The Influence of Structural Features on the Course of Bicyclo[1.1.0]butane Rearrangements Catalyzed by Silver(I) Ion[1,2]

Leo A. Paquette,* Richard P. Henzel,[3a] and Stanley E. Wilson[3b]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 4, 1972*

Abstract: Nine bicyclo[1.1.0]butanes, substituted to varying degrees with alkyl and aryl groups, have been rearranged with catalytic amounts of silver salts. In all cases, 1,3-dienes were produced but the positioning of substituents on this structural framework was found to vary with structure. When C_1 and C_3 are unsubstituted, the cleavage of diametrically opposed edge bonds occurs, a reaction which is kinetically accelerated with 2,2,4,4-tetramethyl substitution. In fact, this pathway also operates exclusively in the 1,2,2,4,4-pentamethyl derivative. Limited kinetic data allow for the possibility that this bond reorganization process is concerted when this level and type of substitution prevail. In those remaining cases in which C_1 and/or C_3 carry substituents, intermediate argento carbonium ion formation operates. 1,2-Hydride or vinyl shift (in that order) to the electron-deficient center and subsequent ejection of Ag^+ leads to the diene products. Stereospecific considerations are also presented.

Four general types of rearrangements have been observed in the Ag^+-catalyzed rearrangement of substituted tricycloheptanes.[4] One is the isomerization to 1,3-cycloheptadienes. This pathway, which proceeds by electrophilic attack of Ag^+ at an edge bond with subsequent diametrically opposite edge bond rupture, operates exclusively in the case of the parent tricyclic hydrocarbon[4,5] and is not affected by alkyl substitution at the "wing" positions.[4a] The second type, recognized to gain importance with substitution of the bridgehead carbons, is the conversion to alkylidenecyclohexenes. Kinetic deuterium isotope effect measurements and other relevant studies have revealed that this rearrangement proceeds by concurrent cleavage of the central bond of the strained ring and an edge bond with generation of intermediate argento carbonium ions.[1,5–7] To the extent that tertiary argento carbonium ions can be formed, this isomerization is facilitated. The third case, the formation of bicyclo[3.2.0]hept-6-enes, is of special interest because a virtual primary isotope effect is observed when deuterium is placed at C_1.[4a,6] A mechanistic rationalization of this rather deep-seated bond reorganization remains to be advanced.[4a,6] Lastly, norcarene production is sometimes encountered, but in the derivatives examined to date, this rearrangement has been only of minor importance.

The present research was initiated in an attempt to gain added insight into the causative factors which underlie this markedly differing behavior, particularly in those bicyclobutanes which lack the added inherent structural rigidity imposed by the *endo,endo*-2,4-trimethylene bridge. Also, these somewhat simpler strained ring systems did allow for greater latitude in the variation of attached groups and in the exo or endo orientation (at C_2 and C_4) of these substituents. As will be delineated, however, very similar substituent effects govern the various bond reorganizations in the several examples whose behavior toward Ag^+ we have assessed.

Results

2,2,4,4-Tetramethylbicyclobutane (**1**), conveniently available from tetramethyl-1,3-cyclobutanedione according to the procedure of Hall, *et al.*,[8] rearranged exothermically and quantitatively to 2,5-dimethyl-2,4-hexadiene (**2**) in $CDCl_3$ containing catalytic quantities of silver fluoroborate. No evidence (nmr and vpc analyses) was obtained for the formation of by-products. Unfortunately, the high symmetry inherent in **1** precludes the possibility of determining unequivocally which bond(s) experiences initial breakage. The exceedingly rapid rate of isomerization of **1** (Table II) does suggest, however, that all four methyl substituents are appropriately positioned to stabilize electron deficiency at the rate-determining transition state. In agreement with the kinetic parameters and precedent established in the tricycloheptane series,[1] this rearrangement may be considered to pass through intermediates **3** and **4**. Conceivably, the formation of argento carbonium ion **6** would be bypassed in this instance because of its secondary nature. However, the involvement of **6** cannot be summarily dismissed, since its independent generation from diazo compound **5** was found to lead chiefly (81%) to **2**. In particular, the preponderance of vinyl migration in **6** conforms to the fact that vinyl groups exhibit a greater relative migratory aptitude to cationic centers than alkyl substituents.[9]

Exposure of 1,3-dimethylbicyclobutane (**7**) to the same conditions resulted in relatively slow (qualitative

---

[1] Part XIV of the series dealing with Ag^+-catalyzed rearrangements. For the previous paper, see L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Amer. Chem. Soc.*, **94**, 7771 (1972).

[2] Various aspects of this work have been presented at the Meeting of the Chemical Institute of Canada, Halifax, Nova Scotia, May, 1971, the 22nd National Organic Chemistry Symposium, Ann Arbor, Mich., June, 1971, and the Second Belgian Chemical Society Symposium on Small Rings and Activated Multiple Bonds, Louvain, Belgium, Sept, 1971.

[3] (a) National Science Foundation Graduate Trainee, 1970–1972; (b) National Institutes of Health Postdoctoral Fellow, 1970–1971; National Science Foundation Postdoctoral Fellow, 1971–1972.

[4] (a) L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, **94**, 7761 (1972); (b) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971); (c) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **92**, 7002 (1970).

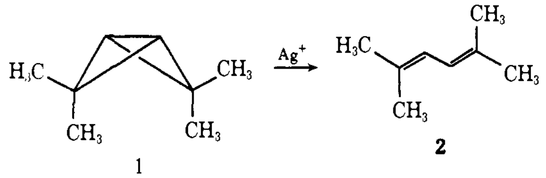
[5] M. Sakai and S. Masamune, *ibid.*, **93**, 4610 (1971).

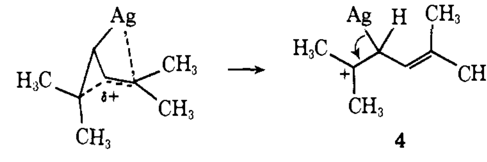
[6] L. A. Paquette and S. E. Wilson, *ibid.*, **93**, 5934 (1971).

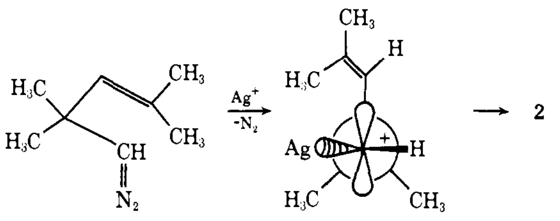
[7] L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971).

[8] H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Sieja, *J. Amer. Chem. Soc.*, **93**, 121 (1971).

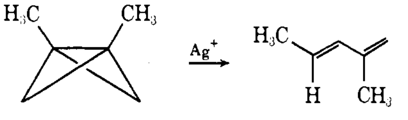
[9] Y. E. Rhodes and T. Takino, *ibid.*, **92**, 5270 (1970), and references therein.

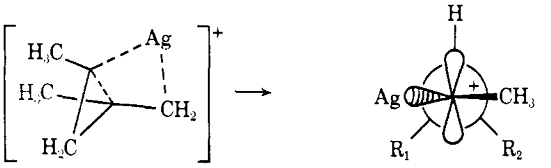

1 2


3 4


5 6

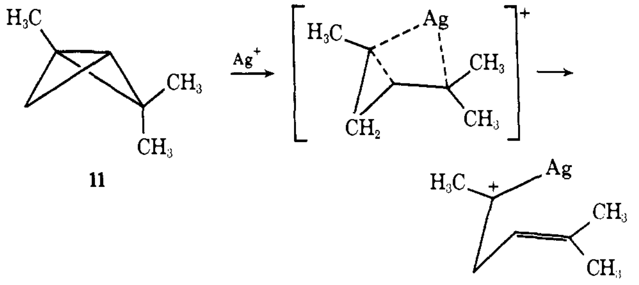
observation) isomerization to diene **8**. If this rearrangement was allowed to proceed beyond approximately 25% conversion, a number of secondary products began to make their appearance. The majority of these substances were of higher molecular weight and were not characterized. The structure of **8** was supported by spin decoupling experiments and confirmed by direct comparison with an authentic commercial sample. In explanation of the fate of **7**, it is proposed that fission of two bonds operates (see **9**) to give argento carbonium ion **10** which then experiences 1,2-hydride shift from one or both of its two possible conformations[10] to provide, upon ejection of Ag^+, the isomer of trans stereochemistry (thermodynamic control).


