Addition of Carbenes to 1,1-Dimethylallene. Formation and Rearrangement of Substituted Methylenecyclopropanes

Xavier Creary[1]

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received September 12, 1977

Addition of photolytically generated carboethyxoxycarbene as well as the copper carbenoid species to 1,1-dimethylallene (1) gives cyclopropanation of both of the allenyl double bonds of 1. Also produced are small amounts of 1-carboethoxymethylene-2,2-dimethylcyclopropanes 4 and 5 as well as C–H insertion products 6 and 7 in the case of the photolytically generated carbene. The photosensitized triplet carbene addition gives similar products in a differing ratio. The intervention of perpendicular trimethylenemethane intermediates is discussed, and a rationale is offered to account for these products. Phenylcarboethoxycarbene, methylcarboethoxycarbene, and substituted phenylcarbenes have also been added to 1. Thermal rearrangements of the methylenecyclopropane products have been observed. The effect of substituents on rate has been determined and is quite small. The substituent effect has been interpreted in terms of an early transition state in the formation of the intermediate perpendicular trimethylenemethane or a concerted process with only partial radical character in the transition state.

The addition of carbenes to olefins forming cyclopropanes has been thoroughly investigated and is of great synthetic utility. Additions to allenes to form methylenecyclopropanes have also been observed. Previous examples include dihalocarbene additions,[2a–e] the copper-catalyzed addition of ethyl diazoacetate,[2d] and the addition of methylene.[2d,e] Additions of dimethylvinylidenecarbene,[2e,g] isopropylidenecarbene,[2f] biscarbomethoxycarbene,[4b] carbomethoxycarbene,[4b] and diphenylcarbene[12] to allene and substituted allenes have also been reported. Our interest in cyclopropanation reactions and trimethylenemethanes has led us to investigate the feasibility of further extending the scope of the reaction of carbenes with allenes to produce a variety of substituted methylenecyclopropanes. The rearrangement of these substrates is also of interest mechanistically. Reported here are the results of a study of the reaction of 1,1-dimethylallene (1) with carboethoxy-, methylcarboethoxy-, phenylcarboethoxy-, and arylcarbenes from a preparative and a mechanistic standpoint. Also presented are data on the thermal rearrangement of the resultant methylenecyclopropanes and the implications concerning reaction mechanism.

Results and Discussion

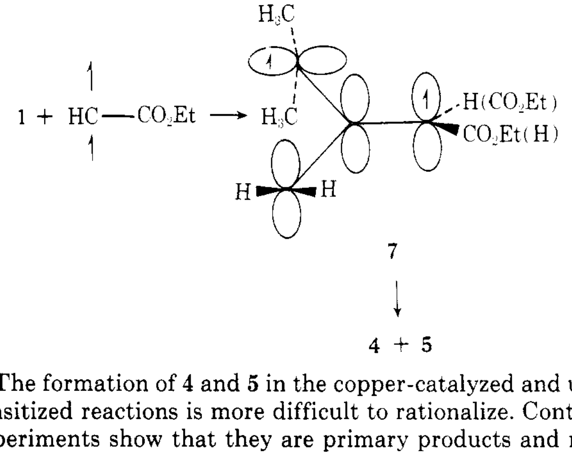
Carboethoxycarbene. The copper-catalyzed reaction of ethyl diazoacetate with 1,1-dimethylallene (1) has previously been carried out and reported to give methylenecyclopropanes 2 and 3 in a 96:4 ratio (Table I).[2d] Carboethoxycarbene (as the carbenoid) generated from the diazoester and copper is relatively nondiscriminating in additions to substituted ethylenes.[3] The reported high selectivity in preference for the more substituted bond in 1,1-dimethylallene (1) was therefore quite surprising. The copper-catalyzed carboethoxycarbene addition to 1 was therefore repeated and results are given in Table I. We have found that the copper carbenoid is indeed quite nonselective, giving similar amounts of methylenecyclopropanes 2 and 3 which arise via addition into both olefinic bonds of the allene. Also produced were small amounts of the two methylenecyclopropanes 4 and 5, which cannot be derived by direct addition of the carbene into the olefinic bonds of the allene. The origin of the discrepancy between the present results and those previously reported is unclear.

The structures of methylenecyclopropanes 4 and 5 and the stereochemistries of the carboethoxy groups were inferred from their NMR spectra. Molecular models indicate that the methylene protons of 5 are in the deshielding region of the carbonyl group. Therefore, the product with the methylene doublet ($J = 2.5$ Hz) at δ 1.33 is assigned structure 5 while the product with the doublet ($J = 1.8$ Hz) at δ 1.11 is assigned to 4. The magnitudes of the coupling constants are also of the same order as in the anti and syn rearrangement products of Feists ester.[11g] Additionally, the methyl groups of 4 are deshielded (δ 1.25) relative to the methyl groups of 5 (δ 1.22).

A study of the reaction of photolytically generated carboethoxycarbene with 1,1-dimethylallene (1) was next undertaken. Direct irradiation of ethyl diazoacetate in the allene as solvent gave the expected addition into both olefinic bonds of the allene in a ratio similar to the copper-catalyzed reaction. The two methylenecyclopropanes 4 and 5 produced in small amounts in the copper-catalyzed reaction are also produced in the direct irradiation. Also formed are the two products 6 and 7, which are formally derived from insertion into the C–H bonds of the methyl group and the allenic C–H bonds.

The benzophenone-sensitized reaction of ethyl diazoacetate with 1,1-dimethylallene (1) gave products of the same structures as the photolytically generated carbene. Product ratios were quite different with the sensitized reaction giving much larger amounts of methylenecyclopropane 3 and only one of the C–H insertion products. In general, these reaction products contrast significantly with those produced in carbomethoxycarbene additions to 1,2-propadiene.[4b]

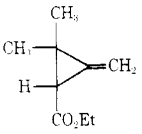
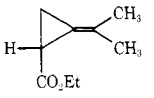
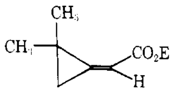
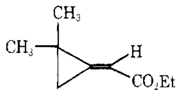
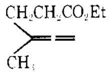
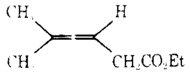
The origin of methylenecyclopropanes 4 and 5 in these reactions is of interest mechanistically. The sensitized reaction can be interpreted in terms of addition of a triplet carboethoxycarbene[4] to the allene, forming a diradical species such as 7. Closure of 7 after spin inversion at the methylene end of the "allylic radical" could produce 4 and 5.



