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The Base-Induced Pyrolysis of Tosylhydrazones of α,β -Unsaturated Aldehydes and Ketones. A Convenient Synthesis of Some Alkylcyclopropenes^{1,2}

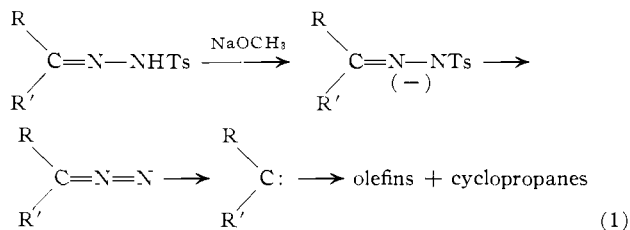
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Tosylhydrazones of a number of α,β -unsaturated aldehydes and ketones have been prepared. On reaction with sodium methoxide in aprotic media at 160–220° alkyl-substituted cyclopropenes are formed. The yields vary from excellent to poor depending mainly on the degree of β -substitution of the tosylhydrazone. The sequence: tosylhydrazone \rightarrow diazoalkene \rightarrow alkenylcarbene \rightarrow cyclopropene is proposed as the most suitable description of the multistep reaction.

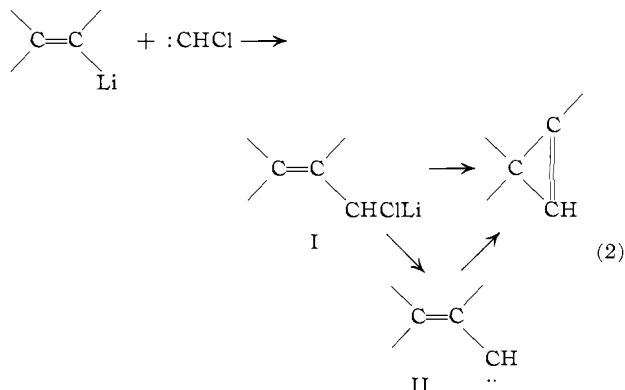
Introduction

Photolysis and pyrolysis in aprotic media of diazoalkanes are generally assumed to proceed through the intermediacy of highly reactive divalent carbon compounds.⁴ Although direct proof for the existence of these species has been brought forth only for relatively few cases,⁵ the nature and distribution of the ultimate products leave little doubt about the generality of this scheme. More recently, it has been shown that the pyrolytic decomposition of the alkali salts of tosylhydrazones of aldehydes and ketones in aprotic solvents yields olefins and cyclopropanes expected to arise from intermediate carbenes.⁶ The most likely sequence of events in these reactions is the primary formation of diazoalkanes by elimination of *p*-toluenesulfinate followed by pyrolytic cleavage of the carbon nitrogen bond (sequence 1). In some cases the diazoalkanes can be isolated when the reaction is carried out at somewhat lower temperature.⁷



The recently reported synthesis of alkylcyclopropenes from alkenyllithium compounds and methylene chloride led to the hypothesis that alkenyl substituted carbenoid intermediates will undergo ring closure to cyclopropenes.⁸ To explain the product formation we assumed that chlorocarbene, generated from the alkenyllithium and methylene chloride,⁹ reacted with the lithium reagent to form the α -chlorolithium compound I. Ring closure to the cyclopropene was then visualized to proceed either directly from I, or possibly, through the intermediacy of alkenylcarbene II (sequence 2).

In this paper we wish to present the results on studies of the base-induced decompositions of tosylhydrazones of α,β -unsaturated aldehydes and ketones and the re-



lated pyrolysis and photolysis of diazoalkenes. This work was undertaken because these reactions could be expected to yield alkenylcarbenes as intermediates, and, if our hypothesis was correct, cyclopropenes as products.

Results and Discussion

The tosylhydrazones III–VIII (Table I) were readily prepared in good yields from the α,β -unsaturated carbonyl compounds by addition of tosylhydrazide to a solution of the aldehyde or ketone in methanol, ethanol, or benzene at temperatures not exceeding 50°. In all cases the products were identified through elemental analyses, and infrared and nuclear magnetic resonance (n.m.r.) spectra. The presence of N–H stretching vibrations in the infrared, the fact that the methyl proton resonances never exceed the shielding of 8.5 τ , and the presence of olefinic proton resonances (with the exception of III) clearly establishes the structures of tosylhydrazones III–VIII. No evidence was found that under the conditions employed cyclizations to the N-tosylpyrazolines (IX) take place. The reaction of mesityl oxide with tosylhydrazide produced two isomeric compounds in approximately equal yields. The higher melting isomer (m.p. 123°) shows in the n.m.r. spectrum besides resonances attributable to the tosyl group, methyl proton resonances at 8.48, 8.21, and 8.08 τ . Small splittings of the two high-field peaks of (0.7 and 1.3 c.p.s., respectively, indicate that these lines should be associated with the allylic methyl groups which are weakly coupled with the olefinic proton. An incompletely resolved multiplet centered at 4.65 τ is assigned to the resonance of the latter. The low melting isomer (m.p. 109°) gives a very similar spectrum. Here, the two allylic methyl resonances are partially overlapping and are centered at 8.26 τ , while the signals for the remaining methyl group and the olefinic proton are found at 8.17 and 4.45 τ , respectively. Since both compounds were found to give the same products upon base-induced decomposition, we believe that the *syn* and *anti* structures IVa and IVb account for the observed differences. This suggestion is in accord with the observation that both isomers are converted to a mixture of the two compounds on heating in

(1) Supported by a grant from the National Science Foundation (NSF G19927).

