A solution of 11.8 mg (0.054 mmol) of **22** in ethyl acetate was hydrogenated in the presence of 10% Pd/C and the product was treated with HCl in isopropyl alcohol to give 11.2 mg (81%) of *trans*-2-*N*-ethylamino-2-phenylcyclohexanol (**23**) hydrochloride,[12] mp 207–209°, identical with an authentic sample.

2-(1-Hydroxycyclopentyl)-2-phenyloxazolidine (**24**).—Treatment of 15.0 g (59.3 mmol) of bromo ketone **18** with 100 ml of 2-aminoethanol as in the preparation of **5** gave 11.5 g (83.6%) of **24** after recrystallization from hexane: mp 94–95°; ir (KBr) 3475 cm^{-1} (OH); ir (CHCl$_3$) 1650 cm^{-1} (weak, C=N); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 208 nm (log ϵ 3.80).

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.01. Found: C, 71.81; H, 8.23; N, 6.03.

2-(2-Hydroxyethylamino)-2-phenylcyclohexanone (**25**).—A solution of 3.04 g (13 mmol) of **24** in 60 ml of freshly distilled *o*-dichlorobenzene was heated at 175° under a N_2 atmosphere for 6 hr. After cooling, the mixture was diluted with ether and extracted with 1 *N* HCl. The aqueous layer was separated, basified with NaOH, and reextracted with ether. The product crystallized from ether on concentration to give 1.06 g (35%) of **25**, mp 97–99°, ir (KBr) 1710 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.01. Found: C, 72.27; H, 8.40; N, 6.23.

Treatment of the mother liquor with picric acid yielded 1.18 g (19.3%) more of **25** as the picrate, mp 185–187° dec.

Anal. Calcd for $C_{20}H_{22}N_4O_9$: C, 51.95; H, 4.80; N, 12.12. Found: C, 51.89; H, 5.03; N, 12.29.

A small sample of **25** was converted to the HCl salt, mp 183–185° dec after recrystallization from methanol–ether.

Anal. Calcd for $C_{14}H_{20}ClNO_2$: C, 62.33; H, 7.47; Cl, 13.14; N, 5.19. Found: C, 62.24; H, 7.69; Cl, 12.95; N, 4.93.

trans-**2-(2-Hydroxyethylamino)-2-phenylcyclohexanol** (**26**).—Aziridinyl alcohol **22** (407 mg, 1.9 mmol) was hydrolyzed with 150 ml of 1 *N* $HClO_4$ as for the preparation of **8** to give 232 mg (52.7%) of **26**, mp 130–132° after recrystallization from ether–pentane.

Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.45; H, 9.00; N, 5.95. Found: C, 71.21; H, 8.81; N, 5.79.

Reduction of 504 mg (1.1 mmol) of **25** picrate with $NaBH_4$ also provided 217 mg (84.8%) of **26**, mp 130–132°. A mixture melting point with the two samples was undepressed.

Registry No.—**2**, 35099-50-4; **3**, 35099-51-5; **5**, 35099-52-6; **5** imine form, 35099-53-7; **6**, 35099-54-8; **7**, 35099-55-9; **8**, 35099-56-0; **9**, 35099-57-1; **11**, 35099-58-2; **11** hydrogen *p*-toluenesulfonate, 35099-59-3; **12**, 35099-60-6; **13** HCl, 35099-61-7; **15**, 35099-62-8; **15** HCl, 35099-63-9; **19**, 35099-64-0; **21**, 35099-65-1; **22**, 35099-66-2; **24**, 35099-67-3; **25**, 35099-68-4; **25** picrate, 35099-69-5; **25** HCl, 35099-70-8; **26**, 35099-71-9; 1-(2-chloroethylamino)-1-phenyl-2-methyl-2-propanol HCl, 35099-72-0; 1-(2-chloroethylamino)-1,1-diphenyl-2-methyl-2-propanol HCl, 35099-73-1.

Acknowledgment.—The authors gratefully acknowledge the National Science Foundation for support of this work through Grant GP 8272.

The Catalytic and Photolytic Decomposition of 1-Chloro-4-diazoalkenes

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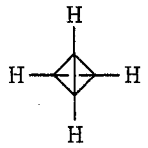
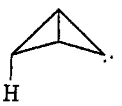
The synthesis of 1-chloro-4-diazo-2,3-dimethyl-1-pentene from 3-methyl-3-penten-2-one and of 1-chloro-4-diazo-2,3-dimethyl-1-butene from methyl acetoacetate is described. The catalytic decomposition of the diazoalkenes was studied; the decomposition of the latter with mercuric iodide gave 1-chloro-2,3-dimethyl-1,3-butadiene, 1-chloro-2-methyl-1,3-pentadiene, and 3-chloro-1,4-dimethylcyclobutene as major products. The mechanism of formation of these products is discussed in terms of the rearrangement of either a metal complexed carbenoid species or a metal complexed bicyclobutane.

The synthesis of tetrahedranes represents a fascinating challenge to the organic chemist.[3] The





availability of such a molecular system would represent a significant development in furthering our understanding of the correlation between chemical bonding and chemical reactivity. Most of the previous unsuccessful approaches evolved around intramolecular insertion of a carbene into a proximate cyclopropene double bond.[2a–c] A more attractive alternative involves intramolecular C–H insertion of a carbene in a suitable bicyclo[1.1.0]butane. Such an intermediate is presumed to be generated in the photodecomposition of carbon suboxide in the presence of cyclopropenes.[3d,e] The subsequent products allow an interpretation of a tetrahedrane intermediate. In an attempt to generate this carbene (or carbenoid) at low temperature in its ground state, we became interested in the synthesis of 2-halobicyclo[1.1.0]butanes.[4] Among the various approaches to such compounds, the catalytic decomposition of diazobutenes appeared particularly suitable.[5,6] We therefore undertook a study of the synthesis and decomposition of 1-chloro-4-diazo-2,3-dimethyl-1-pentene (**1**) and 1-chloro-4-diazo-2,3-dimethyl-1-butene (**2**) as a route to the 2-chlorobicyclo[1.1.0]butanes **3** and **4**. The fascinating rearrangement products obtained relate to the mechanism of decomposition of bicyclobutanes by transition metal catalysis.

Synthesis.—The envisioned precursor of bicyclobutane **3**, 1-chloro-4-diazo-2,3-dimethyl-1-pentene (**1**), was prepared as outlined in Scheme I. Addition of cyanide ion to 3-methyl-3-penten-2-one, saponification of the crude product, and esterification gave the keto ester **5**. Introduction of the chloromethylene group

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[1] National Institutes of Health Predoctoral Fellow.

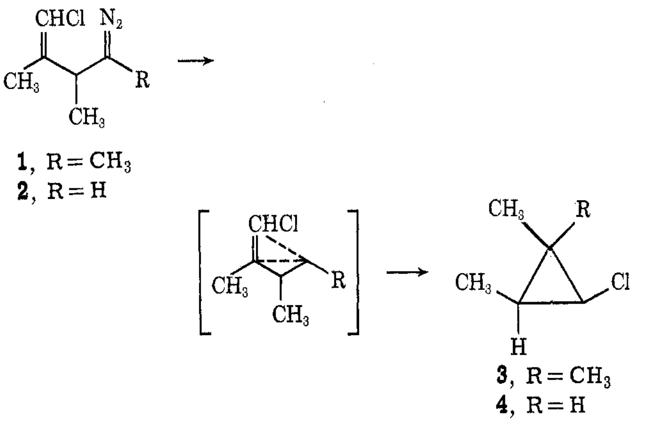
[2] Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.

