Δ^2-2,3-Dipropylcyclopropenyldiazomethanes. Generation from Nitrosourethane and Hydrazone Precursors[1a]

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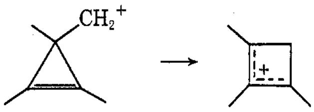
The decomposition of methyl (Δ^2-2,3-dipropylcyclopropenylcarbinyl)-*N*-nitrosourethane (**2**) with several bases has been studied. With potassium *tert*-butoxide the corresponding potassium diazotate salt is formed *via* carbonyl carbon attack. Hydrolysis leads only to carbonium ion products. With lithium ethoxide and sodium methoxide, attack at the nitroso N leads to 3,4-dipropylpyridazine (**8**) and methyl (Δ^2-2,3-dipropylcyclopropenylcarbinyl) carbonate (**6**) as major products *via* the corresponding diazocarbonate **10**. Cyclopropenyldiazomethane **11** is implicated as an intermediate in the formation of **8**. Oxidation of methyl (Δ^2-2,3-dipropylcyclopropenyl) ketohydrazone (**3**) with lead tetraacetate affords methyl (Δ^2-2,3-dipropylcyclopropenyl)carbinyl acetate (**15**). With mercuric oxide, **3** gives 3,4-dipropyl-6-methylpyridazine (**17**). Both reactions appear to involve the corresponding cyclopropenyldiazoalkane **16**.

While a great deal of attention has been focused in recent years on the cyclopropylcarbinyl system, relatively little work has been reported on the chemistry of the cyclopropene ring when joined to an unsaturated center.[2] The solvolysis of diphenyl- and dipropylcyclopropenylcarbinyl alcohol derivatives[3,4] is reported to afford products derived from the cyclobutenyl cation, which results from ring expansion. Although an analysis[3] of kinetic data suggested that the transition state for solvolysis has considerable cyclopropenylcarbinyl character, no report of the successful trapping of this species has appeared.[5]



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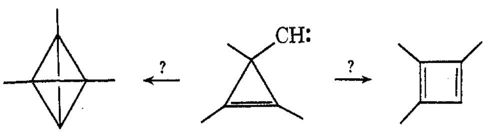
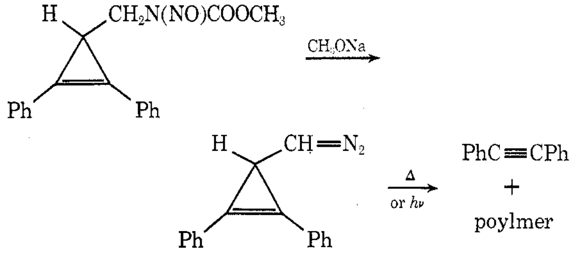
The reactivity of a carbenoid center adjacent to a cyclopropene ring is also of interest because of the formal relationship (eq 2) of a cyclopropenylcarbene



(2)

to cyclobutadiene[6] and tetrahedrane.[7] Closs and Rao[8] have reported that dimers of cyclobutadiene are formed in high yields by treatment of 1,2,3-trimethyl-3-(dichloromethyl)cyclopropene with *n*-butyllithium. White and coworkers[7a] attempted to generate diphenyltetrahedrane from diphenylcyclopropenyldiazomethane (**1**). The diazoalkane **1** was prepared by treating the corresponding nitrosourethane (eq 3) with "solid



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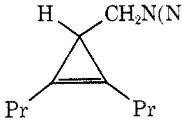
(3)

sodium methoxide containing some methanol of solvation." The thermal and photochemical decomposition of **1** leads mainly to diphenylacetylene and polymer. Masamune and Kato[7b] photolyzed the sodium salt of 1,2-diphenylcyclopropene-3-carboxaldehyde tosylhydrazone and obtained acetylene, diphenylacetylene, and a trace amount of a cyclobutenophenanthrene.

We have been interested for some time in the reactivity of a carbene adjacent to an alkyl-substituted cyclopropene. Of the variety of methods available for the generation of carbenes, the thermal decomposition of an α-diazocyclopropene seemed most appropriate in this case. Diazoalkanes are generally prepared[9] by the base-induced decomposition of *N*-nitrosourethanes or by hydrazone oxidation. We have prepared methyl (Δ^2-2,3-dipropylcyclopropenylcarbinyl)-*N*-nitrosourethane (**2**) and methyl (Δ^2-2,3-dipropylcyclopropenyl) ketohydrazone (**3**). In this paper we



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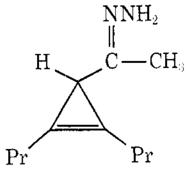

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report on the novel results obtained from studies on the decomposition of **2** using different alkoxide systems and on the oxidation of **3** with lead tetraacetate and mercuric oxide.

