

Palladium-Catalyzed Reactions of 1,3-Dienes with Active Methylene Compounds. II¹

GO HATA,* KUNIYUKI TAKAHASHI, AND AKIHISA MIYAKE

Basic Research Laboratories, Toray Industries, Inc., Kamakura, Japan

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In the presence of palladium and platinum catalysts, 1,3-dienes react with active methylene and methyne compounds such as β -keto esters, β diketones, dialkyl malonates, α -formyl ketones and esters, α -cyano and α -nitro esters, and ethyl phenylsulfonylacetate to form corresponding 2,7-alkadienyl derivatives. In the palladium-catalyzed reactions of active methylene compounds with 1,3-butadiene, 1:2 adducts **1** and 1:4 adducts **2** are obtained as main products, and small amounts of branched 1:2 adduct **3** are isolated as by-products. Addition of isoprene to active methylene compounds gives 2,7-dimethyl-2,7-octadienyl derivatives **4** and **5**, derived from tail-to-tail dimerization of isoprene, almost selectively. In contrast to the addition of isoprene, the reaction of 1,3-pentadiene affords a head-to-tail adduct **6**. In the platinum-catalyzed reaction of 1,3-butadiene with active methylene compounds, a ratio of the branched 1:2 adduct **3** to all the adducts is larger than that observed in the palladium-catalyzed reaction, and 1:1 adduct and 1:3 adduct are isolated as by-products besides **1**, **2**, and **3**. A reaction intermediate **7** involving a four-coordinated palladium system derived from the tertiary phosphine complex of palladium(0) is postulated.

Oligomerization of 1,3-butadiene to cyclic or linear products is catalyzed by some transition metal complexes.^{2,3} Recently, a new type of linear dimerization of 1,3-butadiene catalyzed by transition metal compounds of group VIII of the periodic table, which is completed by addition of a compound having at least one active hydrogen atom, has been found. Tertiary phosphine complexes of palladium(0) were reported to catalyze the reaction of 1,3-butadiene with methanol and phenol to give 1-methoxy-2,7-octadiene and 1-phenoxy-2,7-octadiene, respectively.⁴⁻⁶ A mixture of palladium chloride and sodium phenoxide is quite a selective catalyst for the latter reaction.⁷ Similar reactions have been reported to take place using primary and secondary amines, carboxylic acids,⁵ and active methylene and methyne compounds.^{1,8} A reaction of trimethylsilane with 1,3-butadiene catalyzed with (maleic anhydride)bis(triphenylphosphine)palladium(0)⁹ and that of amines with the diene in the presence of a triethyl phosphite complex of nickel(0)¹⁰ proceed in a little different way to give corresponding 2,6-octadienyl derivatives.

Part of our work on the reaction of the active methylene and methyne compounds with 1,3-dienes has been reported in a preliminary communication.¹ The present paper describes the reaction in detail.

An active and easily available catalyst is prepared by mixing dichlorobis(triphenylphosphine)palladium and basic sodium compounds such as sodium phenoxide, sodium methoxide, sodium carbonate, and sodium salts of the active methylene and methyne compounds used

as the starting reagents. A mixture of palladium chloride and sodium phenoxide showed the same catalytic behavior, but a quite low catalytic activity. Ammonia and pyridine complexes of palladium salts are more effective than palladium chloride but less effective than the triphenylphosphine complex. The low reactivity observed on using palladium chloride and the ammonia and pyridine complexes as catalyst components seems to be due to decomposition of the catalytic species to metallic palladium which appeared during the reaction. On the other hand, in the presence of triphenylphosphine, no separation of metallic palladium was observed and the solution remained pale yellow after completion of the reaction. Zero valent palladium complexes such as tetrakis(triphenylphosphine)palladium(0) and (maleic anhydride)bis(triphenylphosphine)palladium(0) showed catalytic activity without the basic sodium components.

The reaction was applied to compounds with a methylene and methyne group to which two electro-negative groups, such as carbonyl, alkoxy-carbonyl, formyl, cyano, nitro, and sulfonyl groups, are attached. The reaction of the active methylene compounds with butadiene gave two kinds of main products, 1:2 adducts **1** and 1:4 adducts **2**. At an early stage of the reaction the product consisted mainly of **1**. Further addition of butadiene to **1** afforded **2**.

The reaction products were identified by means of elemental analysis, molecular weight measurement, and ir and nmr spectral measurements.

The results on the reaction of 1,3-butadiene with β -keto esters, β diketones, dialkyl malonates and their derivatives, α -formyl ketones, α -formyl esters, α -cyano and α -nitro esters, cyanoacetamide, and ethyl phenylsulfonylacetate are summarized in Tables I and II. The analytical and physical data of the products are listed in Table III. The infrared spectra of the products showed absorptions due to out-of-plane deformation of $-\text{CH}=\text{CH}_2$ near 910 and 990 cm^{-1} , and trans $-\text{CH}=\text{CH}-$ near 960 cm^{-1} . No absorption due to out-of-plane deformation due to cis $-\text{CH}=\text{CH}-$ was observed. This fact indicates that the internal double bond of the 2,7-octadienyl group consists exclusively or mainly of the trans form.

