the solvent *in vacuo* there was obtained 37 mg (60%) of **11b**: mp 105° dec; ν_{max} 3400, 1730, and 1710 cm^{-1}; nmr 0.54 (19-H), 0.73 (18-H), 3.35 ppm (21-CH$_2$); mass spectrum *m/e* 318 (M$^+$ − CO$_2$), 44 (CO$_2$).

3β-Hydroxy-5α-pregnan-20-one (11c).—A solution containing 25 mg of **11b** and 5 ml of 2% potassium hydroxide in 98% methanol was gently heated at reflux temperature for 3 hr. It was then poured into water, extracted with ethyl acetate, washed with water to neutrality, and dried over anhydrous sodium sulfate. After evaporation there was isolated 21 mg (95%) of 3β-hydroxy-5α-pregnan-20-one (**11c**). Recrystallization from methanol gave the pure sample of **11c**: mp 188–190°; [α]D +115°; ν_{max} 3380 and 1705 cm^{-1}. This compound was shown to be identical with an authentic sample of **11c** by mixture melting point, ir, nmr, and tlc analysis.

20-Cyano-3β-acetoxy-5α-pregn-17(20)-ene-21-carboxylic Acid (12a) and 20-Cyano-3β-acetoxy-5α-pregn-17(20)-ene-21-carboxylic Acid (12b).—A mixture of 300 mg of **8c**, 6 ml of ethanol (96%), 3 ml of water, and 300 mg of potassium cyanide was refluxed for 1 hr. Then it was poured into water, acidified with dilute hydrochloric acid to pH 2, and extracted with ethyl acetate. The organic layer was washed to neutrality, dried over anhydrous sodium sulfate, and evaporated to dryness. The product was purified by preparative tlc, using chloroform–methanol (9:1). The less polar fraction (151 mg) corresponded to **12a**. Recrystallization from ethyl acetate afforded the pure sample: mp 196–197°; [α]D ±0°; λ_{max} 223 nm (log ε 4.10); ν_{max} 3100, 2225, 1740, and 1250 cm^{-1}; nmr 0.70 (19-H), 0.89 (18-H), 2.20 (3β-OAc), 3.61 ppm (21-CH$_2$); mass spectrum *m/e* 413 (M$^+$), 353 (M$^+$ − HOAc), 338 (M$^+$ − HOAc − CH$_3$).

The second fraction corresponded to compound **12b** (90 mg). Recrystallization from ethyl acetate gave the pure sample: mp 228–229°; [α]D ±0°; λ_{max} 223–224 nm (log ε 4.13); ν_{max} 3350, 2210, and 1725 cm^{-1}; nmr 0.77 (18-H), 0.86 (19-H), 3.63 ppm (21-CH$_2$); mass spectrum *m/e* 371 (M$^+$), 356 (M$^+$ − CH$_3$), 353 (M$^+$ − H$_2$O).

17-(2′β-Carboxyvinylidene)-5α-androstan-3β-ol (8e).—A solution of 60 mg of **8c** in 10 ml of acetone and 1 ml of sodium hydroxide (2%) in water was refluxed for 2 hr and poured into water. Extraction with ethyl acetate removed the neutral components. The aqueous phase was then acidified with dilute hydrochloric acid, extracted with ethyl acetate, washed with water to neutrality, and dried over sodium sulfate. After evaporation of the solvent 50 mg of **8e** was obtained. Recrystallization from acetone–methylene chloride afforded the analytical sample: mp 144–145°; [α]D −29° (dioxane); λ_{max} 226 nm (log ε 3.98); ν_{max} 3250, 1960, and 1690 cm^{-1}; nmr 0.83 (19-H), 0.93 (18-H), 5.45 ppm (t, *J* = 4 Hz, 22-H); mass spectrum *m/e* 344 (M$^+$), 326 (M$^+$ − H$_2$O), 311 (M$^+$ − H$_2$O − CH$_3$).

Registry No.—**1a**, 10148-98-8; **1b**, 17006-64-3; **2a**, 19646-55-0; **2b**, 38616-25-0; **2c**, 38616-26-1; **2d**, 38616-27-2; **2e**, 38616-28-3; **3a**, 38616-29-4; **3b**, 19516-58-6; **4a**, 38616-31-8; **4b**, 38616-32-9; **4c**, 38616-33-0; **4d**, 38616-34-1; **4e**, 38616-35-2; **5a**, 19516-98-4; **5b**, 38616-37-4; **5c**, 38616-38-5; **5d**, 38616-39-6; **6**, 27741-55-5; **7a**, 21947-63-7; **7b**, 38616-51-5; **7c**, 34091-97-9; **7d**, 34091-98-0; **8a**, 34091-99-1; **8b**, 34092-00-7; **8c**, 34092-02-9; **8d**, 34092-03-0; **8e**, 34092-05-2; **9**, 34092-01-8; **10**, 34092-04-1; **11a**, 34092-06-3; **11b**, 38616-18-1; **11c**, 516-55-2; **12a**, 38400-05-4; **12b**, 38400-06-5; *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine, 357-83-5.

Transition Metal Catalyzed Reactions of Allene[1]

D. ROBERT COULSON

Contribution No. 1967 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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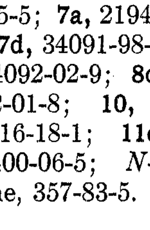
Allene reacts with various amines or carbon acids in the presence of catalytic amounts of certain group VIII metal complexes to give high yields of derivatives of 2,3-dialkyl-1,3-butadienes (**1b–e**). Under the same conditions triethylsilane adds to allene, forming triethylallylsilane. Diels–Alder adducts of the dienes with maleic anhydride are also described. Possible mechanisms for the catalytic reactions are discussed.

Numerous reports of transition metal catalyzed reactions of 1,3-dienes with weak acids[2] or amines[3] have appeared in the literature. By contrast, only one report[4] has dealt with similar reactions of 1,2-dienes. In this report, Shier described the reactions of allene with acetic acid in the presence of palladium acetate. Of the several products isolated, the predominant one was 3-methyl-2-methylene-3-butenyl acetate (**1a**), formally resulting from a condensation of two molecules of allene with one of acetic acid.

Our work in this area resulted from a general interest in the transition metal catalyzed reactions of allene with amines. In the course of our investigations, a series of related reactions were discovered involving highly specific, catalytic condensations of allene with amines as well as with certain carbon acids. The resulting products (**1b–e**) have been shown to be of the



1a, X = OCOCH$_3$; *n* = 1
b, X = NR$_2$; *n* = 1
c, X = CR$_3'$; *n* = 1
d, X = NR; *n* = 2
e, X = CR$_2$; *n* = 2

same structural type as Shier's product, **1a**. As a result of the apparent generality of these reactions, our investigation was primarily directed toward developing the synthetic aspects of this area.