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[1] (a) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract ORGN 154. (b) National Science Foundation Graduate Trainee, 1970–1971.

[2] R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 233–295.

[3] R. Breslow and M. Battiste, *J. Amer. Chem. Soc.*, **82**, 3626 (1960); R. Breslow, J. Lockhart, and A. Small, *ibid.*, **84**, 2793 (1962).

[4] (a) P. Wolf, Ph.D. Thesis, Columbia University, 1964; (b) R. Breslow, H. Bozimo, and P. Wolf, *Tetrahedron Lett.*, 2395 (1970).

[5] A somewhat specialized case of the reverse rearrangement, *i.e.*, cyclobutenyl to cyclopropenylcarbinyl, has recently been discovered in this laboratory: J. Ciabattoni and A. E. Feiring, *J. Amer. Chem. Soc.*, **94**, 5113 (1972).

[6] M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.

[7] (a) E. H. White, G. E. Maier, R. Graeve, U. Zernibl, and E. W. Friend, *J. Amer. Chem. Soc.*, **88**, 611 (1966). (b) S. Masamune and M. Kato, *ibid.*, **87**, 4190 (1965); **88**, 610 (1966). (c) Additional attempts to generate tetrahedrane include H. W. Chang, A. Lautzenheiser, and A. P. Wolf, *Tetrahedron Lett.*, 6295 (1966); R. F. Peterson, R. T. K. Baker, and R. L. Wolfgang, *ibid.*, 4749 (1969); P. B. Shelvin and A. P. Wolf, *J. Amer. Chem. Soc.*, **92**, 406 (1970); H. Ona, H. Yamaguchi, and S. Masamune, *ibid.*, **92**, 7495 (1970); H. J. Hageman and U. E. Wiersum, *Chem. Commun.*, 497 (1971); M. S. Newman and M. W. Logue, *J. Org. Chem.*, **36**, 1398 (1971), and references cited therein.

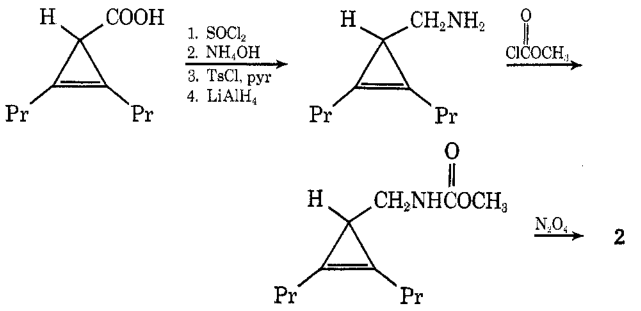
[8] G. L. Closs and V. N. M. Rao, *J. Amer. Chem. Soc.*, **88**, 4116 (1966).

[9] H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961, Chapter 1.

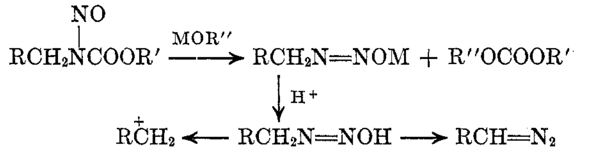
Results and Discussion

Decomposition of 2.—Methyl *N*-(Δ^2-2,3-dipropylcyclopropenylcarbinyl)urethane was prepared from Δ^2-2,3-dipropylcyclopropenecarboxylic acid[10] *via* the acid chloride, the amide, the nitrile, the amine, and reaction of the amine with methyl chloroformate (Scheme I). The *N*-nitrosourethane 2 was prepared by nitrosation of the urethane with dinitrogen tetroxide.[11] The nitrosourethane was purified by chromatography over silica gel and showed no detectable impurities by nmr or tlc.