[3] (a) H. Ona, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, **92**, 7495 (1970); S. Masamune and M. Kato, *ibid.*, **87**, 4190 (1965), and **88**, 610 (1966); (b) E. H. White, G. E. Maier, R. Graeve, V. Zingible, and E. W. Friend, *ibid.*, **88**, 611 (1966); (c) G. L. Closs and V. N. M. Rao, *ibid.*, **88**, 4116 (1966); (d) P. B. Shevlin and A. P. Wolf, *ibid.*, **92**, 406 (1970); (e) R. F. Peterson, R. T. K. Baker, and R. L. Wolfgang, *Tetrahedron Lett.*, 4749 (1969).

[4] B. M. Trost and R. C. Atkins, *Chem. Commun.*, 1254 (1971).

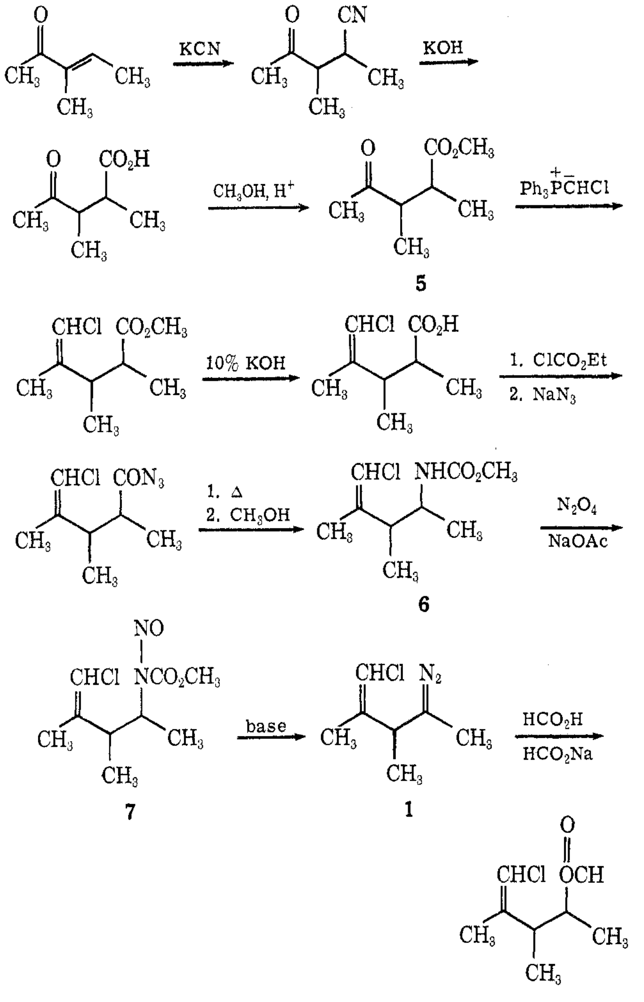
[5] K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 185 (1968).

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



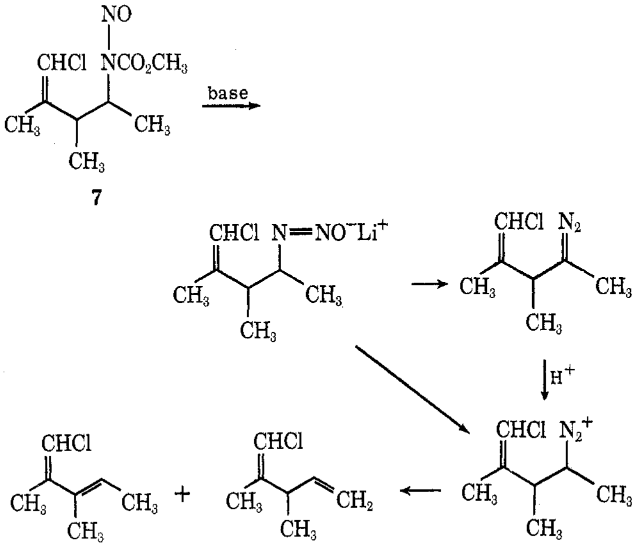
1, R = CH_3
2, R = H
3, R = CH_3
4, R = H

SCHEME I
SYNTHESIS OF 1-CHLORO-4-DIAZO-2,3-DIMETHYL-1-PENTENE (1)



5 **6** **7** **1**

by the Wittig reaction,[7] saponification, and use of the modified[8] Curtius reaction afforded the chloromethylene carbamate **6** in 37% overall yield from **5**. Compound **6** exhibited the expected carbamate ir absorption at 3450, 3400, and 1705 cm^{-1}. The base peak in the mass spectrum was at *m/e* 102 ($CH_3CHNHCO_2CH_3^+$). Nitrosation with dinitrogen tetroxide gave, after rapid chromatography through neutral alumina, an 87% yield of the nitrosocarbamate **7** as an unstable yellow liquid which exhibited no N-H band and a shifted carbonyl band (to 1740 cm^{-1}) in its ir spectrum. Treatment of **7** with base (lithium ethoxide)[9] yielded a pink solution exhibiting strong ir absorption at 2040 cm^{-1}. Characterization of the diazoalkene **1** was achieved through analysis of the formate esters obtained when the solution was quenched with anhydrous formic acid containing sodium formate. The yield of **1** (based on nitrosocarbamate) was found to be only 17%, the major products being the various isomers of 1-chloro-2,3-dimethyl-1,3- and -1,4-pentadienes (**8**, *vide infra*). The predominance of products derived from a carbonium ion intermediate in the reaction of nitrosocarbamate **7** with base is in agreement with other studies[10] related to the generation of a secondary diazoalkene.



7 **8**

It is known[11] that primary diazo systems are more readily generated, and with this consideration in mind the synthesis of 1-chloro-4-diazo-2,3-dimethyl-1-butene (**2**), a precursor to the bicyclobutane **4**, was undertaken (Scheme II). Alkylation of methyl α-methylacetoacetate with methyl bromoacetate yielded the keto diester **9** which, after hydrobromic acid decarboxylation and esterification, gave methyl 3-methyllevulinate (**10**). The *N*-nitrosocarbamate **11**, obtained from **10** in a manner similar to that described in Scheme I, gave on treatment with lithium ethoxide an orange solution of the diazoalkene **2**, ir 2060 cm^{-1}, visible 400–500 nm (ϵ ~17). Quenching of the diazo solution with acetic acid–sodium acetate allowed full characterization of **2** as the acetate. Gas chromatography revealed that elimination products were absent in the formation of **2**.

Decomposition Results.—A detailed analysis of the catalytic decomposition of the secondary diazopentene **1** was precluded by the facile formation of carbonium ion derived products (**8**). Attempts to purify **1** met with failure, and it became necessary to examine the decomposition of **1** in the presence of the previously formed dienes **8**. A variety of catalysts (*vide infra* the study of **2**) were found to yield only the dienes **8**. In view of the difficulties inherent in the secondary

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[7] G. Köbrich, H. Trapp, K. Flory, and W. Drischel, *Chem. Ber.*, **99**, 689 (1966).