The formation of 4 and 5 in the copper-catalyzed and unsensitized reactions is more difficult to rationalize. Control experiments show that they are primary products and not derived from subsequent isomerization of 2 and 3 under the reaction conditions. Products 2 and 3 are photostable both in the absence and presence of benzophenone. Photolysis of pyrazoline intermediates derived from cycloaddition of ethyl

0022-3263/78/1943-1777$01.00/0

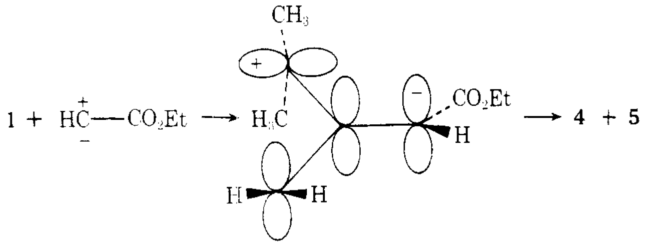
Table I. Reaction of Ethyl Diazoacetate with 1,1-Dimethylallene

Conditions	Total yield, %	Product ratios					
		 2	 3	 4	 5	 6	 7
Cu^a	25	1.0	0.83	0.07	0.04		
hν^b	51	1.0	1.1	0.15	Trace	0.24	Trace
hν/Ph$_2$CO^b	40	1.0	3.4	0.8	1.1	0.37	

^{a} Di-*n*-butyl ether as cosolvent. ^{b} 1,1-Dimethylallene as solvent.

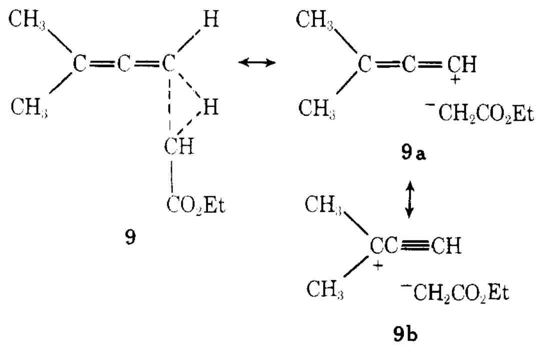
diazoacetate and 1 has also been ruled out as pyrazoline formation is not observable under nonphotolytic conditions. Photoinitiated pyrazoline formation, however, can not be ruled out. Neither can rearrangement from a thermally excited state of 2 or 3. A further possibility to be considered for the formation of 4 and 5 is singlet–triplet interconversion under the conditions of the direct irradiation[5] followed by addition of the triplet carbene to the allene. However, the ratio of 4/5 produced in the sensitized photolysis is 0.7, while the direct irradiation gave a much larger ratio. This argues against a singlet–triplet interconversion mechanism. Such a mechanism is also highly improbable in the copper-catalyzed reaction which is believed to involve a copper-complexed carbene.[6]

A process that should be considered is a stepwise mechanism involving addition of the singlet carbene (or carbenoid) to the allene, giving a zwitterionic intermediate such as 8. Such stepwise singlet carbene processes are rare, but precedents are the addition of iodocarbene to 1,2-dimethylcyclobutene[7a] and the stepwise addition–rearrangements in the reaction of methylene and dihalocarbenes to bicyclobutanes.[7b,c] A favorable electrostatic interaction in 8 might account for the predominance of 4 over 5 in which the carboethoxy group is in closer proximity to the dimethyl grouping.



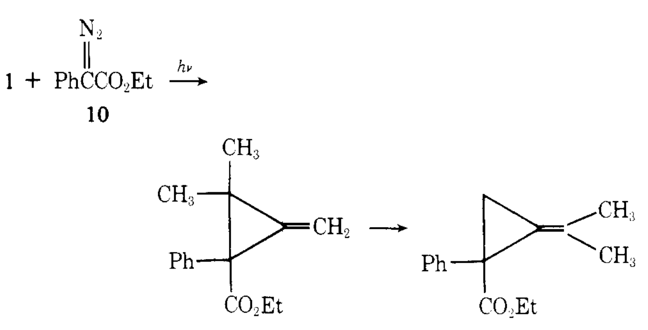
8

The presence of insertion products 6 and 7 in the direct irradiation also deserves comment. These products imply that the same species is not involved in both the photolytic and the copper-catalyzed reaction. The intermediate "photolytic" carbene is even capable of insertion into the allenic C–H bond. Stabilization of the transition state (9) for this type of insertion as indicated by 9a and 9b may account for the unusual insertion into a formally olefinic C–H bond.



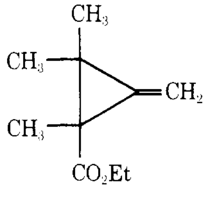
9 9a 9b

Phenylcarboethoxycarbene and Methylcarboethoxycarbene. Direct irradiation of ethyl diazophenylacetate (10) in 1,1-dimethylallene (1) gave methylenecyclopropane 12 as the sole product in 92% yield. This product of formal addition to the *least*-substituted allenic bond was initially quite surprising. Singlet–triplet interconversion of the intermediate carbene was ruled out to account for 12 since it has been found that photochemical addition of 10 to both *cis*- and *trans*-2-butene was stereospecific according to the Skell hypothesis.[8] The possibility that 12 was not a primary product was next investigated. Indeed, when the photolysis was carried out at 0 °C, the methylenecyclopropane 11 was the major photoadduct along with only small amounts of 12. The initial product 11 rearranged thermally to give 12 and accounts for the initial difficulty in detecting this primary product. Rate data will be subsequently presented.



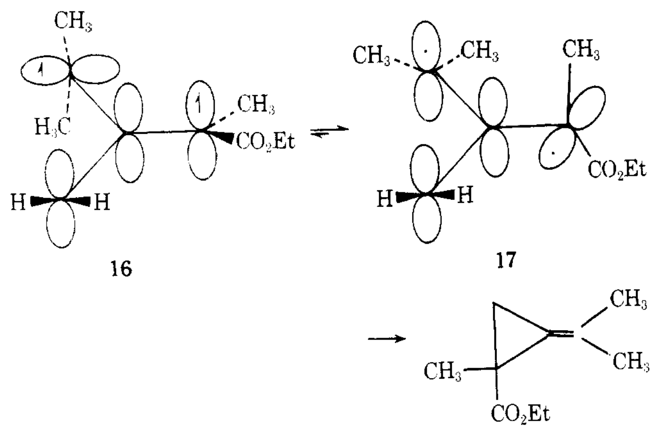
10 11 12

The benzophenone-sensitized irradiation of ethyl diazopropionate (13) in 1 also gave exclusively the product of formal addition into the least-substituted olefinic bond.[9] None of the product from addition to the most-substituted bond of 1, ester 15, was detected. The sole product 14 is in contrast to the photosensitized reaction of ethyl diazoacetate in 1 (Table I) and may reflect the increased ability of an initially formed perpendicular triplet trimethylenemethane 16 to interconvert to forms such as 17.