The reaction of ethyl acetoacetate with 1,3-butadiene in the presence of the $\text{PdCl}_2(\text{PPh}_3)_2\text{-PhONa}$ catalyst

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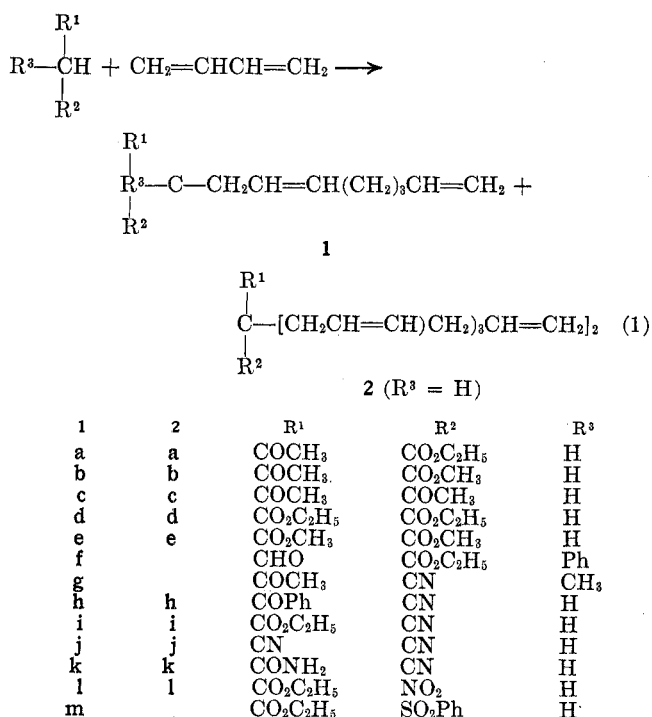
(9) S. Takahashi, T. Shibano, and N. Hagiwara, *Chem. Commun.*, 161 (1969).

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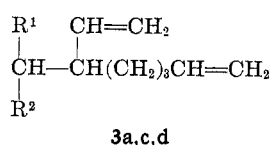
TABLE I
 PALLADIUM-CATALYZED REACTION OF ETHYL ACETOACETATE (0.1 MOL) WITH 1,3-BUTADIENE

Catalyst (mmol)		Butadiene, mol	Temp, °C	Time, min	Products, ^a % ^b	
Pd compd	Basic Na compd				CH ₃ COCHR- CO ₂ C ₂ H ₅	CH ₃ COCR- CO ₂ C ₂ H ₅
PdCl ₂ (Ph ₃ P) ₂ (0.02)	PhONa (2)	0.3	85	25	78	12
PdCl ₂ (Ph ₃ P) ₂ (0.01)	PhONa (1)	0.3	85	60	78	16
PdCl ₂ (Ph ₃ P) ₂ (0.05)	PhONa (3)	0.5	85	210	26	70
PdCl ₂ (Ph ₃ P) ₂ (0.02)	NaCH(COCH ₃)- CO ₂ C ₂ H ₅ (2)	0.3	85	25	52	1
Pd(Ph ₃ P) ₄ (0.25)		0.3	85	30	20	Trace
Pd(Ph ₃ P) ₂ ·MA ^c (0.02)		0.3	85	75	39	0.6
PdCl ₂ (Ph ₃ P) ₂ (0.05)	PhONa (0.4)	0.3	50	30	11	Trace
PdCl ₂ (Ph ₃ P) ₂ (0.05)	PhONa (0.4)	0.3	60	30	59	3
PdCl ₂ (Ph ₃ P) ₂ (0.05)	PhONa (0.4)	0.3	70	30	63	4
PdCl ₂ (Ph ₃ P) ₂ (0.05)	PhONa (0.4)	0.3	85	30	72	28
PdCl ₂ (2)	PhONa (6)	0.3	130	180	63	6
Pd(NO ₂) ₂ (NH ₃) ₂ (0.5)	PhONa (5)	0.3	85	120	70	22
PdCl ₂ (NH ₃) ₂ (0.5)	PhONa (5)	0.3	85	120	82	5
PdCl ₂ (Py) ₂ (0.5)	PhONa (5)	0.3	85	120	69	4
PdCl ₂ (Ph ₃ As) ₂ (0.5)	PhONa (5)	0.3	85	120	53	

^a R = -CH₂CH=CH(CH₂)₃CH=CH₂. ^b Based on ethyl acetoacetate employed. ^c MA = maleic anhydride.



gave 1a and 2a as major products. The reaction occurred slowly at 50° but quite rapidly at 85°, as shown in Table I. Acetylacetone and diethyl malonate reacted with the diene to give 1c and 2c, and 1d and 2d, respectively. Selectivities of the products based on the converted active methylene compounds in the above three reactions were about 90%. As by-products, small amounts of branched 1:2 adducts, *i.e.*, 1-vinyl-5-hexenyl derivatives 3, were isolated. Ethyl aceto-



acetate and acetylacetone were more reactive than diethyl malonate. The effectiveness of the catalyst is shown by the fact that 10,000 molecules of ethyl aceto-


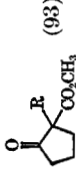

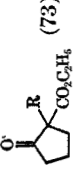

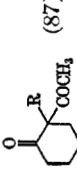

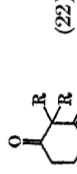
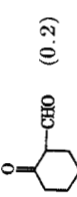
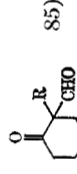
acetate per molecule of dichlorobis(triphenylphosphine)palladium could react in 60 min, as shown in Table I.