7 8

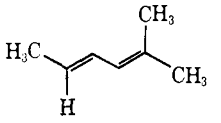

9

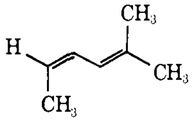
10a, $R_1 = CH_2{=}C(CH_3)$; $R_2 = H$
b, $R_1 = H$; $R_2 = CH_2{=}C(CH_3)$

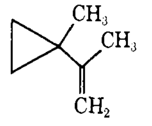
Having demonstrated that two different mechanistic rationales best account for the divergent behavior of **1** and **7**, we now consider the mode of reaction of 1,2,2-trimethylbicyclobutane (**11**) toward Ag^+. Should the C_1 methyl group in **11** be of major importance in controlling its possible competitive rearrangements, argento carbonium ion formation should dominate. In this event, **12** would ultimately lead to isomeric dienes **13** and **14** in which the methyl substituents are bonded to the terminal carbon atoms. This *a priori* reasoning was confirmed by the observation that **11** undergoes essentially quantitative conversion to a mixture of **13** and **14** (90% yield, ratio 4.5:1), together with **15** (8%) and four very minor products, when treated with catalytic amounts of silver fluoroborate (initially at −70°, followed by warming to 40°). The mixture of dienes was efficiently separated by preparative gas chromatography on a silver nitrate–benzonitrile column. Authentic **13** was synthesized by the condensation of isopropylidenetriphenylphosphorane with crotonaldehyde and the stereochemical assignment was supported by double irradiation studies at 100 MHz. Diene **14** was likewise characterized by spectral means (see Experimental Section); additionally, catalytic hydrogenation of the diene mixture led uniquely to 2-methylhexane. Vinylcyclopropane **15** was identified by direct comparison with an authentic sample prepared according to the method of Skattebøl.[11]


11

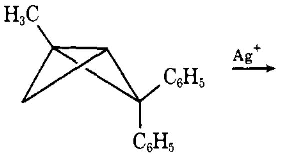
12

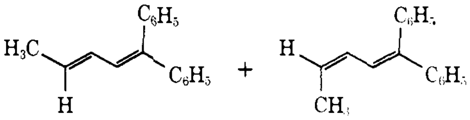

13


14


15

Attention was subsequently turned to two other 1,2,2-trisubstituted bicyclobutanes in which phenyl groups replaced two of the methyl substituents of **11**. At issue was the question posed elsewhere[12] concerning possible mechanistic changeover resulting from prior coordination of Ag^+ to one or the other of the aromatic rings. Synthesis of **16** and **26** was realized by the efficient procedures developed by Moore and Hill.[13] The isomerization of **16** with catalytic amounts of silver fluoroborate in $CDCl_3$ afforded, after preparative thick layer chromatography, the trans (**17**) and cis (**18**) isomers of 1,1-diphenyl-1,3-pentadiene in a combined yield of 67% (ratio 2.5:1). Also formed were three secondary products of higher molecular weight which were not further characterized. The observation was made, however, that if exposure to the catalyst was prolonged well beyond the time when **16** had been consumed (*i.e.*


16


17 18

---

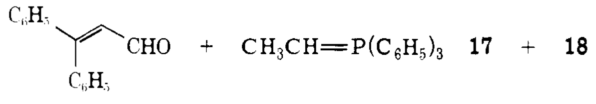
(10) The question of which rotamer experiences more efficient hydride shift is potentially resolvable should the exo and endo sites at C_2 and C_4 be capable of specific deuterium labeling.

(11) L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963).

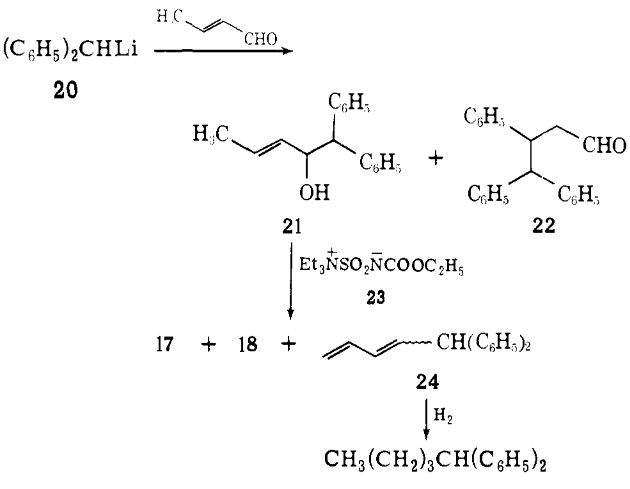
(12) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **94**, 3653 (1972).

(13) W. R. Moore and J. B. Hill, *Tetrahedron Lett.*, 4553 (1970).

2 days), the yield of monomeric $C_{17}H_{16}$ isomers decreased to 21% while the concentration of *cis*-diene **18** dropped almost to zero. Although the preparation of a mixture of **17** and **18** had previously been reported,[14] a method was sought which would provide **17** in highly enriched, if not pure, form. To this end, Wittig condensation of 3,3-diphenylacrolein (**19**) with ethylidenetriphenylphosphorane led to a distribution of **17** to **18** of only 1.85:1 (nmr analysis) and was not further pursued. Similarly, the reaction of crotyltriphenylphosphonium chloride with benzophenone in the presence of *n*-butyllithium gave rise to a 67:23 mixture of **17** and **18**. The most successful approach entailed 1,2 addition of lithium diphenylmethide (**20**) to crotonaldehyde and subsequent dehydration of alcohol **21** with ethyl(carboxysulfamoyl)triethylammonium hydroxide inner salt (**23**).[15] Although the first step was accompanied by 1,4 addition leading to **22** (20%), the yield of **21** (67%) was quite acceptable. As Burgess has noted,[15] **23** is not ideally suited for the dehydration of allylic alcohols because of competitive carbamate formation by S_Ni[1] processes; however, its choice on this occasion was dictated by the exceedingly mild conditions necessary for dehydration, a prerequisite deemed important for the desired enhancement in stereocontrol. By this means, a mixture of **17** and **18** substantially enriched in the trans isomer (5.3:1) was obtained. Diene **24** was also isolated from the hydrocarbon fraction; its nmr spectrum lacked methyl absorption and was characterized by a complex olefinic region. Catalytic reduction of **24** to 1,1-diphenylpentane (**25**) served to rule out the incursion of a structural rearrangement.

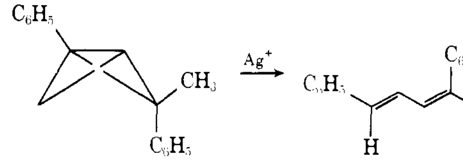


19



The above stereochemical assignments to **17** and **18** depend upon the anticipated predominance of the trans isomer in the various synthetic approaches to these dienes and upon spectral considerations. In particular, the methyl signal of **17** appears as a doublet (J = 6 Hz), whereas that of **18** is seen as a doublet of doublets (J = 1.5 and 7 Hz). These features parallel those exhibited by *trans*- and *cis*-β-methylstyrene, respectively.

Upon similar treatment of **26** with silver fluoroborate, diene **27**, a colorless oil, was obtained as the only characterizable product in 82% yield. Nmr and vpc analysis of the crude reaction mixture gave no evidence of by-product formation and, in fact, provided compelling evidence for the production of only one of the four stereoisomers of 1,4-diphenyl-1,3-pentadiene. By making recourse to the nmr technique developed by Simon[16] and Tobey[17] which relates the geometric structures of relatively unstrained ethylene derivatives to their olefinic proton resonance positions, the two isomers in which the C_4 phenyl group is cis oriented were eliminated from consideration (see Table I).



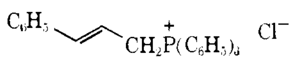
26 **27**

Table I. Calculated and Observed (in Part) Chemical-Shift Values for the Olefinic Protons in the Various Isomers of 1,4-Diphenyl-1,3-pentadiene (Values in δ)[a]

Isomer	H_1	H_2	H_3
Calcd			
trans,trans	6.71	6.91	6.62
trans,cis	6.71	6.91	6.18
cis,trans	6.62	6.44	6.62
cis,cis	6.62	6.44	6.18
Obsd			
27	6.47	6.93	6.27
33	6.62	7.22	6.64

[a] Calculated values taken from ref 14 and 15.

The trans,cis (**27**) and trans,trans isomers (**33**) of 1,4-diphenyl-1,3-pentadiene have previously been described,[18,19] but the nmr data cited were not sufficiently descriptive, nor was there any evidence presented to support the assignments in a precise way. The structure of diene **27** was independently proven by synthesis. Again, however, Wittig reagents were of limited value; for example, the phosphorane derived from **28** was too unreactive toward acetophenone to allow for diene formation in a practical sense. However, condensation of 1-lithioethylbenzene (**31**) with *trans*-cinnamaldehyde did lead chiefly to alcohol **32** (44%). Although the attempted direct generation of **31** by reaction of ethylbenzene with *n*-butyllithium–tetramethyl-



28

---

[14] B. Cheminat and R. Rambaud, *C. R. Acad. Sci., Ser. C*, **264**, 897 (1967).