(2) Reported in part as preliminary communication: G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 2015 (1961).

(3) A. P. Sloan Foundation Research Fellow.

(4) For a recent review, see W. Kirmse, *Angew. Chem.*, **73**, 161 (1961).

(5) Cf. G. Herzberg, *Proc. Roy. Soc. (London)*, **A262**, 291 (1961); R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3214 (1962); R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962); A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).

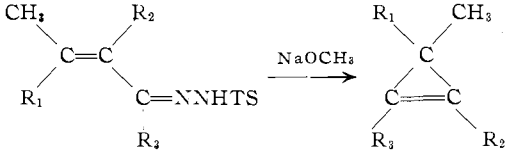
(6) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959); L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); **82**, 1002 (1960).

(7) L. Friedman, private communication; see also W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952), and D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).

(8) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 1003 (1961); **85**, 99 (1963).

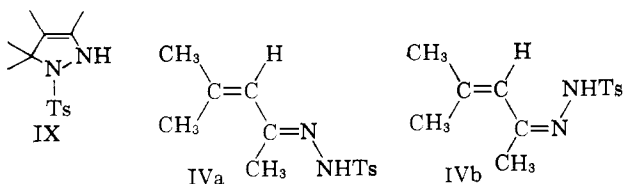
(9) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960); compare also G. L. Closs, *ibid.*, **84**, 809 (1962).

TABLE I



Compd.	R ₁	R ₂	R ₃	Yield of cyclopropene, %
III	CH ₃	CH ₃	H	X, 72
IV	CH ₃	H	CH ₃	X, 39
V	CH ₃	H	H	XI, 50
VI	H	CH ₃	H	XII, 4
VII	H	CH ₃	CH ₃	XIII, 1.5
VIII	H	H	H	XIV, 3

solution. No attempts were made to assign the configurations to the compounds.



Although no extensive search for isomer formation in the other tosylhydrazone preparations has been made, it appears that, if formed at all in these cases (III, V-VIII), a second isomer can be present only in small quantities. Considerations of steric factors readily account for the different behavior of mesityl oxide and the other aldehydes and ketones.

When the tosylhydrazone of α,β -dimethylcrotonaldehyde (III) was added to a suspension of sodium methoxide in refluxing diglyme ($\sim 160^\circ$) a volatile hydrocarbon, C₆H₁₀, was obtained in 72% yield. Through infrared and n.m.r. spectra this compound was identified as 1,3,3-trimethylcyclopropene (X), identical in all properties with a previously prepared sample.⁸ The same cyclopropene, X, was obtained in 38% yield from the tosylhydrazone of mesityl oxide (IV) using identical reaction conditions.¹⁰ The yield was unchanged regardless of whether IVa or IVb was used in this reaction. In addition to the cyclopropene, IV produced a diene which was easily separated from the cyclopropene. On the bases of its spectral properties and physical constants this compound was identified as 4-methyl-1,3-pentadiene (XXIII).

Cyclopropene formation proceeded well from the tosylhydrazone of β -methylcrotonaldehyde (V). The resulting 3,3-dimethylcyclopropene (XI) was obtained in high purity in 50% yield. Hydrogenation to 1,1-dimethylcyclopropane and spectral data confirmed structure XI of the hydrocarbon. The n.m.r. spectrum shows methyl resonance at 8.85 τ (triplet) and a signal for the olefinic proton at 2.68 τ (septuplet) with the expected intensity ratio and a spin coupling between the two groups of 0.7 c.p.s.^{11,12}

The reaction of the tosylhydrazone of tiglaldehyde (VI) with sodium methoxide in Diethyl Carbitol at 190° gave the expected 1,3-dimethylcyclopropene (XII) in only 4% yield. The main product was identified as 3,4-dimethylpyrazole. The structure of cyclopropene XII was confirmed by hydrogenation yielding *cis*-1,2-di-

(10) The preparation of cyclopropene X from mesityl oxide constitutes a more convenient synthesis of X than the decomposition of the tosylhydrazone III. Although the latter reaction proceeds with a higher yield, α,β -dimethylcrotonaldehyde is relatively difficult to prepare.⁸

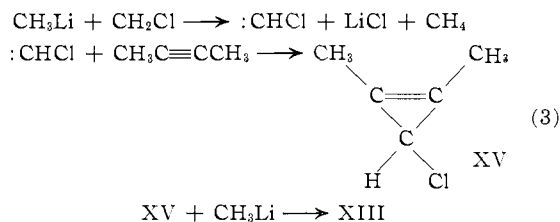
(11) The chemical shift values reported here refer to carbon tetrachloride solutions with tetramethylsilane as internal standard. The previously reported values for XI were determined on the neat compound.⁸

(12) A comprehensive discussion of the n.m.r. and infrared spectra of all cyclopropene derivatives prepared in this Laboratory is in preparation.

methylcyclopropane, *trans*-1,2-dimethylcyclopropane, and isopentane in a ratio of 10:1:6, respectively. The predominant formation of the *cis* isomer is in agreement with the expectation that adsorption on the catalyst surface occurs with the least hindered side of the cyclopropene ring.

