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Organic Syntheses by Means of Noble Metal Compounds. XXVIII. Syntheses of a New Type of π-Allylic Palladium Complexes from α, β- and β, γ-Unsaturated Esters and Their Carbonylation[1, 2]

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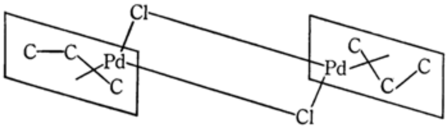
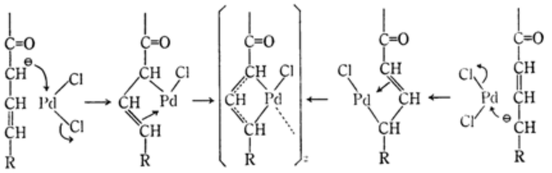
A general method of synthesizing a new type of π-allylic complex of palladium from compounds with an allylic hydrogen activated by a carbonyl group is described. Ethyl 3-butenoate and ethyl 2-butenoate give the same carbethoxy-substituted π-allyl complex, with hydrogen chloride eliminated, when treated with palladium chloride. Unsaturated diesters, such as diethyl glutaconate and diethyl 3-hexenedioate, also react with palladium chloride to give the corresponding π-allylic complexes. The structures of these complexes are discussed by means of a study of their NMR spectra. The carbonylation of these complexes proceeds smoothly, and carbon monoxide is introduced to form unsaturated esters. 3-Butenoate and then glutaconate are prepared, starting from allyl chloride, by a series of complex formations and carbonylation reactions. The possible synthetic application of this method of step-by-step introduction of carbon monoxide to other olefins is suggested. Diethyl 3-hexenedioate gives the complex, which is then converted into diethyl muconate by the elimination of palladium by the action of a base or carbon monoxide.

The π-allylic complex is a class of complexes formed with several transition metal compounds.³⁾ The simplest complex, π-allylpalladium chloride, has the structure shown below:



A number of π-allylic-type complexes of palladium chloride are known; they can be prepared from the following compounds: 1) Allylic halide or allylic alcohol and palladium chloride.⁴⁾ 2) Conjugated dienes and bisbenzonitrile dichloropalladium.⁵⁾ 3) Allene and bisbenzonitrile dichloropalladium.⁶⁾ 4) Substituted olefin and palladium chloride.⁷⁾ 5) Mesityl oxide and palladium chloride.⁸⁾

However, systematic studies of the preparation of π-allylic complexes with one or more functional groups have only once been attempted.⁹⁾ The only exception is the complex of mesityl oxide, which has a ketonic group. A consideration of the mechanism of these allylic complex formations led us to expect that compounds with an active hydrogen at an allylic position should form π-allylic complexes, eliminating hydrogen chloride, in the manner shown below:



As the most suitable compounds, α, β- and β, γ-unsaturated carbonyl compounds were chosen; the reactions of these compounds with palladium chloride were investigated. We have found that ethyl 3-butenoate formed a yellow complex when treated with palladium chloride, while ethyl 2-butenoate gave rise to the complex expected. Then the investigation of complex formation was

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1) A preliminary account of a part of this work has already been given, J. Tsuji, S. Imamura and J. Kiji, *J. Am. Chem. Soc.*, **86**, 4491 (1964).

2) Part XXVII: J. Tsuji and K. Ohno, *ibid.*, **88**, 3452 (1966).

3) A review article on π-allylic complexes has been published: M. L. H. Green and P. L. I. Nagy, "Advances in Organometallic Chemistry," Vol. 2, Academic Press, New York (1964), p. 325.

4) J. Smidt and W. Hafner, *Angew. Chem.*, **71**, 284 (1959).

5) B. L. Shaw, *Chem. Ind.*, **1962**, 1190.

6) R. G. Schultz, *Tetrahedron*, **20**, 2809 (1964); *Tetrahedron Letters*, **1964**, 301; M. S. Lupin and B. L. Shaw, *ibid.*, **1964**, 883.

7) R. Hüttel and H. Christ, *Chem. Ber.*, **96**, 3101 (1963).

8) G. W. Parshall and G. Wilkinson, *Chem. Ind.*, **1962**, 261.

9) Recently, the preparation of π-allylic complexes from α, β-conjugated cyclic ketones as an extension of the work described in this paper has been reported briefly: A. Kasahara, Y. Tanaka and K. Asamiya, Abstracts of Papers Presented at the 19th Annual meeting of Japan Chemical Society (1966), p. 324.

extended to various compounds with allylic hydrogens activated by carbonyl groups.