SCHEME I



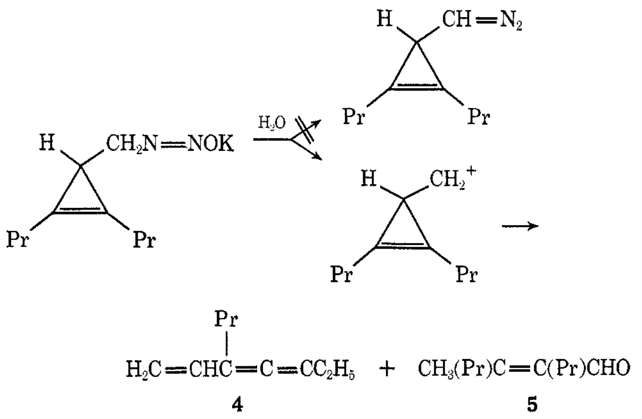
The reaction of alkoxide bases on nitrosourethanes is known to proceed *via* initial attack of base on either the carbonyl carbon or the nitroso N, depending on the type of substrate, base, and solvent used.[12] Attack of base at the carbonyl carbon affords a diazotate salt which is isolatable in the absence of a proton source. Protonation[13] of the diazotate salt affords a diazotic acid which partitions between diazoalkane and carbonium ion formation depending upon the structure of the alkyl group and the nature of the reaction medium. In 1966, Moss[13] reported that treatment of nitrosourethanes with potassium *tert*-butoxide in ether



$$\begin{array}{c} RCH_2\overset{NO}{N}COOR' \xrightarrow{MOR''} RCH_2N{=}NOM + R''OCOOR' \\ \downarrow H^+ \\ R\overset{+}{C}H_2 \longleftarrow RCH_2N{=}NOH \longrightarrow RCH{=}N_2 \end{array}$$

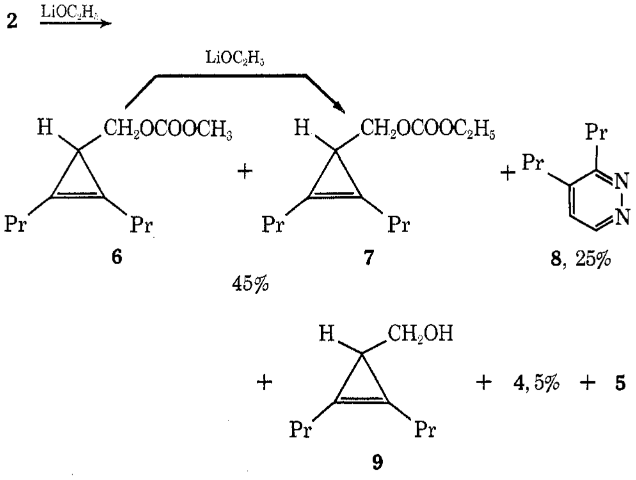
affords, *via* carbonyl attack, the corresponding potassium diazotate salts. For the particular case of the dipropylcyclopropenylcarbinyl system (Scheme II), hydrolysis of the diazotate salt afforded none of the expected diazoalkane but exclusively products 4 and 5 derived from a cyclopropenylcarbinyl cation.[4a] In our hands, addition of 2 to a slurry of potassium *tert*-butoxide in ether resulted in rapid disappearance of the yellow nitrosourethane color but no gas evolution. Subsequent hydrolysis after 20 min resulted in vigorous N_2 evolution. Glpc examination of the colorless ethereal solution was consistent with that reported[13] (Scheme II). No trace of diazoalkane could be detected.

SCHEME II



In contrast, addition of 2 to an ethereal slurry of anhydrous lithium ethoxide resulted in the gradual (*ca.* 0.5 hr) evolution of 75% of the theoretical yield of N_2. Conventional isolation procedures afforded methyl (Δ^2-2,3-dipropylcyclopropenylcarbinyl) carbonate (6), ethyl (Δ^2-2,3-dipropylcyclopropenylcarbinyl)-carbonate (7) (combined yields of 6 + 7, 45%), 3,4-dipropylpyridazine (8, 25%), 3-propyl-1,3,4-heptatriene (4, 5%), and trace amounts of Δ^2-2,3-dipropylcyclopropenylcarbinyl alcohol (9) and *cis*- and *trans*-2-propyl-3-methyl-2-hexenal (5) (Scheme III). Appropriate control experiments demonstrated that ethyl carbonate 7 and alcohol 9 were secondary products arising from attack of ethoxide ion on the initially formed methyl carbonate 6. The relative amounts of 6 and 7 varied as a function of reaction time; a longer reaction time increased the yield of 7 at the expense of 6.