[8] J. Weinstock, *J. Org. Chem.*, **26**, 3511 (1961).

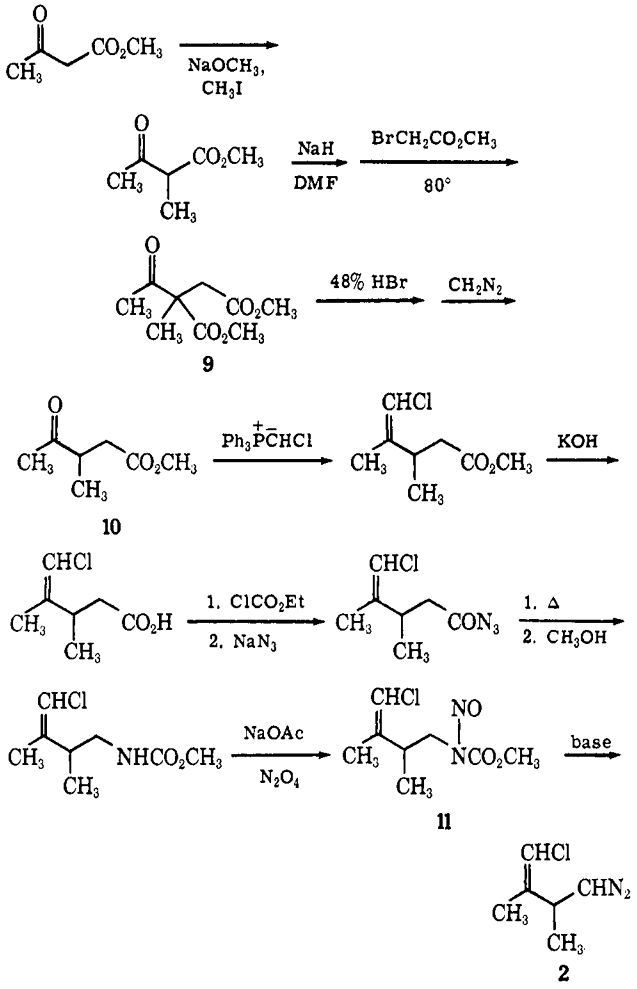
[9] W. M. Jones and D. L. Muck, *J. Amer. Chem. Soc.*, **88**, 3798 (1966).

[10] J. Meinwald and T. N. Wheeler, *ibid.*, **92**, 1009 (1970).

[11] R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966).

SCHEME II

SYNTHESIS OF 1-CHLORO-4-DIAZO-2,3-DIMETHYL-1-BUTENE (**2**)



diazo system, attention was focused on the study of the decomposition of the primary diazobutene **2**.

The catalytic decomposition of **2** was investigated under a variety of conditions (see Table I), all of which failed to produce detectable quantities of any bicyclobutane.[12–14] As a representative example, the addition of a pentane solution of **2** to a dimethyl ether solution of mercuric iodide[12] at −78° led to a disappearance of the 2060-cm^{-1} ir band. Gas chromatography of the resulting mixture allowed identification of the products shown in Scheme III.[15]

TABLE I

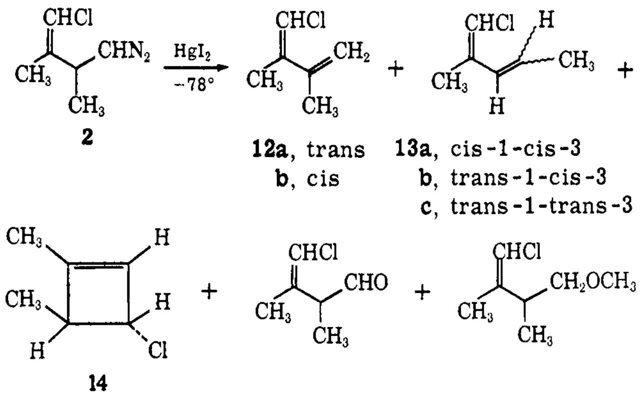
PRODUCT DISTRIBUTION FROM DECOMPOSITION OF DIAZOALKANE 2

Catalyst	12a	12b	13a	13b + 13c	14	15
HgI_2[a]	12	37	3	20	3	
CuCN[b]	25	47	4	6	9	
$CuBF_4$	35	63			2.5	
LiBr[c]	25	50	3	10	5	
$ZnCl_2$[d]	20	60		15	5	
$h\nu$	17	31				52

[a] Reference 12. [b] Reference 6. [c] Reference 13. [d] Reference 14.

SCHEME III

REACTION OF **2** WITH MERCURIC IODIDE



The major product of the reaction, the 1,3-butadiene **12**, exhibited nmr absorption at δ 5.1, 4.9 (br s, CH_2), 5.86, 6.23 (m, =CHCl, anti and syn chlorine, respectively), and ir absorption at 890 cm^{-1} ($R_2C{=}CH_2$). The 1,3-pentadiene structure of **13** was evident from the spectral data: nmr δ 1.81 (d, J = 6 Hz, =$CHCH_3$), 5.8–6.2 (m, *cis*-methyl isomer **13a**), 6.68 (d, J = 15 Hz, *trans*-methyl isomer **13b**). The assignment of the cyclobutene structure rests on the spectroscopic data and its precursor structure. The high resolution mass spectrum established a formula of C_6H_9Cl. The nmr spectrum indicated a vinylic methyl group (δ 1.72, finely coupled singlet) and a secondary saturated methyl group (δ 1.19, d, J = 7 Hz). The methine proton coupled to the methyl group is also allylic (2.9, bm). A single vinylic proton (δ 5.76, br s) and a saturated methine proton geminate to a chlorine (δ 4.22, br s) complete the spectrum. Lack of observable coupling between the vicinal protons is common in trans-3,4-disubstituted cyclobutenes. Two minor products also isolated, 2,3-dimethyl-4-chloro-3-butenal and 2,3-dimethyl-4-methoxy-1-butene, arise as byproducts in the preparation of the diazo compound.

The available data failed to suggest the presence of any bicyclobutanes in the reaction mixture. Careful gas chromatography, including variation of injector, detector, and column temperatures, did not alter the number or relative amounts of the products obtained. In an effort to explore the possible existence of bicyclobutanes in the reaction prior to gas chromatography, a solution of diazobutene **2** was prepared in fluorotrichloromethane (Freon 11) and reacted with mercuric iodide in dimethyl ether at −78°. After removal of the majority of solvent under reduced pressure at −20° and filtration, a −25° nmr spectrum was recorded. Only the presence of dienes (absorption due to allylic methyl groups) was noted.[16] A further indication that bicyclobutanes were absent from the reaction mixture (at least at −20°) arises from consideration of the rapid rearrangement of bicyclobutanes when exposed to acidic media.[17] Stirring an aliquot of the reaction solution with glacial acetic acid followed by gas chroma-

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(12) E. J. Corey and K. Achiwa, *Tetrahedron Lett.*, 2245 (1970).

(13) G. L. Closs and R. B. Larrabee, *ibid.*, 287 (1965).

(14) S. H. Goh, L. E. Closs, and G. L. Closs, *J. Org. Chem.*, **34**, 25 (1969).

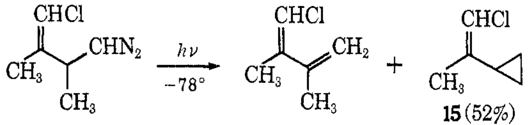
(15) The molecular formula of all products was confirmed by high resolution mass spectrometry—see Experimental Section.