Because the hydrogenation came to a complete stop after the uptake of 1.3 equivalents of hydrogen, it is assumed that under the conditions employed the isopentane does not arise from a consecutive hydrogenation of the dimethylcyclopropane but that ring cleavage and saturation of the double bond are consequences of the same adsorption process. The n.m.r. spectrum of XII further supports the structure assignment by exhibiting resonances characteristic of saturated and allylic methyl groups in addition to the resonances of the olefinic and saturated ring protons.¹²

A very poor yield of 1,2,3-trimethylcyclopropene (XIII) resulted from the decomposition of the tosylhydrazone of 3-methyl-3-penten-2-one (VII). The main product was identified as 3,4,5-trimethylpyrazole. The n.m.r. spectrum of the hydrocarbon is in agreement with structure XIII, showing allylic methyl resonance at 8.18 τ , a doublet for the saturated methyl group at 9.07 τ , and a multiplet for the ring proton at 8.7 τ .¹² Further support for the structure assignment arises from the fact that the same compound is available in better yield from the reaction of methyl lithium with methylene chloride in the presence of 2-butyne. The formation of XIII in this reaction is readily explained on the basis of sequence 3. The initially formed chlorocarbene^{9,13} is visualized to add to butyne to form 1,2-dimethyl-3-chlorocyclopropene. Facile displacement of the chlorine atom in XV by a methyl group is to be expected in view of the known stability of cyclopropenium ions.¹⁵



Finally, a poor yield of 3-methylcyclopropene (XIV) was obtained from the tosylhydrazone of crotonaldehyde (VIII). The very unstable olefin was characterized through its n.m.r. and infrared spectrum. Additional evidence for the cyclopropene structure of this compound follows from the Diels-Alder addition to cyclopentadiene. The reaction proceeded smoothly at 0° to give the tricyclic compound XVI. The very close analogy of the n.m.r. and infrared spectra of XVI with those of the cyclopropene adduct of cyclopentadiene¹⁶ strongly support the structure.

It should be noted that only one isomer was formed to which we assign the stereochemistry as indicated in XVI. This assignment is based on the known *endo* addition of cyclopropene¹⁶ and the failure of 3,3-dimethylcyclopropene to add to cyclopentadiene even at elevated temperatures. The latter observation seems to indicate a strong steric factor opposing the *endo*

(13) The recently reported discrepancy between the reactivities of the intermediates in photolysis or pyrolysis of chlorodiazomethane on one hand, and in the reaction of alkyl lithium with methylene chloride on the other, leaves some doubt about the intermediacy of a free carbene in the latter reaction.¹⁴ However, until more light is shed on the mechanism of this reaction, we will continue to formulate the reaction of methylene chloride with alkyl lithium in terms of a carbene mechanism.

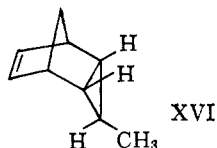
(14) G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4350 (1962).

(15) R. Breslow, H. Hover, and H. W. Chang, *ibid.*, **84**, 3168 (1962), and references cited therein.

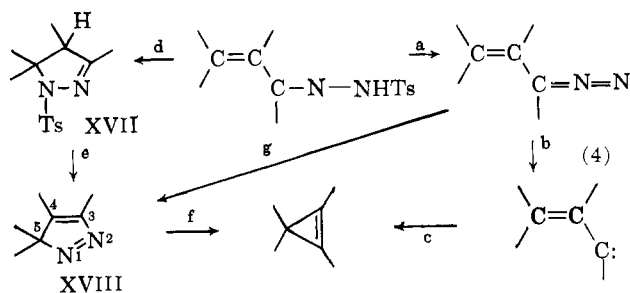
(16) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

orientation of the methyl group in the transition state.

In summary, it can be stated that the base-induced decomposition of tosylhydrazones of α,β -unsaturated aldehydes and ketones appears to give good yields of cyclopropenes when the β -carbon atom is fully substituted with alkyl groups. The presence of one hydrogen atom at the β -position suffices to diminish the cyclopropene yield substantially, and we have not yet been able to obtain any cyclopropane from tosylhydrazones with two hydrogens at the β -position.

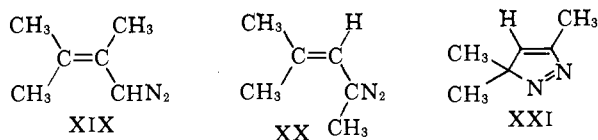


Although the formation of cyclopropenes from tosylhydrazones of α,β -unsaturated aldehydes and ketones seemed to confirm our original hypothesis, additional information about the intermediates in this multistep reaction was clearly desirable. Scheme 4 is a



summary of possible sequence capable of describing cyclopropene formation. Instead of assuming the intermediacy of an alkenylcarbene (reaction sequence a, b, c), it appeared entirely reasonable to invoke a pyrazolenine (XVIII) as immediate precursor for the cyclopropene. Such a mechanism (reaction sequence d, e, f or a, g, f) seems attractive because it can account readily for the formation of pyrazoles in those cases where a β -hydrogen is present in the tosylhydrazone. Tautomerization of a pyrazolenine with a hydrogen at position 5 to a stable pyrazole can be expected to compete successfully with the elimination of nitrogen.