SCHEME III



The results of the lithium ethoxide decomposition of 2 are most readily explained by assuming initial attack of base on the nitroso N[12] to generate a cyclic intermediate (Scheme IV) followed by ring opening to generate the diazocarbonate 10. Intermediate 10 is similar to that proposed in the thermal decomposition of nitrosoamide derivatives.[14] The nature of the products indicates two modes of decomposition of 10. Loss of nitrogen generates a cyclopropenylcarbinyl cation–carbonate anion ion pair which, in the nonpolar solvent, largely collapses to 6 before rearrangement can occur. The small amounts of rearranged carbonium ion products (*i.e.*, 4 and 5) result from the

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[10] R. Breslow, H. Hover, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

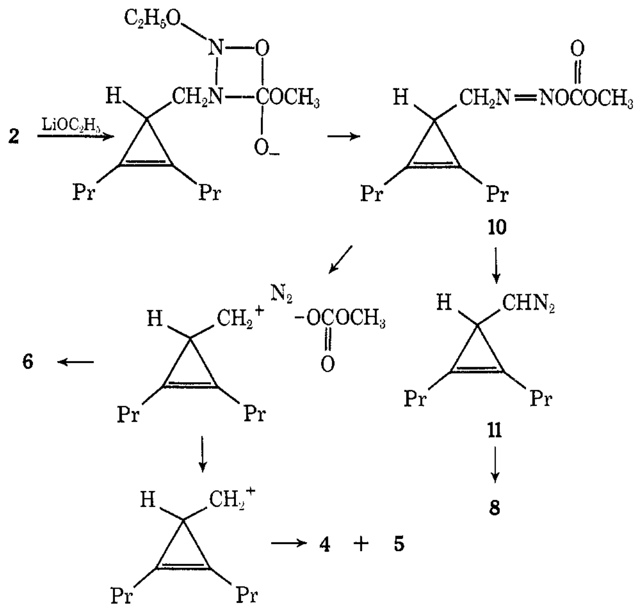
[11] E. H. White, *ibid.*, **77**, 6008 (1955).

[12] W. M. Jones and D. L. Muck, *ibid.*, **88**, 3798 (1966).

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

[14] E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 440–458.

SCHEME IV

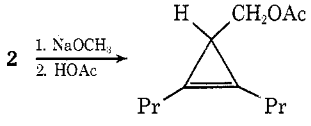


small proportion of cyclopropenylcarbinyl cation which escapes from the solvent cage before collapse to **6**. A second mode for decomposition of **10** is suggested by the formation of pyridazine **8**. Under the basic reaction conditions, loss of an α proton from **10** followed by or simultaneous with loss of carbonate anion generates diazoalkane **11**. Thermal rearrangement of **11** affords the observed regiospecific 3,4-dipropylpyridazine (**8**). Apparently the rate of rearrangement of **11** is competitive with its rate of formation, as its presence under the above conditions (*vide infra*) could not be directly detected. Quenching of a reaction mixture with acetic acid before completion afforded only a mixture of the above products plus unchanged starting material.

While we have not been able to obtain direct evidence for this mechanism, it appears attractive for several reasons. First, it accounts for N_2 loss and product formation prior to hydrolysis. Second, the observation of a high percentage of carbonate product with the unrearranged cyclopropenylcarbinyl system appears to require some intermediate (*i.e.*, **10**) which can efficiently produce a cyclopropenylcarbinyl cation–carbonate anion ion pair under the reaction conditions. If intermolecular attack by carbonate anion on some other intermediate were the source of **6**, the lack of observed products arising from attack of the more nucleophilic ethoxide ion, present in excess, is difficult to explain. Finally the rearrangement of **11** to **8** has precedent[2] in other rearrangements of cyclopropene derivatives to form six-membered rings. Although the tendency for lithium alkoxide bases to promote attack on the nitroso N has been previously observed,[12] we are unaware of another example in which the change in base effects the radical change in product composition observed in this case.

More definitive evidence for the intermediacy of diazoalkane **11** was obtained by decomposition of **2** with sodium methoxide. Addition of **2** to an ethereal slurry of sodium methoxide containing some methanol[7a] resulted in a rapid (*ca.* 5 min) evolution of 52% of the theoretical yield of N_2 and the simultaneous formation of a pink color in the ether solution. An infrared spectrum of the mixture at this point showed a strong band at 2050 cm^{-1} consistent with the presence of diazoalkane. After several hours the color faded with little additional gas evolution. The products, in addition to considerable quantities of nonvolatile residue, were **6** (15%), **8** (15%), **4**(15%), and a large number of trace products (by glpc), two of which were identified as alcohol **9** and unsaturated aldehyde **5**. Examination of the crude reaction mixture by glpc indicated the absence of 4-octyne and methyl (Δ^2-2,3-dipropylcyclopropenylcarbinyl) ether in the mixture (the latter was independently synthesized for comparison of glpc retention times). Despite the fact that nmr of the crude mixture showed complete destruction of the nitrosourethane, only 12% dimethyl carbonate was detected by glpc.