Results

Catalytic Reactions of Allene with Amines.—In the presence of various compounds of palladium or rhodium, *e.g.*, PdCl$_2$, RhCl$_3$·3H$_2$O, [P(Ph)$_3$]$_4$Pd, or [P(Ph)$_3$]$_2$Pd·olefin, allene and various amines reacted to give

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[1] Part of this work was disclosed at the 163rd National Meeting of American Chemical Society, Division of Petroleum Chemistry, Symposium on "New Routes to Olefins," Boston, Mass., April 1972.

[2] (a) G. Hata, K. Takahashi, *et al.*, *J. Org. Chem.*, **36**, 2116 (1971); (b) E. S. Brown, and E. A. Rick, *Chem. Commun.*, 112 (1969); (c) E. J. Smutny, *J. Amer. Chem. Soc.*, **89**, 6793 (1967); (d) W. E. Walker, R. M. Manyik, *et al.*, *Tetrahedron Lett.*, **No. 43**, 3817 (1970).

[3] (a) S. Takahashi, T. Shibano, and N. Hagihara, *Bull. Chem. Soc. Jap.*, **41**, 454 (1968); (b) T. Mitseyusu, M. Hara, *et al.*, *Chem. Commun.*, 345 (1971).

[4] G. D. Shier, *J. Organometal. Chem.*, **10**, 15 (1967).

TABLE I

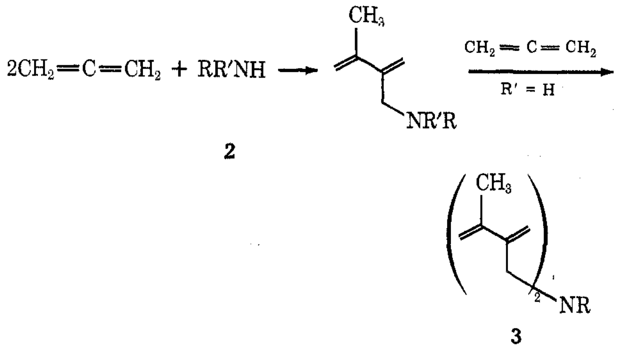
CATALYTIC CONDENSATIONS OF AMINES AND ALLENE[a]

Registry no.	Amine	Yield[c] of mono-dienylamine, %	Bp, °C (mm)	Yield[c] of bis-(dienyl)-amine, %	Bp, °C (mm)	Mole ratios of allene:amine:catalyst
7664-41-7	Ammonia	23	77.5–78 (100)	25	60 (0.4)	200:1200:1
	Ammonia[b]	2	77.5–78 (100)	50	60 (0.4)	200:1200:1
74-89-5	Methylamine	42	85.5–86.5 (100)	20	56–57.5 (0.3)	500:600:1
	Methylamine			58	46–57.5 (0.3)	1200:300:1
75-04-7	Ethylamine	29	47 (7)			500:200:1
	Ethylamine			60	49.5 (0.08)	800:200:1
75-31-0	Isopropylamine	44	30–33 (0.7)			500:200:1
107-10-8	Propylamine	30	54 (8)			580:230:1
75-64-9	*tert*-Butylamine	32	64–66 (11)			800:200:1
108-91-8	Cyclohexylamine	75	45 (0.4)			500:400:1
62-53-3	Aniline	12	76 (0.2)			500:200:1
768-94-5	Adamantane amine	75	108–113 (0.4)			500:200:1
124–40–3	Dimethylamine	70	136.5 (750)			250:600:1
110-68-9	*n*-Butylmethylamine	79	81–84 (7)			300:100:1
123-75-1	Pyrrolidine	78	71–74 (7)			500:200:1
110-89-4	Piperidine	79	71 (5.2)			500:200:1
110-91-8	Morpholine	41	60–61.5 (0.4)			500:200:1
100–60–7	*N*-Methylcyclohexylamine	67	80–81 (0.5)			500:200:1
109-89-7	Diethylamine	77	59–60.5 (7)			500:200:1
5459-93-8	*N*-Ethylcyclohexylamine	84	80–81 (0.4)			500:200:1
100-61-8	*N*-Methylphenylamine	62	90–90.5 (0.1)			500:200:1
141-43-5	*β*-Aminoethanol	37	62.5–63 (0.22)			500:200:1

[a] All the reactions were carried out under the conditions described for the preparation of 2 ($R' = H$; $R = CH_3$) in the Experimental Section. [b] Temperature 140°. [c] Yields are based on the limiting component.

derivatives of 3-methyl-2-methylene-3-butenylamine (Scheme I).

SCHEME I



R = H, alkyl
R′ = H, alkyl, aryl

By employing ammonia or primary amines, both mono(dienyl)amines, 2, and bis(dienyl)amines, 3, were formed. Either product could usually be made the predominant product by varying the reaction temperature or mole ratio of the reactants. In most cases, the only side reaction observed was a competing, and usually negligible, homopolymerization of allene. Table I gives examples of the products obtained from these reactions.

The reactions could be easily performed by passing allene into a solution of the amine and catalyst in hexamethylphosphoramide at *ca.* 1-atm pressure. This solvent was chosen over several others because of a relatively greater ease of product separation. Temperatures of at least 70–90° were usually required for reasonable reaction times (<18 hr). When shorter reaction times were desired the reactions were conducted in sealed stainless steel vessels using lower boiling solvents, *e.g.*, tetrahydrofuran or benzene, and higher temperatures (*ca.* 100–140°).

Palladium complexes were generally superior to those of rhodium and most of the work described here involves the use of palladium catalysts. Of the several Pd(0) complexes tested, bis(triphenylphosphine)-(maleic anhydride)palladium[5] was used most frequently because of its high solubility and stability in air. With these catalysts, product–catalyst mole ratios of 75–100 were routinely achieved but values of 500–1000 could be easily reached, although at the expense of a decreased reaction rate.

It was observed that both Pd(0) and Pd(II) complexes were effective catalysts except when ammonia was employed in place of an amine. In this case, only Pd(0) complexes were found to be active.

In an attempt to gain some insight into the effects of reaction variables on these reactions, a brief study was made of the effect of changing the solvent and catalyst in the reaction of *n*-butylmethylamine with allene. Table II summarizes the results of this study.

The structural assignments of the products were based mainly on the results of studies of their physical properties. The properties found for 2 ($R = CH_3$; $R' = H$) may be regarded as typical. The infrared spectrum[6] of this compound revealed a single strong absorption at 1607 cm^{-1}. The ultraviolet spectrum showed an absorption (λ_{max} 225 mμ, ϵ 17,200 in EtOH)

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[5] S. Takahashi and N. Hagihara, *J. Chem. Soc. Jap., Pure Chem. Sect.*, **88**, 1306 (1967).

[6] The infrared[7] and ultraviolet[8] (EtOH) spectra of 2,3-dimethylbutadiene contain absorptions at 1600 cm^{-1} and λ_{max} 227 mμ, respectively.

[7] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 149.

[8] W. J. Bailey and J. C. Goosens, *J. Amer. Chem. Soc.*, **78**, 2804 (1956).