15

The direct irradiation of ethyl diazopropionate (13) in 1 gave an extremely complex product mixture from which the product of addition into the more-substituted bond (15), as well as 14, could be isolated.

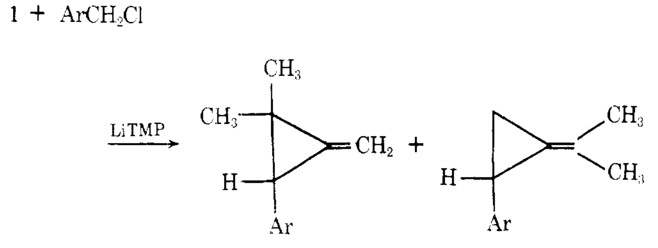


16

17

14

Arylcarbenes. The behavior of arylcarbenes with 1,1-dimethylallene (1) contrasts with that of the carboethoxy-substituted carbenes. Table II summarizes the reaction of arylcarbenoids generated from benzyl halides and lithium tetramethylpiperidide (LiTMP). As implied by our previous work,[10] there is a distinct preference for addition into the more-substituted bond in contrast to carboethoxycarbene. The products 19 are primary products and do not result from rearrangement of 18 under the reaction conditions. Yields were fair with electron-donating groups on the benzyl halide, but they were poor with carbenoids generated from benzyl halides bearing electron-withdrawing substituents. In fact, *p*-nitrobenzyl chloride and *p*-trifluoromethylbenzyl chloride gave no cyclopropanation products. The benzophenone-sensitized reaction of phenyldiazomethane and 1 also gave a predominance of addition into the more-substituted bond of the allene. However, the product ratio is reduced to 1.8. Of interest is the fact that there is no crossover into the benzylidenecyclopropane series of products and no significant amounts of C–H insertion products.



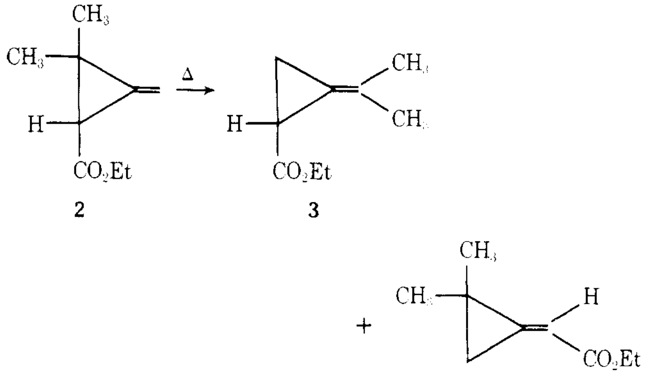
18

19

Table II. Reaction of Benzyl Halides and LiTMP with 1,1-Dimethylallene

Benzyl halide	Registry no.	Yield[a] of 18 and 19, %	Ratio[b] 18/19
$PhCH_2Cl$	100-44-7	35[c]	4.1
p-CH_3PhCH_2Cl	104-82-5	33[c]	3.9
p-CH_3OPhCH_2Cl	824-94-2	31[c]	Large
p-$ClPhCH_2Cl$	104-83-6	21	5.1
1-Naphthyl-CH_2Cl	86-52-2	20	3.0
m-$ClPhCH_2Cl$	620-20-2	7	~4[d]
m-CH_3OPhCH_2Cl	824-98-6	33	3.9
m-$FPhCH_2Cl$	456-42-8	13	4.1
$PhCH(=N_2)$[e]	766-91-6	54	1.8

[a] After chromatography and/or distillation. [b] Determined by NMR spectroscopy. [c] See ref 9 for a discussion of the formation of an acetylenic side product. [d] Impurity prevents precise determination. [e] Benzophenone-sensitized reaction.

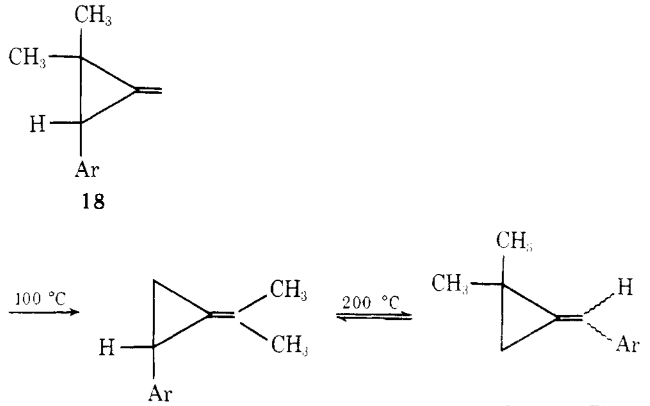


2

3

5

Thermal Rearrangements of Substituted Methylenecyclopropanes. The availability of a variety of substituted methylenecyclopropanes by reaction of 1,1-dimethylallene with carbenes has led us to examine rearrangement rates to isomeric methylenecyclopropanes as a function of substitution. This type of rearrangement has been a subject of continuing interest with respect to mechanism[11] since the observation of the thermal rearrangement of Feists ester.[11a] Recently the effect of alkoxy substituents on the course of the rearrangement has been reported.[11i] The effect of aryl and carboethoxy substituents is now reported. Table III gives rearrangement rates of a series of substituted methylenecyclopropanes as determined by NMR spectroscopy. Rearrangement of 2 gave methylenecyclopropanes 3 and 5. Unlike the carbene addition reaction, little if any of the isomeric 4 is produced. The aryl-substituted methylenecyclopropanes 18 gave the exocyclic isopropylidenecyclopropanes 19 as the sole thermal rearrangement products at 100 °C. At 200 °C further rearrangement of 19 (Ar = Ph) occurred to produce an equilibrium mixture of 19 (55%) and two benzylidenecyclopropanes 20a and 20b (45%). No indenes were produced as in the thermal rearrangement of 2,2-diphenylmethylenecyclopropane.[11h,12]



18

19

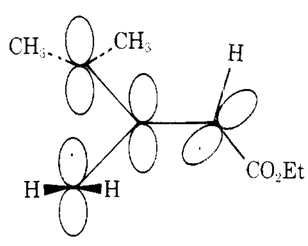
20a,b (Ar = Ph)

Diradical mechanisms have been suggested for the methylenecyclopropane rearrangement.[11d–i] In terms of such diradical mechanisms, the formation of 3 and 5 in the rearrangement of 2 would be consistent with the involvement of 21 and 22, respectively. The fact that 5 (and not 4) is produced suggests that the opening of 3 occurs to give the carboethoxy group anti to the dimethyl grouping, as in 22. Rearrangement of 18 at 100 °C gives only 19, which implies only one type of diradical (23) is involved. Diradical 23 should be more stable than 24 due to the low demand for further conjugation at the stabilized "aryl radical center." The demand for further conjugation at the "dimethyl-substituted radical center" is not satisfied in 24. This precludes formation of 24 at lower temperatures, which acccounts for the absence of benzylidenecyclopropanes 20 despite thermodynamic stability