Quenching of a 5-min-old slurry of **2** and sodium methoxide in ether with excess glacial acetic acid produced a second vigorous evolution of N_2 and immediate disappearance of the pink color. Nmr of the crude mixture (which in this case contained little nonvolatile material) showed complete destruction of the nitrosourethane **2**. Glpc of the reaction mixture was compatible with that obtained above, except that in this case no pyridazine **8** was present. Instead a new product, comprising 38% of the mixture by glpc, was present, which was collected by preparative glpc and identified as Δ^2-2,3-dipropylcyclopropenylcarbinyl acetate (**12**).



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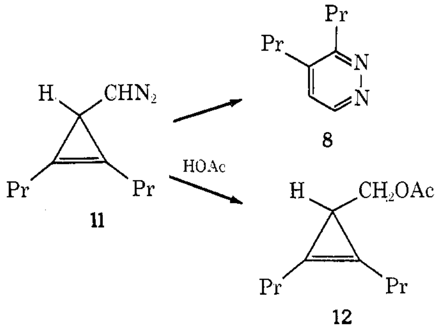
The isolation of only 12% dimethyl carbonate from the sodium methoxide decomposition of **2** suggests that this reaction also proceeds largely from attack of base on the nitroso N (Scheme IV). In this case, however, formation of the diazoalkane **11** appears to be much faster than in the lithium ethoxide case. This results in a buildup of **11** in solution, as evidenced by the solution color and infrared spectrum. The isolation of acetate **12** confirms the structure of **11**,



as diazoalkanes are known to react rapidly with carboxylic acids to give unrearranged product esters.[15] Furthermore, the fact that the acetic acid quench eliminated formation of the pyridazine **8** with little effect on the other reaction products suggests that pyridazine alone arises from the diazoalkane intermediate.

It is interesting to note that little nonvolatile ma-

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[15] D. Y. Curtin and S. M. Gerber, *J. Amer. Chem. Soc.*, **74**, 4052 (1952).

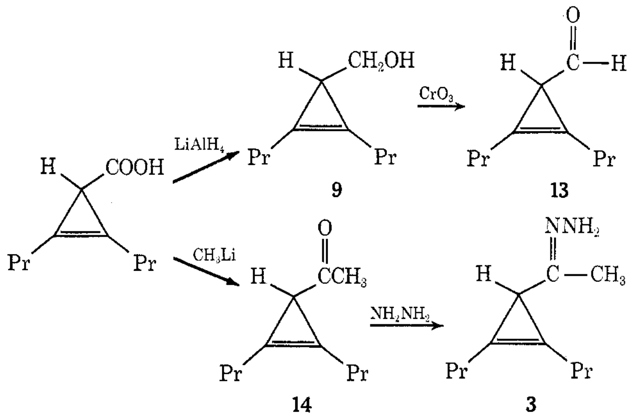
terial was obtained from the reaction mixture quenched by acetic acid and that the residue from the mixtures which were allowed to proceed without quenching showed a strong band at 1640 cm^{-1} in the infrared. These facts suggest that azine formation may be partially responsible for the low overall product yields in the sodium methoxide case. Quenching the mixture with acetic acid is seen to eliminate azine formation as well as pyridazine formation, accounting for the somewhat higher yield of acetate **12** (38% by glpc) as compared to the yield of pyridazine in unquenched reactions (20% by glpc, see Experimental Section). The somewhat cleaner results obtained from the lithium ethoxide reaction may, therefore, be due in part to slower initial attack of base on the nitrosourethane. The rate of formation of diazoalkane is roughly the same as its rate of unimolecular rearrangement to pyridazine; its concentration in solution remains low, thereby largely eliminating bimolecular reaction to form azine. The reason for the difference in rate of attack by lithium ethoxide and sodium methoxide is, however, not known.

The possibility that some of the results reported here might be due to a thermal decomposition of nitrosourethane **2** was ruled out by the finding that **2** was completely stable to the reaction conditions in the absence of base for over 24 hr (no detectable impurities by nmr). The compound could be recovered in pure form in 73% yield by column chromatography after 24-hr reflux in cyclohexane.