TABLE II

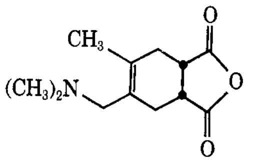
EFFECT OF SOLVENT AND CATALYST ON REACTION OF ALLENE WITH n-BUTYLMETHYLAMINE[a]

Registry no.	Catalyst	Solvent	Yield[c] of 2,[b] %
7647-10-1	$PdCl_2$	Benzene	83
	$PdCl_2$	Hexamethylphosphoramide	81
	$PdCl_2$	Acetonitrile	68
	$PdCl_2$	Tetrahydrofuran	41
16520-27-7	$PdCl_2 + P(Ph)_3$	Tetrahydrofuran	71
16520-27-7	$[P(Ph)_3]_2Pd \cdot MA$[d]	Tetrahydrofuran	98

[a] The reactions were run at 110° for 3 hr in an 80-cc stainless steel autoclave using 300 mmol of allene, 100 mmol of amine, 1 mmol of catalyst, and 25 ml of solvent. [b] R = CH_3; R′ = $CH_3(CH_2)_3$. [c] Yields are based on the amine and were determined by glpc analysis. [d] Maleic anhydride.

expected for a 2,3-dialkyl-1,3-diene.[6] A relatively simple nmr spectrum gave singlets corresponding to the NH (δ 0.60 ppm, exchangeable with D_2O), NCH_3 (2.21 ppm), olefinic CH_3 (1.82 ppm), and allylic methylene (3.27 ppm) groups. The olefinic hydrogens were assigned to a complex multiplet covering a range of δ 4.9–5.15 ppm. The corresponding bis(dienyl)amine **3** (R = CH_3) possessed similar spectral properties with the exceptions of an enhanced ultraviolet absorption at λ_{max} 222 mμ (ϵ 26,600 in EtOH) and the absence of an NH nmr absorption. All of the compounds described in Table I possessed similar spectral properties with generally predictable variations. Table III gives a compilation of the nmr spectral characteristics for all of these compounds.

Further verification of these structural assignments came from the reactions of the tertiary amines with maleic anhydride. Thus, **2** (R′ = R = CH_3) reacted with 1 equiv of maleic anhydride to give the expected Diels–Alder adduct, **4**. A similar reaction occurred with **3** (R = CH_3), giving **5** as a mixture of syn and anti ring-junction isomers.



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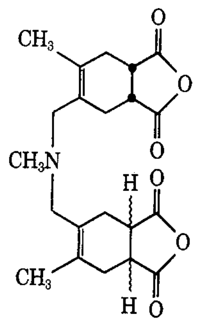

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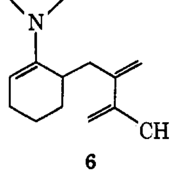
Although tertiary amines were found to be unreactive toward allene, enamines presented an exception. Thus, when 1-(1-cyclohexenyl)pyrrolidine was treated with allene under the usual conditions, the condensation product **6** was obtained in 34% yield.



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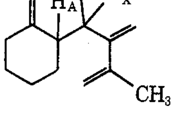

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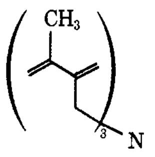
The structure of **6** was supported by its nmr spectrum, which revealed resonances attributable to an enamine hydrogen (δ 4.7–5.2 ppm, 4 H). The infrared spectrum indicated the presence of both the characteristic 1,3-diene unit (1592 cm^{-1}) and an enamine (1666 cm^{-1}). Furthermore, acidic hydrolysis of **6** gave a ketone to which structure **7** was assigned. This ketone had retained the 1,3-diene unit according to nmr analysis (δ 4.9–5.2 ppm, 4 H). Further information resulted from the observation of an unusual nmr resonance, assigned to H_X. This particular hydrogen appeared as a four-line pattern attributed to an ABX type spectrum (δ 3.33 ppm, $|J_{AX} + J_{BX}|$ = 17 Hz). The unusual character of this resonance is probably due to the effect of an adjacent asymmetric center enhanced by the local field effect of the carbonyl group. Conformational preferences could also affect this resonance.

Attempts to prepare **8** directly from allene and ammonia were unsuccessful. However, by replacing the ammonia with **3** (R = H) and a trace of a radical trapping agent, phenothiazine, a material was obtained which appeared to be a sample of slightly impure **8**, bp 94–96° (0.36 mm). All further attempts to purify this material induced its polymerization. The nmr spectrum of this material revealed the familiar pattern of absorptions at δ 5.43–5.13 (m, 3 H), 4.98 (m, 1 H), 3.20 (s, 2 H), and 1.84 (s, 3 H). None of the protons appeared to exchange with D_2O.



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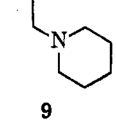
The formation of appreciable amounts of 1:1 allene–amine adducts was not observed in any of the reactions studied. For example, careful examination of the reaction products arising from the reaction of dimethylamine with allene revealed the formation of a *ca.* 1% yield of N,N-dimethylallylamine accompanied by a 70% yield of **2** (R = R′ = CH_3).

As part of a study of the reaction mechanism, N-deuteriopiperidine (>99% d_1) was treated with allene to give **9**.



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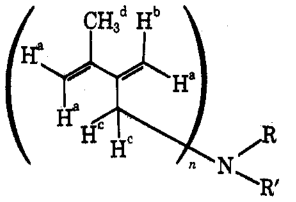
Nmr and mass spectral analysis revealed a total incorporation of 0.80 ± 0.05 deuterium atoms per molecule with 95 ± 3% of this amount located in the methyl group.

Catalytic Reactions of Allene with Carbon Acids.— In most respects, the reactions of allene with carbon acids were found to exactly parallel those found with amines (Scheme II). A singular exception to this generalization was the complete ineffectiveness of Pd(II) or Rh(III) complexes as catalysts. As in the case of the amines, Pd(0) complexes were found to be

TABLE III

NMR SPECTRAL DATA FOR MONO- AND BIS(DIENYL)AMINES (2 AND 3) (IN BENZENE)