[15] E. M. Burgess, H. R. Penton, Jr., and E. A. Taylor, *J. Amer. Chem. Soc.*, **92**, 5224 (1970).

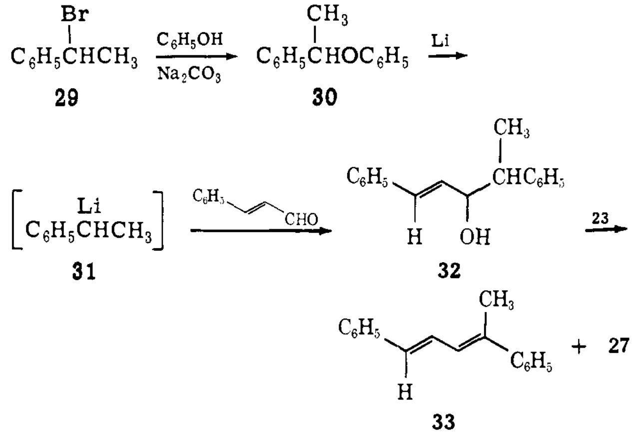
[16] C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

[17] S. W. Tobey, *J. Org. Chem.*, **35**, 1281 (1969).

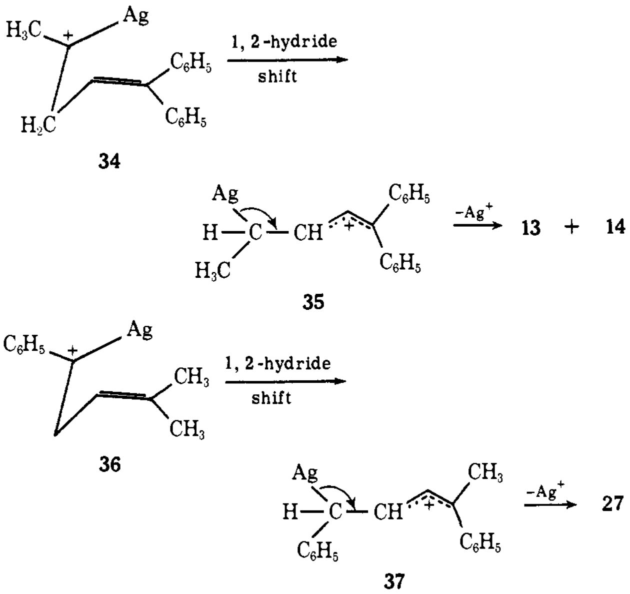
[18] H. Igeta, T. Tsuckiya, and T. Nakai, *Tetrahedron Lett.*, 2667 (1969).

[19] B. M. Mikhailov, G. S. Ter-Sarkisian, and F. B. Tutorskaya (*Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 831 (1959); *Chem. Abstr.*, **54**, 1416c (1960)) report the preparation of an isomer, mp 98–99° (from ethanol). Subsequently, the uv spectrum of this compound was disclosed: $\lambda_{\max}^{\text{heptane}}$ 320 (ϵ 43,000) and 235 nm (13,340) [A. N. Nikitin, M. D. Galanin, G. S. Ter-Sarkisian, and B. M. Mikhailov, *Opt. Spectrosc. (USSR)*, 6, 226 (1959)].

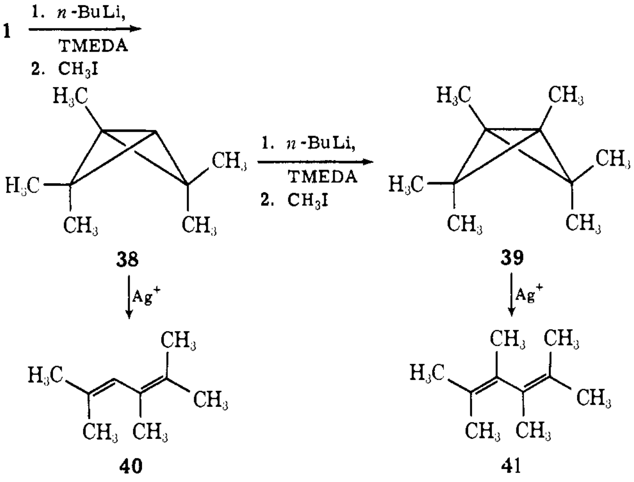
ethylenediamine was rather unsuccessful, the desired anion was obtained in good yield *via* the phenoxy ether route previously employed for allyl-[20] and cyclohexenyllithium.[1] Alcohol **32** was obtained as a mixture of two diastereomers as revealed by the nmr spectrum in which the methyl absorption appears as a pair of doublets. Treatment of **32** with **23** as before resulted in rapid dehydration and the formation of an equimolar mixture of **27** and its trans,trans counterpart **33**. These isomeric dienes were readily separated by preparative scale gas chromatography and identified by their individual nmr and uv spectra. The oily first component which has been assigned trans,cis stereochemistry (**27**) showed $\lambda_{max}^{C_2H_5OH}$ 303 nm (ϵ 30,000) and was identical in all respects with the Ag^+-catalyzed rearrangement product of **26**. The crystalline product of longer retention time, formulated as the trans,trans isomer **33**, exhibited longer wavelength absorption [$\lambda_{max}^{C_2H_5OH}$ 322 nm (ϵ 41,000)] as a result of the absence of steric inhibition to resonance and the rough agreement of its olefinic proton chemical shifts to theory (Table I). Additionally, the melting point of **33** corresponded to that assigned previously to this isomer.[19,20]



It is interesting at this point to contrast the high stereoselectivity encountered in the formation of **27** with the much lower level of stereocontrol observed in the Ag^+-catalyzed rearrangements of **11** and **16**. In view of the product structures, there seems to be little doubt that the presence of phenyl substituents does not promote a mechanistic changeover. In actuality, argento carbonium ions **12**, **34**, and **36** very likely intervene in these respective rearrangements. As a result, the alignment of substituents at C_1 in **27** is a direct consequence of the stereochemistry of its bicyclobutane precursor **26**. The requisite assumption is that rotation about the incipient double bond on the pathway to **37** and about the alkyl cation center in **37** does not occur. Such assumptions appear quite valid. In contrast, the stereochemistry at C_4 arises at the time of departure of Ag^+ from allylic cations such as **35** and **37**. As discussed previously (see **10**, for example), there are two possible rotamers of these intermediates which are properly disposed in an electronic sense for the generation of the second double bond. The stereochemical results derived from this step should reflect a combination of steric, kinetic, and thermodynamic factors. Not unexpectedly, a phenyl substituent at the carbon bonded to the transition metal is capable of greater control (to give ultimately trans product) than is a methyl group.



The effect of exhaustive alkyl substitution upon the course of such bicyclobutane rearrangements was evaluated next. To this end, the 1,2,2,4,4-pentamethyl (**38**) and hexamethyl derivatives (**39**) were prepared.



These strained hydrocarbons have previously been described,[21,22] but we have found it exceedingly convenient to prepare them by stepwise methylation of **1**. Previously, it was demonstrated that 2,2,4,4-tetramethyl substitution of the bicyclobutane ring leads to very rapid rearrangement in the presence of Ag^+ (see the case of **1**, Table II) with the formation of dienes in which the methyl groups are positioned exclusively at the terminal carbons of the conjugated system. However, the placement of substituents at C_1 and C_3 of a bicyclobutane ring is also known to promote the incursion of competitive argento carbonium ion pathways. To this time, the rates of reactions proceeding by this latter pathway have always been much slower than, for example, the rate of isomerization of **1**.[1,4a] It was of interest, therefore, to study the behavior of **38** and **39**.

When exposed to catalytic quantities of silver perchlorate in anhydrous benzene, **38** reacted violently and

---

(20) J. J. Eisch and A. M. Jacobs, *J. Org. Chem.*, **28**, 2145 (1963).

(21) D. P. G. Hamon, *Tetrahedron Lett.*, 3143 (1969).

(22) D. P. G. Hamon, *J. Amer. Chem. Soc.*, **90**, 4513 (1968).