For the complex formation, the following three methods were used: 1) An α,β- or β,γ-unsaturated carbonyl compound was refluxed in an ethanolic solution of sodium tetrachloropalladate for 5—20 min. 2) Palladium chloride was mixed with an excess of the unsaturated compound and heated for 0.5—20 hr, and the reaction mixture was extracted with chloroform. 3) The unsaturated compound was mixed with a benzene solution of bisbenzonitrile dichloropalladium and then left for several days at room temperature. Each of these methods has its own merits and faults. The method 1 is a homogeneous reaction and proceeds rapidly, but a considerable amount of palladium chloride is reduced by ethanol to metallic palladium. The method 2 is heterogeneous and, hence, a slow reaction. This method gives a rather pure product, but it is not suitable for the preparation of those complexes which tend to decompose upon long heating

TABLE 1. π-ALLYLIC COMOLEXES

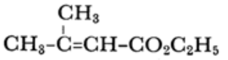
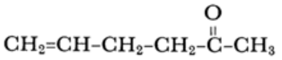
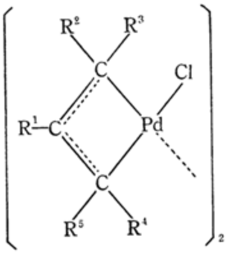
Starting material	Method of preparation	Yield %	Mp °C	MW found (calcd.)	Anal. found (calcd.) C%	H%	Cl%
$CH_2\text{=}CH\text{-}CH_2\text{-}CO_2H$	3	73	195—210	—	21.66 (21.17)	2.33 (2.22)	14.99 (15.62)
$CH_2\text{=}CH\text{-}CH_2\text{-}CO_2CH_3$	1	33	190	—	24.97 (24.92)	2.95 (2.93)	14.87 (14.71)
$CH_2\text{=}CH\text{-}CH_2\text{-}CO_2C_2H_5$	2	44	141—143	497.6 (509.9)	28.44 (28.26)	3.60 (3.56)	14.08 (13.90)
$CH_2\text{=}CH\text{-}CH_2\text{-}CO_2C_3H_7$	1	68	78—79	530.3 (537.8)	31.46 (31.25)	4.16 (4.12)	13.23 (13.19)
$CH_3\text{-}CH\text{=}CH\text{-}CH_2\text{-}CO_2C_2H_5$	1	37	140—150	527.4 (537.8)	31.35 (31.25)	4.11 (4.12)	13.21 (13.19)
 $CH_3\text{-}\overset{\overset{CH_3}{\mid}}{C}\text{=}CH\text{-}CO_2C_2H_5$	2	26	173	—	31.55 (31.25)	4.04 (4.12)	13.28 (13.19)
$C_2H_5O_2C\text{-}CH\text{=}CH\text{-}CH_2\text{-}CO_2C_2H_5$	2	17	175—176	658.8 (654.1)	33.29 (33.05)	4.09 (4.01)	10.89 (10.84)
 $CH_2\text{=}CH\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\parallel}}{C}\text{-}CH_3$	1	54	155—163	—	30.01 (30.16)	3.73 (3.80)	15.25 (14.83)
$H_5C_2OOC\text{-}CH_2\text{-}CH\text{=}CH\text{-}CH_2\text{-}CO_2C_2H_5$	1	75	148—151	690.0 (682.1)	35.45 (35.21)	4.43 (4.43)	10.54 (10.40)
$CH_3O_2C\text{-}CH_2\text{-}CH\text{=}CH\text{-}CH_2\text{-}CO_2CH_3$	1	80	147—148	617.0 (626.1)	30.90 (30.69)	3.55 (3.54)	11.40 (11.33)

TABLE 2. NMR SPECTRA OF π-ALLYLIC COMPLEXFS



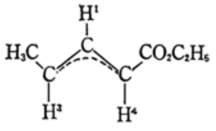
No.	R^1	R^2	R^3	R^4	R^5	τ τ_1	τ_2	τ_3	τ_4	Coupling constant (cps) J_{12}	J_{13}	J_{14}	Other
I	H	H	H	H	H	4.55	5.98	7.05		7.1	12.1		
II	H	H	H	H	$CO_2C_2H_5$	3.90	5.80	6.71	6.36	7.2	12.5	11.3	
III	H	H	H	H	$CO_2C_3H_7$	3.90	5.77	6.64	6.30	7.1	12.3	10.8	
IV	H	CH_3	H	H	$CO_2C_2H_5$	4.10		5.78	6.56		11.0	11.0	CH_3 8.65 τ doublet
V	CH_3	H	H	H	$CO_2C_2H_5$		6.04	7.05	6.55	—	—	—	CH_3 7.50 τ singlet
VI	H	$CO_2C_2H_5$	H	H	$CO_2C_2H_5$	3.25		6.10				11.5	
VII	H	$CH_2CO_2C_2H_5$	H	H	$CO_2C_2H_6$	3.98		5.82	6.42	—	11.0	11.0	$\text{-}CH_2\text{-}$ 7.28 τ