Registry no.	Substituents R	R′	n	H^a	H^b	H^c	H^d	R	R′
38644-47-2	H	H	1	5.19–4.95 m	4.86 m	3.33 m	1.81 m	0.80 s	Same as R
38644-48-3	H		2	5.3–5.07 m	4.90 m	3.35 s	1.82 m	0.95 s	
38644-49-4			3	5.43–5.13 m	4.98 m	3.20 s	1.84 s		
38644-50-7	CH_3	H	1	5.15 m	4.90 m	3.27 m	1.82 m	2.21 s	0.60 s
38644-51-8	CH_3		2	5.40–5.00 m	4.89 m	3.05 s	1.95 m	2.20 s	
38644-52-9	C_2H_5	H	1	5.35–5.13 m	4.98 m	3.38 m	1.87 m	0.99 t $J = 7$ Hz 2.53 q $J = 7$ Hz	0.62 s
38644-53-0	C_2H_5		2	5.41–5.15 m	4.98 m	3.20 s	1.87 m	0.98 t $J = 7$ Hz 2.44 q $J = 7$ Hz	
38644-54-1	$(CH_3)_2CH$	H	1	5.37–5.12 m	4.98 m	3.41 s	1.87 m	2.71 p $J = 6.5$ Hz 0.99 d $J = 6.5$ Hz	0.72 s
38644-55-2	C_3H_7[c]	H	1	5.30–5.09 m	5.05 m	3.48 s	1.95 m	2.62 t $J = 7$ Hz 1.80–0.75 m	Obscured by R
38644-56-3	$t\text{-}C_4H_9$	H	1	5.31–5.07 m	4.91 m	3.31 m	1.85 m	0.99 s	0.55 s
38644-57-4	$(CH_2)_5CH$	H	1	5.35–5.1 m	4.98 m	3.45 s	1.88 m	2.0–0.75 m 2.65–2.1 m	Obscured by R
38644-58-5	C_6H_5[b]	H	1	5.31–5.01 m	5.01 m	3.83 m	1.94 m	7.32–6.32 m	Variable
38644-59-6	1-Adamantyl	H	1	5.56–5.15 m	5.01 m	3.45 s	1.91 m	2.15–1.8 m 1.75–1.45 m	0.55 s
38644-60-9	CH_3	CH_3	1	5.33–5.07 m	5.01 m	3.05 m	1.90 m	2.13 s	Same as R
38644-61-0	CH_3	$n\text{-}C_4H_9$	1	5.46–5.11 m	4.98 m	3.05 s	1.85 m	2.07 s	1.55–0.65 m 2.45–2.05 m
38644-62-1	$(CH_2)_2$	$(CH_2)_2$	1	5.52–5.12 m	5.01 m	3.23 s	1.88 m	1.64–1.47 m 2.62–2.20 m	Same as R
38644-63-2	$(CH_2)_3$	$(CH_2)_2$	1	5.60–5.14 m	5.01 m	3.06 s	1.87 m	1.76–1.15 m 2.50–2.15 m	Same as R
38644-64-3	$(CH_2)_2O$	$(CH_2)_2$	1	5.48–5.06 m	5.02 m	3.01 s	1.88 m	2.39–2.12 m 3.72–3.48 m	Same as R
38644-65-4	CH_3	$(CH_2)_5CH$	1	5.44–5.13 m	4.98 m	3.21 s	1.89 m	2.15 s	1.9–0.75 m 2.53–2.05 m
38644-66-5	C_2H_5	C_2H_5	1	5.17–5.49 m	4.95 m	3.18 m	1.89 m	0.93 t $J = 7$ Hz 2.45 q $J = 7$ Hz	Same as R
38644-67-6	CH_3[a]	C_6H_5	1	5.21–4.89 m	4.89 m	4.04 m	1.91 m	2.85 s	7.7–6.4 m
38644-68-7	C_2H_5	$(CH_2)_5CH$	1	5.54–5.17 m	4.97 m	3.27 m	1.90 m	1.0 t $J = 7$ Hz 2.48 q $J = 7$ Hz	2.0–0.85 m 2.75–2.2 m
38644-69-8	$HO(CH_2)_2$[b]	H	1	5.36–5.03 m	4.96 m	3.72–3.19 Obscured by R′	1.90 m	2.62 t $J = 6$ Hz 3.72–3.19 m	3.72–3.19 Obscured by H^c

[a] CD_3CN solution. [b] CCl_4 solution. [c] $CDCl_3$ solution.

the catalysts of choice. Consequently, in all of the work described here, bis(triphenylphosphine)(maleic anhydride)palladium was the only catalyst used. Table IV gives some results of the reactions that were performed with several carbon acids.

The structures assigned to **10** and **11** were based primarily on the evidence obtained from comparisons of their spectral properties with those of the previously discussed dienylamines. All of the carbon acid adducts possessed the spectral characteristics attributed to the presence of a 2,3-dialkyl-1,3-butadiene unit. In this respect, the spectral properties described for **10** ($R = R' = CO_2Et$) in the Experimental Section may be regarded as typical for these compounds. The corre-

Table IV

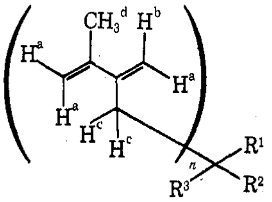
Catalytic Condensation Reactions of Carbon Acids and Allene[a]

Registry no.	Carbon acid	Yield of 10, %	Bp, °C (mm)	Yield of 11, %	Bp, °C (mm)	Mole ratios of acid:allene:catalyst
123-54-6	Acetylacetone	60[b]	90–92 (1.4)	<5		600:500:1
		<5		47	109.5 (0.5)	200:1000:1
141-97-9	Ethyl acetoacetate	58	89–89.5 (0.4)	<5		600:500:1
		<10		38	92 (0.05)	200:1000:1
105-53-3	Diethyl malonate	86[c]	80–80.5 (0.2)	0		100:100:1
105-56-6	Ethyl cyanoacetate	28	95.5 (0.35)	0		800:400:1
109-77-3	Malononitrile	47[d]	73 (0.5)	<5		600:500:1
		<5		73	100–101 (0.15)	200:500:1

[a] Unless otherwise noted, all of the reactions were carried out under the conditions described for the preparation of 10 ($R^1 = R^2 = CO_2Et$) in the Experimental Section at a temperature of 120°. Yields are based on the limiting reagent. [b] Reaction temperature 50°. [c] Reaction temperature 100°. [d] Reaction temperature 60°.

Table V

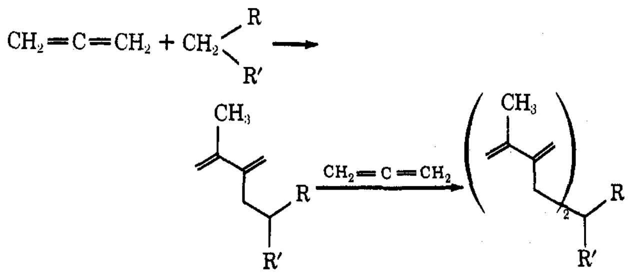
Nmr Spectral Data for Mono- and Bis(dienyl)carbon Acids (10 and 11) (in CCl_4)



Registry no.	Substituents R¹	R²	R³	n	Hᵃ	Hᵇ	Hᶜ	Hᵈ	R¹	R²	R³
38644-70-1	CH_3CO	CH_3CO[a]	H	1	5.22–4.76 m	5.22–4.76 m	2.75 d J = 7.5 Hz	1.96 s	2.06 s	2.06 s	3.83 t J = 7.5 Hz
38644-71-2	CH_3CO	CH_3CO		2	5.09 s 4.83 m 4.70 m	4.97 m	2.92 m	1.74 m	2.00 s	2.00 s	
38644-72-3	CH_3CO[a]	CO_2Et	H	1	5.07–4.92 m	4.90 m	2.75–2.6 m	1.87 m	2.10 s	1.22 t J = 7 Hz 4.10 q J = 7 Hz	3.67–3.39 m
38644-73-4	CH_3CO	CO_2Et		2	5.25–4.82 m	5.05 m	2.92 s	1.86 s	2.05 s	1.28 t J = 7 Hz 4.11 q J = 7 Hz	
38644-74-5	CO_2Et	CO_2Et	H	1	5.13 m	5.02 m	2.86 d J = 7.5 Hz	1.91 s	1.27 t J = 7 Hz 4.19 q J = 7 Hz	Same as R′	3.48 t J = 7.5 Hz
38644-75-6	CO_2Et	CN	H	1	5.25–4.90 m	5.02 m	3.18–2.25 m	1.90 m	1.28 t J = 7 Hz 4.18 q J = 7 Hz		3.77–3.42 m
38644-76-7	CN	CN	H	1	5.55–5.12 m 5.55–5.01 m	5.15 m 5.12 m	2.97 d J = 8 Hz	1.97 s			3.91 t J = 8 Hz
38644-77-8	CN	CN		2	5.55–5.3 m 5.12 m	5.12 m	2.86 s	1.97 s			

[a] Contains enol form; data given is for keto form.