Table II. Isomerization Rate Data (C_6H_6 Solution)[a]

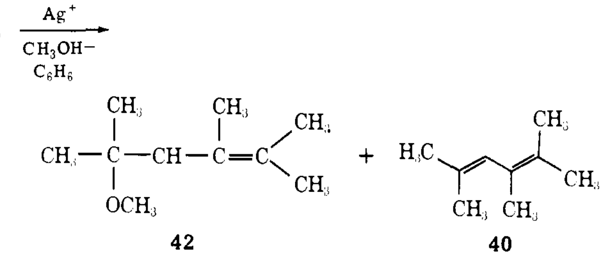
Hydrocarbon	$AgClO_4$, N	T, °C	k_{Ag}, M^{-1} sec^{-1}	Rel rate
	8.45×10^{-5}	40.0	2.26×10^{-3}[b]	1
45	4.03×10^{-2}	40.1	6.5×10^{-3}	3
48	2.02×10^{-2}	40.1	1.4×10^{-2}	6
1	4.65×10^{-5}	40.1	46.6	21,000
	4.65×10^{-5}	40.1	47.9	

[a] These rate data pertain to the initial rate of disappearance of bicyclobutane. [b] Taken from ref 4a.

very exothermically to give exclusively **40**. In contrast, treatment of hexamethyl derivative **39** under identical conditions did not result in a vigorous reaction. Rather, heating at 40° for a minimum of 30 min was required to achieve complete conversion to diene **41**. Product assignments were confirmed by comparison with literature data for authentic samples.

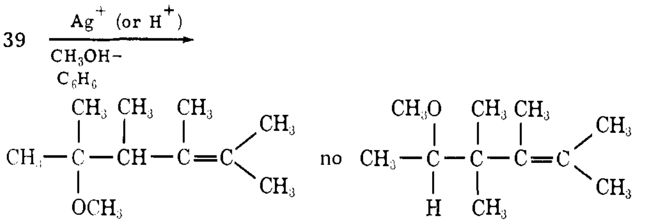
Kinetically speaking, the dissimilarity of (qualitative) isomerization rates for **38** and **39** suggests that these molecules rearrange in quite different fashion. Again, symmetry precludes additional refinement of this question. Further studies with silver perchlorate in methanol–benzene did reveal, however, that quite different mechanistic factors may be at play in protic media. As can be seen, both **38** and **39** gave rise to homoallylic methyl ethers (**42** and **43**, respectively). The pentamethyl derivative rearranged so rapidly, however, that 40% of diene **40** was also formed; no diene was seen in the case of **39**. The structural assignments to **42** and **43** follow convincingly from their nmr spectra (see Experimental Section); **43** was also prepared unequivocally by acid-catalyzed methanolysis of **39**. The point of particular significance is that no evidence for the formation of ether **44** could be found. We intend to comment further elsewhere on the nature of Ag^+ catalysis in protic solvent systems.

38



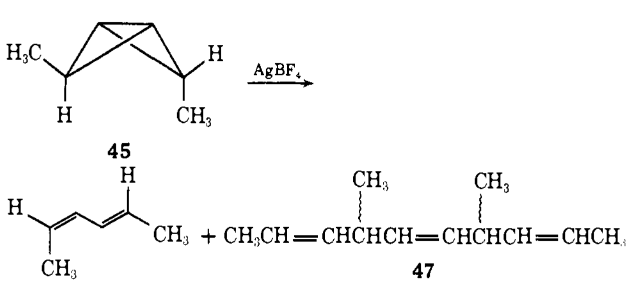
42 **40**

39

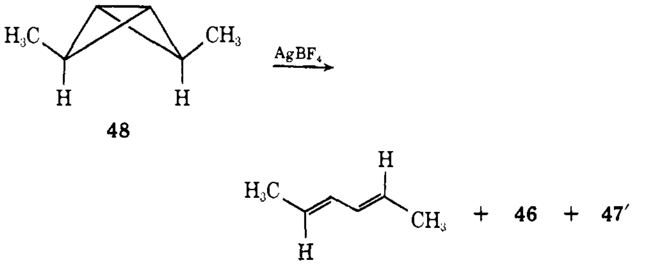


43 **44**

The Ag^+-catalyzed reactions of the isomeric 2,4-dimethylbicyclobutanes **45** and **48** give rise to 2,4-hexadienes whose stereochemistries are virtually the reverse of those encountered on thermolysis.[23] Whereas **45** exhibited very high levels of stereospecificity (≥95% of **46**), **48** led to both **46** and **49** albeit with a 3:1 preference for the trans,trans isomer.[4c, 24] Kinetic measurements relating to the initial rates of disappearance of **45** and **48** are listed in Table II together with comparable data for **1** and tricyclo[4.1.0.0^{2,7}]heptane. These data reveal an interesting gradual rate increase in proceeding from the endo,endo to the endo,exo and finally to the exo,exo 2,4-disubstituted derivatives. The substantial rate enhancement exhibited by **1** once again attests to a mechanistic changeover; a most direct interpretation centers about the operation of a concerted or near-concerted bond reorganization in this instance.[1]



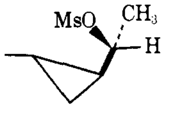
45 **46** **47**



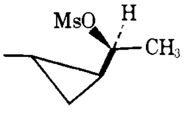
48 **49**

Dimer formation (**47** and **47′**) also was encountered under the conditions employed herein ($AgBF_4$, $CDCl_3$, 40°). The structural assignment to these dimers (of differing geometric and configurational stereochemistry) follows convincingly from their high-resolution mass spectra, their nmr features (see Experimental Section), and independent catalytic hydrogenation to 4,7-dimethyldecane. These dimers do not appear to arise from any of the combinations diene + diene, diene + cyclobutene, cyclobutene + cyclobutene, and cyclobutene + bicyclobutane; in actuality, **46** and **49** as well as *cis*- and *trans*-3,4-dimethylcyclobutenes[25] are stable to the reaction conditions. It has not proven possible to confirm which of the several remaining possibilities obtains; however, the capability of "cross-breeding" a 2,4-hexadiene of improper stereochemistry with a bicyclobutane in the presence of Ag^+ has been demonstrated.

The diene product distributions are remarkably similar to those which arise from base-catalyzed elimination of methanesulfonic acid from cyclopropylcarbinyl mesylates **50** and **51**.[24] Because **50** and **51** are inter-



50



51

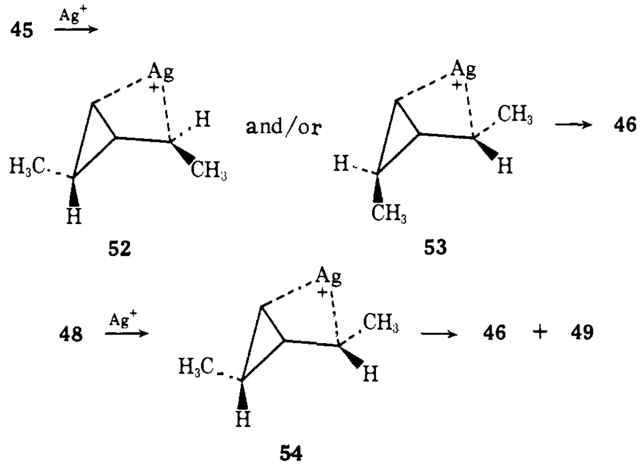
---

[23] G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968).

[24] M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971).

[25] R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965). We thank Professor Winter for a sample of the cis isomer and for directions describing an improved synthesis of the trans congener.

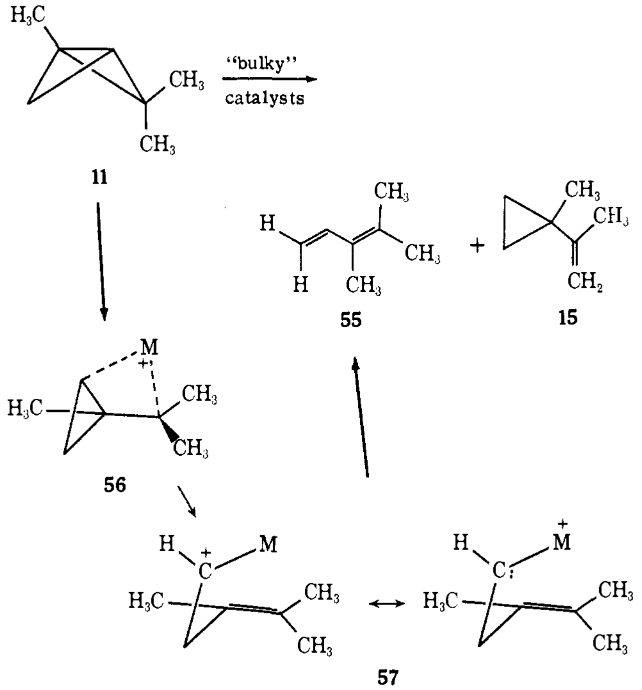
related with **45** and **48** through somewhat similar carbonium ion structures, it is reasonable to assume that the subsequent bond reorganizations are controlled chiefly by the cationic nature of such intermediates rather than the presence of the silver ion in the catalyzed processes. In the case of **45**, it is not yet known which edge bond exhibits kinetically more rapid cleavage (see **52** and **53**). This detail in presently being examined.