Ethyl 2-oxocyclopentanecarboxylate, 2-acetylcyclohexanone, and trimethyl 1,1,3-propanetricarboxylate reacted with the diene to yield the corresponding 2,7-octadienyl derivatives in 73, 87, and 83% yields, respectively. The reaction of the diene with 2-oxocyclohexanecarbaldehyde, 2-oxocyclododecanecarbaldehyde, and ethyl phenylformylacetate also afforded the 1:2 adducts in high yields. Ethanolysis of 2-acetyl-2-(2,7-octadienyl)cyclohexanone which was obtained from the above reaction resulted in the formation of 2-(2,7-octadienyl)cyclohexanone. The same compound was obtained by elimination of the formyl group of 1-(2,7-octadienyl)-2-oxocyclohexanecarbaldehyde, as expected. Although it seemed certain that the product from the reaction of 1,3-cyclohexanedione with the diene contained a 1:2 adduct besides a 1:4 adduct, the 1:2 adduct has not been identified owing to a poor separation in a fractional distillation.

β-Keto esters, β diketones, α-formyl ketones, and α-formyl esters are in equilibrium between keto and enol forms. Therefore, it might be possible that the hydroxy groups of the enol forms react with 1,3-butadiene to yield 2,7-octadienyl derivatives in which the octadienyl group is bonded to the oxygen atom, as methanol and phenol do. No such products, however, were observed. The addition of 1,3-butadiene to the carbon atom of the active methylene and methyne is quite selective.

Compounds having a cyano group in place of a carbonyl or an ester group of β-keto esters reacted in the same way. The reaction of ethyl cyanoacetate with 1,3-butadiene gave the linear adducts 1i and 2i with a small amount of a branched adduct, ethyl (1-vinyl-5-hexenyl)cianoacetate. The results on the reaction of the diene with 3-oxo-2-methylbutyronitrile, cyanoacetamide, benzoylacetonitrile, and malononitrile are listed in Table II. Low yields of the products in the reaction of the diene with nitroacetone and ethyl nitroacetate seem to be due to decomposition of the catalyst. Ethyl (phenylsulfonyl)acetate reacted with the diene to yield 1m in a 91% yield.

TABLE II
 PALLADIUM-CATALYZED REACTION OF ACTIVE METHYLENE AND METHYNE COMPOUNDS WITH 1,3-BUTADIENE

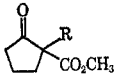
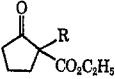
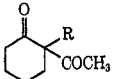
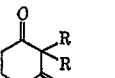
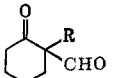
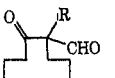
Active methylene and methyne compd (mol)	BD, ^a mol	Catalyst, mmol PdCl ₂ (Ph ₃ P) ₂	Basic Na compd	Temp, °C	Time, min	Products, ^b (%)
CH ₂ COCH ₂ CO ₂ CH ₃ (0.1) CH ₃ COCH ₂ CO ₂ CH ₃ (0.25)	0.3	0.02	PhONa (2)	85	25	CH ₂ COCH ₂ CO ₂ CH ₃ (61)
	0.6	0.07	MeONa (4)	85	140	CH ₃ COCH ₂ CO ₂ CH ₃ (43) CH ₃ COCH ₂ CO ₂ CH ₃ (7) CH ₃ COCH ₂ CO ₂ CH ₃ (11)
 (0.053)	0.2	0.02	PhONa (1.5)	85	90	 (93)
 (0.053)	0.2	0.02	PhONa (1.5)	85	90	 (73)
CH ₂ CO ₂ CH ₃ CH(COCH ₃)CO ₂ CH ₃ (0.09)	0.4	0.05	CH ₃ ONa (1)	85	180	CH ₂ CO ₂ CH ₃ (83) CH(COCH ₃)CO ₂ CH ₃
CH ₂ COCH ₂ COCH ₃ (0.1) CH ₃ COCH ₂ COCH ₃ (0.1) CH ₃ COCH ₂ COCH ₃ (0.15)	0.3	0.02	PhONa (2)	85	180	CH ₂ COCH ₂ COCH ₃ (62)
	0.3	0.02	PhONa (2)	85	25	CH ₃ COCH ₂ COCH ₃ (13)
	0.45	3 ^d	NaCH(COCH ₃) ₂ (9)	135	180	CH ₂ COCH ₂ COCH ₃ (7) CH ₃ COCH ₂ COCH ₃ (18)
 (0.2)	0.5	0.02	PhONa (1)	85	130	 (87)
 (0.036)	0.11	0.2	MeONa (2)	85	60	 (22)
CH ₂ (CO ₂ C ₂ H ₅) ₂ (0.1) CH ₂ (CO ₂ CH ₃) ₂ (0.1) CH ₂ CO ₂ CH ₃ (0.09)	0.3	0.02	PhONa (2)	85	180	RCH(CO ₂ C ₂ H ₅) ₂ (47)
	0.3	0.2	PhONa (6)	85	180	RCH(CO ₂ CH ₃) ₂ (49) CH ₂ CO ₂ CH ₃
	0.3	0.5	CH ₃ ONa (5)	85	105	CH ₂ CO ₂ CH ₃ (83) CH(CO ₂ CH ₃) ₂
 (0.2)	0.5	0.03	PhONa (1)	85	90	 (85)