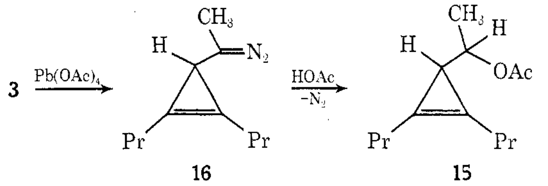
Oxidation of 3.—Oxidation[9] of the hydrazone of Δ^2-2,3-dipropylcyclopropenecarboxaldehyde (**13**) was expected to provide an independent synthesis of the diazoalkane **11** implicated in the alkoxide decomposition of **2**. The aldehyde **13** was prepared as shown in Scheme V. The reduction of Δ^2-2,3-dipropylcyclopropenecarboxylic acid[10] with $LiAlH_4$ is reported[4a] to lead to a mixture of the cyclopropenylcarbinyl alcohol **9** and a saturated alcohol arising from homoconjugate reduction of the double bond. We have found that carrying out the reduction in ether at −40° eliminates overreduction, providing in high yield the desired unsaturated alcohol **9**. Careful oxidation of **9** with dipyridine–chromium trioxide complex in methylene chloride (the Collins reagent[16]) afforded the aldehyde **13**. In our hands, however, the aldehyde was a rather unstable oil which was difficult to purify and did not provide satisfactory derivatives.

We turned out attention, therefore, to the corresponding methyl ketone **14**, which was prepared according to published procedures[17] from Δ^2-2,3-dipropylcyclopropenecarboxylic acid and methyllithium. Treatment of **14** with excess hydrazine in methanol afforded, in excellent yield, the corresponding hydrazone **3** as a colorless oil which decomposed rapidly neat but was stable for prolonged periods in solution. It could be recovered unchanged after refluxing for 8 hr in ethanol.[18] The samples used for oxidation were freshly prepared and contained no detectable impurities by nmr or ir spectroscopy.

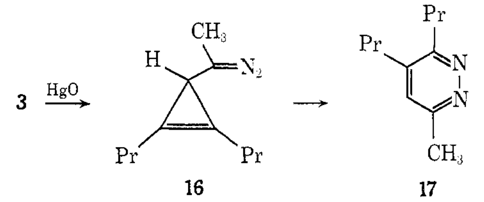
Scheme V



Addition of a methylene chloride solution of **3** to a slight excess of lead tetraacetate[19] in methylene chloride resulted in immediate nitrogen evolution and formation of a white precipitate of lead diacetate. Conventional isolation procedures involving silica gel chromatography afforded a 51% yield of methyl (Δ^2-2,3-dipropylcyclopropenyl)carbinyl acetate (**15**). This reaction is believed to involve[19] oxidation of the hydrazone to the corresponding diazoalkane **16** followed by reaction of the diazoalkane with the *in situ* generated acetic acid. As in the case of the sodium methoxide decomposition of **2** followed by quenching with acetic acid, reaction of the diazoalkane with acid is faster than rearrangement to a pyridazine.



Pyridazine product, however, was obtained from the mercuric oxide oxidation of **3**. Stirring a suspension of red mercuric oxide and hydrazone **3** at high speed for 24 hr in pentane resulted in little gas evolution. Work-up afforded in 58% isolated yield (67% by nmr of the crude reaction mixture) an oil the structure of which was assigned as 3,4-dipropyl-6-methylpyridazine (**17**).



These results, when combined with those from the alkoxide-induced decomposition of **2**, leave little doubt that dipropylcyclopropenyldiazomethanes rearrange with reasonable efficiency to the corresponding pyridazines. The mechanism of this rearrangement appears to involve a formal 1,4-sigmatropic shift of a cyclopropene σ bond. An alternate possibility (Scheme VI) that rearrangement involves an intramolecular 1,3-dipolar cycloaddition of the diazoalkane group to

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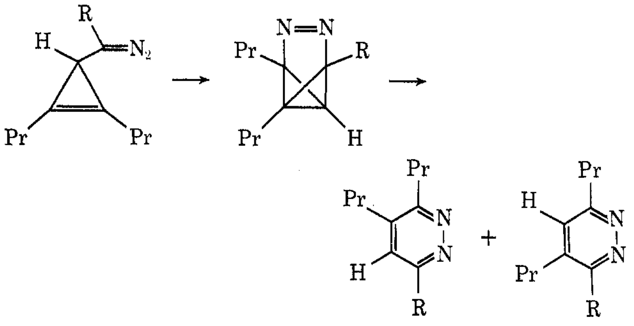
[16] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

[17] M. Vidal, E. Chollet, and P. Arnaud, *ibid.*, 1073 (1967).

[18] Phenyl (Δ^2-2,3-dipropylcyclopropenyl) ketohydrazone is reported to rearrange under the conditions of its synthesis (refluxing ethanol) to a dihydropyridazine: R. Breslow, R. Boikess, and M. Battiste, *ibid.*, **No. 26**, **42** (1960); N. Obata and I. Moritani, *Bull. Chem. Soc. Jap.*, **39**, 2250 (1966).