Table III. Rearrangement Rates of Substituted Methylenecyclopropanes in Isooctane

Compd	Registry no.	Temp, °C	10^5k, s^{-1}	$k_{rel}^{100\ °C}$	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
18 (*p*-H)	65108-25-0	200.0	1.56×10^{5a}			
		100.0	35.5	1.0	28.6	2
		80.0	3.77			
18 (*p*-CH_3)	65108-26-1	100.0	46.5	1.3	27.1	−2
		80.0	5.55			
18 (*p*-Cl)	65354-61-2	100.0	47.5	1.3	29.5	5
		80.0	4.72			
18 (*p*-OCH_3)	65108-27-2	100.0	61.6	1.7	26.6	−2
		80.0	7.63			
18 (1-naphthyl)	65354-62-3	100.0	56.5	1.6	27.7	0
		80.0	4.64			
18 (*m*-Cl)	65354-63-4	100.0	33.0	0.9	29.9	4
		80.0	3.47			
18 (*m*-OCH_3)	65354-64-5	100.0	34.0	1.0	27.4	−1
		80.0	3.97			
18 (*m*-F)	65354-65-6	100.0	31.7	0.9	28.8	2
		80.0	3.33			
18 (*p*-Br)	65354-66-7	100.0	48.8	1.4	27.4	−1
		80.0	5.72			
2		150.0	19.7		33.4	3
		130.0	2.63			
		100.0	0.0849^a	2.4×10^{-3}		
11	65354-67-8	38.0	19.1			
		49.9	80.5	1.0×10^{3b}	23.4	0
25	4372-94-5	200.0	5.33^c	3.4×10^{-5d}		

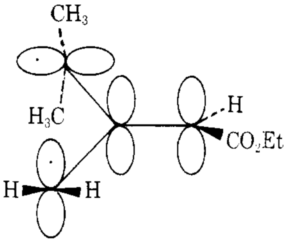
[a] Extrapolated value. [b] Comparison made at 499 °C. [c] The solvent was *n*-dodecane. [d] Comparison made at 200 °C.



21

↓

3

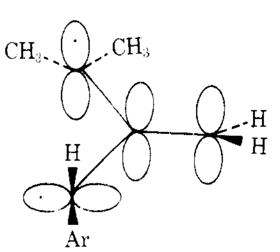


22

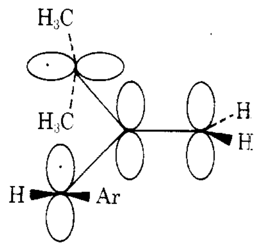
↓

5

comparable to that of **19**. Further rearrangement of **19** (Ar = Ph) to **20** at 200 °C would involve the intervention of **24** at the elevated temperatures.

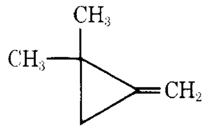


23



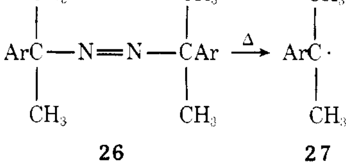
24

The kinetic data is of interest when one considers the perpendicular trimethylenemethane diradical intermediate suggested for the methylenecyclopropane rearrangement. Initially apparent are the rate enhancements relative to dimethylmethylenecyclopropane **25**. The rate enhancing effect of the aryl group is larger than the carboethoxy group. However, the rate enhancement is only 2.7×10^2 for the carboethoxy group and 2.9×10^4 for the phenyl group. These rate enhancements must be considered quite small in light of the resonance stabilization energy of a benzyl radical (13.5 kcal/mol).[13] If aryl stabilization in **23** is comparable to that of a benzyl radical, then the rate enhancement of **18** vs. **25** should be *greater than*[14] 2.9×10^4.



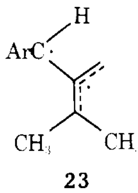
25

The effect of substituents on the aryl group is also minimal. The entire spread in rate in **18** is only a factor of two between the slowest and fastest. Differences in enthalpies and entropies of activation were also found to be small. This data raises the question of the actual intermediacy of discrete radical intermediates such as **23**. If an intermediate with "full radical character" is involved, what is the expected substituent effect? It is known that, in general, substituent effects on rate of formation of free radicals are small. Data have been presented showing that polar factors can contribute to radical reactions.[15] However, polar effects should be minimal in the methylenecyclopropane rearrangement, and there is no reason to expect correlation of rate with σ or σ^+ substituent constants.



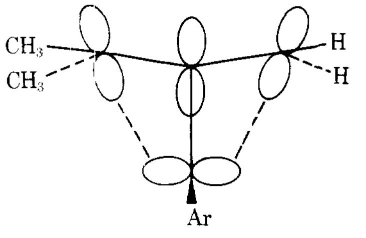
$$\mathrm{ArC(CH_3)_2{-}N{=}N{-}C(CH_3)_2Ar} \xrightarrow{\Delta} \mathrm{ArC(CH_3)_2\cdot}$$

26 **27**



23

Kovacic, Shelton, and Liang have examined substituent effects in the pyrolysis of para-substituted azocumenes **26** and have found a small rate effect.[16] These effects were attributed to resonance effects in the intermediate radical **27**. These azocumene pyrolyses should be relatively devoid of the polar effects seen in many radical reactions. The rate effects in these azocumene pyrolyses are somewhat larger than in the pyrolysis of **18** *despite the fact that a tertiary radical is involved.* The cumyl radical **27** should require *less* of a substituent stabilizing effect than benzylic radical **23**. If **23** is involved in the pyrolysis of **18**, then the transition state has less radical character at the benzylic position than in the pyrolysis of azocumene **26**. The origin of the reduced radical character in the transition state could be an early transition state in the methylenecyclopropane rearrangement. Alternately, the minimal substituent effect is not inconsistent with a concerted process having a transition state resembling **27**, in which there



27

is only partial radical character at the benzylic position. Without further data on the effect of substituents on radical reactions devoid of polar character, a choice between these two suggestions cannot be made.

Experimental Section

NMR spectra were recorded on a Varian A-60A spectrometer or a Varian XL-100 spectrometer using the Fourier transform mode. Infrared spectra were recorded on a Perkin-Elmer Infracord spectrometer.