(16) An estimated limit of detection of bicyclobutane was 5%.

(17) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970).

tography yielded a chromatogram which was identical with that obtained from the solution which had not been exposed to acid.

The photolytic decomposition of diazobutene **2** was studied in a further attempt to generate the bicyclobutane **4**. Known[18] to be an efficient method of generating carbenes from diazoalkanes, direct photolysis of **2** led to formation of the butadiene **12** and, as the major product, the vinyl cyclopropane **15**.



2 **12** (48%) **15** (52%)

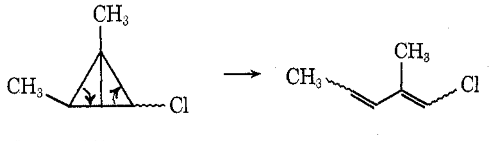
The vinyl cyclopropane structure of **15** was evident from the nmr [(CCl_4) δ 0.8–0.4 (br m), 1.66 (allylic methyl), 5.80 and 5.95 (=CHCl, mixture of isomers)] and ir (3130, 3050, 920 cm^{-1}) spectra. Insertion of the singlet carbene into the neighboring methyl group (to yield **15**) is not unexpected in view of the work by Kirmse[18b] on the reactions of α-methyl-substituted carbenes. Attempts to generate the triplet carbene *via* sensitized photolysis failed owing to the low solubility of the sensitizers under the photolysis conditions (pentane, −78°). In all cases singlet carbene products (*i.e.*, **15**) were observed.

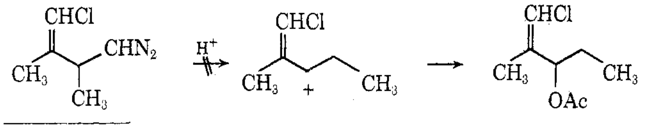
Discussion

The products obtained in the catalytic decomposition of diazobutene **2** allow a discussion of the mechanistic possibilities related to their formation. The terminal butadiene **12** is the product to be expected from either hydrogen migration of a carbenoid species or elimination of a diazonium cation.

Of greater interest is the mechanism of formation of the dienes **13** and the cyclobutene **14**. Possible considerations of the origin of **13** include: (a) thermal ring opening of a bicyclobutane (in what would formally be a retro [$2_s + 2_a$] process); (b) metal catalyzed ring opening of a bicyclobutane; (c) migration in a cationic diazonium species; (d) migration in a metal complexed carbenoid species.

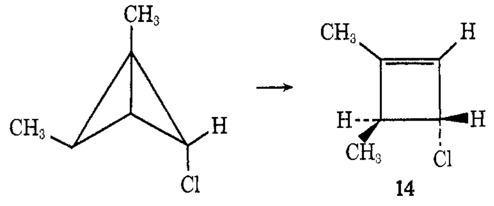
Thermal ring opening (mechanism a) of a bicyclobutane generally requires temperatures on the order of 200°. The experimental data require that any pathway involving such intermediate be capable of taking place at below −25°. Thus, such a course is rendered unlikely. Migration in a cationic species (mechanism c) is equally unlikely. Thus, carbonium ion products resulting from treatment of **2** with acid do not possess such rearranged structures. In this case, methyl migration in the homoallylic cation is at least slower than solvent capture, whereas significant methyl migration occurs in the acetolysis of isobutyldiazonium cation.[19] This discrepancy may relate to partial stabilization of the primary cation center by the proximate double bond.





The data available do not allow a clear distinction between the two remaining mechanistic possibilities—metal catalyzed rearrangement of a bicyclobutane (mechanism b) and migration in a metal complexed carbenoid (mechanism d). Recent studies[20] involving the rearrangement of bicyclobutanes to butadienes with silver, palladium, or rhodium catalysts have all involved temperatures of 25° or above. As noted above, the low temperature product analysis precludes the presence of bicyclobutanes at temperatures above −20°. Alternatively, it has been shown that migration of a metal complexed carbenoid is rapid at low temperature.[20a–c] These observations have led to the interpretation that such metal complexed carbenes are intermediates in the bicyclobutane rearrangement.[20a–c] Alternatively, organosilver cations have been invoked to rationalize rate data in the silver perchlorate catalyzed rearrangement.[20a]

In the present experiments, two types of rearrangement products **13** and **14** must be reconciled. The cyclobutene **14** most simply arises from thermal rearrangement of the desired bicyclobutane system (**4**) with an endo chlorine. We have previously shown that 2,2-dichloro-1,3,4-trimethylbicyclo[1.1.0]butane rearranges to the corresponding cyclobutene even at −70°. The dienes **13** may be rationalized by either a methyl shift or a vinyl shift. If the latter, the same bicyclobutane (**4** chlorine endo or exo) may be invoked; however, the higher temperatures usually required for metal catalyzed rearrangement make this pathway unattractive also. A partitioning most likely occurs earlier in the sequence. To differentiate between the Gassman and Paquette views of the reaction is exceedingly difficult since they clearly merge. Vinyl migration in the metal complexed carbene **16** is undoubtedly preceded by interaction of the π electrons with the carbenoid center. The question factors to whether the species **17** is an intermediate or a transition state. Such an important but fine distinction is not allowed at the present time. Assuming that cyclobutene **14** has its origin in **4**, the low yields of bicyclobutane products may be attributed to (1) diminished double-bond participation as envisioned in species **17**



4 **14**

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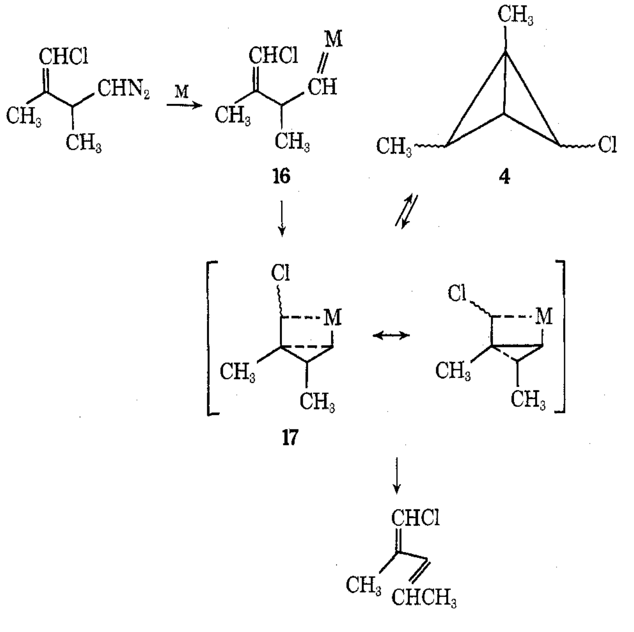
[18] (a) D. M. Lemal and K. S. Shim, *Tetrahedron Lett.*, 3231 (1964); (b) W. Kirmse and D. Groszmass, *Chem. Ber.*, **99**, 1746 (1966).

[19] J. H. Bayless, A. T. Jurewicz, and L. Friedman, *J. Amer. Chem. Soc.*, **90**, 4466 (1968).