Scheme II



10 11

R, R′ = CN, CO_2Et, $COCH_3$

sponding bisdienes, 11, differed primarily in that the ultraviolet absorptions were enhanced by the presence of an extra chromophore and the nmr spectrum lacked evidence for a methine hydrogen. Finally, a slight complication was introduced into the spectral interpretations of 10 ($R = R' = COCH_3$ and $R = COCH_3$, $R' = CO_2Et$), since these compounds contained substantial amounts of their respective enol forms, depending upon the solvent employed. Table V gives a compilation of the nmr spectral characteristics of these compounds, excluding the enol forms.

Because of the occurrence of side reactions, it was necessary to perform the allene condensations with acetylacetone and malononitrile at temperatures below 100°. When the reaction with malononitrile was performed above this temperature, the only product obtained was an intractable yellow solid. Although this material could not be adequately characterized, it seems reasonable to suggest that it arose from an intermolecular condensation of 10 ($R = R' = CN$). In this regard, it should be noted that the dimerization of malononitrile to give 1,1,3-tricyano-2-amino-1-propene has been reported[9] to be catalyzed by tetrakis(triphenylphosphine)palladium. The side reaction is apparently suppressed when excess allene is employed. In this case a good yield of 11 ($R = R' = CN$) may be obtained at 120° (see the last entry in Table IV). This finding supports the view that the side reaction is similar to the catalytic dimerization of malononitrile, since one would not expect 10 ($R = R' = CN$) to undergo such a condensation.

In the reaction of acetylacetone with allene, it was found that a material isomeric to 10 ($R = R' = CH_3CO$) was obtained as the major product when the

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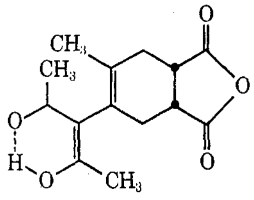
[9] K. Schorpp, P. Kreutzer, and W. Beck, *J. Organometal. Chem.*, **37**, 397 (1972).

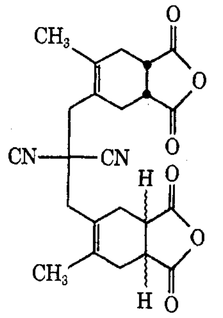
reaction was carried out above *ca.* 100°. This material was apparently formed from **10** ($R = R' = CH_3CO$), since performing the reaction at lower temperatures (*ca.* 60°) gave good yields of **10** ($R = R' = CH_3CO$). Upon isolation, this isomeric material proved to be an inseparable mixture of at least two compounds; therefore, the structures of these compounds remain unassigned.

Our apparent inability to prepare the compounds **11** ($R = R' = CO_2Et$ and $R = CO_2Et$; $R' = CN$) may be the result of the instability of these compounds under the isolation conditions. The crude reaction mixtures gave evidence for product formation; however, rearrangements to complex mixtures appeared to occur on attempted distillation.

As with the amino dienes, maleic anhydride reacted smoothly with **10** and **11** to give the expected Diels–Alder adducts. Thus, **10** ($R = R' = COCH_3$) and **11** ($R = R' = CN$) gave the expected adducts **12** and **13**, respectively.

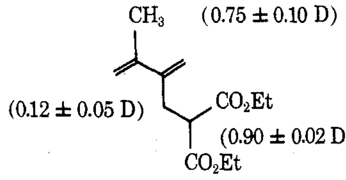


12

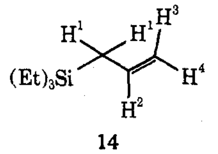


13

The reaction of allene with diethyl 2,2-dideuteriomalonate (>94% D_2) gave a labeled sample of **10** ($R = R' = CO_2Et$). Mass spectral and nmr analysis revealed the following deuterium distribution.



Catalytic Reaction of Allene with Triethylsilane.— Numerous attempts were made to effect catalytic reactions between allene and other active hydrogen compounds. During this work, it was found that triethylsilane cleanly reacted with allene in the presence of bis(triphenylphosphine)(maleic anhydride)palladium to form triethylallylsilane (**14**).[10] The structure was



14

assigned mainly on the basis of its nmr spectrum. A doublet at δ 1.55 ($J_{12} = 8$ Hz) was assigned to the allylic hydrogens. The olefinic protons, δ 4.6–6.2, displayed a pattern characteristic of a vinyl group.

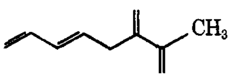
Discussion

Insufficient information is in hand to reasonably define any single mechanism for these catalytic reactions of allene. However, certain experimental facts shall be discussed which must be accommodated by any proposed mechanism.

It appears from the results of several experiments that the presence of either a Pd(0) or a Rh(I) species is necessary for catalysis to occur. The apparent activity of Pd(II) or Rh(II) complexes in the reactions of amines with allene is readily explained as resulting from the *in situ* reduction of these complexes by the amines. In support of this hypothesis, it was noted that palladium dichloride reacted with representative alkyl amines at temperatures of 80–100° to slowly deposit metallic palladium. If, as seems likely, the oxidation of the amines involves carbon–hydrogen bonds,[11] a similar oxidation pathway would not be available for ammonia, thus accounting for the observed inactivity of Pd(II) complexes in the ammonia–allene reactions.

The results of the deuterium-labeling experiments require a mechanism which places the active hydrogen of the amine or carbon acid predominantly in the olefinic methyl group of the product. In the case of the reaction of piperidine-d_1 with allene, all of the deuterium was found in the methyl group of the product. This finding is of little help in distinguishing between mechanisms, since all of the apparently reasonable mechanisms considered require this particular placement of hydrogen. However, the situation with the carbon acids is not so clear-cut. Thus, in the case of the reaction of allene with 2,2-dideuteriodiethyl malonate, some deuterium is found on the allylic methylene group. This does not appear to be the result of a slow exchange following product formation, although the uncertainty of the analytical method employed does leave some doubt. It may also be noted that this observed lack of significant exchange of **10** ($R = R' = CO_2Et$) with 2,2′-dideuteriodiethyl malonate under typical reaction conditions rules out the possibility of the rapid, reversible formation of **10** ($R = R' = CO_2Et$).