Copper-Catalzyed Reaction of Ethyl Diazoacetate with 1,1-Dimethylallene. A solution of 5.00 g of ethyl diazoacetate in 5 mL of dry di-*n*-propyl ether was added dropwise over 6 h to a mixture of 7 g of 1,1-dimethylallene[17] and 8 mL of di-*n*-propyl ether containing 70 mg of copper acetylacetonate. The mixture was heated in an oil bath at 60–70 °C during the addition. Initially no nitrogen evolution was observed. After 1 h, 300 mg of copper bronze was added. Shortly thereafter nitrogen evolution began and was spontaneous with the addition of the diazoester. Upon completion of the addition, heating was continued for an additional hour. The solvents were removed under reduced pressure, and the residue was distilled at 0.5 mm with the bath temperature below 90 °C. The distillate (2.73 g) was analyzed by gas chromatography on a 5 ft, 5% SE-30 on Chromosorb G column at 75 °C. Samples of each product, esters **2–5,** ethyl fumarate, and ethyl maleate, were isolated by preparative gas chromatography with the injector and detector temperatures below 140 °C. The yields of esters **2**, **3**, **4**, and **5** are given in Table I along with the ratios as determined by gas chromatography. The distillate also contained 37% of ethyl fumarate and ethyl maleate as determined by NMR spectroscopy. The NMR spectrum of **2**[2d] (CCl_4) showed δ 5.35 (2 H, t, $J = 2$ Hz), 4.07 (2 H, q, $J = 7$ Hz), 1.94 (1 H, t, $J = 2$ Hz), 1.29 (6 H, s), and 1.24 (3 H, t, $J = 7$ Hz); NMR of **3** (CCl_4) δ 4.08 (2 H, q, $J = 7$ Hz), 2.05 (1 H, m), 1.80 (6 H, m), 1.58 (2 H, m), 1.23 (3 H, t, $J = 7$ Hz); NMR of **4** ($CDCl_3$) δ 6.08 (1 H, t, $J = 1.8$ Hz), 4.21 (2 H, q, $J = 7$ Hz), 1.32 (3 H, t, $J = 7$ Hz), 1.25 (6 H, s), 1.11 (2 H, d, $J = 1.8$ Hz); NMR of **5** ($CDCl_3$) δ 6.20 (1 H, t, $J = 2.5$ Hz), 4.22 (2 H, q, $J = 7.2$ Hz), 1.30 (3 H, t, $J = 7.2$ Hz), 1.33 (2 H, d, $J = 2.5$ Hz), 1.22 (6 H, s).

The reaction of ethyl diazoacetate with **1** in di-*n*-butyl ether using copper bronze powder under conditions similar to those described above gave a similar product ratio to the reaction in di-*n*-propyl ether.

Photolysis of Ethyl Diazoacetate in 1,1-Dimethylallene. A solution of 120 mg of ethyl diazoacetate (Aldrich Chemical Co.) in 5.5 mL of 1,1-dimethylallene under nitrogen was degassed at 0.1 mm and sealed in a Pyrex tube under vacuum. The mixture was irradiated at room temperature for 3 h using a 450-W Hanovia medium-pressure lamp with a Pyrex filter. Upon completion of the irradiation the yellow color had faded substantially. The solvent was removed under vacuum, and the residue was distilled at 0.08 mm to give 83 mg (51%) of a mixture of esters **2–7.** Samples of each product were isolated by preparative gas chromatography on a 6 ft, 10% XE-60 on Chromosorb P column at 105 °C with the injector and detector temperatures below 140 °C. Ester **5** was separated on an SE-30 column since the retention time on the XE-60 column was identical to **2**. Ester **6** showed the following: NMR ($CDCl_3$) δ 4.64 (2 H, sextet, $J = 3.2$ Hz), 4.13 (2 H, q, $J = 7$ Hz), 2.43 (2 H, m), 2.23 (2 H, m), 1.71 (3 H, t, $J = 3.2$ Hz), 1.25 (3 H, t, $J = 7$ Hz); IR 5.09 μm. Ester **7** showed the following: NMR ($CDCl_3$) δ 5.08 (1 H, m), 4.16 (2 H, q, $J = 7$ Hz), 2.98 (2 H, d, $J = 7$ Hz), 1.69 (6 H, d, $J = 3$ Hz), 1.27 (3 H, t, $J = 7$ Hz). The product ratios in Table I were also determined by gas chromatography.

Benzophenone-Sensitized Photolysis of Ethyl Diazoacetate in 1,1-Dimethylallene. A degassed solution of 150 mg of ethyl diazoacetate and 0.5 g of benzophenone in 6 mL of 1,1-dimethylallene was sealed in a Pyrex tube under vacuum and irradiated for 3 h with Pyrex-filtered light from a 450-W Hanovia medium-pressure source. After completion of the irradiation, the ester products **2–6** were isolated by distillation as previously described, giving 81 mg (40%) of products. Product separation was carried out by gas chromatography using an XE-60 or SE-30 column. The product ratios were also determined by gas chromatography. In a second run, the ratio of benzophenone to ethyl diazoacetate was doubled, but the product ratio was the same as before.

Sensitized and Direct Irradiation of 2 and 3. Control Experiments. A 16.4-mg sample of **2** was dissolved in 3 mL of 1,1-dimethylallene containing 250 mg of benzophenone, degassed, and sealed under vacuum. The mixture was irradiated with Pyrex-filtered light from a Hanovia 450-W medium-pressure source and a General Electric sunlamp for 2 h and 15 min. Gas chromatographic analysis of the mixture after irradiation showed only ester **2**.

Similar irradiation of 13.2 mg of ester **3** in 3 mL of 1,1-dimethylallene containing 250 mg of benzophenone gave only unchanged **3**. Direct irradiation of degassed solutions of **2** and **3** for 3 h with a Hanovia 450-W medium-pressure source also gave no observable change.

Photolysis of Ethyl Diazophenylacetate in 1,1-Dimethylallene. A degassed solution of 140 mg of ethyl diazophenylacetate[18] in 5 mL of 1,1-dimethylallene was sealed under vacuum and irradiated for 3 h with Pyrex-filtered light from a 450-W Hanovia high-pressure source. During the irradiation, the temperature was approximately 35 °C. After completion of the irradiation, the solvent was removed under vacuum. The NMR spectrum of the crude residue showed only ester **12**. Distillation of the residue gave 156 mg (92%) of ester **12**: bp 86–87 °C (0.1 mm); NMR ($CDCl_3$) δ 7.10 (5 H, s), 3.95 (2 H, q, $J = 7$ Hz), 2.14 (1 H, m), 1.73 (6 H, m), 1.36 (1 H, m), 1.00 (3 H, t, $J = 7$ Hz); mass spectrum, *m/e* 230.1320 (calcd for $C_{15}H_{18}O_2$, 230.1307).