[19] D. H. R. Barton, J. F. McGhie, and P. L. Batton, *J. Chem. Soc. C*, 1033 (1970).

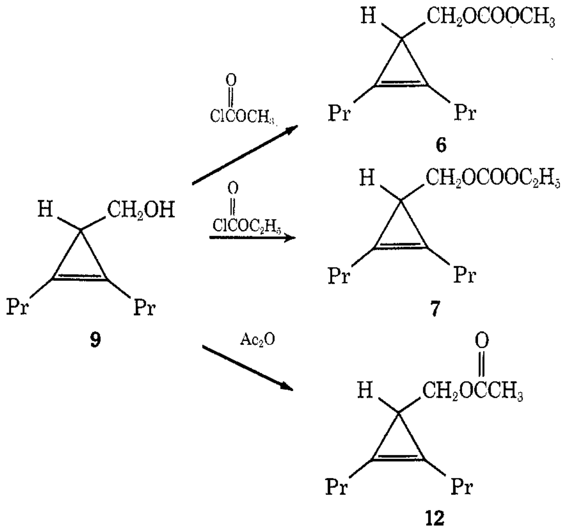
Scheme VI



the cyclopropene double bond[20] followed by a bicyclobutane–butadiene type of rearrangement[21] is less likely, since it should lead to the production of two isomeric pyridazines, contrary to what was observed.

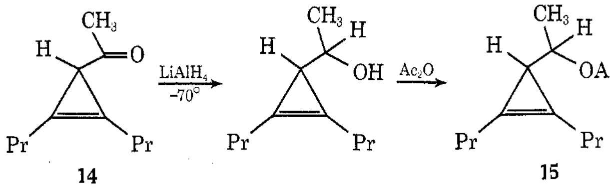
It is interesting to note that, for diphenylcyclopropenyldiazomethane,[7a] nitrogen loss followed by or simultaneous with fragmentation to acetylene and diphenylacetylene is the major mode of decomposition, whereas in the dipropyl case rearrangement to pyridazine predominates (no 4-octyne was detected in any experiment).

Product Identification.—In addition to their nmr and ir spectra (see Experimental Section), the identities of reaction products which are derivatives of Δ^2-2,3-dipropylcyclopropenylcarbinyl alcohol (**9**) were confirmed by independent synthesis. Treatment of **9** with methyl or ethyl chloroformate in pyridine afforded samples of **6** and **7**, respectively, identical with the products from the lithium ethoxide induced decomposition of **2**. Acylation of **9** with acetic anhydride afforded in acetate identical with **12**.



Lithium aluminum hydride reduction of methyl (Δ^2-2,3-dipropylcyclopropenyl) ketone at −70°, followed by acylation with acetic anhydride in pyridine, afforded an acetate **15** identical with the product from the lead tetraacetate oxidation of hydrazone **3**.

The pyridazine structure **8** was assigned on the basis of the following data. Elemental analysis and mass spectrum (*m/e* 164) were consistent with the formula $C_{10}H_{16}N_2$. A prominent ion at *m/e* 136 ($M^+ - N_2$) was also observed in the mass spectrum.[22] The ir showed sharp absorptions at 1580 and 1560 cm^{-1}, and the uv showed maxima at 254, 258, and 335 mμ, characteristic of the pyridazine structure.[23] The nmr spectrum, in addition to two nonequivalent propyl groups, showed clean one-proton doublets at 7.27 and 8.92 ppm with a coupling constant of 5.2 Hz. The chemical shifts and coupling constants of the aromatic protons are consistent only with the assigned pyridazine substitution pattern; the observed coupling constants for pyridazine protons are $J_{3,4} = 5.05$ and $J_{3,5} = 2.0$ Hz.[23]



In a similar fashion, the elemental analysis and mass spectrum (*m/e* 178) of **17** established its formula as $C_{11}H_{18}N_2$. Its ir and uv spectra closely resembled those obtained for pyridazine **8**. The nmr showed, in addition to the nonequivalent propyl groups, sharp singlets at 2.62 (CH_3) and 7.10 ppm (aromatic H).