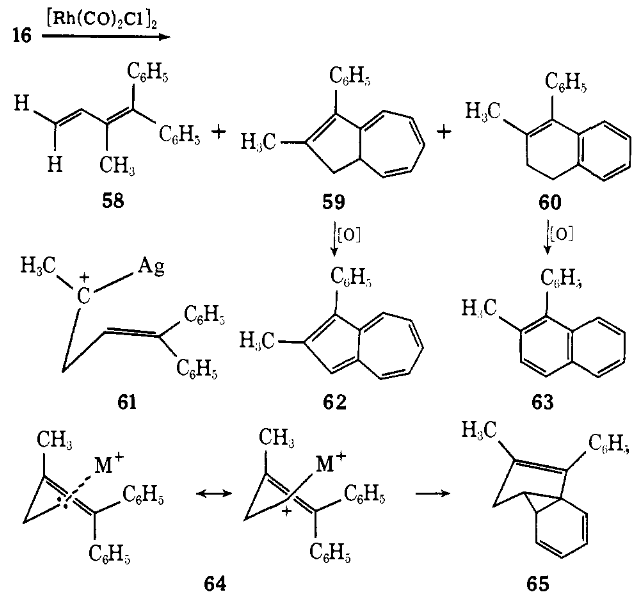


Discussion

With Pd(II) and Rh(I) catalysts, **45** and **48** afford, in addition, substantial quantities of 1,3-dimethylbutadiene,[26] presumably due to competitive carbenoid–metal complex formation as discussed in the preceding paper.[1] In this connection, 1,2,2-trimethylbicyclobutane (**11**) undergoes rearrangement to **56** (major) and **15** when treated with catalytic quantities of rhodium and iridium carbonyl chloride dimers[27] and $Pd(C_6H_5CN)_2Cl_2$.[28] This dramatic difference in product diene formation suggests that initial approach of such exceedingly bulky catalysts to the C_1–C_2 bond is not kinetically competitive with attack at the C_2–C_3 linkage. As a result of this steric factor and the marked propensity of these metals for complexed carbene–carbonium ion formation, **56** is formed and experiences ring opening to **57**.

Significantly, the isomerization of **16** by rhodium dicarbonyl chloride dimer serves to provide a major point of distinction between the chemical reactivities of argento carbonium ions and metal-complexed carbenoid intermediates. Thus, the formation of **17** and **18** is explicable on the basis of C_1C_2 and C_1C_3 bond cleavage to afford **61**, with subsequent hydride migration and ultimate loss of Ag^+. On the basis of the primary products (**58**–**60**) obtained with the rhodium catalyst,[29] it would appear that oxidative addition again operates for steric reasons at the less hindered C_2C_3 bond to provide **64** which exhibits sufficient carbenoid character to produce norcaradiene derivative **65**, a probable precursor of **59** and **60**, or to engage in direct insertion into a phenyl C–H bond. No comparable carbenoid reactions have yet been encountered under conditions of Ag^+ catalysis.





Experimental Section

Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer and apparent coupling constants are cited. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Rearrangement of 1. A solution of 42.6 mg of pure **1**[8] in 150 μl of $CDCl_3$ was placed in an nmr tube and cooled to −78°. Solid anhydrous silver fluoroborate (2 mg) was added and the tube was allowed to warm slowly to room temperature with agitation during 3–5 min. At this point, the nmr spectrum was recorded and **1** was seen to have been completely converted to **2**.[30] The reaction mixture was quenched with saturated sodium chloride solution and diluted with ether. Centrifugation permitted ultimate decantation of the ether layer; preparative vpc scale isolation of **2** gave 31.5 mg of material whose ir spectrum corresponded exactly with that in the Sadtler collection (no. 5315).

Preparation of 1-Diazo-2,2,4-trimethylpent-3-ene (5). A. 2,2,4-Trimethyl-3-pentenal Oxime. To a stirred solution of 15.47 g

---

(26) M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Commun.*, 486 (1971).

(27) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, 92, 7631 (1970).

(28) P. G. Gassman, G. R. Meyer, and F. J. Williams, *Chem. Commun.*, 842 (1971).

(29) P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, 93, 5897 (1971).

(30) A spectrum of authentic 2,5-dimethyl-2,4-hexadiene appears in the Varian Spectra Catalog, No. 515.

(0.123 mol) of 2,2,4-trimethyl-3-pentenal[31] and 10.3 g (0.148 mol) of hydroxylamine hydrochloride in a mixture of 50 ml of 95% ethanol and 40 ml of water was added portionwise 12.5 g (0.148 mol) of solid sodium bicarbonate. Upon completion of the addition, the mixture was refluxed for 2.5 hr, cooled, and extracted with ether. The dried ether extracts were evaporated *in vacuo* to give 16.68 g (96%) of the oxime, mp 43–45° (from methanol–water).

Anal. Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68 26; H, 10.53; N, 9.92.

B. 2,2,4-Trimethyl-3-pentenylamine. To a refluxing slurry of 7.80 g (0.205 mol) of lithium aluminum hydride in 350 ml of anhydrous ether was slowly added during 1 hr a solution of 19.35 g (0.137 mol) of oxime in 100 ml of ether. After heating for 40 hr, the reaction was processed in the standard alkaline fashion (8 ml of water, 8 ml of 30% potassium hydroxide solution, and 23 ml of water). The basic compounds were extracted into 1 *M* hydrochloric acid. This solution was extracted with ether and neutralized and the liberated amine was taken up in ether. Distillation of the product afforded 9.26 g (53%) of colorless oil: bp 62–68° (24 mm); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.98–5.12 (m, 1, olefinic), 2.54 (br s, 2, NH_2), 1.72 (br s, 6, $=C(CH_3)_2$), and 1.04 (br, s, 6, remaining CH_3).

The picrate was prepared, mp 163–164° (from ethanol).

Anal. Calcd for $C_{14}H_{20}N_4O_7$: C, 47.19; H, 5.66; N, 15.72. Found: C, 47.04; H, 5.71; N, 15.75.

C. Methyl *N*-(2,2,4-Trimethyl-3-pentenyl)carbamate. An 8.90-g (0.070 mol) sample of this amine was treated with 6.63 g (0.070 mol) of methyl chloroformate and 2.87 g (0.0718 mol) of sodium hydroxide according to the general procedure described in the preceding paper.[1] The carbamate so produced (11.60 g, 89%) was purified by molecular distillation at 40–43° (0.74 mm).

Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.66; H, 10.38; N, 7.56.

D. Methyl *N*-Nitroso-*N*-(2,2,4-trimethyl-3-pentenyl)carbamate. This compound was prepared from 7.42 g (0.040 mol) of carbamate, 2.95 ml (0.048 mol) of dinitrogen tetroxide, and 6.55 g (0.080 mol) of sodium acetate as before.[1] The crude product obtained (8.16 g, 95%) was further purified by molecular distillation at 42–50° (0.07 mm). The nitrosocarbamate is a bright yellow liquid: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.03 (m, 1, olefinic), 4.07 (s, 3, OCH_3), 3.78 (s, 2, CH_2N<), 1.72 (superimposed d, 6, $=C(CH_3)_2$), and 0.96 (s, 6, remaining CH_3).

Anal. Calcd for $C_{10}H_{18}N_2O_3$: C, 56.05; H, 8.47; N, 13.08. Found: C, 56.04; H, 8.76; N, 13.03.

E. Generation of 5. A solution of the nitrosocarbamate (2.00 g, 9.35 mmol) in 5 ml of benzene was added to an ice-cold mixture of 10 ml of 50% potassium hydroxide, 10 ml of benzene, and 10 ml of Carbitol. After stirring for 20 min, more water was added and the layers were separated. The aqueous phase was extracted once with benzene and the combined benzene layers were washed with water and dried over KOH pellets at 0°.