Photolysis of Ethyl Diazophenylacetate in 1,1-Dimethylallene at 0 °C. A degassed solution of 100 mg of ethyl diazaophenylacetate in 4 mL of 1,1-dimethylallene was sealed under vacuum and immersed in an ice-water mixture in a Pyrex crystallizing dish. The mixture was irradiated at 0 °C for 2.5 h. The solvent was then removed under vacuum, and the temperature was not allowed to exceed 0 °C. The NMR spectrum of the crude residue showed methylenecyclopropanes **11** and **12** in an approximate ratio of 4:1. Compound **11**: NMR ($CDCl_3$) δ 7.7–7.2 (5 H, m), 5.83 (1 H, s), 5.63 (1 H, s), 4.12 (2 H, q, $J = 7$ Hz), 1.38 (3 H, s), 1.20 (3 H, t, $J = 7$ Hz), 0.85 (3 H, s).

Rearrangement of **11** to **12** occurs in the probe of the NMR instrument with a half-life of approximately 50 min. Rate data in isooctane is given in Table III.

Benzophenone-Sensitized Photolysis of Ethyl Diazopropionate in 1,1-Dimethylallene. A mixture of 140 mg of ethyl diazopropionate[19] in 7 mL of 1,1-dimethylallene and 500 mg of benzophenone in a Pyrex tube was sealed under nitrogen. The mixture was irradiated for 3 h with the usual Pyrex-filtered light. After removal of the solvent under vacuum, the residue was distilled with the pot temperature below 90 °C to give 69 mg (38%) of ester **14**: bp 48 °C (1.6 mm); NMR (CCl_4) δ 4.07 (2 H, q, $J = 7$ Hz), 2.1–1.7 (7 H, m), 1.5–1.2 (4 H, m, with a 3-H s at δ 1.33), 1.20 (3 H, t, $J = 7$ Hz). Ester **14** has been previously reported,[9] but no spectral data were given.

Photolysis of Ethyl Diazopropionate in 1,1-Dimethylallene. A solution of 180 mg of ethyl diazopropionate in 6 mL of 1,1-dimethylallene was degassed and sealed in a Pyrex tube under vacuum. After a 3-h irradiation and removal of the solvent under reduced pressure, 57 mg of volatile products was isolated by distillation at 0.1 mm. Gas chromatographic analysis of the mixture on 5 ft, SE-30 column showed a complex, poorly resolved mixture of at least six components. Isolation of two of the major components was accomplished by preparative gas chromatography with the injector and detector temperatures below 140 °C. The product of longer retention time was shown to be ester **14** by spectral comparison with a sample produced as described above.

The product of shorter retention time, ester **15**, showed the following: NMR ($CDCl_3$) δ 5.37 (1 H, s), 5.33 (1 H, s), 4.14 (2 H, q, $J = 7$ Hz), 1.37 (3 H, s), 1.24 (3 H, t, $J = 7$ Hz), 1.22 (6 H, s). Ester **15** has

Table IV. NMR Spectra (δ) of 18 in CCl_4 and 19 in $CDCl_3$

Compd	Registry no.	Ar	CH_2	HCAr	OCH_3	CH_3
18 (*p*-Cl		7.1	5.54	2.40		1.33, 0.83
18 (1-naphthyl)		8.2–7.2	5.68	2.78		1.53, 0.73
18 (*m*-Cl)		7.1	5.55	2.38		1.34, 0.86
18 (*m*-OCH_3)		6.7	5.53	2.39	3.73	1.33, 0.86
18 (*m*-F)		7.4–6.6	5.56	2.42		1.35, 0.87
18 (*p*-Br)[a]		7.6–7.0	5.58	2.42		1.33, 0.83
19 (*p*-Cl)	57765-59-0	7.4–6.8	1.70, 1.07	2.52		1.91, 1.77
19 (1-naphthyl)	65354-68-9	8.5–7.0	1.78, 0.90	3.06		1.97
19 (*m*-Cl)	65354-69-0	7.4–6.9	1.70, 1.10	2.52		1.91, 1.78
19 (*m*-OCH_3)	65354-70-3	7.4–6.6	1.70, 1.10	2.55	3.78	1.91, 1.79
19 (*m*-F)	65354-71-4	7.4–6.6	1.70, 1.10	2.54		1.91, 1.77
19 (*m*-Br)[b]	65354-72-5	7.5–6.8	1.70, 1.10	2.48		1.91, 1.77

[a] In $CDCl_3$. [b] In CCl_4.

been previously reported,[9] but no spectral data were given.

Reaction of Benzyl Chlorides with Lithium Tetramethylpiperidide in 1,1-Dimethylallene. General Procedure. A mixture of 6 mmol of the appropriately substituted benzyl chloride, 3.5 g of 1,1-dimethylallene, and 3 mL of ether was placed in a water bath at room temperature under nitrogen. A solution of 77 mmol of lithium tetramethylpiperidide prepared from tetramethylpiperidine and methyllithium in ether was added dropwise over a 2-h period. After stirring for an additional hour an aqueous workup followed. Tetramethylpiperidine was removed by extraction with dilute hydrochloric acid, and the products were isolated by distillation and/or chromatography on neutral alumina with pentane elution. Products 18 (*p*-Cl, 1-naphthyl, *m*-Cl, *m*-OCH_3, and *m*-F) were all chromatographed before distillation. Product 18 (1-naphthyl) was not distilled. The ratio of 18/19 was determined by NMR integration of the olefinic protons of 18 vs. the methyl protons of 19. Pure samples of 19 were isolated by preparative gas chromatography on the thermolysis products of 18. NMR spectral data are given in Table IV. Data on 18 and 19 (*p*-H, *p*-CH_3, and *p*-OCH_3) have been reported.[10]

Thermal Rearrangement of Substituted Methylenecyclopropanes. Kinetics Procedure. Approximately 80 mg of 18 and an internal standard (dimethyl phthalate) were dissolved in isooctane in an NMR tube and sealed under nitrogen. The tube was heated in a constant temperature bath at the appropriate temperature for a given amount of time. Periodically the tube was analyzed for remaining 18 by integration of the signal at δ 5.5–5.7. Integrals were corrected for detector response, and rate constants were calculated by the least-squares method. Correlation coefficients were in all cases better than 0.999. For product analyses the sample was heated for a minimum of ten half-lives and the tube contents were analyzed by gas chromatography. Samples of each product 19 were also isolated by preparative gas chromatography or by distillation of the thermolysis product of neat 18. 19 (1-naphthyl) was not stable to gas chromatographic conditions.

The rearrangement of ester 2 was monitored by gas chromatography with the injection port temperature below 140 °C. A sample of approximately 10 mg of 2 and 5 mg of mesitylene (internal standard) was diluted to 1 mL with isooctane, and portions were sealed in tubes under nitrogen. The tubes were immersed in a constant temperature bath, and at appropriate time intervals the contents of the various tubes were analyzed by gas chromatography on an SE-30 column at 72 °C for remaining 2. Rate constants were calculated in the usual manner. Samples of products 3 and 5 were also isolated for identification purposes by preparative gas chromatography.