Apparently the presence of so-called "active hydrogen" compounds may not be necessary for the formation of products containing the characteristic 2,3-dialkyl-1,3-diene unit described here. In related work[12] reported recently, it was shown that butadiene reacts with allene in the presence of bis(triphenylphosphine)(maleic anhydride)palladium to give a 78% yield of **15**.



15

A possible mechanism for these reactions could involve the initial formation of a metal hydride, possibly by an oxidative addition of an amine or carbon acid to the metal. However, if such intermediates were formed, one would expect them to be reactive toward monoolefins. All attempts to observe such reactions have thus far failed.

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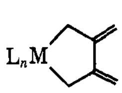
[10] A. D. Petrov and V. F. Mironov, *Dokl. Akad. Nauk SSSR*, **75**, 707 (1950).

[11] Compare with the oxidation of alcohols with palladium(II) salts: W. G. Lloyd, *J. Org. Chem.*, **32**, 2816 (1967).

[12] D. R. Coulson, *J. Org. Chem.*, **37**, 1253 (1972).

Alternative mechanisms not requiring a hydride intermediate could conceivably involve intermediates such as **16**, since metal–carbon bond cleavage of such



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species with an amine or carbon acid would lead to the observed products. However, the evidence for such intermediates is purely circumstantial at this point.

The reaction of triethylsilane with allene obviously differs from the other reactions discussed here, since *only* a 1:1 addition product could be isolated. In this case an oxidative addition of the silane to the metal is likely to be a necessary step. This suggestion is corroborated by recent mechanistic studies[13] concerned with the catalytic additions of silanes to monoolefins.

Experimental Section

Melting points and boiling points are uncorrected. Nuclear magnetic resonance spectra were recorded at 60 MHz using a Varian Associates A-60A instrument. Chemical shifts are reported with tetramethylsilane (δ 0.00) as an internal standard. The proton integrations for all new compounds were found to be within ±5% of their theoretical values. The infrared spectra were recorded on pure liquids or KBr pellets of solids. All new compounds discussed previously but not described in this section gave satisfactory elemental analyses for carbon, hydrogen, and nitrogen, where applicable (within ±0.5 units of the calculated percentages).

***N*,3-Dimethyl-2-methylene-3-butenylamine, 2 ($R' = H$, $R = CH_3$).**—A solution of allene (10 g, 250 mmol), methylamine (11 g, 300 mmol), and bis(triphenylphosphine)(maleic anhydride)palladium (0.364 g, 0.5 mmol) in 25 ml of tetrahydrofuran was heated to 120° for 6 hr in an 80-cc stainless steel lined autoclave. The resulting solution was directly distilled, giving 5.8 g (42% yield) of *N*,3-dimethyl-2-methylene-3-butenylamine, **2** ($R' = H$, $R = CH_3$): bp 85.5–86.5° (100 mm); ir 1607 cm^{-1} (C═C); uv (EtOH) λ_{max} 225 mμ (ε 17,200); nmr, see Table III.

Anal. Calcd for $C_7H_{13}N$: C, 75.6; H, 11.8; N, 12.6. Found: C, 75.45; H, 11.59; N, 12.60.

Reaction of *N*,*N*,3-Trimethyl-2-methylene-3-butenylamine, 2 ($R = R' = CH_3$), with Maleic Anhydride.—A solution of **2** (6.9 g, 55 mmol) in 10 ml of benzene was added over 30 min to maleic anhydride (4.9 g, 50 mmol) in 30 ml of benzene. After standing for 18 hr the solution was directly distilled, giving 6.50 g of an oil, bp 151–152° (1.1 mm). This oil was purified by recrystallization from hot hexane, giving 3.30 g of white needles of **4**: mp 79–80°; ir 1775 and 1838 cm^{-1} (anhydride bands); nmr (benzene) δ 1.5 (s, 3 H, olefinic methyl), 1.8–2.2 (m, 8 H, *N*-methyl and methylene), 2.35–2.85 (m, 6 H, methylene and methine).

Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.65; H, 7.68; N, 6.28. Found: C, 64.48; H, 7.80; N, 6.49.

***N*-(3-Methyl-2-methylene-3-butenyl)piperidine, 2 [$R = (CH_2)_2$; $R' = (CH_2)_3$].**—A solution of piperidine (10.0 ml, 100 mmol) and palladium chloride (0.177 g, 1 mmol) in 20 ml of hexamethylphosphoramide was warmed to 70°. Allene at *ca.* 1-atm pressure was allowed to be absorbed by the solution. After an initial slow rate of uptake the rate of absorption accelerated to *ca.* 20 ml/min. After 17 hr the absorption had essentially ceased and the dark solution was poured into 130 ml of water. The mixture was extracted with three 50-ml portions of pentane. The pentane extracts were combined, dried over magnesium sulfate, and distilled. A fraction was collected boiling at 71–75° (5 mm) and weighing 10.76 g. This material was identified as **2** [$R = (CH_2)_2$; $R' = (CH_2)_3$] and corresponded to a 65% yield based on piperidine charged: ir 1608 cm^{-1} (1,3-diene); nmr, see Table III.

Anal. Calcd for $C_{11}H_{19}N$: C, 79.95; H, 11.59; N, 8.47. Found: C, 79.89; H, 11.51; N, 8.75.

***N*-[6-(2-Methyl-3-methylene-1,3-butadiene)-1-cyclohexenyl]pyrrolidine (6).**—A mixture of *N*-(1-cyclohexenyl)pyrrolidine (15.1 g, 100 mmol), bis(triphenylphosphine)(maleic anhydride)palladium (2.2 g, 3 mmol), and allene (10 g, 250 mmol) in 25 ml of tetrahydrofuran was heated to 120° for 6 hr in an 80-cc stainless steel pressure vessel. The resulting solution was distilled, giving 7.75 g (34% yield) of *N*-[6-(2-methyl-3-methylene-1,3-butadiene)-1-cyclohexenyl]pyrrolidine (**6**): bp 92–96° (0.2 mm); ir 1592 (C═C, 1,3-diene), 1633 cm^{-1} (C═C, enamine); nmr (benzene) 1.95–2.4 (m, 3 H, methylene + methine), 2.4–3.35 (m, 6 H, allylic methylene), 4.45 (t, 1 H, $J = 4$ Hz, enamine hydrogen), 4.78–5.25 (m, 4 H, olefinic).

Anal. Calcd for $C_{16}H_{25}N$: C, 83.05; H, 10.9; N, 6.05. Found: C, 82.65; H, 10.79; N, 5.64.