Malonates

β Diketones

α -Formyl Ketones and α -Formyl Esters

TABLE III
PHYSICAL AND ANALYTICAL DATA OF THE PRODUCTS^a

Product ^b	Registry no.	Bp, °C (mm)	n_D^{25}	Empirical formula	Molecular weight Calcd	Molecular weight Found
RCH(COCH ₃) ₂	29330-76-5	135-6 (7)	1.4800	C ₁₃ H ₂₀ O ₂	208	208 ^c
R ₂ C(COCH ₃) ₂	29330-77-6	170-1 (3)	1.4837	C ₂₁ H ₃₂ O ₂	316	316
CH ₂ =CH(CH ₂) ₃ CH=CHCH ₂ C- (CH ₂ CH=CHCH ₃)(COCH ₃) ₂	29331-16-6	129-30 (3)	1.4800 ^d	C ₁₇ H ₂₆ O ₂	264	257
CH ₂ =CH(CH ₂) ₃ CH(CH=CH ₂)- CH(COCH ₃) ₂	26450-24-8	105-7 (11)	1.4630	C ₁₃ H ₂₀ O ₂		
CH ₂ =CHCH(CH ₃)CH(COCH ₃) ₂	29149-83-5	199	1.4497	C ₉ H ₁₄ O ₂	154	155
RCH(COCH ₃)CO ₂ C ₂ H ₅	26561-31-9	139 (5)	1.4580	C ₁₄ H ₂₂ O ₃	238	238 ^c
R ₂ C(COCH ₃)CO ₂ C ₂ H ₅	26561-32-0	189 (5)	1.4758	C ₂₂ H ₃₄ O ₃	346	346 ^c
CH ₂ =CH(CH ₂) ₃ CH(CH=CH ₂)- CH(COCH ₃)CO ₂ C ₂ H ₅	29085-37-8	98-102 (20)	1.4539	C ₁₄ H ₂₂ O ₃	238	232
RCH(COCH ₃)CO ₂ CH ₃	29330-83-4	111 (1.5)	1.4588	C ₁₃ H ₂₀ O ₃	224	228
R ₂ C(COCH ₃)CO ₂ CH ₃	29330-84-5	181 (3.5)	1.4775	C ₂₁ H ₃₂ O ₃	332	335
RCH(CO ₂ CH ₃) ₂	29330-85-6	111-7 (1)	1.4563	C ₁₈ H ₂₀ O ₄	240	238
R ₂ C(CO ₂ CH ₃) ₂	29330-86-7	162 (1)	1.4735	C ₂₁ H ₃₂ O ₄	348	351
RCH(CO ₂ C ₂ H ₅) ₂	29330-87-8	134-5 (3)	1.4496	C ₁₅ H ₂₄ O ₄	268	276
R ₂ C(CO ₂ C ₂ H ₅) ₂	29330-88-9	179 (2)	1.4672	C ₂₃ H ₃₆ O ₄	376	376 ^c
CH ₂ =CH(CH ₂) ₃ CH(CH=CH ₂)- CH(CO ₂ C ₂ H ₅) ₂	29330-89-0	100 (1.3)	1.4483	C ₁₅ H ₂₄ O ₄	268	263
	29453-58-5	130 (2)	1.4776	C ₁₅ H ₂₂ O ₃	250	256
	29330-90-3	137-8 (3)	1.4739	C ₁₆ H ₂₄ O ₃	264	260
	29330-91-4	149 (3.5)	1.4759	C ₁₆ H ₂₄ O ₂	248	246
	29330-92-5	149-151 (0.001)	1.4983	C ₂₂ H ₃₂ O ₂	328	325
CH ₃ O ₂ CCH ₂ CH ₂ CR(COCH ₃)CO ₂ CH ₃	29453-59-6	154-7 (1)	1.4655	C ₁₇ H ₂₆ O ₆	310	311
CH ₃ O ₂ CCH ₂ CH ₂ CR(CO ₂ CH ₃) ₂	29330-93-6	161-2 (1)	1.4652	C ₁₇ H ₂₆ O ₆	326	323
	29330-94-7	158 (4.5)	1.4880	C ₁₅ H ₂₂ O ₂	234	234
	29330-95-8	169-173 (0.02)	1.4993	C ₂₁ H ₃₄ O ₂	318	311
PhCR(CHO)CO ₂ C ₂ H ₅	29330-96-9	156-9 (0.1)	1.5075	C ₁₉ H ₂₄ O ₃	300	306
RCH(CN) ₂	29330-97-0	115 (2)	1.4626	C ₁₁ H ₁₄ N ₂	174	170
R ₂ C(CN) ₂	29330-98-1	174-6 (4)	1.4800	C ₁₉ H ₂₆ N ₂	282	278
RCH(CN)COOC ₂ H ₅	29453-60-9	120-120.5 (2)	1.4553	C ₁₈ H ₁₉ NO ₂	221	221
R ₂ C(CN)COOC ₂ H ₅	29330-99-2	161-2 (2)	1.4747	C ₂₁ H ₃₁ NO ₂	329	317
CH ₃ CR(CN)COCH ₃	29331-00-8	111-2 (4)	1.4652	C ₁₈ H ₁₉ NO	205	199
R ₂ C(CN)CONH ₂	29331-01-9	172 (0.002)		C ₁₉ H ₂₈ N ₂ O	300	294
RCH(CN)COPh	29331-02-0	134-6 (10 ⁻⁴)	1.5293	C ₁₇ H ₁₉ NO	253	261
R ₂ C(CN)COPh	29331-03-1	156-8 (10 ⁻⁴)	1.5210	C ₂₅ H ₃₁ NO	361	353
RCH(NO ₂)COOC ₂ H ₅	29331-04-2	110-2 (2)	1.4619	C ₁₂ H ₁₉ NO ₄	241	239
R ₂ C(NO ₂)COOC ₂ H ₅	29331-05-3	154-6 (2)	1.4820	C ₂₀ H ₃₁ NO ₄	349	330
RCH(SO ₂ Ph)COOC ₂ H ₅	29331-06-4	156-7 (10 ⁻⁴)	1.5176	C ₁₈ H ₂₄ SO ₄	336	334

^a All compounds in Tables III and V gave C, H (and N when present) analyses within ± 0.4 . The analytical data were made available to the editors and to the referees. ^b R = -CH₂CH=CH(CH₂)₃CH=CH₂. ^c Determined by mass spectroscopy. The others were measured by vapor pressure osmometry. ^d n_D^{20} .