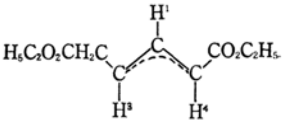
The method 3 is a mild one, but sometimes the separation of the allylic complex formed by the reaction from bisbenzonitrile dichloropalladium is not easy. In all cases, the reaction mixture should be left for a long time, sometimes for a month, with the occasional evaporation of a part of the solvents, in order to secure a miximum yield, because the complex has considerable solubility in organic solvents and precipitates slowly. Most of the complexes are moderately soluble in ordinary organic solvents. Chloroform, methylene chloride, and tetrahydrofuran seem to be the most suitable solvents for recrystallization. For this type of complex formation, several α,β- and β,γ-unsaturated esters were used; the results of the experiments are summarized in Table 1. In addition, the complex formation with a ketone with homoallylic hydrogens activated by a carbonyl group was attempted. Thus, 5-hexen-2-one formed the complex presumably after the migration of the double bond to the β,γ-position.

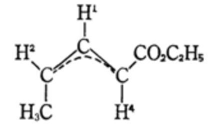
The Structure of the Complexes. The molecular-weight determination clearly indicates that the complexes have the dimeric structure. In addition, the infrared spectra of the complexes show an absorption due to the ester carbonyl, indicating that the carbonyl group does not take part in the complex formation. The most convincing evidence for the π-allylic structure was obtained by a study of the NMR spectra. The spectra of a large number of π-allyl complexes have been reported.³⁾ They are all essentially similar and may best be interpreted in terms of the sandwich structure. In Table 2, the τ values and coupling constants (J) of the complexes prepared from various α,β- and β,γ-unsaturated carbonyl compounds are shown and compared with the reported value of the related complex. For example, the spectrum of π-allylpalladium chloride (complex I) is analyzed thoroughly; it is known that the peak of H^1 appears as the lowest one (τ 4.55). In addition, in an allylic system, the syn protons (H^2) appear at a lower field than the anti protons (H^3). Anlike the simple assignment for the complex I, an important problem to be solved in the substituted complexes (II—VII) is the determination of the orientation of the substituted groups in the complexes.

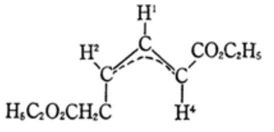
The assignment of the complexes of 3-butenoates (II and III) is straightforward and can be reasonably explained.¹⁰⁾ For example, the NMR spectrum of n-propyl 3-butenoate (III) can be explained in the following way. The peaks for H^1 (τ 3.90) and H^2 (τ 5.77) are reasonable. H^4 is affected by the $COOC_3H_7$ group; hence, its peak appears at τ 6.30. Therefore, the highest peak, at τ 6.64, can be assigned to H^3 without ambiguity. The coupling constants also support this assignment. H^1 couples with the two trans protons (H^3 and H^4), and their coupling constants were found to be $J_{13}=12.3$ and $J_{14}=10.8$ respectively. In addition, H^1 couples with the cis proton (H^2), and its coupling constant was found to be $J_{12}=7.1$. As a result of these couplings, the peak of H^1 was found to be an octet. Thus, it may be concluded that the orientation of the ester group is "syn."

On the other hand, the spectra of the complexes of ethyl 3-pentenoate (IV) and diethyl 3-hexenedioate (VII) need some comment. It is apparent that the ester groups have a syn orientation. Thus for these complexes, the following structures (IV-A and -B, and VII-A and -B) should be considered, depending on the orientation of the methyl and carboethoxymethyl groups.