[20] (a) P. G. Gassman, T. J. Akins, and F. J. Williams, *ibid.*, **93**, 1812 (1971); (b) P. G. Gassman and F. J. Williams, *Tetrahedron Lett.*, **No. 18**, 1409 (1971); (c) M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Commun.*, 486 (1971); (d) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 4611 (1971), and references therein; (e) L. A. Paquette and S. E. Wilson, *ibid.*, **93**, 5934 (1971), and references therein.



due to the negative inductive effect of the chloride and (2) diminished metal–C$_1$ interaction in species **17** due to the ability of chlorine to stabilize adjacent positive charge. The important role of the metal cation in both processes is demonstrated by the absence of both types of rearrangement products in the photolysis experiments.

Experimental Section[21]

Preparation of Methyl 2,3-Dimethyl-4-ketopentanoate (5).—Following the procedure of Haworth, *et al.*,[22] 20.0 g (0.20 mol) 3-methyl-3-penten-2-one was dissolved in 500 ml of 95% ethanol. Potassium cyanide (14.3 g, 0.22 mol) in 50 ml water was added over 5 min. The cloudy mixture was heated to 75° with stirring for 18 hr. After cooling to 0°, ether and saturated brine were added and the reaction was extracted. Drying over magnesium sulfate and solvent removal gave 17 g of a viscous yellow oil, which exhibited the spectral characteristics expected for an amide:[23] ir ($CHCl_3$) 3650, 3450, 3200, 1660 cm^{-1}.

Saponification of 12.68 g (0.089 mol) of the crude product in 250 g of refluxing 20% potassium hydroxide for 26 hr, followed by hydrochloric acid acidification, extraction with ether, and drying over magnesium sulfate, gave 7.06 g (55%) of crude 2,3-dimethyl-4-ketopentanoic acid: ir ($CHCl_3$) 3000 (br), 1750, 1700 cm^{-1}; nmr ($CDCl_3$) δ 9.2 (br, 1 H). Heating the total product on a steam bath overnight in 500 ml of methanol containing 3 ml of concentrated sulfuric acid, followed by extraction with ether and washing with sodium bicarbonate, afforded 6.7 g (86%) of crude ester. Distillation gave 5.20 g (67%) of clear, colorless product: bp 30° (0.05 mm); ir (CCl_4) 1740, 1710 cm^{-1}; nmr (CCl_4) δ 3.62 (s, 3 H), 2.72 (m, 2 H), 2.12 (s, 3 H), 1.10 (m, 6 H); mass spectrum *m/e* (rel intensity) 158 (4), 143 (5), 127 (21). *Anal.* Calcd for $C_8H_{14}O_3$: 158.09429. Found: 158.09089.

Preparation of Chloromethyltriphenylphosphonium Chloride.—Chloromethyltriphenylphosphonium chloride was prepared according to the procedure of Kobrich.[7] The material obtained (36.0 g, 44%) exhibited hydroxyl absorption in the ir, indicating the presence of either water or hydroxymethyltriphenylphosphonium salt. Purification attempts met with failure, and the salt was used in an impure state.

Preparation of Methyl 5-Chloro-2,3,4-trimethyl-4-pentenoate.—To 300 ml of freshly distilled ether was added 19.1 g (0.055 mol) of chloromethyltriphenylphosphonium chloride and 4.42 g (0.052 mol) of *n*-butyllithium was added over 15 min to yield a dark orange suspension. After this mixture stirred for 15 min at 0°, 3.50 g (0.022 mol) of keto ester **5** was added dropwise. After stirring 0.5 hr at room temperature, the reaction mixture was quenched with 25 ml of water and extracted with ether. Evaporation of solvent, dissolving the residue in hexane, and filtration enabled removal of the triphenylphosphine oxide. The filtrate was washed with 5% hydrochloric acid, dried over magnesium sulfate, and evaporated. Distillation (short path) yielded 2.078 g (50%) of a clear colorless liquid: ir (CCl_4) 1740, 1630 cm^{-1}; nmr (CCl_4) δ 5.74 (m, 1 H), 3.58 (s, 3 H), 2.4 (m, 2 H), 1.70 (finely coupled s, J = 1.5 Hz, 3 H), 1.0–1.2 (complex m, 6 H).

Anal. Calcd for $C_9H_{15}O_2Cl$: C, 56.69; H, 7.93; Cl, 18.59. Found: C, 56.96; H, 7.80; Cl, 18.79.

Preparation of Methyl *N*-4-(1-Chloro-2,3-dimethyl-1-pentenyl)-carbamate (6).—Saponification of 0.445 g (2.34 mmol) of methyl 5-chloro-2,3,4-trimethyl-4-pentenoate in 20 ml of 10% aqueous potassium hydroxide containing 2 ml of ethanol by refluxing for 1 hr yielded, after work-up, 0.383 g (93%) of the corresponding acid: ir ($CHCl_3$) 3000, 1700 cm^{-1}; nmr ($CDCl_3$) δ 10.5 (br m, 1 H).

Subjecting the acid to the modified Curtius reaction[8] enabled the desired carbamate to be prepared as follows. To a solution of 1.65 g (9.40 mmol) of the acid prepared above in 25 ml of acetone containing 5 ml of water in a 100-ml three-neck flask was added 1.10 g (10.9 mmol) triethylamine in 5 ml of acetone at 0°. Ethyl chloroformate (1.32 g, 12.2 mmol in 5 ml of acetone) was added dropwise from a syringe over 10 min. After the mixture stirred for 0.5 hr at 0°, sodium azide (0.925 g, 14.2 mmol in 8 ml of water) was added dropwise from a funnel over 15 min. The reaction mixture was then stirred at 0° for 1 hr, poured onto ice, and extracted with ether. After drying (magnesium sulfate) and evaporation (without heating), an oil was obtained which exhibited strong azide ir absorption at 2140 cm^{-1}.

The oil was dissolved in 25 ml of dry toluene and heated to 90–100° for 1 hr. After gas evolution had ceased, 20 ml of dry methanol was added and the solution was refluxed for 3 hr. Distillation over a short path (bath temperature 125°, 0.05 mm) yielded 1.55 g (80%) of a pale yellow liquid exhibiting the following spectral characteristics: ir ($CHCl_3$) 3450, 3400, 1705, 1630 cm^{-1}; nmr ($CDCl_3$) δ 5.9 (m, 1 H), 4.5 (br s, 1 H), 3.65 (s, 3 H), 2.2 (m, 2 H), 1.75 (finely coupled m, 3 H), 1.2 (complex m, 6 H); mass spectrum *m/e* (rel intensity) 102 (100, $CH_3CHNHCO_2CH_3^+$).

Anal. Calcd for $C_9H_{16}NO_2Cl$: C, 52.55; H, 7.84; N, 6.81; Cl, 17.24. Found: C, 52.85; H, 7.85; N, 6.83; Cl, 17.06.