TABLE V
 PHYSICAL AND ANALYTICAL DATA OF THE PRODUCTS^a

Product	Registry no.	Bp, °C (mm)	n_D^{20}	Molecular weight	
				Calcd	Found
$\text{CH}_2=\text{C}(\text{CH}_3)(\text{CH}_2)_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}(\text{COCH}_3)\text{COOC}_2\text{H}_5$	29085-27-6	103-104 (0.05)	1.4629	266	270
$[\text{CH}_2=\text{C}(\text{CH}_3)(\text{CH}_2)_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2]_2\text{C}(\text{COCH}_3)\text{COOC}_2\text{H}_5$	29085-29-8	160-162 (0.01)	1.4847	402	395
$\text{CH}_2=\text{C}(\text{CH}_3)(\text{CH}_2)_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}(\text{COCH}_3)_2$	29085-32-3	96-98 (0.02)	1.4808	236	234
$[\text{CH}_2=\text{C}(\text{CH}_3)(\text{CH}_2)_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2]_2\text{C}(\text{COCH}_3)_2$	29085-33-4	150-152 (0.001)	1.4910	372	377
$\text{CH}_2=\text{CHCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3)\text{CH}(\text{COCH}_3)\text{COOC}_2\text{H}_5$	29331-11-1	104-105 (0.35)	1.4569	266	265
$\text{CH}_2=\text{CHCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3)\text{CH}_2\text{COOC}_2\text{H}_5$	29331-12-2	74-76 (0.02)	1.4482	224	223
$\text{CH}_2=\text{C}(\text{CH}_3)-$	29085-31-2	122 (3)	1.4700	294	290
$\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}(\text{COCH}_3)\text{COOC}_2\text{H}_5$					

^a See footnote a in Table III.

$\text{PdCl}_2(\text{Ph}_3\text{As})_2$, ²¹ $\text{PtCl}_2(\text{Ph}_3\text{P})_2$, ²² and $\text{Pt}(\text{Ph}_3\text{P})_4$, ²² were prepared by the previously reported methods.

Acetylacetone, ethyl acetoacetate, methyl acetoacetate, diethyl malonate, dimethyl malonate, and malononitrile were purified by distillation under vacuum. Ethyl 2-oxocyclopentanecarboxylate, ²³ methyl 2-oxocyclopentanecarboxylate, ²³ 2-acetylcyclohexanone, ²⁴ 1,3-cyclohexanedione, ²⁵ cyanoacetamide, ²⁶ 3-oxo-2-methylbutyronitrile, ²⁷ ethyl nitroacetate, ²⁸ and ethyl (phenylsulfonyl)acetate ²⁹ were prepared by the methods described in the literature. Dimethyl 2-acetyl-1,3-propanedicarboxylate and trimethyl 1,1,3-propanetricarboxylate were prepared by reactions of methyl acrylate with methyl acetoacetate and dimethyl malonate, respectively, in the presence of sodium methoxide. 2-Oxocyclohexanecarbaldehyde was synthesized by the reaction of cyclohexanone and methyl formate. ³⁰ 2-Oxocyclododecanecarbaldehyde ³¹ and ethyl phenylformylacetate were prepared by the same method as employed in the preparation of 2-oxocyclohexanecarbaldehyde.

Purification of 1,3-butadiene was accomplished by vaporization of the liquid diene containing triethylaluminum. Isoprene, 1,3-pentadiene, and 2,3-dimethyl-1,3-butadiene were distilled under argon atmosphere.

General Procedure for Reaction of Active Methylene or Methyne Compounds with 1,3-Dienes.—A 100-ml stainless steel autoclave was charged with an active methylene or methyne compound and catalyst components, followed by cooling with Dry Ice-methanol. After removal of the air within the autoclave under vacuum, 1,3-butadiene was vaporized from the liquid diene containing triethylaluminum to be condensed in the autoclave. The reaction was carried out by stirring at 85°. The reaction mixture was distilled and analyzed by vpc without further treatment.