IV-A


VII-A


IV-B


VII-B

At first glance, the IV-B structure seems probable because of the following assignments: H^1 (τ 4.10), H^2 (τ 5.78), and H^4 (τ 6.56), based on the assumption that the peak of H^2 will appear at a lower field than H^4. If the IV-B structure is the correct one, however, the trans coupling, J_{14}, is larger than the cis coupling, J_{12}, and hence the peak of H^1 should appear as a quartet. Actually, however, the peak of H^1 was observed as a clear triplet, showing that the coupling constants are of nearly the same order. Therefore, it can be concluded that the structure IV-A expresses the correct structure of the complex, and J_{14} and J_{13} may be calculated to be 11 each. They are reasonable values for trans couplings.

The same situation was observed with the spectrum of the complex VII; the conclusion is that the structure VII-A is the correct one. In this case also, H^3 (τ 5.82) appears at the field lower than that of H^4 (τ 6.42). These conclusions seem rather unusual, for H^4 is next to the carbonyl group and H^3 is next to the methyl or methylene, and hence H^4 should appear at the lower field due to the effect of the carbonyl group.¹¹⁾ It seems

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10) The NMR spectra of allylic complex of methyl 3-butenoate with iron carbonyl have recently been reported by H. D. Murdoch, *Z. Naturforsch.*, **20b**, 179 (1965).

11) The structure of the complex IV given on the basis of the assignment of the NMR spectrum described in the preliminary communication (Ref. 1) was not correct and should be modified.

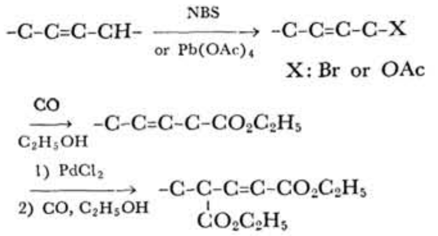
likely that H^4 is located closer to palladium than H^3. These conclusions were confirmed by the analyses of the spectra with a decoupling technique and by detailed calculations. The complete analyses of the spectra of the complexes IV and VII leading to these conclusions will be given in a separate paper.

The Carbonylation of the Complexes. We have previously reported that π-allylic complexes obtained from allylic compounds and conjugated dienes can be carbonylated to form β, γ-unsaturated esters in alcohol.[12,13] For example, ethyl 3-butenoate can be obtained by the carbonylation of allyl chloride or allyl alcohol catalyzed by palladium chloride. Therefore, it may be expected that all the complexes obtained here will be carbonylated. Actually, the complex II was carbonylated to form ethyl glutaconate, accompanied with β-ethoxyglutarate. It seems likely that the latter is formed by the Michael addition of ethanol to ethyl glutaconate. Ethyl glutaconate has allylic hydrogens activated by the two carbethoxy groups. Therefore, glutaconate formed the complex VI more easily than was expected.

In view of the facts that π-allyl complex is carbonylated to give the β, γ-unsaturated ester and that the resulting β, γ-unsaturated ester can form π-allylic complex when reacted with palladium chloride, there is an interesting synthetic application of these reactions. In other words, by this sequence of complex formation and carbonylation reaction, carbon monoxide can be introduced one after another forming β, γ-unsaturated esters. Thus, starting from allyl chloride or allyl alcohol, the following sequence of the reactions is established:

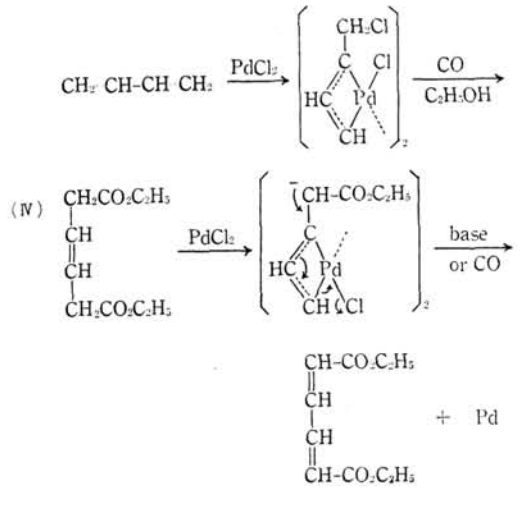
$$\begin{gathered}CH_2{=}CH{-}CH_2{-}Cl \xrightarrow{PdCl_2} \pi\text{-allyl complex I}\\ \xrightarrow[C_2H_5OH]{CO} CH_2{=}CH{-}CH_2CO_2CH_5 \xrightarrow{PdCl_2} \text{complex II}\\ \xrightarrow[C_2H_5OH]{CO} H_5C_2O_2C{-}CH{=}CH{-}CH_2{-}CO_2C_2H_5\\ \xrightarrow{PdCl_2} \text{Complex VI}\end{gathered}$$