Rearrangement of 19 (Ar = Ph) at 200 °C. A 30-mg sample of 19 (Ar = Ph) was sealed under nitrogen and heated at 200 °C for 1 h. Gas chromatographic analysis on a 6 ft, 10% XE-60 on Chromosorb P column at 110 °C showed unchanged 19 (Ar = Ph) (approximately 55%) along with *syn*-2,2-dimethylbenzylidenecyclopropane (**20a**; 20%) and *anti*-2,2-dimethylbenzylidenecyclopropane (**20b**; 25%). Further heating for 1.5 h at 220 °C did not change the ratio. Samples of each product were isolated by preparative gas chromatography, and structures of **20a** and **20b** were assigned by NMR spectroscopy. *syn*-2,2-Dimethylbenzylidenecyclopropane (**20a**) showed the following: NMR ($CDCl_3$) δ 7.42–7.10 (5 H, m), 6.66 (1 H, t, J = 1.8 Hz), 1.32 (6 H, s), 1.05 (2 H, d, J = 1.8 Hz). *anti*-2,2-Dimethylbenzylidenecyclopropane (**20b**) showed the following: NMR ($CDCl_3$) δ 7.60–7.20 (5 H, m), 6.75 (1 H, t, J = 2.5 Hz), 1.27 (2 H, d, J = 2.5 Hz), 1.24 (6 H, s).

The same mixture of 19 (Ar = Ph), **20a**, and **20b** could be produced by heating **20b** at 205 °C for 1 h.

Preparation of 1,1-Dimethyl-2-methylenecyclopropane (25).[2a] Potassium *tert*-butoxide (120 mg) was dissolved in 3 mL of dry dimethyl sulfoxide, and 260 mg of 1,3,3-trimethylcyclopropene[20] was added. A mildly exothermic reaction followed. After 15 min, NMR analysis showed no remaining cyclopropene. *n*-Dodecane (3 mL) was added followed by 8 mL of water. The dodecane extract was dried over sodium sulfate and used directly for the kinetics experiments. The NMR spectrum of 25 in the dodecane extract showed the characteristic olefinic multiplet at δ 5.3.[2a]

Thermal Rearrangement of 1,1-Dimethyl-2-methylenecyclopropane (25). A solution of 25 in dodecane prepared as described above and 16 mg of dimethyl phthalate (internal standard) were sealed in an NMR tube. The tube was heated in refluxing methyl benzoate (200.0 °C) for an appropriate amount of time and analyzed for remaining 25 by integration of the olefinic signal. The isomerization gives an equilibrium mixture[21] of isopropylidenecyclopropane and 25 in a ratio of 4.4:1 as determined by NMR integration of the remaining 25 after 20 half-lives. Rate constants were calculated from data acquired during the first half-life only.

Acknowledgment. The author wishes to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for support of this work.

Registry No.—**2**, 30762-78-8; **3**, 65354-58-7; **4**, 65354-59-8; **5**, 65354-60-1; **6**, 20387-99-9; **7**, 30333-01-8; **10**, 22065-57-2; **12**, 65354-73-6; **13**, 6111-99-5; **14**, 65354-74-7; **15**, 65354-75-8; **19** (Ar = Ph), 56701-47-4; **20a**, 65454-76-9; **20b**, 65354-77-0; ethyl diazoacetate, 623-73-4; 1,1-dimethylallene, 598-25-4; 1,3,3-trimethylcyclopropene, 3664-56-0; isopropylidenecyclopropane, 4741-86-0.

References and Notes

(1) Alfred P. Sloan Fellow, 1977–1979.

(2) (a) W. Rahman and H. G. Kuivila, *J. Org. Chem.*, **31**, 772 (1966); (b) P. Battioni, L. Vo-Quang, and Y. Vo-Quang, *Bull. Soc. Chim. Fr.*, 3938 (1970); (c) R. R. Kostikov and A. I. Ioffe, *J. Org. Chem. USSR (Engl. Transl.)*, **6**, 2639 (1970); (d) P. Battioni, L. Vo-Quang, and Y. Vo-Quang, *Bull. Soc. Chim. Fr.*, 3942 (1970); (e) W. von E. Doering, J. C. Gilbert, and P. A. Leermakers, *Tetrahedron*, **24**, 6863 (1968); (f) R. F. Bleicholder and H. Shechter, *J. Am. Chem. Soc.*, **86**, 5032 (1964); (g) G. Kolrich, H. Heinemann, and W. Zundorf, *Tetrahedron*, **23**, 565 (1967). We thank a referee for informing us of several examples of which we were previously unaware.

(3) R. A. Moss, *Carbenes 1973*, **1**, 194 (1973).

(4) For representative examples of benzophenone-sensitized triplet carbene reactions, see (a) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 1015 (1962); (b) M. Jones, Jr., W. Ando, M. E. Hendrick, A. Kulczycki, Jr., P. M. Howley, K. F. Hummel and D. S. Malament, *ibid.*, **94**, 7469 (1972); (c) M. Jones, Jr., A. Kulczycki, Jr., and K. F. Hummel, *Tetrahedron Lett.*, 183 (1967); (d) M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *ibid.*, 1391 (1961).

(5) An analogous interconversion occurs for phenylcarbene in frozen matrices: see (a) R. A. Moss and U-H. Dolling, *J. Am. Chem. Soc.*, **93**, 954 (1971); (b) R. A. Moss and M. A. Joyce, *ibid.*, **99**, 1262 (1977).

(6) W. R. Moser, *J. Am. Chem. Soc.*, **91**, 1135, 1141 (1969).

(7) (a) N. C. Yang and T. A. Marolowski, *J. Am. Chem. Soc.*, **90**, 5644 (1968); (b) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); (c) W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Lett.*, 991 (1965).

(8) R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 3383 (1959).

(9) Photosensitized decomposition of a pyrazoline also gave **14** as a major product. Other methylenecyclopropane isomers of **14** were also produced; see T. Sanjiki, H. Kato, and M. Ohta, *Chem. Commun.*, 496 (1968).

(10) X. Creary, *J. Am. Chem. Soc.*, **99**, 7632 (1977).

(11) For a discussion of this general class of rearrangements, see (a) G. A. R.