Reaction of Acetylacetone with 1,3-Butadiene.—A mixture of 0.1 mol of acetylacetone, 0.02 mmol of $\text{PdCl}_2(\text{Ph}_3\text{P})_2$, 2 mmol of sodium phenoxide, and 0.3 mol of the diene was stirred at 85° for 3 hr. The products consisted of **3c** (0.6 g, 3%), **1c** (12.9 g, 62%), **2c** (5.8 g, 18%), and a residue (0.5 g). Spectroscopic data of the products are as follows. **3c**: ν_{max} 1703 (ketone), 1644, 996, and 915 cm^{-1} ($-\text{CH}=\text{CH}_2$); τ 8.7 (m, $-\text{CCH}_2\text{C}-$), ~ 8.0 ($=\text{CCH}_2\text{CCH}_2\text{C}=\text{C}$), 8.0 and 7.9 ($\text{CH}_3\text{CO}-$), 7.1 (m, $-\text{CHCCO}-$), 6.3 (d, $-\text{CHCO}-$), and 4.0-5.3 (m, olefinic protons). **1c**: ν_{max} 1723, 1703, and 1610 (β diketone), 1639, 993, and 911 ($-\text{CH}=\text{CH}_2$), 969 cm^{-1} (trans $-\text{CH}=\text{CH}-$); τ 8.6 (m, $-\text{CCH}_2\text{C}-$), ~ 8.0 ($-\text{CH}_2\text{CCH}_2-$), 8.0 and 7.9 ($\text{CH}_3\text{CO}-$), 7.5 (t, $-\text{CH}_2\text{CCO}-$, keto form), 7.1 (br s, $-\text{CH}_2\text{CCO}-$, enol form), 6.3 (t, $-\text{CHCO}-$, keto form), 4.6-5.0 (olefinic protons), and -6.7 [s, $-\text{C}(\text{OH})=\text{CCO}-$, enol form]. **2c**: ν_{max} 1702 (ketone), 1644, 994, and 912 ($-\text{CH}=\text{CH}_2$), 967 cm^{-1} (trans $-\text{CH}=\text{CH}-$); τ 8.6 (m, $-\text{CCH}_2\text{C}-$),

~ 8.0 ($=\text{CCH}_2\text{CCH}_2\text{C}=\text{C}$), 8.0 (s, $\text{CH}_3\text{CO}-$), 7.5 (d, $-\text{CH}_2\text{CCO}-$), and 4.0-5.1 (m, olefinic protons).

Reaction of Ethyl Acetoacetate with Isoprene.—A mixture of 0.1 mol of ethyl acetoacetate, 0.3 mol of isoprene, 0.1 mmol of $\text{PdCl}_2(\text{Ph}_3\text{P})_2$, and 2 mmol of sodium phenoxide was stirred at 85° for 20 hr. The product consisted of **4a** (17.8 g, 67%), **5a** (11.0 g, 28%), and a residue (0.9 g). The former compound showed the following spectral characteristics: ν_{max} 1740 and 1718 (keto ester), 1652 and 886 cm^{-1} ($>\text{C}=\text{CH}_2$); τ 8.8 and 5.9 (t, and q, $-\text{OCH}_2\text{CH}_3$), ~ 8.5 ($-\text{CCH}_2\text{C}-$), 8.4 and 8.3 [2 s, $-\text{C}(\text{CH}_3)=\text{C}-$], ~ 8.0 (m, $=\text{CCH}_2\text{CCH}_2\text{C}=\text{C}$), 7.9 ($\text{CH}_3\text{CO}-$), 7.6 (d, $-\text{CH}_2\text{CCO}-$), 6.5 (t, $-\text{CHCO}-$), 5.4 (s, $>\text{C}=\text{CH}_2$), and 4.8 (t, $-\text{CH}=\text{C}<$). The latter compound showed following spectral characteristics: ν_{max} 1740 sh and 1712 (keto ester), 1651 and 886 cm^{-1} ($>\text{C}=\text{CH}_2$); τ 8.8 and 5.9 (t, and q, $-\text{OCH}_2\text{CH}_3$), ~ 8.5 ($-\text{CCH}_2\text{C}-$), 8.5 [s, $-\text{C}(\text{CH}_3)=\text{C}-$], 8.3 [s, $-\text{C}(\text{CH}_3)=\text{C}-$], ~ 8.0 ($=\text{CCH}_2\text{CCH}_2\text{C}=\text{C}$), 7.9 (s, $\text{CH}_3\text{CO}-$), 7.4 (s, $-\text{COCCH}_2-$), 5.4 (s, $>\text{C}=\text{CH}_2$), and 4.9 (t, $-\text{CH}=\text{C}<$).

Reaction of Acetylacetone with Isoprene.—A mixture of 0.1 mol of acetylacetone, 0.3 mol of isoprene, 0.25 mmol of $\text{PdCl}_2(\text{Ph}_3\text{P})_2$, and 2.5 mmol of sodium phenoxide in 15 ml of benzene was stirred under the same conditions as those of the previous experiment to yield **4c** (15.8 g, 67%) and **5c** (9.0 g, 24%). The former compound showed the following spectral characteristics: ν_{max} 1728 sh, 1700, and 1602 (β diketone), 1649 and 886 cm^{-1} ($>\text{C}=\text{CH}_2$); τ ~ 8.5 ($-\text{CCH}_2\text{C}-$), ~ 8.4 [$-\text{C}(\text{CH}_3)=\text{C}-$], 8.0 ($=\text{CCH}_2\text{CCH}_2\text{C}=\text{C}$), 8.0 and 7.9 (s, $\text{CH}_3\text{CO}-$), 7.5 (d, $-\text{CH}_2\text{CCO}$, keto form), 7.1 (s, $-\text{CH}_2\text{CCO}-$, enol form), 6.3 (t, $-\text{CHCO}-$), 5.4 (s, $>\text{C}=\text{CH}_2$), and 4.9 ($-\text{CH}=\text{C}<$). The latter compound exhibited the following spectral characteristics: ν_{max} 1699 (ketone), 1651 and 886 cm^{-1} ($>\text{C}=\text{CH}_2$); τ ~ 8.5 ($-\text{CCH}_2\text{C}-$), 8.6 and 8.3 [2 s, $-\text{C}(\text{CH}_3)=\text{C}-$], ~ 8.1 ($=\text{CCH}_2\text{CCH}_2\text{C}=\text{C}$), 8.0 (s, $\text{CH}_3\text{CO}-$), 7.3 (s, $-\text{CH}_2\text{CCO}-$), 5.4 (s, $>\text{C}=\text{CH}_2$), and 4.9 (t, $-\text{CH}=\text{C}<$).