Preparation of Methyl *N*-Nitroso-*N*-4-(1-chloro-2,3-dimethyl-1-pentenyl)carbamate (7).—Nitrosation[24] was effected by filtration of a solution of 1.042 g (5.1 mmol) of distilled carbamate **6** in 20 ml of dry ether through sodium sulfate into a 50-ml side-arm flask, addition of 1.64 g (20 mmoles) anhydrous sodium acetate, and cooling to −20°. Dinitrogen tetroxide was distilled into the flask for 1 hr, during which time the color became green. After an additional 2 hr at −20°, the mixture was carefully poured onto 250 ml of ice-cold 10% sodium bicarbonate, causing vigorous bubbling and the elution of a brown vapor. Extraction with cold ether, washing with water, and drying over magnesium sulfate yielded a yellow solution which was stored at −20°. The absence of any N–H band in the ir (at 3400 cm^{-1}) was noted in the crude material. Chromatography of the crude product (1.35 g, 100%) through neutral alumina (Woelm, activity III) using hexane as the eluent afforded 1.036 g (87%) of the pure nitrosocarbamate: ir ($CHCl_3$) 1740, 1630 cm^{-1}; nmr ($CDCl_3$) δ 5.8 (m, 1 H), 4.05 (s, 3 H), 0.80–1.80 (complex m, 9 H); tlc (alumina, 6% ether-hexane) R_f 0.52. The product was stored in ether solution at −20°. Attempts to obtain an analytically pure sample met with failure.

Preparation of 1-Chloro-4-diazo-2,3-dimethyl-1-pentene (1).—Lithium ethoxide[25] (195 mg, 3.8 mmol) was added to a solution of

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[21] All ir spectra were recorded on a Beckman IR-8 spectrophotometer, all uv spectra on a Cary Model 15 spectrophotometer, and all nmr spectra on a Varian Model A-60A spectrometer fitted with a variable-temperature probe. Chemical shifts are reported in parts per million downfield from TMS as an internal standard. Mass spectra were obtained on an AEI MS-902 double focusing instrument at an ionizing voltage of 70 eV. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Vpc analyses were performed on an Aerograph Model A90-P3 gas chromatograph using a 15-ft 20% SE-30 on Chromasorb W column.

[22] R. D. Haworth, B. G. Hutley, R. G. Leach, and G. Rodgers, *J. Chem. Soc.*, 2720 (1962); A. Bowers, *J. Org. Chem.*, **26**, 2043 (1961).

[23] Haworth[22] found that extended reflux times resulted in partial saponification of the cyano group to an amide.

[24] E. H. White, *J. Amer. Chem. Soc.*, **77**, 600 (1955).

[25] T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *ibid.*, **84**, 1371 (1962).

173 mg (3.3 mmol) N nitrosocarbamate **7** in 6 ml of anhydrous ethanol cooled to −20°. After stirring for 1 hr at −20°, the orange solution was diluted with 50 ml of pentane and washed with three portions of dilute aqueous potassium hydroxide. Drying the organic phase over potassium hydroxide pellets yielded a pink solution having strong ir absorption at 2040 cm^{-1}.

Characterization of the diazo solution was achieved by addition of an aliquot to a rapidly stirring mixture of 1.5 g of sodium formate in 5 ml anhydrous formic acid (prepared by refluxing 90% formic acid over phthalic anhydride and distilling[26]). The pink color was immediately discharged. After extraction of ether, washing with sodium bicarbonate, and drying over potassium carbonate, vpc analysis allowed isolation and characterization of the formate ester of **1**, 4-(1-chloro-2,3-dimethyl-1-pentenyl)-formate: ir (CCl_4) 3100, 1730, 1630, 1180 cm^{-1}; nmr (CCl_4) δ 7.90 (br s, 1 H), 5.80 (br s, 1 H), 1.72 (finely coupled s, J = 1.5 Hz, 3 H), 1.1 (complex m, 6 H); mass spectrum *m/e* (rel intensity) 178, 175 (weak, ratio 1:3, M$^+$ for $C_8H_{13}ClO_2$), 132 (10), 130 (30), 95 (30). The yield was determined to be 17%.

Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.39; H, 7.42; Cl, 20.07. Found: C, 54.56; H, 7.44; Cl, 20.30.

The major products from the reaction were shown to be the various isomers of 1-chloro-2,3-dimethyl-1,4-pentadiene and 1-chloro-2,3-dimethyl-1,3-pentadiene (**8**, 30% yield): ir (CCl_4) 3100, 1630, 1370, 1100, 910 cm^{-1}; nmr (CCl_4) δ 5.5–6.0 (m, 2 H), 5.14, 4.92 (br m, 2 H), 1.5–1.9 (complex m, 6 H), 1.13 (two overlapping doublets, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 132 (6), 130 (17), 115 (4), 95 (100).

Anal. Calcd for $C_7H_{11}Cl$: C, 64.36; H, 8.49; Cl, 27.15. Found: C, 64.49; H, 8.53; Cl, 27.09.

Two additional products were shown to have arisen from reaction with solvent (ethanol) and by air oxidation. In an effort to eliminate the former, freshly distilled hexamethylphosphoramide was employed as the solvent for generating the diazo compound. It was found, however, that the yield of formate esters dropped to 14%, and the yield of dienes rose to 56%.

Preparation of Methyl 3-Carbomethoxy-4-keto-3-methylpentanoate (9).—Into a 250-ml three-neck flask fitted with a reflux condenser and dropping funnel was put 3.93 g (0.090 mol) sodium hydride–mineral oil dispersion which was washed with hexane. Freshly distilled dimethylformamide (90 ml) was added and stirred. Methyl α-methylacetoacetate (12.00 g, 0.0925 mol), prepared according to the procedure of Marvel[27] from methyl acetoacetate, was added dropwise over 20 min. After the mixture stirred at room temperature for 0.5 hr, 15.30 g (0.10 mol) methyl bromoacetate (diluted in DMF) was added dropwise over 1 hr. After the reaction was heated to 80° for 3 hr an aliquot was found to be neutral to moist litmus. After cooling, water was added and the reaction mixture was concentrated on a rotary evaporator fitted with a vacuum pump. Extraction with ether, washing with water, and drying over magnesium sulfate gave, after concentration, 15.98 g (89%) crude product. Distillation afforded 12.24 g (68%) of pure product as a clear, colorless liquid, bp 61–70° (0.05 mm). A vpc-collected sample had the following spectral properties: ir ($CHCl_3$) 1725, 1710 cm^{-1}; nmr ($CDCl_3$) δ 3.76 (s, 3 H), 3.66 (s, 3 H), 2.90 (s, 2 H), 2.25 (s, 3 H), 1.50 (s, 3 H); mass spectrum *m/e* (rel intensity) 202 (1), 171 (45), 160 (55), 128 (100).

Anal. Calcd for $C_9H_{14}O_5$: C, 53.45; H, 6.97. Found: C, 53.42; H, 6.84.

Preparation of Methyl 4-Keto-3-methylpentanoate (Methyl 3-Methyllevulinate, 10).—To 50 ml of hydrobromic acid (48%) was added 12.24 g (0.60 mol) keto diester **9** (neat). After refluxing for 3 hr, the mixture was cooled, extracted with ether, then sodium bicarbonate, and ether again, following acidification. After drying (magnesium sulfate), solvent was removed to give a colorless oil: ir ($CHCl_3$) 3000, 1700 cm^{-1}; nmr ($CDCl_3$) δ 10.1 (br s, 1 H).

To an ethereal solution of the crude acid cooled to 0° was added an excess of diazomethane (prepared from EXR-101 in ether). The usual work-up gave 2.97 g (35%) of a clear, pale yellow liquid. Analytical samples, collected on the vpc, exhibited the following spectral properties: ir (CCl_4) 1730, 1700, 1350 cm^{-1}; nmr (CCl_4) δ 3.60 (s, 3 H), 2.2–3.0 (complex m, 3 H), 2.14 (s, 3 H), 1.12 (d, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 144 (4), 129 (10), 113 (44), 102 (40), 87 (67).

Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.21; H, 8.40.

Preparation of Methyl *N*-Nitroso-*N*-4-(1-chloro-2,3-dimethyl-1-butenyl)carbamate (11).—The remainder of the synthesis was identical with that described above for the synthesis of the N nitrosocarbamate **7**. Reaction of 2.93 g (20.4 mmol) of the keto ester **10** with triphenylphosphonium chloromethylide gave the chloro olefin ester, which, after saponification, yielded 1.83 g (56%) of the corresponding acid. The ester exhibited the following spectral data: ir (CCl_4) 3100, 1740, 1630 cm^{-1}; nmr (CCl_4) δ 5.75, 5.90 (br s, 1 H), 3.60 (s, 3 H), 2.3 (m, 3 H), 1.7 (two finely coupled s, J = 1.5 Hz, 3 H), 1.10 (two overlapping d, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 178, 176 (weak, ratio 1:3), 161 (1), 141 (50), 105 (23), 103 (70).

Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.39; H, 7.42; Cl, 20.07. Found: C, 54.64; H, 7.39; Cl, 19.99.

Curtius rearrangement of the acid (1.83 g, 11.3 mmol) yielded, after distillation, 1.736 g (80%) of the desired carbamate: ir ($CHCl_3$) 3450, 3400, 3100, 1700, 1630, 1500 cm^{-1}; nmr ($CDCl_3$) δ 5.90 (br s, 1 H), 4.7 (br m, 1 H), 3.66 (s, 3 H), 3.12 ("triplet," J = 7 Hz, 2 H), 2.4 (complex m, 1 H), 1.75 and 1.69 (two finely coupled s, J = 1.5 Hz, 3 H), 1.05 (two overlapping d, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 88 (100, $CH_2NHCO_2CH_3^+$).

Anal. Calcd for $C_8H_{14}N_2OCl$: C, 50.13; H, 7.36; N, 7.31; Cl, 18.50. Found: C, 50.29; H, 7.33; N, 7.27; Cl, 18.42.

Reaction of 0.960 g (5.00 mmol) of the carbamate with dinitrogen tetroxide, followed by alumina chromatography as before, yielded 0.880 g (80%) yellow N nitrosocarbamate **11**: ir ($CHCl_3$) 1750, 1630 cm^{-1}; uv (EtOH) λ_{max} 238 nm (ϵ 1830), 401 (55), 421 (52). An attempt to obtain an analytically pure sample failed.

Preparation of 1-Chloro-4-diazo-2,3-dimethyl-1-butene (2).—Following the procedure previously described, 39.3 mg (0.18 mmol) of the nitrosocarbamate **11** was treated with 85 mg (1.6 mmol) lithium ethoxide in ethanol. Extraction into pentane, washing with dilute potassium hydroxide, and drying over potassium hydroxide pellets afforded a yellow solution exhibiting strong ir absorption at 2060 cm^{-1} and visible absorption from 400 to 500 nm (ϵ ~17). Addition of an aliquot to a mixture of anhydrous sodium acetate in glacial acetic acid, followed by extraction with ether, washing with sodium bicarbonate, and drying over potassium carbonate, allowed isolation of the acetate adduct of **2**. Vpc analysis enabled the adducts to be identified as *cis*-4-acetoxy-1-chloro-2,3-dimethyl-1-butene (22.5% yield) and *trans*-4-acetoxy-1-chloro-2,3-dimethyl-1-butene (19.5% yield). The spectral properties were as follows.

Cis isomer: ir (CCl_4) 3050, 1740, 1630, 1240, 950 cm^{-1}; nmr (CCl_4) δ 5.93 (br s, 1 H), 2.3 (m, 1 H), 2.00 (s, 3 H), 1.84 (d, J = 1.5 Hz, 3 H), 1.22 (d, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 141 (4), 118 (32), 116 (100).

Anal. Calcd for $C_8H_{13}O_2Cl$: C, 54.39; H, 7.41; Cl, 20.07. Found: C, 54.21; H, 7.59; Cl, 20.38.

Trans isomer: ir (CCl_4) 3050, 1740, 1630, 1230 cm^{-1}; nmr (CCl_4) δ 5.89 (br d, J = 7.5 Hz, 2 H), 2.4 (broad m, 1 H), 1.98 (s, 3 H), 1.75 (d, J = 1.5 Hz, 3 H), 1.08 (d, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 141 (4) 118 (32), 116 (100).

Anal. Calcd for $C_8H_{13}O_2Cl$: C, 54.39; H, 7.41; Cl, 20.07. Found: C, 54.19; H, 7.48; Cl, 20.35.

Decomposition of 1-Chloro-4-diazo-2,3-dimethyl-1-pentene (1).—The decomposition of the diazopentane **1** by cuprous cyanide, cuprous chloride, tri-*n*-butylphosphinecopper(I) iodide, and photolysis was studied. In a typical experiment, 110 mg (1.2 mmol) cuprous cyanide was added to a solution of diazoalkane **1** [prepared from 84 mg (0.36 mmol) nitrosocarbamate **7** and 70 mg (1.8 mmol) lithium ethoxide] in 40 ml of ether cooled to −78°. After warming to −20° and stirring for 2 hr, the reaction mixture was analyzed by vpc. The only identifiable products were the diene mixture **8**.

Decomposition of 1-Chloro-4-diazo-2,3-dimethyl-1-butene (2).—The previously described pentane solution of diazobutene **12** [prepared from 304 mg (1.38 mmol) nitrosocarbamate **11**] was added over 0.5 hr dropwise from a temperature-controlled dropping funnel (cooled to −78°) to a solution of 420 mg (0.97 mmol) of mercuric iodide dissolved in 75 ml of dimethyl ether and cooled to −78°. The diazobutene solution was deaerated in the dropping funnel by the bubbling of nitrogen through the

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(26) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, Oxford, 1966, p 170.

(27) C. S. Marvel and F. D. Hager, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 248.

solution. After the solution stirred for 1.5 hr at −78°, an ir spectrum was taken of the now colorless solution; the absorption at 2060 cm^{-1} was absent.