This sequence of reactions can be extended further to simple olefins in order to prepare unsaturated mono- or diesters. At first the olefin is treated with *N*-bromosuccinimide or lead tetraacetate in order to introduce a halogen or an acetoxy group at an allylic position. Thus, the allylic position can be carbonylated to give a β, γ-unsaturated ester. In turn, the ester gives a complex with palladium chloride. The carbonylation of this complex gives rise to a diester:



$$\begin{gathered}{-}C{-}C{=}C{-}CH{-} \xrightarrow[\text{or } Pb(OAc)_4]{NBS} {-}C{-}C{=}C{-}C{-}X \quad X\text{: Br or OAc}\\ \xrightarrow[C_2H_5OH]{CO} {-}C{-}C{=}C{-}C{-}CO_2C_2H_5\\ \xrightarrow[2)\ CO,\ C_2H_5OH]{1)\ PdCl_2} {-}C{-}\underset{\displaystyle CO_2C_2H_5}{\underset{|}{C}}{-}C{=}C{-}CO_2C_2H_5\end{gathered}$$

Another interesting application of this method is shown by the reaction of the complex of ethyl 3-hexenedioate (complex VII). Ethyl 3-hexenedioate can be obtained in a low yield by the carbonylation of the butadiene - palladium chloride complex.[13] The complex of hexenedioate has an active methylene, and it may be expected that the treatment of this complex with a base will give rise to muconate by the reductive elimination of palladium. This proved to be the case; the treatment of the complex with dimethyl sulfoxide anion in dimethyl sulfoxide gave rise to ethyl *trans, trans*-muconate. The most effective method of muconate formation was found to be the treatment with carbon monoxide. On the attempted carbonylation of this complex in benzene, muconate was produced. This method consists of an indirect oxidation of hexenedioate to muconate by palladium chloride. In other words, palladium chloride was utilized for the abstraction of two hydrogens in a unique fashion. By this method, muconic acid can be prepared from butadiene through complex formation, carbonylation, complex formation, and carbonylation, as is shown below, although the first step of the series, that is, the carbonylation of the butadiene complex, produces only a low yield.



Experimental

The NMR spectra were determined on Varian high-resolution spectrometers, Models DP 60 and HR 100,

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[12] J. Tsuji, J. Kiji, S. Imamura and M. Morikawa, *J. Am. Chem. Soc.*, **86**, 4359 (1964).

[13] J. Tsuji and S. Hosaka, *ibid.*, **87**, 4075 (1965).

using tetramethylsilane as an internal standard in $CDCl_3$; the peak positions are expressed in terms of τ values. The molecular weights were determined in benzene using a Mechrolab vapor-pressure osmometer.

Materials. Ethyl 3-butenoate was prepared by the carbonylation of allyl chloride in ethanol.[12] The other 3-butenoates were prepared by the esterification of 3-butenoic acid which had been prepared by the known method.[14] Ethyl 3-pentenoate was prepared by the palladium-catalyzed carbonylation of butadiene in ethanol.[15] 5-Hexen-2-one was prepared by the hydrolysis of ethyl allylacetoacetate, followed by decarboxylation. Commercially-available 3-hexenedioic acid was used after esterification.

The Preparation of the Complexes. Only typical examples will be shown below.

a) Sodium tetrachloropalladate (29 g) was dissolved in warm methanol (300 m*l*), and then methyl 3-butenoate (15 g) was added. After the mixed solution had been refluxed for 5 min, yellow crystals began to precipitate. After it had stood in an ice box for one day, the complex (8 g, 33% based on palladium chloride) was collected by filtration and recrystallized from tetrahydrofuran.

b) Ethyl 2-butenoate (13 g) was mixed with palladium chloride (1.5 g); the mixture was then refluxed for 14 hr, and the reaction mixture was extracted with chloroform. The chloroform solution was concentrated, and the residue was recrystallized from chloroform to give the complex (1.3 g, 60%).

c) 3-Butenoic acid (1 g) and an equivalent amount of bisbenzonitrile dichloropalladium were dissolved in benzene. After the mixture had stood at room temperature for a few days, long, yellow crystals appeared, giving 1.93 g (73%) of the complex.

d) Ethyl 3-hexenedioate (16 g) and sodium tetrachloropalladate (24 g) were dissolved in 150 m*l* of ethanol, and the mixed solution was refluxed for 30 min. The solution was then filtered to remove the precipitated metallic palladium, and the filtrate was allowed to stand at room temperature for one day. The precipitated yellow crystals were collected by filtration and washed successively with water, alcohol, and ether. From the filtrate, a 3-g portion of the complex was collected after 3 days. After one month, a total of 20.5 g (75%) of the complex had been obtained.