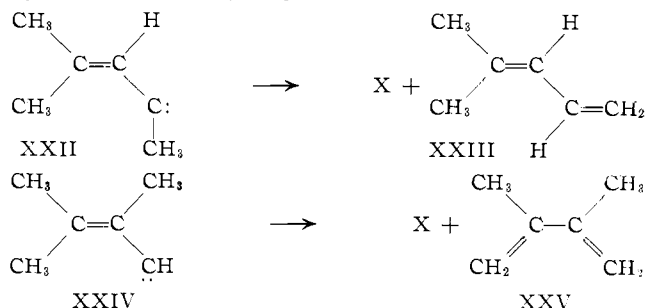
Evidence for the occurrence of reaction a in the base-induced pyrolysis of tosylhydrazones III and IV was obtained by lowering the reaction temperature to 70–90°. Under those conditions the corresponding diazoalkenes XIX and XX were isolated. Pyrolysis of both XIX and XX yielded 1,3,3-trimethylcyclopropene (X).



Similarly, the cyclopropene X was obtained in excellent yield *via* the photolytic decomposition of XIX at -20° . While these observations demonstrate that diazoalkenes are probable intermediates in the tosylhydrazone pyrolysis, the possibility of bypassing the alkenylcarbene through sequence a, g, f still existed.

Through variation of reaction conditions, 3,3,5-trimethylpyrazolenine (XXI) was finally obtained from the sodium salt of IV in 36% yield. The structure assignment of XXI is based on spectral data [infrared: strong band at 1640, $=C-H$ 3095 cm^{-1} ; ultraviolet: λ_{max} 257 (2250), 350 $m\mu$ (270); n.m.r.: singlet 8.65, doublet 7.63, and quadruplet 3.70 τ , J 1.7 c.p.s.]. While the diazoalkene XX might be an intermediate in the formation of XXI (sequence a, g), it seems that the

internal Michael addition followed by elimination of sulfinate (sequence d, e) is a better description of the reaction because the simultaneously formed XX appeared to be stable under the reaction conditions. Somewhat surprisingly, XXI resisted pyrolytic conversion to X and was found to be perfectly stable at temperatures at which cyclopropene formation from IV proceeded smoothly.¹⁷ This result eliminates pyrazolenines as possible precursors of cyclopropenes in tosylhydrazone pyrolysis and constitutes strong support for a carbene mechanism (sequence a, b, c). The formation of diene XXIII as side product in the pyrolysis of IV can be regarded as further support for the intermediacy of alkenylcarbene XXII, since 1,2-hydrogen shifts are well known reactions of alkylcarbenes.^{6,9} Similarly, the small amount of 2,3-dimethylbutadiene (XXV) formed in both pyrolysis and photolysis of XIX can be explained on the basis of carbene XXIV as intermediate by invoking a 1,4-hydrogen shift.¹⁸



To account for the large variation in yields of cyclopropenes, we suggest that the relative rates of reactions a, b, d, and possibly g are strongly dependent on the degree of substitution of the β -carbon atom. Both steric and electronic effects resulting from increasing methyl substitution at the β -position will retard the rates of the cyclization steps d and g. In contrast, elimination steps a and b will be accelerated by the electron-releasing power of the alkyl groups. The resulting shift of the product balance in favor of heterocyclic compounds with decreasing methyl substitution corresponds to the experimental observation.

Finally, the synthesis of cyclopropenes X–XIV and the previously reported preparations of tetramethylcyclopropene⁸ and 1,2-dimethylcyclopropene¹⁹ enable us to make a qualitative comparison of the thermostabilities of these strained systems as a function of methyl substitution. The generally observed stabilizing influence of methyl groups on small ring compounds appears to be effective in the cyclopropene series as well. In particular, the 3,3-dimethyl substituted compounds X, XI, and tetramethylcyclopropene were found to be completely stable at room temperature. Methyl substitution at the olefinic carbon atoms, while still adding to the stability of the system, seems to be considerably less effective. Thus, 1,2-dimethylcyclopropene is reported to polymerize at room temperature. Similarly, XII, XIII, and XIV with only one methyl group at position 3 were found to polymerize readily, with XIV being the least stable.

Experimental

All boiling points are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian V 4300-B spectrometer

(17) The photolytic conversion of XXI and similar pyrazolenines to cyclopropenes (G. L. Closs and W. A. Böll, *Angew. Chem.*, **75**, 640 (1963)), might well be a two-quantum process, in which the first step is the conversion of the pyrazolenine to the diazoalkene. Additional work is in progress to clear up this point.

(18) For a detailed discussion of the cyclization of alkenylcarbenes to cyclopropenes see ref. 8.

(19) W. v. E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

operating at 40 Mc. Infrared spectra were obtained on a Beckman IR-7.

α,β -Dimethylcrotonaldehyde Tosylhydrazone (III).—Tosylhydrazide (55 g., 0.29 mole) was added to a solution of α,β -dimethylcrotonaldehyde⁸ (28.9 g., 0.29 mole) in ethanol (270 ml.). The temperature was not allowed to exceed 50°. After 30 min. the solution was cooled to 0° and the tosylhydrazone was allowed to crystallize for 12 hr. (61 g., 0.23 mole, 79%). Recrystallization from ethanol gave pure material melting at 128–130°; n.m.r.,²⁰ 8.24 (s), 2.0 (s), 1.61 (broadened s) τ in ratio of 9:1:1; infrared, 3250, 1665, 1605 cm.⁻¹.