Reaction of Ethyl Acetoacetate with 1,3-Pentadiene.—The reaction was carried out under the same conditions as those in the reaction of ethyl acetoacetate with isoprene. The product (8.5 g, 32%) was identified as ethyl 2-acetyl-3,7-dimethyl-4,9-decadienoate: ν_{max} 1742 sh and 1716 (keto ester), 1644, 994, and 912 ($-\text{CH}=\text{CH}_2$), and 972 cm^{-1} (trans $-\text{CH}=\text{CH}-$); τ 9.2 [d, $-\text{C}(\text{CH}_3)-$], 9.0 [2 d, $-\text{C}(\text{CH}_3)-$], 8.8 (2 t, $-\text{OCCH}_3$), 8.4 (m, $=\text{CCCHCC}=\text{C}$), 8.1 (m, $=\text{CCH}_2\text{CCH}_2\text{C}=\text{C}$), 7.9 and 8.0 ($\text{CH}_3\text{CO}-$), 7.1 (m, $=\text{CCHCCO}-$), 6.8 (d, $-\text{CHCO}-$), 5.9 (2 q, $-\text{OCH}_2\text{C}-$) and 4.0-5.2 (m, olefinic protons). Two kinds of the signals due to acetyl, ethyl, and one of the methyl groups on the side chain indicate that the compound is a mixture of the erythro and three isomers. Refluxing the product with sodium ethoxide in ethanol gave ethyl 3,7-dimethyl-4,9-decadienoate: ν_{max} 1740 (ester), 1644, 992, and 911 ($-\text{CH}=\text{CH}_2$), and 971 cm^{-1} (trans $-\text{CH}=\text{CH}-$); τ 9.2 [d, $-\text{C}(\text{CH}_3)-$], 9.0 [d, $-\text{C}(\text{CH}_3)-$], 8.8 (t, $-\text{OCCH}_3$), 8.5 (m, $=\text{CCCHCC}=\text{C}$), 8.0 (m, $=\text{CCH}_2\text{CCH}_2\text{C}=\text{C}$), 7.8 (d, $-\text{CH}_2\text{CO}-$), 7.4 (m, $=\text{CCHCCO}-$), 6.0 (q, $-\text{OCH}_2\text{C}$), 4.0-5.1 (olefinic protons).

Reaction of Ethyl Acetoacetate with 2,3-Dimethyl-1,3-butadiene.—A mixture of 0.05 mol of ethyl acetoacetate, 0.15 mol of 2,3-dimethyl-1,3-butadiene, 0.25 mmol of $\text{PdCl}_2(\text{Ph}_3\text{P})_2$, and 2.5 mmol of sodium phenoxide in 15 ml of benzene was stirred at 85° for 20 hr. The product (1.0 g, 7%) was identified as ethyl 2-acetyl-4,5,8,9-tetramethyl-4,9-decadienoate: ν_{max} 1742 and 1720 (keto ester), 1647, 890 cm^{-1} ($>\text{C}=\text{CH}_2$); τ 9.0 [d, $-\text{C}(\text{CH}_3)-$], 8.8 (t, $-\text{OCCH}_3$), 8.4 and 8.5 [s, $=\text{C}(\text{CH}_3)-$], 8.1 (m, $=\text{CCCH}_2\text{CC}=\text{C}$), 7.9 (s, $\text{CH}_3\text{CO}-$), 7.5 (d, $-\text{CH}_2\text{CCO}-$), 6.6 (t, $-\text{CHCO}-$), 5.8 (q, $-\text{OCH}_2\text{C}$), and 5.4 (s, olefinic protons).

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2-(2,7-Octadienyl)cyclohexanone.—A mixture of 150 ml of ethanol, 0.5 g of sodium metal, and 39.8 g of 2-acetyl-2-(2,7-octadienyl)cyclohexanone was heated at 80° for 2 hr. After the usual workup, the product was distilled; the first fraction had bp 110–120° (2 mm), 7.6 g, and the second fraction had bp 168–176° (2 mm), 27.0 g. Redistillations of both fractions gave 2-(2,7-octadienyl)cyclohexanone [bp 116° (3 mm); n_D^{25} 1.4809; ν_{\max} 1712 (>C=O), 1644, 990, and 910 (–CH=CH₂), and 970 cm⁻¹ (trans –CH=CH–)] and ethyl 6-acetyl-8,13-tetradecadienoate [bp 181° (3.5 mm); n_D^{25} 1.4635; ν_{\max} 1737 (ester), 1713 (>C=O), 1642, 993, and 910 (–CH=CH₂), and 970 cm⁻¹ (trans –CH=CH–)], respectively.

Anal. Calcd for C₁₄H₂₂O: C, 81.50; H, 10.75; mol wt, 206. Found: C, 81.23; H, 10.65; mol wt, 205. *Anal.* Calcd for C₁₈H₃₀O₂: C, 73.43; H, 10.27; mol wt, 294. Found: C, 73.57; H, 10.19; mol wt, 294.

2-(2,7-Octadienyl)cyclohexanone was also obtained by refluxing an aqueous sodium hydroxide solution of 1-(2,7-octadienyl)-2-oxocyclohexanecarbaldehyde in a 87% yield.