Decomposition of 5. Approximately one-half of the above solution was added to 5 ml of cold 0.202 *M* silver perchlorate in benzene, whereupon 84 ml of nitrogen was evolved. This solution was immediately washed with water and saturated sodium chloride solution, filtered, and vacuum transferred. Vpc analysis and separation on a $^1/_4$ in. × 12 ft 15% squalene on Chromosorb W column at 65° showed that 2,5-dimethyl-2,4-hexadiene (**2**) was the major product (81%). Also produced was 3,5-dimethyl-2,4-hexadiene (6%) and 13% of a mixture of six unidentified hydrocarbons of isomeric structure.

Rearrangement of 7. To a solution of 144.3 mg of **7**[32] in 0.5 ml of $CDCl_3$ was added 10.3 mg of anhydrous silver fluoroborate. After standing at room temperature for 4 hr, the reaction mixture was quenched with aqueous sodium chloride solution, diluted with pentane, and centrifuged. The resulting isomeric product was separated by preparative vpc and shown to be identical with authentic 2-methyl-1,3-pentadiene:[33] $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.3–6.4 (complex m, 2, H_3 and H_4), 4.72 (br s, 2, H_1), and 1.77 (m, 6, methyls).

Rearrangement of 11. A solution of 55.9 mg of pure **11**[34] in 120 ml of $CDCl_3$ was cooled in a Dry Ice–acetone bath. Anhydrous silver fluoroborate (~3 mg) was added and the solution was allowed to warm slowly to room temperature with agitation. This mixture was allowed to stand at room temperature until nmr analysis no longer showed unreacted **11** (~2 hr), and was then diluted with ether and quenched with saturated sodium chloride solution. The components of the resulting mixture were analyzed on a $^1/_4$ in. × 24 ft column packed with 5% SF-96 on Chromosorb G at 50°, giving the percentage composition discussed in the text. Products were isolated by the same technique from a preparative scale run (387.1 mg of **11**), except that a squalene column was utilized to separate **15** from the diene mixture and a silver nitrate–benzonitrile column was employed subsequently to separate **13** efficiently from **14**: for **13**, $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.2–6.5 (m, $J_{3,4}$ = 10.8 Hz, $J_{1,5}$ = 15.6 Hz, and $J_{3,5} \cong 0$ Hz, 3, olefinic) and 1.72 (br s, 9, methyls); $\nu_{\max}^{\mathrm{neat}}$ 980 and 950 cm^{-1} (strong); for **14**, $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.1–6.3 (m, $J_{3,4}$ = 11 Hz, $J_{4,5}$ = 8.5 Hz, and $J_{3,5}$ = 1.8 Hz, 3, olefinic) and 1.72 (three-line m, 9, methyls); $\nu_{\max}^{\mathrm{neat}}$ 717 cm^{-1} (strong); for **15**, $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.74 (m, 2, $=CH_2$), 1.68 (m, 3, $=CCH_3$), 1.18 (s, 3, other CH_3), 0.65 (m, 2, cyclopropyl), and 0.46 (m, 2, cyclopropyl).[9]

Hydrogenation of 13 and 14. A mixture of dienes **13** and **14** (96 μl) was hydrogenated over 15 mg of 10% Pd/C in 3 ml of ether at atmospheric pressure and 30°. The catalyst was removed by filtration and the lone product was isolated by preparative vpc ($^1/_4$ in. × 10 ft column packed with 15% squalene on Chromosorb W at 75°) and shown to be identical with authentic 2-methylhexane.[33]

***trans*-2-Methyl-2,4-hexadiene (13).** To the phosphorane prepared from 5.75 g (0.0153 mol) of isopropyltriphenylphosphonium bromide and 10 ml of 1.6 *N* *n*-butyllithium in pentane under nitrogen in 55 ml of anhydrous ether was added a solution of 1.07 g (0.0153 mol) of freshly distilled crotonaldehyde in 5 ml of ether. The deep red color was discharged almost immediately. After being heated at reflux for 14 hr, the mixture was cooled in ice and water was added. The layers were separated and the aqueous phase was extracted with ether. The combined organic layers were washed with water, dried, and distilled through a Vigreux column to remove solvent. The residue was treated with pentane to precipitate organophosphorus compounds, filtered, and again carefully fractionated. Pure **13** was isolated by preparative vpc ($^1/_4$ in. × 20 ft column packed with 5% QF-1 on Chromosorb G) and was shown to be identical in all respects with the material isolated above.

Rearrangement of 16. To a solution of 432 mg (1.96 mmol) of **16**[11] in 2.2 ml of $CDCl_3$ was added 25 mg of anhydrous silver fluoroborate. After 30–40 min at nmr probe temperatures, analysis revealed the complete disappearance of **16** and the mixture was diluted with ether and quenched with saturated sodium chloride solution. Evaporation of the solvent gave 408 mg (95%) of viscous oil. This material was chromatographed on two 20 × 20 × 0.2 in. silica gel plates and the band of highest R_f (294 mg) was found by vpc to be composed of **17** (71%), **18** (27%), and three very minor products (2%). Control experiments showed **17** and **18** to be stable to silica gel. This mixture was examined additionally by nmr methods and the stereochemistry of the dimer was assigned on the basis of ensuing work.

***trans*-5,5-Diphenyl-2-penten-4-ol (21).** Into a three-necked 100-ml flask fitted with a stirring bar, dropping funnel, screw stopper, thermometer, and nitrogen inlet was placed 50 ml of dry tetrahydrofuran. After cooling to −20°, 20.7 ml (0.03 mol) of *n*-butyllithium was introduced, followed by the dropwise addition of 5.04 g (0.03 mol) of diphenylmethane. When allowed to warm to room temperature, the solution slowly developed a deep orange-red coloration. TMEDA (1 ml) was added and after an additional 1.5 hr this solution was added *via* syringe to a solution of 2.1 g (0.03 mol) of crotonaldehyde in 10 ml of dry tetrahydrofuran cooled in a Dry Ice–acetone bath. Upon completion of the addition, the reaction mixture was allowed to warm to 0° and quenched with water. Extraction with ether and removal of solvent left 6.70 g of crude oil which was chromatographed on silica gel. Elution with 5% benzene in ether gave 1.45 g (20%) of aldehyde **22**, the 2,4-dinitrophenylhydrazone of which melted at 155–158° (from ethanol).

Anal. Calcd for $C_{23}H_{22}N_4O_4$: C, 66.01; H, 5.30; N, 13.39. Found: C, 65.93; H, 5.34; N, 13.30.

Elution with ether gave 4.86 g (68%) of alcohol **21**. An analytical sample of **21** was obtained by preparative tlc purification and molecular distillation: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.8–7.4 (m, 10, aromatic), 5.3–5.9 (m, 2, olefinic), 4.71 (m, 1, >CHOH), 3.90 (d, J = 8 Hz, 1, Ar_2CH), 2.03 (br, 1, OH), and 1.48 (d, J = 5 Hz, 3, CH_3).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.53; H, 7.68.

Dehydration of 21. A solution of 1.00 g (4.19 mmol) of **21** and 1.03 g (4.62 mmol) of ethyl(carboxysulfamoyl)triethylammonium

---

(31) R. H. Hasek, R. D. Clark, and J. H. Chaudet, *J. Org. Chem.*, 26, 3130 (1961).

(32) (a) W. von E. Doering and J. F. Coburn, *Tetrahedron Lett.*, 991 (1965); (b) K. Griesbaum and P. E. Butler, *Angew. Chem., Int. Ed. Engl.*, 6, 444 (1967).

(33) Obtained from Chemical Samples Co., Columbus, Ohio.

(34) (a) R. Skattebøl, *Tetrahedron Lett.*, 2361 (1970); (b) W. R. Moore, K. G. Taylor, P. Muller, S. S. Hall, and Z. L. F. Geibel, *ibid.*, 2365 (1970).

hydroxide inner salt[18] in 50 ml of dry tetrahydrofuran was stirred at 30–40° for 45 min. After concentration and extraction with ether, the solvent was removed to give 1.01 g of oil which was chromatographed on silica gel. Elution with hexane gave a total of 36 mg (35%) of hydrocarbons. Diene **24** was eluted first upon subsequent vpc purification on the 5% QF-1 column at 180°: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.0–7.5 (m, 10, aromatic), 5.9–6.8 (m, 3, nonterminal olefinic), 4.6–5.2 (m, 3, $=CH_2$ and Ar_2CH). The ratio of **17** to **18** which subsequently eluted was 5.3:1.