2-(3-Methyl-2-methylene-3-butenyl)cyclohexanone (7).—A solution of *N*-[6-(2-methyl-3-methylene-1,3-butadiene)-1-cyclohexenyl]pyrrolidine (1.15 g, 5 mmol) and concentrated hydrochloric acid (0.395 ml, 4.5 mmol) in 10 ml of methanol was stirred for 3 hr. The solution was then evaporated of solvent and the residue was extracted with pentane. The pentane layer was dried over magnesium sulfate and evaporated of solvent. The residual oil weighed 0.75 g. Glpc collection (retention time 14 min, 155°, 20% silicone gum nitrile; 8 ft × 0.25 in. column) afforded a pure sample of **7**: ir 1592 (C═C, 1,3-diene unit), 1709 cm^{-1} (C═O); nmr (CCl_4) δ 1.0–2.7 (m, 13 H, methylene and methyl), 3.03 (m, 1 H, methine), 4.9–5.2 (m, 4 H, C═C); derivative 2,4-dinitrophenylhydrazone, mp 117.8–118° from ethanol.

Anal. Calcd for $C_{18}H_{22}N_4O_4$: C, 60.35; H, 6.19; N, 15.62. Found: C, 60.0; H, 6.13; N, 15.56.

Diethyl (3-Methyl-2-methylene-3-butenyl)malonate (10) ($R = R' = CO_2Et$).—A solution of diethyl malonate (30.6 ml, 200 mmol), allene (8 g, 200 mmol), and bis(triphenylphosphine)(maleic anhydride)palladium (1.46 g, 2 mmol) in 25 ml of tetrahydrofuran was heated to 100° for 6 hr in an 80-cc stainless steel lined autoclave. The resulting solution was directly distilled giving 20.62 g (86% yield), bp 80–80.5° (0.2 mm), of **10** ($R = R' = CO_2Et$): uv (EtOH) λ_{max} 232 mμ (ε 18,480); ir 1605 (1,3-diene), 1740 cm^{-1} (C═O); nmr, see Table V.

Anal. Calcd for $C_{13}H_{20}O_4$: C, 65.0; H, 8.38. Found: C, 64.64; H, 8.62.

Reaction of *N*-Deuteriopiperidine and Allene.—A solution of *N*-deuteriopiperidine[14] (>98% d_1) (5.0 ml, 50 mmol) and bis(triphenylphosphine)(maleic anhydride)palladium (0.364 g, 0.5 mmol) in 10 ml of hexamethylphosphoramide (redistilled) was placed under an atmosphere of allene at 75° with rapid stirring. Absorption of allene was allowed to proceed for 25 hr. The solution was then poured into 70 ml of water and extracted with 3 × 25 ml of pentane. The pentane layer was dried over $MgSO_4$ and filtered. The clear solution was distilled, giving 2.9 g (35% yield) of monodeuterated 2-methyl-3-(piperidinomethyl)-1,3-butadiene (**9**). Nmr analysis revealed a total of 0.78 ± 0.05 atoms of deuterium per molecule, all of which appeared to be on the methyl carbon. Mass spectral analysis gave d_0 17% and d_1 83%, in close agreement with the nmr analysis.

Reaction of Bis(2,3-dimethylenebutyl)dicyanomethane (12) with Maleic Anhydride.—A solution of maleic anhydride (2.16 g, 22 mmol) in 15 ml of benzene was added to a solution of **11** ($R = R' = CN$) (2.27 g, 10 mmol) in 5 ml of benzene over 45 min with stirring. The solution was allowed to stand overnight, giving a white, crystalline mass which was filtered directly, giving 3.9 g of a white powder after washing with 3 × 15 ml of benzene. This powder could not be properly recrystallized but could be precipitated from methylene chloride by addition of ether. A white powder, 1.95 g, mp 217–218°, resulted. The formation of two stereoisomers is possible here and could account for the amorphous character of the product. The product was assigned the structure **13** on the following basis: ir 1775, 1840 cm^{-1} (anhydride); nmr (DMSO-d_6) δ 1.78 (s, 6 H, methyl), 2.2–2.6 (m, 8, methylene), 2.65–3.65 (m, 8 H, methylene and methine).

Anal. Calcd for $C_{23}H_{22}N_2O_6$: C, 65.4; H, 5.25; N, 6.63. Found: C, 65.92; H, 5.09; N, 6.47.

Attempted Preparation of Tris(3-methyl-2-methylene-3-butenyl)amine (8).—A solution of **3** ($R = H$) (8.85 g, 50 mmol), bis(triphenylphosphine)(maleic anhydride)palladium (0.364 g,

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[13] (a) A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965); (b) L. H. Sommer, J. E. Lyons, and H. Fujimoto, *ibid.*, **91**, 7051 (1969); (c) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964).

[14] The *N*-deuteriopiperidine was prepared by heating *N*-deuteriopiperidinium deuteriochloride, obtained by exchange with D_2O, with freshly calcined calcium oxide.

0.50 mmol), and a trace of phenothiazine in 25 ml of tetrahydrofuran was charged to an 80-cc stainless steel presure vessel. Allene (6.0 g, 150 mmol) was added and the resulting mixture was heated to 120° for 6 hr. The solution was distilled directly, giving a middle fraction weighing 3.14 g, bp 94–96° (0.36 mm). Two other fractions (bp 93–97°) accounted for 3.52 g and the residue remaining in the distillation pot weighed 6.92 g. The middle fraction was analyzed by nmr; see Table III. Thus, the sample appeared to be *ca.* 90–95% pure **8**. All attempts to further purify this material resulted in polymer formation.

Separation of Products from Reaction of Acetylacetone with Allene.—A preparation of **10** (R = R′ = $COCH_3$) carried out at 120° according to the procedure described for the preparation of **10** (R = R′ = CO_2Et) gave a product containing *ca.* 70% of an unknown material. This product (10.0 g, >30 mmol) and maleic anhydride (5.44 g, 55.5 mmol) were allowed to stand for 4 days in 50 ml of benzene solution. The solution was then evaporated of solvent by rotary evaporation and the resulting green-yellow oil was treated with 55 ml of ether. Cooling to 0° gave crystal formation. Filtration gave 3.43 g of **12**. The filtrate was directly distilled, giving maleic anhydride (*ca.* 3.2 g) and a fraction of bp 61–65 (0.35 mm) (3.7 g) containing <5% maleic anhydride (0.32 mm) by nmr analysis.

A sample of this fraction was purified by preparative glpc (20% silicone gum nitrile column): ir 1674, 1650–1510 cm^{-1} (β-diketone, chelate); mass spectrum, parent peak at *m/e* 180 corresponding to $C_{11}H_{15}O_2$ (mol wt, 180.24); uv (EtOH) λ_{max} 271 mμ (ϵ 11,750) [note: **10** (R = R′ = $COCH_3$) possesses λ_{max} 275 mμ (ϵ 8350), enol form, and λ_{max} 223 mμ (ϵ 8000)]; nmr (CCl_4) δ 4.95 (m, 1.65 H), 4.87 (m, 0.30 H), 3.09 (m, 1.47 H), 2.90–2.70 (m, 0.60 H), 2.22–2.0 (m, 0.60 H), 1.79 (m, 0.85 H), 1.40 (m, 5.05 H).