Anal. Calcd. for C₁₃H₁₈N₂O₂S (266.36): C, 58.62; H, 6.89; N, 10.52. Found: C, 58.72; H, 6.97; N, 10.60.

Mesityl Oxide Tosylhydrazones (IVa and IVb).—Mesityl oxide (27 g., 0.27 mole) was added slowly to a solution (40°) of tosylhydrazide (50 g., 0.27 mole) in methanol (100 ml.). The temperature was not allowed to exceed 50°. After 20 min., water (25 ml.) was added and the product was allowed to crystallize. The mixture of IVa and IVb was filtered off, washed with methanol-water, and dried. This crude product (50.5 g., 0.19 mole, 70%, m.p. 105–110°) was utilized without further purification for the cyclopropene synthesis.

Separation of Isomers IVa and IVb.—The crude tosylhydrazone of mesityl oxide (17 g., 0.064 mole) was stirred in diglyme (35 ml.) for 10 min. at room temperature. The undissolved portion was filtered off and washed with diglyme and pentane. Recrystallization from ether gave a tosylhydrazone (4.95 g., 0.019 mole), 30%, m.p. 122.5–123.5°; n.m.r., see Discussion; infrared, 3260, 1662, 1602 cm.⁻¹.

Anal. Calcd. for C₁₃H₁₈N₂O₂S (266.36): C, 58.62; H, 6.89. Found: C, 58.75; H, 6.75.

The diglyme filtrate was poured onto ice-water (200 ml.). The precipitate was filtered off and was partly dissolved in methanol. The filtered methanol solution was chilled to -20° and the resulting crystals (m.p. 107–109°) were collected. Mixture melting point with the higher melting isomer, 104–107°. The n.m.r. analysis showed that small amounts of the high melting isomer were still present, infrared 3220, 1660, 1598 cm.⁻¹.

Anal. Calcd. for C₁₃H₁₈N₂O₂S (266.36): C, 58.62; H, 6.89; N, 10.52. Found: C, 58.52; H, 6.92; N, 10.74.

β -Methylcrotonaldehyde Tosylhydrazone (V).— β -Methylcrotonaldehyde (9.3 g., 0.11 mole) was added to a solution of tosylhydrazide (20.8 g., 0.11 mole) in methanol (40 ml.) at 40°. The solution was chilled to -15° and the tosylhydrazone (20.9 g., 0.083 mole, 75%) was allowed to crystallize. Recrystallization from ethanol gave a pure sample melting at 97–98°.

Anal. Calcd. for C₁₂H₁₆N₂O₂S (252.33): C, 57.11; H, 6.39; N, 11.10. Found: C, 56.78; H, 6.39; N, 11.13.

Tiglaldehyde Tosylhydrazone (VI).—Tiglaldehyde (22.0 g., 0.26 mole) was added slowly to a suspension of tosylhydrazide (46.0 g., 0.25 mole) in benzene (100 ml.). To the cooled solution was added pentane (300 ml.). The tosylhydrazone was allowed to crystallize, filtered, and dried (59 g., 0.23 mole, 92%). A sample was recrystallized from ethanol (m.p. 83.5–84.0°); infrared: 3210, 1645, 1597 cm.⁻¹; n.m.r. 8.3 (m), 4.2 (m), 2.58 (s), 1.65 (s) τ with intensity ratios 6:1:1:1.

Anal. Calcd. for C₁₂H₁₆N₂O₂S (252.33): C, 57.11; H, 6.39; N, 11.10. Found: C, 57.00; H, 6.45; N, 11.13.

3-Methyl-3-penten-2-one Tosylhydrazone (VII).—3-Methyl-3-penten-2-one (40.0 g., 0.41 mole) was added to a solution of tosylhydrazide (64.0 g., 0.40 mole) in methanol (100 ml.). The temperature was not allowed to exceed 45°. The solution was cooled to -15° and the tosylhydrazone was allowed to crystallize (69 g., 0.26 mole, 65%), infrared: 3230, 1642, 1600 cm.⁻¹; n.m.r. 8.3 (m), 8.13 (s), 4.0 (m) 2.2 (s) τ with relative intensities of 6:3:1:1.

Crotonaldehyde Tosylhydrazone (VIII).—Tosylhydrazide (37.2 g., 0.20 mole) was added to a chilled solution of crotonaldehyde (15.4 g., 0.22 mole) in benzene (120 ml.). Addition of pentane (120 ml.) completed the precipitation of the tosylhydrazone (46 g., 0.19 mole, 96%). Recrystallization from methylene chloride-pentane gave pure material melting at 125°; infrared, 3220, 1653, 1600 cm.⁻¹; n.m.r.,²⁰ 8.26 (d), 4.1 (m), 2.8 (s), 1.4 (s) τ with relative ratios of 3:2:1:1.

Anal. Calcd. for C₁₁H₁₄N₂O₂S (238.31): C, 55.44; H, 5.92. Found: C, 55.46; H, 5.85.