After the solution was warmed to −20° and the dimethyl ether was allowed to distil from the reaction, the residue was filtered and concentrated by careful distillation under reduced pressure into a flask cooled to −78°. The distillate was concentrated in a similar manner (the residue flask was kept at or below −10°, and the combined residues were analyzed by gas chromatography (the residue solution was kept at the storage temperature of −20°). After initial separation of the complex mixture into two major fractions, the individual components were isolated and identified by preparative gas chromatography. The products isolated were as follows.

trans-1-Chloro-2,3-dimethyl-1,3-butadiene (**12a**, 12.7% rel yield): ir (CCl_4) 3130, 1630, 1375, 890 cm^{-1}; nmr (CCl_4) δ 5.86 (br s, 1 H), 5.09, 4.95 (br s, 2 H), 1.9 (complex m, 6 H); mass spectrum *m/e* (rel intensity) 118 (25), 116 (80), 81 (100). *Anal.* Calcd for C_6H_9Cl: 116.03927. Found: 116.03888.

cis-1-Chloro-2,3-dimethyl-1,3-butadiene (**12b**, 37.2%): ir (CCl_4) 3130, 1630, 1375, 890 cm^{-1}; nmr (CCl_4) δ 6.23 (br s, 1 H), 5.10, 4.98 (br s, 2 H), 1.9 (complex m, 6 H); mass spectrum *m/e* (rel intensity) 118 (24), 116 (64), 81 (100). *Anal.* Calcd for C_6H_9Cl: 116.03927. Found: 116.03915.

cis-1-Chloro-2-methyl-*cis*-1,3-pentadiene (**13a**, 22.6% total **14a** and **14b**): nmr (CCl_4) δ 5.97 (br s, 1 H), 5.8–5.2 (m, 2 H), 1.90 (finely coupled s, 3 H), 1.81 (d, J = 6 Hz, 3 H); mass spectrum *m/e* (rel intensity) 118 (16), 116 (46), 81 (100). *Anal.* Calcd for C_6H_9Cl: 116.03927. Found: 116.03840.

trans-1-Chloro-2-methyl-*cis*-1,3-pentadiene (**13b**): ir (CCl_4) 3080, 3030, 1600, 1440, 950, 850 cm^{-1}; nmr (CCl_4) δ 6.2–5.5 (complex m with br s at 5.92, 3 H), 1.85 (finely coupled s, 3 H), 1.79 (d, J = 5 Hz, 3 H); mass spectrum *m/e* (rel intensity) 118 (13), 116 (40), 81 (100). *Anal.* Calcd for C_6H_9Cl: 116.03927. Found: 116.03930.

1-Chloro-2-methyl-*trans*-1,3-pentadiene (**13c**): ir (CCl_4) 3080, 3030, 1630, 1440, 960, 850 cm^{-1}; nmr (CCl_4) δ 6.68 (d, J = 15 Hz, 1 H), 6.1–5.6 (m, 2 H), 1.8 (complex m, 6 H); mass spectrum *m/e* (rel intensity) 118 (15), 116 (45), 81 (100). *Anal.* Calcd for C_6H_9Cl: 116.03927. Found: 116.03915.

3-Chloro-1,4-dimethylcyclobutene (**14**): nmr (CCl_4) δ 5.76 (br s, 1 H), 4.22 (br s, 1 H), 2.9 (br m, 1 H), 1.72 (finely coupled s, 3 H), 1.19 (d, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 118 (12), 116 (36), 81 (100). *Anal.* Calcd for C_6H_9Cl: 116.03927. Found: 116.03915.

The remaining products were identified as having arisen from reaction with solvent (methanol) and air during generation of the diazobutene.

4-Chloro-2,3-dimethyl-3-butenal (6.5%): ir (CCl_4) 2820, 2750, 1730, 1630 cm^{-1}; nmr (CCl_4) δ 9.61 (s, 1 H), 6.12 (br s, 1 H), 3.87 (q, J = 7 Hz, 1 H), 1.69 (finely coupled s, 3 H), 1.20 (d, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 134 (1), 132 (4), 105 (13), 103 (40), 97 (52). *Anal.* Calcd for C_6H_9ClO: 132.03419. Found: 132.03065.

1-Chloro-2,3-dimethyl-4-methoxy-1-butene (8.1%): ir (CCl_4) 3050, 1630, 1120 cm^{-1}; nmr (CCl_4) δ 5.82 (br s, 1 H), 3.25 (s, 3 H), 2.2 (m, 3 H), 1.79 (finely coupled s, 3 H), 1.09 (d, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 150 (1), 148 (4), 113 (3), 81 (9). *Anal.* Calcd for $C_7H_{13}ClO$: 148.06548. Found: 148.06533.

Four additional minor components (total 7.9%) were not identified. Nmr spectra of each indicated they were probably decomposition products.

Stirring an aliquot of the reaction mixture (prior to gas chromatography) for 0.5 hr with glacial acetic at room temperature, followed by vpc analysis, did not alter the chromatogram obtained with respect to the number or relative yields of the products present. Generation of the diazobutene in methanol followed by extraction into fluorotrichloromethane (Freon 11) allowed nmr analysis to be performed on the crude reaction mixture after reaction with mercuric iodide at −78° and warming to −25° to remove the dimethyl ether present. Only absorption due to allylic methyl groups (δ 1.7–2.0) was noted at −25°. An estimated limit of detection of bicyclobutane was 10%.

Photochemical Decomposition of Diazobutene 2.—A pentane solution (∼0.1%) of the diazobutene **2**, prepared from the reaction of 36 mg (0.16 mmol) of nitrosocarbamate **11** with 90 mg (1.7 mmol) of lithium ethoxide, was deaerated with nitrogen in a Pyrex photolysis tube and cooled to −78°. The solution was photolyzed 1.5 hr at −78° (methanol heat exchanger and recirculating pump using Dry Ice as coolant) with a Hanovia 450-W high pressure mercury vapor lamp. The ir spectrum of the now colorless solution lacked absorption at 2060 cm^{-1}. Concentration of the solution (at −10° as described above) afforded a colorless solution which was analyzed by vpc.

In addition to a 48% relative yield of the 1,3-butadiene **12**, the major product of the reaction was found to be 1-chloro-2-cyclopropylpropene (**15**, 52%): ir (CCl_4) 3130, 3050, 920 cm^{-1}; nmr (CCl_4) δ 5.95, 5.80 (br s, 1 H), 1.9 (m, 1 H), 1.66 (d, J = 1.5 Hz, 3 H), 0.8–0.4 (m, 4 H); mass spectrum *m/e* (rel intensity) 118 (15), 116 (46), 81 (100). *Anal.* Calcd for C_6H_9Cl: 116.03927. Found: 116.04120.

The attempted triplet sensitized photolysis of the diazoalkane in pentane containing benzophenone and in 1:1 pentane–acetone gave identical product mixtures as did the direct photolysis above. It was found, however, that both acetone and benzophenone are insoluble in pentane at −78°.

Registry No.—**1**, 35147-19-4; **2**, 35191-78-7; **5**, 35140-52-4; **6**, 35140-53-5; **7**, 35191-79-8; **8** (1,3-diene), 35140-54-6; **8** (1,4-diene), 35191-80-1; **9**, 35140-55-7; **10**, 25234-83-7; **11**, 35191-81-2; **12a**, 35140-57-9; **12b**, 35140-58-0; **13a**, 35140-59-1; **13b**, 35140-60-4; **13c**, 35140-61-5; **14**, 35140-62-6; **15**, 5296-54-8; methyl 5-chloro-2,3,4-trimethyl-4-pentenoate, 35140-64-8; 5-chloro-2,3,4-trimethyl-4-pentenoic acid, 35140-65-9; 4-(1-chloro-2,3-dimethyl-1-pentenyl) formate, 35140-66-0, methyl 5-chloro-3,4-dimethyl-4-pentenoate, 35191-82-3; methyl *N*-4-(1-chloro-2,3-dimethyl-1-butenyl)carbamate, 35140-67-1; *cis*-4-acetoxy-1-chloro-2,3-dimethyl-1-butene, 35140-68-2; *trans*-4-acetoxy-1-chloro-2,3-dimethyl-1-butene, 35140-69-3; 4-chloro-2,3-dimethyl-3-butenal, 35140-70-6; 1-chloro-2,3-dimethyl-4-methoxy-1-butene, 35140-71-7.

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