The Carbonylation of the Complex. *In Ethanol.* Complex III (4.6 g) was dissolved in 30 m*l* of ethanol, and the solution was poured into a glass vessel equipped with a gas inlet capillary. The vessel was set in an autoclave, and the carbonylation was carried out at 90°C under carbon monoxide pressure (150 kg/cm^2) for 16 hr. After the usual work-up, diethyl glutaconate (1 g, 30%) and ethyl β-ethoxyglutarate (0.8 g, 19%) were separated by preparative gas chromatography. Ethyl glutaconate was identified by comparing its NMR and infrared spectra with those of an authentic sample. Ethyl glutaconate was reduced with palladium on carbon, and the reduced product was hydrolyzed in ethanolic potassium hydroxide. Glutaric acid was obtained and identified by a mixed-melting-point determination (96—97°C). Also, ethyl glutaconate was hydrolyzed in ethanolic potassium hydroxide to give glutaconic acid, mp 129—131°C.

Ethyl ethoxyglutarate was identified by means of its NMR and infrared spectra; the NMR spectrum showed the following peaks: τ 8.78 (triplet) and τ 5.92 (quartet), due to two ethyl ester groups; τ 8.92 (triplet) and τ 6.50 (quartet), due to one ethyl ether, and τ 7.53 (doublet), due to two $-CH_2-$ groups.

Found: C, 56.78 ; H, 8.57%; mol wt, 230.3. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68%; mol wt, 232.3.

In Benzene. The complex (9 g) and benzene (50 m*l*) were set in the autoclave as has been described above, and the reaction was carried out under the same conditions. After the reaction mixture had been filtered, 20 m*l* of ethanol was added and the mixture was refluxed for 1.5 hr. Ethyl *trans*-glutaconate (2.76 g, 43%) and ethyl ethoxyglutarate (0.76 g., 9.5%) were thus obtained.

The Formation of Muconate. *With Carbon Monoxide.* The complex of ethly 3-hexenedioate (8.7 g) and 40 m*l* of benzene were set in the autoclave as has been described above, and the mixture was shaken for 20 hr at 100°C under carbon monoxide pressure (100 kg/cm^2). After the reaction, the reaction mixture was filtered, 40 m*l* of ethanol was added, and the solution was refluxed for 1 hr. Ether was added and dried. By distillation, 5.1 g of the product was obtained at 95—125°C/4 mmHg. Gas chromatographic analysis (thermol-3, 180°C and silicone DC 550 at 180°C) showed two peaks corresponding to ethyl 3-hexenedioate (2.3 g) and ethyl *trans, trans*-muconate (2.8 g). The product was redistilled at 95—96°C/4 mmHg. During the distillation, a crystalline substance began to deposit; it was collected. Purified by sublimation, the crystalline substance was determined to be ethyl muconate. Ethyl muconate: mp 59.5—61°C. λ_{max}^{MeOH} 262 mμ (ε=36500).[16]

Found: C, 60.68; H, 7.12%; mol wt, 200. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12%; mol wt, 198.2.

The NMR spectrum showed the following peaks; τ 8.70 (triplet) and τ 5.78 (quartet), due to two ethyl ester groups; τ 3.83 (quartet), due to two α-protons, and τ 2.68 (quartet), due to two β-protons.

With the DMSO Anion. Sodium hydride (50%, 1.2 g) was dissolved in 20 m*l* of DMSO by warming it to 50—60°C for 30 min. The complex (8 g) was then dissolved in DMSO (40 m*l*). The DMSO anion solution was stirred into the solution of the complex, drop by drop, at room temperature for 15 min. The mixture was stirred at room temperature for 1 hr, and then at 80°C for 30 min. The mixture was filtered, and a large amount of ether was added to the filtrate. The ethereal solution was washed well with water. The solution was dried, and the ether was evaporated. The distillation of the residue gave 2.5 g (53%) of ethyl muconate.

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14) E. C. Horning, "Organic Syntheses," Vol. III, p. 851 (1960).

15) J. Tsuji, J. Kiji and S. Hosaka, *Tetrahedron Letters*, **1964**, 605.

16) J. A. Elvidge, R. P. Linstead, P. Sim and B. A. Orkin, *J. Chem. Soc.*, **1950**, 2235.