Cyclopropene Formation from Tosylhydrazones. General Procedure.—The tosylhydrazone was usually dissolved or suspended in 2 to 3 parts of the glyme solvent. Prior to use the glyme solvent was purified by distillation *in vacuo* over sodium. This solution, or suspension, was added over a period of 30 to 60 min. to a suspension of sodium methoxide in 1 part glyme solvent heated to a suitable temperature (160 to 220°) in a flask equipped

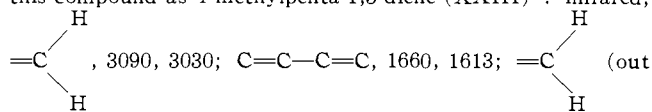
with mechanical stirrer, thermometer, addition funnel, and a short Vigreux column. The column head was connected to a flask immersed in a Dry Ice-acetone bath. For the more volatile cyclopropenes a second cold trap was connected in series with the flask. The addition rate of the tosylhydrazone solution and the heating of the reaction flask were controlled in such manner to allow the methanol, generated in the reaction, to distil from the mixture, maintaining the selected reaction temperature. After addition was completed, the apparatus was usually swept with nitrogen for a few minutes to drive all products into the collection flask. The contents of the collection flask (methanol and cyclopropene and other volatile compounds) was diluted with a suitable hydrocarbon (pentane, hexane, or heptane, depending on the boiling point of the product), washed with ice-water, and distilled over a Heli-pack column.

1,3,3-Trimethylcyclopropene (X) from α,β -Dimethylcrotonaldehyde Tosylhydrazone (III).—A solution of III (26.6 g., 0.10 mole) in diglyme (120 ml.) was added as described above to a suspension of sodium methoxide (11 g., 0.2 mole) in diglyme (100 ml.) at approximately 160°. The reaction distillate was diluted with *n*-heptane and worked up as described above. 1,3,3-Trimethylcyclopropene (5.9 g., 0.072 mole, 72%) was collected from the distillation column at 42.8–43.3°, *n*_D²⁰ 1.3892. The infrared and n.m.r. spectra of this sample were found identical with the spectra of a previously prepared sample of X.⁸

1,3,3-Trimethylcyclopropene from Mesityl Oxide Tosylhydrazone (IV).—A suspension of IV (120 g., 0.45 mole) in diglyme (250 ml.) was added as described above to a suspension of sodium methoxide (56 g., 1.03 moles) in diglyme (85 ml.) at approximately 160°. It was found advantageous to stir the slurry in the addition funnel to assure smooth addition of IV. Fractionation of the reaction distillate (diluted with *n*-heptane) gave 1,3,3-trimethylcyclopropene (b.p. 42.5–43.5°, 14.5 g., 0.18 mole, 39%).

Separate reactions utilizing the isomeric tosylhydrazones IVa and IVb under identical conditions gave 38 and 42% yields of 1,3,3-trimethylcyclopropene.

The higher boiling fractions of several runs were combined and redistilled over an efficient Heli-pack column. A fraction boiling at 71–73° was obtained. Infrared and n.m.r. spectra identified this compound as 4-methylpenta-1,3-diene (XXIII)²¹: infrared,



of plane) 890 cm.⁻¹; n.m.r., 8.2 (m), 5.2 (m), 4.6–3.5 (m) τ in ratios 3:1:1. From v.p.c. analysis of the original reaction mixture the yield of XXIII was 3–4% based on IV.

3,3-Dimethylcyclopropene from β -Methylcrotonaldehyde Tosylhydrazone (V).—A solution of V (40.0 g., 0.16 mole) in Diethyl Carbitol (200 ml.) was added as described above to a suspension of sodium methoxide (18 g., 0.35 mole) in Diethyl Carbitol (50 ml.) at approximately 180°. The reaction distillate was diluted with *n*-hexane (20 ml.) and washed with water while keeping the separatory funnel in an ice bath. Fractional distillation over a chilled column gave 3,3-dimethylcyclopropene (b.p. 14.5°, 5.40 g., 0.08 mole, 50%).

1,3-Dimethylcyclopropene from Tiglaldehyde Tosylhydrazone (VI).—A solution of VI (102 g., 0.405 mole) in Diethyl Carbitol (250 ml.) was added to a refluxing suspension of sodium methoxide (50 g., 0.95 mole) in Diethyl Carbitol (60 ml.). The reaction distillate was poured on ice-water and was extracted with mineral oil (10 ml.), keeping the separatory funnel in an ice bath. The mineral oil layer was washed several times with water. The volatile hydrocarbon was distilled from the oil *in vacuo* into a trap cooled with liquid nitrogen. 1,3-Dimethylcyclopropene (1.0 g., 0.015 mole, 4%) was pipetted from the trap at -20°, thus separating the compound from small amounts of water. The purity of the compound was estimated from the n.m.r. spectrum to be better than 90%; infrared, 3120, 3065, 1774 cm.⁻¹. A capillary boiling point determination gave a value of 33°. The half-life of the compound at room temperature was found to be less than 5 hr. A separate run (0.05 mole) in diglyme gave a somewhat smaller yield of 1,3-dimethylcyclopropene (2.5%). The remaining reaction mixture in this run was diluted with water and extracted with ether several times. The combined ether extracts were washed with water to remove the diglyme. After removal of the ether a crystalline residue remained (2.85 g., 0.03 mole, 60%), identified as 3,4-dimethylpyrazole by comparison with an authentic sample (m.p. 56–57°).