Platinum-Catalyzed Reaction of Acetylacetone with 1,3-Butadiene.—A mixture of 0.1 mol of acetylacetone, 0.5 mmol of Pt(Ph₃P)₄, 7 mmol of sodium phenoxide, and 0.3 mol of 1,3-butadiene was stirred at 85° for 16 hr. The product was com-

posed of 3-(1-methylallyl)-2,4-pentanedione (2.0 g, 13%), 1c (4.5 g, 21%), 3c (4.8 g, 24%), 3-(2-butenyl)-3-(2,7-octadienyl)-2,4-pentanedione (2.6 g, 10%), and 2c (3.3 g, 11%). The 1:1 adduct showed the following spectral characteristics: ν_{\max} 1722 sh and 1700 (ketone), 1644, 998, and 922 cm⁻¹ (–CH=CH₂); τ 9.0 (d, –CCH₃), 8.0 and 7.9 (CH₃CO–), 7.0 (m, =CCH–), 6.4 (d, –CHCO–), 4.8–5.2 (m, CH₂=C–), and 4.0–4.6 (m, –CH=C–). The 1:3 adduct exhibited the following spectral characteristics: ν_{\max} 1723 sh and 1702 (ketone), 1643, 991, and 910 (–CH=CH₂), 967 cm⁻¹ (trans –CH=CH–); τ 8.6 (m, =CCCH₂CC=), 8.3 (d, =CCH₃), ~8.0 (=CCH₂CCH₂C=), 8.0 (CH₃CO–), 7.5 (d, –CH₂CCO–), 4.0–5.2 (m, olefinic protons).

A mixture of 0.1 mol of acetylacetone, 0.5 mmol of PtCl₂(Ph₃P)₂, 7 mmol of sodium phenoxide, and 0.3 mol of 1,3-butadiene in 15 ml of benzene was stirred at 85° for 5 hr. The adducts 1c, 3c, and 2c were obtained in 18, 12, and 44% yields, respectively.

Registry No.—2-(2,7-Octadienyl)cyclohexanone, 29331-14-4; ethyl 6-acetyl-8,13-tetradecadienoate, 29331-15-5; 3-(2-butenyl)-3-(2,7-octadienyl)-2,4-pentanedione, 29331-16-6.

Preparation of Alkylmagnesium Fluorides¹

SIMON H. YU AND E. C. ASHBY*

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

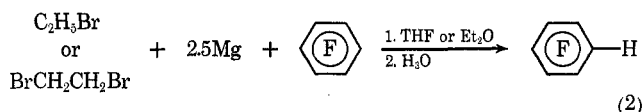
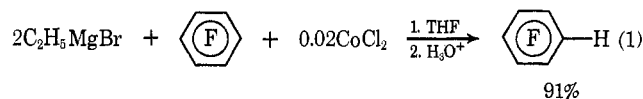
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Alkylmagnesium fluorides have been prepared in high yield by the reaction of alkyl fluorides with magnesium in ether solvents in the presence of specific catalysts. The reaction rate was found to depend significantly on the solvent, reaction temperature, and catalyst. The best solvents for the reaction were found to be tetrahydrofuran and 1,2-dimethoxyethane and the best catalyst found was iodine. Under conditions of atmospheric pressure reflux using iodine as a catalyst, *n*-hexylmagnesium fluoride was produced in 90% yield in 14 days in diethyl ether, in 92% yield in 1.2 days in tetrahydrofuran, and in 92% yield in 4 hr in 1,2-dimethoxyethane. Under the most favorable conditions fluorobenzene and benzyl fluoride failed to react with magnesium.

For over half a century organic chemists have been interested in the preparation of organomagnesium fluorides; however, all attempts to prepare and isolate this class of compounds have been uniformly unsuccessful. The first attempt to prepare an organomagnesium fluoride was reported in 1921 by Swarts.² He found that the reaction of amyl fluoride with iodine-activated magnesium in diethyl ether after 100-hr reflux produced decane and magnesium fluoride. In 1931 Schiemann and Pillarsky³ reported that neither fluorobenzene nor its ortho methyl or para nitro derivatives reacted with magnesium to form the corresponding Grignard reagent. The same year Gilman and Heck⁴ reported that a small quantity of biphenyl was formed when fluorobenzene was heated with magnesium at 300° for 200 hr in a sealed tube without solvent. When fluorobenzene was sealed in a tube with activated magnesium-copper alloy⁵ in diethyl ether at room temperature for 6 months, the reaction mixture gave a negative color test⁶ for the presence of an active organometallic compound; however, at the end of 18 months the color test was positive. Several attempts were made by Bernstein and coworkers⁷ to prepare a Grignard reagent

from benzyl fluoride. At reflux temperature in diethyl ether, no reaction took place. Addition of an iodine crystal or of phenylmagnesium bromide failed to initiate reaction. Under more vigorous conditions in di-*n*-butyl ether, polymerization of the benzyl fluoride occurred. While ordinary magnesium gave no reaction, bibenzyl was obtained from the reaction of benzyl fluoride with activated magnesium in diethyl ether at 100° for 10 days in an autoclave. Thus all attempts to prepare fluoro Grignard reagents were frustrated either by a lack of reaction between the organo fluorides and magnesium or the formation of coupling product.

During our study the possible intermediacy of perfluoroarylmagnesium fluorides was indicated by the reaction of perfluoroaryl compounds with 2 molar equiv of ethylmagnesium bromide and a catalytic amount of certain transition metal halides in tetrahydrofuran⁸ (eq 1) and from the reaction of hexafluorobenzene with



magnesium and an equal molar amount of an entrainer such as ethyl or ethylene bromide in tetrahydrofuran

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