with a two-fold excess of $LiCuMe_2$ in ether at -25°C. Yields in the range of 40-80% are obtained with a wide variety of alkyl, aryl and vinylcuprate reagents. Typically, the reaction produces a single goemetric isomer, the trans configuration, as shown for 31.

The reaction can also be carried out with a Grignard reagent as the alkylating agent. A cuprous salt is used as a catalyst to promote the initial conjugate addition to the C=C bond. For example, 6-methoxy-2-naphthylmagnesium bromide gives 32 in 53% yield when cuprous chloride is used as the catalyst.



32

The requirement for an excess of organometallic reagent in this reaction arises from the fact that products such as 31 and 32 possess an enolizable hydrogen α to the carbomethoxy group. While this structural feature of the product complicates the original synthesis, it is a significant advantage in terms of adding desired structural features to a cyclopentanoid product. This virtue is illustrated in a simple synthesis of dihydrojasmone 34.



33 34

Deprotonation of 31 with potassium hydride followed by alkylation with amyl iodide produces mixed geometrical isomers of 33. The nature of the mixture is not significant in this instance because the following step, oxidative decarboxylation to form 34, erases the stereochemical complexity. The yield of dihydrojasmone from 31 is 42%. The synthesis of dihydrojasmone is not particularly significant in itself, but it illustrates the virtues of this methodology in synthesis of 2,3-disubstituted cyclopentanones.

SUMMARY

These five examples from our organic synthesis research at Du Pont demonstrate the usefulness of organometallic methods in solving problems of potential industrial significance. We anticipate that such methods will be used more extensively as organic chemists become familiar with their capabilities. Some organometallic reactions approach enzymatic selectivity in producing desired molecular configurations. One of the major questions for the future is the relative importance of organometallic and enzymatic methods in synthesis of complex organic molecules.

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