1,2,3-Trimethylcyclopropene from 3-Methyl-3-penten-2-one Tosylhydrazone (VII).—A partial suspension of VII (65 g., 0.24 mole) in diglyme (250 ml.) was added to a refluxing suspension of sodium methoxide (27 g., 0.5 mole) in diglyme (80 ml.). The reaction distillate was worked up as described for 1,3-dimethylcyclopropene. The volatile hydrocarbon mixture (0.5 g.) was shown to contain 1,2,3-trimethylcyclopropene (1.7%)

(20) The signals arising from the tosyl group have been omitted since they are approximately the same for all tosylhydrazones (7.6 (s) and 2.4 (m) τ).

(21) G. B. Bachman and C. G. Goebel, *J. Am. Chem. Soc.*, **64**, 788 (1942).

yield) by comparison of the infrared and n.m.r. spectra with those of a pure sample. Attempts of further purification were unsuccessful because of the instability of the cyclopropene.

The remaining reaction mixture was diluted with water and exhaustively extracted with ether. The combined ether extracts were extracted with 2 *N* hydrochloric acid and the nonbasic compounds were removed from the aqueous layer by repeated ether extraction. Neutralization with potassium carbonate and extraction with ether gave, after removal of the solvent, 3,4,5-trimethylpyrazole (5.4 g., 0.05 mole, 21%, m.p. 137–138°).

3-Methylcyclopropene from Crotonaldehyde Tosylhydrazone (VIII).—A solution of VIII (120 g., 0.5 mole) in triglyme (300 ml.) was added to a suspension of sodium methoxide (54 g., 1.0 mole) in triglyme (120 ml.) at 200–220°. Distillation of the volatile reaction products over a Heli-pack column afforded 3-methylcyclopropene (0.9 g.). On the basis of the n.m.r. spectrum the product was estimated to be 80–85% pure (2.6% yield). Due to the extreme instability no further purification was possible. The boiling point was estimated to be in the vicinity of –5°; infrared, C=C (stretch) 1639 cm.⁻¹; n.m.r. 8.9 (m), 8.5 (m), and 2.8 (m) τ in intensity ratios of 3:1:2.

1,2,3-Trimethylcyclopropene from 2-Butyne.—Methylolithium (0.2 mole) in ether (120 ml.) was added dropwise at 0° to a mixture of 2-butyne (24 g., 0.43 mole) and methylene chloride (8.5 g., 0.1 mole) under vigorous stirring. The reaction mixture was poured on ice-water (350 ml.) containing ethanol (70 ml.). The hydrocarbons were extracted with mineral oil (30 ml.). The mineral oil layer was washed with ice-water-ethanol mixtures (once with 350 ml. of water containing 50 ml. of ethanol, followed by 350 ml. of water containing 30 ml. of ethanol and finally 250 ml. of water). The volatile components of the mineral oil layer were distilled *in vacuo* at room temperature into a trap cooled with liquid nitrogen. The distillate (11 g.) was distilled over a short spiral column with bath temperature not exceeding 55°. The fraction distilling up to 25° contained most of the 2-butyne. The distillation residue (3.12 g.) was shown by v.p.c. to contain 43% of 1,2,3-trimethylcyclopropene (1.32 g., 16.1 moles, 16%). The final purification was accomplished by v.p.c. on a column of di-2-ethylhexyl sebacate on base-washed firebrick at 20°. The relative order of retention times on this column are: butyne, ether, 1,2,3-trimethylcyclopropene, methylene chloride. A larger sample of the cyclopropene was prepared by repeated injections of 0.1 ml. of concentrate; infrared, C=C, 1880 cm.⁻¹; n.m.r., see Discussion.

Hydrogenation of 1,3-Dimethylcyclopropene.—1,3-Dimethylcyclopropene (0.33 g., 4.85 mmoles) was hydrogenated in *n*-heptane (1 ml.) using platinum oxide (45 mg.) as catalyst. The temperature was kept at 0°. The hydrogenation came to a complete stop after the uptake of 151 ml. (6.3 mmoles, 1.3 equiv.). The catalyst was filtered off and the solution was analyzed by v.p.c. (30% TCP on firebrick at 32°). The chromatogram showed the presence of three compounds which were isolated by trapping from the v.p.c. column. Comparison of v.p.c. retention times, infrared, and n.m.r. spectra with authentic samples showed these compounds to be *cis*-1,2-dimethylcyclopropane, *trans*-1,2-dimethylcyclopropane, and isopentane. According to v.p.c. analysis (assuming identical thermoconductivity) these products were formed in ratios of 10:1:6.

Hydrogenation of 3,3-Dimethylcyclopropene.—3,3-Dimethylcyclopropene (0.478 g., 0.007 mole) was dissolved in ethanol (3 ml.) and hydrogenated over 5% palladium-on-charcoal (50 mg.) at 0°. Hydrogen uptake (0.0064 mole) was complete within 7 min.; v.p.c. analysis showed the hydrogenation product to consist of 95% 1,1-dimethylcyclopropane with only one other component (unidentified). Isolation of the cyclopropane by v.p.c. was carried out on 12-ft. column using TCP firebrick as substrate at 22°. The material was identified by comparison of its infrared and n.m.r. spectra with an authentic sample of 1,1-dimethylcyclopropane.