Kon and H. R. Nanji, *J. Chem. Soc.*, 2557 (1932); (b) M. G. Ettlinger, *J. Am. Chem. Soc.*, **74**, 5805 (1952); (c) E. F. Ullman, *ibid.*, **82**, 505 (1960); (d) J. P. Chesick, *ibid.*, **85**, 2720 (1963); (e) J. J. Gajewski, *ibid.*, **90**, 7178 (1968); (f) R. Noyari, H. Takaya, Y. Nakanisi, and H. Nozaki, *Can. J. Chem.*, **47**, 1242 (1969); (g) T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *J. Am. Chem. Soc.*, **87**, 3026 (1965); (h) J. C. Gilbert and J. R. Butler, *ibid.*, **92**, 2168 (1970); (i) W. E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970); (j) J. J. Gajewski, *J. Am. Chem. Soc.*, **93**, 4450 (1971); (k) W. Kirmse and H.-R. Marawski, *J. Chem. Soc., Chem. Commun.*, 122 (1977).

(12) M. Jones, Jr., M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Lett.*, 845 (1970).

(13) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 221 (1969).

(14) The 13.5 kcal/mol value corresponds to a $10^{6.2}$ rate difference at 200 °C.

(15) (a) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963); (b) B. R. Kennedy and K. U. Ingold, *ibid.*, **44**, 2381 (1966); (c) R. D. Gilliom and B. F. Ward, Jr., *J. Am. Chem. Soc.*, **87**, 3944 (1965); (d) K. M. Johnston, G. H. Williams, and H. J. Williams, *J. Chem. Soc. B*, 114 (1966).

(16) J. R. Shelton, C. K. Liang, and P. Kovacic, *J. Am. Chem. Soc.*, **90**, 354 (1968).

(17) W. J. Bailey and C. R. Pfeiffer, *J. Org. Chem.*, **20**, 95 (1955).

(18) M. Regitz and F. Menz, *Chem. Ber.*, **101**, 2622 (1968).

(19) M. B. Sohn, M. Jones, Jr., M. E. Hendrick, R. R. Rando, and W. von E. Doering, *Tetrahedron Lett.*, 53 (1972).

(20) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).

(21) The isomerization of **24** to give isopropylidenecyclopropane in the gas phase has been reported; see R. J. Crawford and H. Tokunaga, *Can. J. Chem.*, **52**, 4033 (1974).

Hydrogenation of 2,5-Diacetoxy-2,5-dimethyl-3-hexyne over Palladium[1a]

Donald R. Paulson,* L. Scott Gilliam,[1b] Virgil O. Terry,[1c] Susanne M. Farr,
Earl J. Parker, Franklin Y. N. Tang, Rudiger Ullman, and George Ribar

Department of Chemistry, California State University, Los Angeles, Los Angeles, California 90032

Received July 19, 1977

The hydrogenation of **1** over 10% palladium on charcoal proceeds to give seven products (**2**–**8**). Alkene **2** is the precursor of the other products. A concerted process including hydrogenation, hydrogenolysis, and isomerization is postulated to account for the direct formation of **5** from **2**. The effect of added nitrogen bases on the product distribution is presented, and several mechanistic alternatives are discussed.

One of the most useful reactions for the preparation of pure cis olefins has been the catalytic hydrogenation of acetylenes over deactivated catalysts at room temperature and atmospheric pressure.[2] The classic catalyst for this reaction is Lindlar's catalyst, lead-poisoned palladium on calcium carbonate.[3] The partial hydrogenation of acetylenic carbinols has been studied by many workers. These are useful synthetic intermediates due both to their ease of synthesis and to the possibility of transforming them into molecules containing different functionality.[4] Thus, much of the work on acetylenic carbinols has been directed toward their selective hydrogenation to the olefinic stage without any further reduction to the alkane system.

Moderation of palladium catalysts with added pyridine has been employed to hydrogenate acetylenic carbinols to allylic alcohols.[5] The pyridine apparently functions to poison the catalyst by being absorbed more strongly on the catalyst surface than the alkene but less strongly adsorbed than the acetylene. This could result in selective hydrogenation,[6] although recently it has been suggested that selectivity in alkyne hydrogenation is not due to different strenghts of adsorption of alkenes and alkynes but rather to different kinds of surface adsorption sites.[7] The self-poisoning effect of pyridine on its own hydrogenation has been reviewed.[8] The reduction of pyridine to piperidine results in even stronger catalyst poisoning by the piperidine. The unshared electron pair on the nitrogen atom apparently causes the effect since pyridinium salts are readily hydrogenated without any self-poisoning of the catalyst.

Many other catalyst inhibitors have been employed for partial hydrogenation of acetylenes over palladium. These include, for example, morpholine,[9] barium carbonate,[10] calcium carbonate,[11] combinations of lead acetate and quinoline with calcium carbonate,[12] barium sulfate,[11] potassium hydroxide,[13] etc.

Although palladium is one of the most commonly used hydrogenation catalysts, isomerization[14] or hydrogenolysis[15] can be serious problems with this catalyst. In some cases catalyst modifiers can be employed to prevent these reactions. For example, potassium hydroxide prevents the hydrogenolysis of the hydroxyl groups of propargyl alcohols.[16]

We have undertaken a study of the hydrogenation of 2,5-diacetoxy-2,5-dimethyl-3-hexyne (**1**) over 10% palladium on charcoal in the presence of pyridine and piperidine as catalyst modifiers. We had inadvertently observed that upon hydrogenation of **1**, varying quantities of 2-acetoxy-2,5-dimethyl-4-hexene (**5**) were produced.[1a] The production of this novel reaction product involves hydrogenation, isomerization, and hydrogenolysis. The hydrogenation of **1** has been previously reported, but the only isolated product was the alkene **2**.[17]

Results and Discussion

Hydrogenation of **1** over 10% palladium on charcoal at atmospheric pressure in absolute ethanol results in the formation of seven different compounds (**2**–**8**, Scheme I) along with acetic acid from hydrogenolysis of some of the acetate groups. The composition of the reaction mixture was followed as a function of equivalents of hydrogen absorbed by the system. This plot is shown in Figure 1. Examination of the figure shows that the concentrations of **2** and **5** steadily increase to a maximum and then decrease as they are further transformed. Figure 2 shows the data for hydrogenation of **2** under similar conditions. It is clear that **2** is the precursor to the other reaction products, while **4**, **7**, and **8** are end products which are not further transformed. Scheme I shows a plausible sequence to account for each of the products observed.

The initial hydrogenation of **1** proceeds to give predominantly the cis alkene (**2**) along with a small quantity of the trans alkene (**3**). The trans alkene could have been formed directly from the acetylene[18] or as a result of isomerization of the cis alkene over the palladium catalyst.[19] The former is preferred since **3** is not formed during hydrogenation of **2** nor is **2** formed during hydrogenation of **3**. Presumably, in either case, formation of **3** would be due to a stepwise addition of hydrogen atoms, with the first addition step being reversible.[20]

0022-3263/78/1943-1783$01.00/0