Hydrogenation of 24. Purified **24** (10.1 mg) was hydrogenated over 15 mg of 10% Pd/C in 5 ml of ether. Removal of the catalyst, evaporation of the solvent, and preparative vpc isolation afforded 7.3 mg of 1,1-diphenylpentane which proved identical in all respects with an authentic sample.[35]

Rearrangement of 26. To 14.7 mg of silver fluoroborate (dried overnight at 0.1 mm) in an nmr tube was added under nitrogen 176.6 mg of **26** dissolved in 1 ml of degassed $CDCl_3$. When **26** had been completely converted to **27** (15 min, nmr analysis), the customary work-up was followed and the crude product was purified by preparative tlc. There was obtained 145 mg (82%) of pure *trans,cis*-1,4-diphenyl-1,3-pentadiene (**27**); see below for spectral data.

α-Methylbenzyl Phenyl Ether (30). α-Phenethyl bromide (22.2 g, 0.12 mol), phenol (10.5 g, 0.125 mol), and sodium carbonate (18.0 g, 0.13 mol) were refluxed in 250 ml of acetone for 42 hr. At the end of this time, the analysis showed the reaction to be incomplete; accordingly, the solids were filtered and 27.0 g of sodium carbonate was added. After 24 hr of heating, the mixture was cooled, concentrated *in vacuo*, and extracted with ether and water. The combined organic layers were washed with 30% KOH solution to remove phenol, dried, and distilled to give 18.92 g (79.5%) of **30**, bp 77° (0.05 mm) [lit.[36] bp 143–145° (10 mm)].

***trans*-1,4-Diphenyl-1-penten-3-ol (32).** Into a three-necked 100-ml flask fitted with a stirrer, nitrogen inlet tube, thermometer, and dropping funnel was introduced 560 mg (0.08 g-atom) of lithium wire and 25 ml of anhydrous tetrahydrofuran. A few crystals of biphenyl and a small portion of the solution comprised of 3.96 g (0.02 mol) of **30** dissolved in 25 ml of the same solvent were added. After stirring for 3 hr, an intense red color had developed; the solution was cooled to −45° whereupon the remainder of the phenoxy ether was added. This solution was stirred at −50° to −78° for 5 hr and added *via* syringe to 2.64 g (0.02 mol) of *trans*-cinnamaldehyde in 10 ml of dry tetrahydrofuran cooled to −78°. The reaction mixture was allowed to warm slowly to 0°, quenched by the addition of water, and extracted with ether. Evaporation of the ether gave 5.17 g of yellow oil of approximately 50% purity (tlc analysis). Chromatography on silica gel and elution with 2–5% ether in petroleum ether furnished 2.11 g (44%) of pure **32**. An analytical sample was obtained by molecular distillation at high vacuum: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.9–7.5 (m, 10, aromatic), 5.80–6.7 (nine-line m, 2, olefinic), 4.1–4.4 (m, 1, $>CHOH$), 2.6–3.1 (m, 1, benzylic), 2.1 (br s, 1, OH), and 1.1–1.4 (d, J = 7 Hz, 3, CH_3).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.53; H, 7.71.

Dehydration of 32. Alcohol **32** (1.48 g, 6.2 mmol) and ethyl(carboxysulfamoyl)triethylammonium hydroxide inner salt (1.51 g, 6.8 mmol) were dissolved in 75 ml of dry tetrahydrofuran and stirred at 30–40° for 3 hr. Work-up as before and chromatography of the crude product on silica gel afforded 590 mg (43%) of an approximately 50:50 mixture of **27** and **33**. These dienes were readily purified and separated by preparative vpc on a ¼ in. × 6 ft column packed with 5% QF-1 on Chromosorb G at 180°: for **27**, $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.0–7.4 (m, 10, aromatic), 6.1–7.0 (m, 3, olefinic), 2.13 (d, J = 1 Hz, 3, CH_3); $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ 228 (ε 15,000), 236 (14,000), and 303 mm (30,000); see also Table I; for **33**, mp 95.5–97.0° (lit mp 94–95°[16] and 98–99°[17]); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.1–7.6 (m, 10, aromatic), 6.4–7.4 (m, 3, olefinic), and 2.23 (d, J = 1 Hz, CH_3); $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ 233 (ε 11,000) and 322 mm (41,000); see also Table I.

1,2,2,4,4-Pentamethylbicyclo[1.1.0]butane (38). Under a nitrogen atmosphere, 8 ml of TMEDA was added to a cooled solution of 45 ml (59 mmol) of 1.3 *M* *n*-butyllithium in pentane. This was followed by the rapid addition of 6.0 g (55 mmol) of **1**. A light yellow solid precipitated during the course of the reaction which was permitted to extend overnight at room temperature. The mixture was cooled in an ice bath and 9.1 g (64 mmol) of methyl iodide was added dropwise over a 10-min period. After being washed with 10 ml of water, the organic layer was treated with 10 ml of aqueous cupric sulfate solution and dried. Most of the solvent was distilled through a short Vigreux column. The remaining material was vacuum transferred at 30 mm and 90° and the volatile substances were condensed at −78°. Preparative vpc (¼ in. × 4 ft 5% OV-11 column at 70°) isolation of **38** gave 1.74 g (25%) of colorless liquid having spectral properties consistent with those reported earlier.[19]

Rearrangement of 38. A benzene solution of silver perchlorate (1.5 ml of 0.188 *M*) was cooled in an ice bath. An extremely exothermic reaction ensued as **38** (219 mg, 1.77 mmol) was added cautiously over 30 sec. Approximately 1 min after this addition, 1 ml of saturated sodium chloride solution was added and the benzene layer was removed by means of a pipet. The aqueous phase was extracted with a small amount of pentane and the combined organic layers were dried. Preparative vpc isolation on the OV-11 column at 100° of the major product (trace quantities of unknown substances were also seen) furnished 136 mg (62%) of **40** whose nmr spectrum was in agreement with that described for this diene.[37]

Hexamethylbicyclo[1.1.0]butane (39). A 536-mg (4.32 mmol) sample of **38** was metallated with 4.0 ml of 1.3 *M* *n*-butyllithium (3.2 mmol) and 1.0 ml of TMEDA as before. Addition of 1.1 g (7.7 mmol) of methyl iodide, followed by the usual work-up, gave 120 mg (20%) of **39** (preparative vpc on the OV-11 column at 70°). The nmr spectrum of this hydrocarbon compared well with that reported earlier.[20]

Rearrangement of 39. Equilibration of 1.0 ml of 0.188 *M* silver perchlorate in benzene at 40° was followed by the rapid addition of 98 mg (0.71 mmol) of **39**. No vigorous reaction was seen. An initial slight cloudiness developed and with time a silver mirror appeared on the walls of the vial. Conditions were maintained for 30 min and the reaction was quenched by addition of 1 ml of saturated sodium chloride solution. Work-up as before and preparative vpc isolation furnished 61 mg (62%) of tetramethyl-2,4-hexadiene (**41**).[38]

Reaction of 38 with Silver Perchlorate in Methanol–Benzene. A solution consisting of 1.0 ml of 0.188 *M* silver perchlorate in benzene and 1.0 ml of methanol was thermally equilibrated in an ice bath for 15 min. Rapid addition of 150 mg (1.36 mmol) of **38** resulted in the formation of an immediate dark color. After 1 min in the ice bath, the reaction was quenched with 1 ml of saturated brine. The aqueous layer was extracted with 1 ml of pentane and the combined organic layers were dried. Vpc analysis (5% OV-17 column at 115°) revealed the presence of two major components and traces of two very minor unidentified components. The first component to elute was identified as **40** (60 mg, 40%). The second component (72 mg) was characterized as ether **42**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.25 (s, 3, OCH_3), 2.30 (s, 2, CH_2), 1.71 (s, 9, $=CCH_3$), and 1.17 (s, 6, CH_3).

Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.72; H, 12.94.

Reaction of 39 with Silver Perchlorate in Methanol–Benzene. A solution comprised of 1.0 ml of 0.188 *M* silver perchlorate in benzene and 1.0 ml of methanol was equilibrated at 40.0° for 20 min. Cloudiness developed with injection of 103 mg (0.75 mmol) of **39**. After going undisturbed for 20 min, the reaction was quenched and processed as above to give 70 mg of **43**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.21 (s, 3, OCH_3), 2.88 (q, J = 7 Hz, 1, methine), 1.65 (m, 9, $=CCH_3$), and 0.90–1.17 (m, 9, CH_3).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.43; H, 12.86.

Ring Opening of 39 with Perchloric Acid in Methanol–Benzene. A methanolic perchloric acid solution was prepared by adding 1 drop of 70% perchloric acid to 3 ml of methanol. A vigorous exothermic reaction ensued as 98 mg (0.71 mmol) of **39** was added to a mixture of 1 ml of the above solution and 1 ml of benzene. After 5 min, 1.0 ml of dilute aqueous sodium hydroxide was introduced. The aqueous layer was extracted with pentane and the combined organic layers were processed as described earlier to give 66 mg of **43**, identical in all respects with the material isolated above.