Diels–Alder Reaction of (2,3-Dimethylenebutyl)diacetylmethane 10 (R = R′ = CH_3CO) with Maleic Anhydride.—A solution of maleic anhydride (4.9 g, 50 mmol) in 30 ml of benzene was added to **10** (R = R′ = $COCH_3$) (9.75 g, 55 mmol) in 25 ml of benzene. The solution was allowed to stand for 22.5 hr and was then evaporated of volatiles on a rotary evaporator (35°, 20 mm). The residue was a yellow oil. This oil, on mixing with 50 ml of ether, gave a white, crystalline solid. Filtration and washing of the solid gave 2.5 g of a white, crystalline solid, mp 122–123°. This compound is assigned the structure **12** on the following basis: ir 1775, 1838 cm^{-1} (anhydride); nmr (CD_3CN) δ 1.78 (s, 3 H, CH_3), 2.02 (s, 6 H, CH_3CO), 2.1–2.5 (m, 4 H, methylene), 3.08 (s, 2 H, methylene), 3.4–3.6 (m, 2 H, CHCO), 13.76 (s, 1 H, OH).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 64.75; H, 6.51. Found: C, 65.35; H, 6.59.

Reaction of 2-Methyl-3-dimethylaminomethyl-1,3-butadiene (2, R = R′ = CH_3) with Maleic Anhydride.—A solution of 6.9 g (55 mmol) of 2-methyl-3-dimethylaminomethyl-1,3-butadiene in 10 ml of benzene under nitrogen was added with stirring over 30 min to 4.9 g (50 mmol) of maleic anhydride in 30 ml of benzene. The solution was allowed to stand for 18 hr and was then evaporated of volatiles on a rotary evaporator. The residue was directly distilled, giving 6.50 g of an oil, bp 151–152° (1.1 mm). This substance was further purified by recrystallization from hot hexane, giving 3.30 g of white needles, mp 79–80°. This compound was assigned the structure **4** on the basis of the following physical evidence: ir 1775, 1838 cm^{-1} (anhydride); nmr (benzene) δ 1.50 ppm (s, 3 H, methyl), 1.75–2.25 (m, 8 H, methyl and methylene), 2.25–2.9 (m, 6 H, methylene and methine).

Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.65; H, 7.68; N, 6.28. Found: C, 64.48; H, 7.71; N, 6.50.

Diels–Alder Reaction of Bis(2,3-dimethylenebutyl)methylamine (3, R′ = CH_3) with Maleic Anhydride.—A solution of 1.91 g (10 mmol) of **3** (R′ = CH_3) in 5 ml of benzene was added to 2.16 g (22 mmol) of maleic anhydride in 15 ml of benzene. The solution, after standing overnight, was evaporated of volatiles on a rotary evaporator (35°, 20 mm), giving a syrupy material. On mixing with 30 ml of ether the material solidified and the mixture was filtered, giving 3.62 g of a tan solid. This solid was recrystallized from benzene–hexane, giving 2.05 g of a microcrystalline material, mp 140–147°. This melting range is probably explainable by the fact that two stereoisomers are likely to be formed in this reaction. The structure assigned to this material, **5**, was found to be consistent with the following physical evidence: ir 1775, 1840 cm^{-1} (anhydride); nmr (benzene) δ 1.75 (s, 6 H, CH_3), 1.92 (s, 3 H, CH_3), 2.2–2.65 (m, 8 H, allylic methylene), 2.84 (s, 4 H, allylic methylene), 3.25–3.5 (m, 4 H, CHCO).

Anal. Calcd for $C_{21}H_{25}NO_6$: C, 65.15; H, 6.51; N, 3.62. Found: C, 65.42; H, 6.60; N, 3.52.

Catalytic Reaction of 2,2′-Dideuteriodiethyl Malonate with Allene.—A solution of 15.5 ml (100 mmol) of 2,2′-dideuteriodiethyl malonate,[15] >94% d_2, 0.182 g (0.25 mmol) of bis(triphenylphosphine)(maleic anhydride)palladium, and 4.0 g (100 mmol) of allene in 15 ml of dry tetrahydrofuran was placed in a 50-cc Carius tube and sealed. The tube was heated to 120° for 6 hr. The resulting mixture was directly distilled, affording a pure sample of deuterium-labeled diethyl (3-methyl-2-methylene-3-butenyl) malonate, bp 80° (0.2 mm). Nmr analysis of the sample in carbon tetrachloride provided the following distribution of deuterium, on the reasonable assumption that the ethyl substituents did not undergo hydrogen–deuterium exchange during the reaction: methyl group, 0.75 ± 0.10 D; methylene group, 0.12 ± 0.05 D; methine group, 0.90 ± 0.02 D. Within the limits of the measurement (±5% of the respective integration areas) there appeared to be no deuterium residing on the olefinic carbons.

A similar reaction was carried out in which the allene was replaced by a pure sample of diethyl (3-methyl-2-methylene-3-butenyl) malonate. Reisolation of the ester followed by nmr analysis showed that less than 0.05 D was present in either the methyl or the methylene group. Thus, within the limits of this method, essentially no exchange was found.

Triethylallylsilane (14).—A solution of allene (10 g, 250 mmol), triethylsilane (14.5 g, 125 mmol), and bis(triphenylphosphine)-(maleic anhydride)palladium in 25 ml of tetrahydrofuran was heated to 120° for 6 hr in an 80-cc stainless steel lined pressure vessel. The resulting solution was directly distilled, giving 9.4 g (48% yield) of **14**: bp 37° (3 mm); ir 1660 cm^{-1} (C=C); nmr (CCl_4) δ 0.25–1.30 (m, 15 H, ethyl), 1.55 (d, J_{12} = 8 Hz, 2 H, allylic hydrogens), 4.6–5.05 (m, 2 H, olefinic methylene), 5.4–6.2 (m, 1 H, J_{23} = 16 Hz, J_{24} = 8 Hz, olefinic methine).

Anal. Calcd for $C_9H_{20}Si$: C, 69.15; H, 12.89. Found: C, 69.71; H, 13.23.

Registry No.—**4**, 38644-78-9; *cis,cis*-**5**, 38644-79-0; *cis,trans*-**5**, 38644-80-3; **6**, 38644-81-4; **7**, 38644-82-5; **7** DNP, 38644-83-6; **8**, 38644-49-4; **9**, 38644-85-8; **12**, 38644-86-9; *cis,cis*-**13**, 38644-87-0; *cis,trans*-**13**, 38677-70-2; **14**, 17898-21-4; allene, 463-49-0; maleic anhydride, 108-31-6; *N*-(1-cyclohexenyl)pyrrolidine, 1125-99-1; *N*-deuteriopiperidine, 694-586; 2,2′-dideuteriodiethyl malonate, 4303-49-5; diethyl (3-methyl-2-methylene-3-butenyl)malonate, 38644-74-5; triethylsilane, 617-86-7.

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(15) The diethyl 2,2-dideuteriomalonate was prepared from commercially available perdeuteriomalonic acid and ethanol-*O*-d_1.