Addition of 3-Methylcyclopropene to Cyclopentadiene.—To a solution of cyclopentadiene (2.5 g., 0.038 mole) in methylene chloride (15 ml.) was added at –20° 3-methylcyclopropene (0.70 g., approximately 80% pure, 0.01 mole). The solution was allowed to sit for 30 min. before the solvent was removed *in vacuo*.

The residue was distilled over a small Vigreux column. The addition product XVI was collected at 80° (70 mm.); 0.95 g., 0.007 mole, 70%. Final purification was accomplished by v.p.c. on a polyadipate column on firebrick at 110°; infrared, 2.22 (m), 913, 897 cm.⁻¹; n.m.r., 8.8–9.6 (m), 8.35 (t), 7.25 (m), 4.33 (t) τ .

Anal. Calcd. for C₉H₁₂ (120.20): C, 89.94; H, 10.06. Found: C, 90.15; H, 10.17.

1-Diazo-2,3-dimethyl-2-butene (XIX).— α,β -Dimethylcrotonaldehyde (10 g., 0.037 mole) was dissolved in tetraglyme (50 ml.) containing sodium methoxide (4 g., 0.075 mole). The reaction flask was equipped with a take-off arm connected to a flask immersed in Dry Ice-acetone. The solution was heated *in vacuo* (0.4–0.5 mm.) to 70–75° bath temperature. Under these conditions the diazo compound distilled into the receiver flask while it was formed. The reaction was completed after about 40 min. The contents of the receiver flask was diluted with *n*-heptane to give a solution of the diazoalkene. Titration with benzoic acid was used to analyze the solution (0.026 mole, 70%); infrared, 2055 cm.⁻¹; vis.-methanol, λ_{\max} 515 m μ , ϵ 55.

Photolysis of 1-Diazo-2,3-dimethyl-2-butene (XIX).—A solution of XIX (0.025 mole) in *n*-heptane (50 ml.) was irradiated at –20° with a Hanovia high pressure arc (500 watt). The cylindrical reaction vessel was made of Pyrex, thus eliminating light with shorter wave length than 300 m μ . After approximately 3 hr. the solution was colorless. The reaction mixture was distilled and all volatile components boiling up to 95° were collected. Analysis of this distillate (4.6 g.) by v.p.c. and infrared showed, besides *n*-heptane, 1,3,3-trimethylcyclopropene (1.45 g., 0.018 mole, 70%) and 2,3-dimethyl-1,3-butadiene (1%). The latter compound was identified through comparison of its v.p.c. retention times with those of an authentic sample on two different columns.

Pyrolysis of 1-Diazo-2,3-dimethyl-2-butene (XIX).—A solution of XIX (0.022 mole) in diglyme (30 ml.) was added within 30 min. to refluxing diglyme (30 ml.). The reaction flask was equipped with a short Vigreux column which was connected with a receiver flask immersed in Dry Ice-acetone. The addition of the diazo compound and the heating of the reaction flask were regulated to prevent the solvent from distilling over the column while maintaining a gentle reflux. The distillate was washed with water twice and analyzed by v.p.c. and infrared spectrum. The mixture was found to be essentially pure 1,3,3-trimethylcyclopropene (1.5 g., 0.018 mole, 82%) containing some 2,3-dimethyl-1,3-butadiene (1.5%). The latter compound was identified by comparison of its v.p.c. retention times with those of an authentic sample on two different columns.

Preparation and Pyrolysis of 4-Diazo-2-methyl-2-pentene (XX).—Mesityl oxide tosylhydrazone (26 g., 0.1 mole) was added to a suspension of sodium hydride (0.12 mole) in triglyme (50 ml.). The mixture was heated *in vacuo* (100° bath temperature, 0.5 mm.) and the reaction product was allowed to distill into a receiving flask, containing diglyme, cooled with Dry Ice-acetone. The resulting dark red solution (vis., λ_{\max} 520 m μ) was pyrolyzed in a glass spiral heated to 180°. The volatile components from this pyrolysis were collected in trap cooled to –70°. Fractionation of the distillate gave 1,3,3-trimethylcyclopropene (1.5 g., 0.018 mole, 18%, m.p. 42–43°).

3,3,5-Trimethylpyrazolenine.—Sodium methoxide (8.1 g., 0.15 mole) was added to a cooled suspension of mesityl oxide tosylhydrazone (37.3 g., 0.14 mole) in tetraglyme (100 ml.). The resulting methanol was removed by distillation *in vacuo*. The remaining solution was slowly heated within 2 hr to 95°. The product was then distilled (0.5 mm.) from the reaction mixture by gradually warming the mixture to the boiling point of the solvent. Fractionation of the distillate gave 3,3,5-trimethylpyrazolenine (5.5 g., 0.05 mole, 36%) boiling at 75° (51 mm.); for physical data see Discussion. The compound proved to be stable to 180° and was distilled unchanged at 147–148° (750 mm.).

Anal. Calcd. for C₆H₁₀N₂ (110.16): C, 65.41; H, 9.15. Found: C, 65.49; H, 9.39.

(22) These values should be compared with the reported frequencies for the des-methyl compound.¹⁹