Rearrangement of 48. Addition of *ca.* 3 mg of anhydrous silver fluoroborate to a sample of **48**[23] dissolved in $CDCl_3$ caused rapid disappearance of the bicyclobutane (nmr analysis) and the development of absorption corresponding to **46** and **49**. The reaction was complete after 1 hr at the nmr probe temperature, at which time additional peaks due to dimer formation were in evidence. Satu-

---

(35) A. Maercker, *Justus Liebigs Ann. Chem.*, 732, 151 (1970).

(36) H. Hart and H. S. Eleuterio, *J. Amer. Chem. Soc.*, 76, 516, 519 (1959).

(37) P. M. Collins and H. Hart, *J. Chem. Soc. C*, 1197 (1967).

(38) W. F. Forbes, R. Shilton, and A. Balasubramanian, *J. Org. Chem.*, **29**, 3527 (1964).

rated aqueous sodium chloride solution was added and the organic phase was filtered through a short column of alumina and analyzed by vpc. The ratio of dimers to **49** and **46** (ratio 3:1) was 86:14. The dienes were separated ($^1/_4$ in. × 12 ft 5% squalene on Chromosorb G at 40°) and assigned stereochemistry on the basis of spectral comparisons with authentic samples. The two major dimers (ratio 1.5:1) were isolated by preparative scale vpc on a 5% SF-96 column operated at 120°: dimer I, *m/e* calcd, 164.1565; found, 164.1563; dimer II, *m/e* calcd, 164.1565; found, 164.1563. The first isomer exhibited the following nmr spectrum: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.1–5.5 (m, 6, olefinic), 2.9–3.4 (m, 2, bisallylic), 1.66 (m, 6, sp^2 CCH_3), and 1.03 (d, J = 7 Hz, 6, sp^2 CCH_3). The second dimer had a very similar spectrum: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.3–5.5 (m, 6), 2.5–3.0 (m, 2), 1.68 (m, 6), and 1.06 (d, J = 7 Hz, 6).

Rearrangement of 45. Exposure of **45**[23] to catalytic quantities of anhydrous silver fluoroborate as above gave a product mixture composed of *cis,trans*-2,4-hexadiene (**46**, 62%) and two dimers (ratio 1:1) in 38% yield. The nmr spectrum ($CDCl_3$) of this dimer mixture showed δ 5.25–5.55 (m, 6), 2.6–3.0 (m, 2), 1.67 (m, 6), and 1.03 (d, J = 7 Hz, 6).

Hydrogenation of the Dimers. A mixture of dimers (7.9 mg) was hydrogenated in 2 ml of ethyl acetate over 15 mg of 10% palladium on carbon at room temperature and atmospheric pressure. The processed solution was freed of solvent by preparative vpc ($^1/_4$ in. × 20 ft 5% QF-1 on Chromosorb G at 130°). There was obtained 7.3 mg of 4,7-dimethyldecane which was identical in all respects with the authentic sample prepared below.

4,7-Dimethyldecane. A solution of 3.00 g (0.015 mol) of 4,7-dimethyl-5-decyne-4,7-diol (K&K Laboratories) in 40 ml of absolute ethanol containing 150 mg of 10% palladium on carbon was hydrogenated in a Parr apparatus at 50 psig. After 20.5 hr, the catalyst was separated by filtration and the solvent was removed by distillation through a short Vigreux column. The hydrocarbon product was separated from residual hydroxylic material by vpc isolation as above: *m/e* calcd, 170.2034; found, 170.2032.

Acknowledgment. Partial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Photochemical Reorganizations in the 1,3-Diazabicyclo[3.1.0]hex-3-ene System[1]

Albert Padwa*[2] and Edward Glazer

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214.

Received March 21, 1972

Abstract: The irradiation of a triaryl-substituted 1,3-diazabicyclo[3.1.0]hex-3-ene in benzene results in ring opening to an enediimine intermediate which undergoes subsequent thermal disrotatory closure to a *cis*-dihydropyrazine. The same enediimine intermediate was formed on irradiation of a *cis*- or *trans*-dihydropyrazine. An intriguing variation of the normal reaction pathway occurs when the irradiation is carried out in an alcoholic medium. Photolysis of *endo*- or *exo*-2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**5** and **6**, respectively) in methanol gave 2,4-diphenyl-1-methoxybenzylimidazoline (**25**). The photoreaction can be formulated as proceeding *via* an azomethine ylide by cleavage of the aziridine C–C bond. The azomethine ylide will lead to imidazoline **25** by addition of methanol. Irradiation of **5** or **6** in an ethanol glass produced a bright red color which was rapidly discharged by the addition of dimethyl acetylenedicarboxylate. The formation of a cycloadduct supports the postulate that the photochemistry of the diazabicyclo ring proceeds *via* the formation of an azomethine ylide which subsequently opens to an enediimine.

Light-induced transformations of cyclic dienes have been the subject of recent intensive study.[3,4] Derivatives of 1,3-cyclohexadiene, for example, have been transformed into a vast array of photoproducts *via* ring-opening processes,[5] valence-bond tautomerism reactions,[6] bond switching mechanisms,[7] and dimerization pathways.[8] Despite the fact that photochemical isomerizations of cyclic dienes have been well documented, investigation of suitable heterocyclic analogs in light-induced reactions has been somewhat limited,[9,10] even though the generality of the photochemical ring-opening reactions for systems isoelectronic with 1,3-cyclohexadienes was predicted by Barton 13 years ago.[11] One exception is the work of Beak and Miesel who reported the ready photoisomerization of 2,3-dialkyl-2,3-dihydropyrazines (**1**) to sub-

---

(1) Photochemical Transformations of Small Ring Heterocyclic Compounds. XLII. For part XLI, see A. Padwa, L. Brodsky, and S. Clough, *J. Amer. Chem. Soc.*, **94**, 6767 (1972).

(2) Alfred P. Sloan Foundation Fellow, 1968–1972, and National Institutes of Health Special Postdoctoral Fellow, 1972.

(3) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(4) G. J. Fonken in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 222.

(5) (a) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960); (b) P. de Mayo and S. T. Reid, *Quart. Rev., Chem. Soc.*, **15**, 393 (1961); (c) E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961); (d) E. Havinga, *Chimia*, **16**, 146 (1962); (e) R. L. Autrey, D. H. R. Barton, A. K. Ganguly, and W. H, Reusch, *J. Chem. Soc.*, 3313 (1961); (f) R. Srinivason, *J. Chem. Phys.*, **38**, 1039 (1963); (g) G. J. Fonken and K. Mehrotra, *Chem. Ind. (London)*, 1025 (1964); (h) W. G. Dauben and R. M. Coates, *J. Org. Chem.*, **29**, 2761 (1964); (i) J. Meinwald and P. H. Mazzochi, *J. Amer. Chem. Soc.*, **88**, 2851 (1966).

(6) (a) W. G. Dauben and R. M. Coates, *ibid.*, **86**, 2490 (1964); (b) H. Prinzbach and J. H. Hartenstein, *Angew. Chem.*, **74**, 651 (1962); **75**, 639 (1963); E. E. van Tamelen, S. P. Pappas, and K. L. Kirk, *J. Amer. Chem. Soc.*, **93**, 6092 (1971).

(7) (a) D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958); (b) W. G. Dauben and G. J. Fonken, *J. Amer. Chem. Soc.*, **81**, 4060 (1959); (c) D. H. R. Barton, R. Bernasconi, and J. Klein, *J. Chem. Soc.*, 511 (1960); (d) G. R. Evanega, W. Bergmann, and J. English, Jr., *J. Org. Chem.*, **27**, 13 (1962); (e) H. Hart and A. J. Waring, *Tetrahedron Lett.*, 325 (1965); (f) M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, **93**, 6615 (1971); (g) J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967).

(8) (a) L. A. Paquette and G. Slomp, *ibid.*, **85**, 765 (1963); (b) E. C. Taylor, R. O. Kan, and W. W. Paudler, *ibid.*, **85**, 776 (1963).

(9) D. R. Arnold, V. Y. Abraitys, and D. Mcleod, Jr., *Can. J. Chem.*, **49**, 823 (1971).

(10) P. Beak and W. R. Messer in "Organic Photochemistry," Vol. II, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, p 117.

(11) D. H. R. Barton, *Helv. Chim. Acta*, 42, 2604 (1959).