Structural assignments for **4** and **5** are based on their glpc and spectroscopic (ir and nmr) identity with the major products from the potassium *tert*-butoxide decomposition of **2**.[13]

Experimental Section

Melting points were obtained on a Kofler micro heating stage; all melting and boiling points are uncorrected. Infrared and ultraviolet spectra were recorded with a Perkin-Elmer 337 spectrophotometer and a Cary Model 14 recording spectrophotometer, respectively. Infrared spectra were recorded as films unless otherwise indicated; only bands important for structure proof are reported. All nmr spectra were run on a Varian A-60A instrument in the indicated solvents. Chemical shifts are reported in parts per million from tetramethylsilane and the number in parentheses indicates the number of protons responsible for the signal. The letter denotes the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad singlet. Mass spectra were obtained with an Hitachi RMU-6D instrument. Gas–liquid partition chromatographic (glpc) analyses were obtained with an Aerograph A-90P instrument using a 10 ft × 0.25 in. column of 15% SE-30 on Chromosorb W. Relative peak areas were measured by disk integration and are not corrected for detector response.

Gas evolution was measured by water displacement; reported volumes are corrected for the vapor pressure of water and to standard conditions of temperature and pressure. All reactions were run in an atmosphere of prepurified nitrogen or argon.

The purity of all new compounds was checked by glpc or tlc, and, where stability permitted, by elemental analysis (Galbraith Laboratories, Knoxville, Tenn.).

Materials.—Ethyl ether, benzene, and hydrocarbon solvents were freshly distilled from $LiAlH_4$. Pyridine was distilled from BaO. The following reagents were obtained from the indicated source and were used as received: anhydrous sodium methoxide (Matheson Coleman and Bell), anhydrous potassium *tert*-butoxide (MSA Research Corp.), methyllithium (Alfa), lithium ribbon (City Chemical Corp.), dinitrogen tetroxide ("nitrogen dioxide," Matheson), methyl and ethyl chloroformate (Aldrich), 4-octyne (Farchan), mercuric oxide (Baker). Lead tetraacetate (G. Fredrich Smith Co.) was recrystallized from glacial acetic acid and dried *in vacuo* immediately before use. Tosyl chloride

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[20] H. M. Cohen, *J. Heterocycl. Chem.*, **4**, 130 (1967).

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

[22] S. J. Weininger and E. R. Thornton, *ibid.*, **89**, 2050 (1967); M. H. Benn, T. S. Saensen, and A. M. Hagg, *Chem. Commun.*, 574 (1967).

[23] M. Tisler and B. Stanovnik in "Advances in Heterocyclic Chemistry," Vol. 9, A. R. Katritsky and A. J. Baulton, Ed., Academic Press, New York, N. Y., 1968.

was purified according to Fieser.[24] Lithium ethoxide was prepared according to a published procedure.[25] The product was dried for 6 hr at 100° (2 mm) and used immediately. Column chromatography was performed using Baker 60–200 mesh silica gel; thin layer chromatography (tlc) was performed on precoated silica gel plates purchased from E. Merck & Co.

Δ^2-2,3-Dipropylcyclopropenecarboxamide.—Freshly distilled thionyl chloride (25 ml) was added dropwise over 0.5 hr to a stirred solution of 25.2 g (0.15 mol) of Δ^2-2,3-dipropylcyclopropenecarboxylic acid[10] in 25 ml of benzene. The dark mixture was then refluxed under nitrogen for 3 hr and cooled and the benzene and excess thionyl chloride were removed *in vacuo*. The dark brown oil was distilled to give the colorless acid chloride: bp 72° (0.5 mm) [lit.[26] bp 59–61° (0.2 mm)]; ir 1900 (w), 1780 cm^{-1} (s).

The acid chloride was dissolved in 100 ml of ether and added dropwise to a stirred mixture of 300 ml of concentrated NH_4OH and 600 ml of ether. The layers were separated and the aqueous solution was extracted once with 50 ml of ether. The combined ether solutions were washed twice with water and twice with saturated aqueous NaCl solution. Evaporation of the ether *in vacuo* left a white solid which was recrystallized from cyclohexane to give 21 g (85%) of white needles: mp 107–109° (lit.[26] mp 106–106.5°); ir (KBr) 3350 (s), 3275 (s), 1890 (w), 1630 cm^{-1} (s); nmr ($CDCl_3$) δ 0.97 (6 H, t), 1.55 (4 H, m), 1.95 (1 H, s), 2.43 (4 H, t), 6.0 (2 H, bs).

1-Cyano-2,3-dipropylcycloprop-2-ene.—Freshly purified tosyl chloride[24] (22.9 g, 0.12 mol) was added portionwise over 0.5 hr to a stirred solution of 14 g (0.084 mol) of Δ^2-2,3-dipropylcyclopropenecarboxamide in 125 ml of dry pyridine. The solution temperature was maintained between 5 and 10° by means of an ice bath. A thick precipitate which formed during the addition required that an additional 50 ml of pyridine be added to maintain stirring. The mixture was stirred at 5° for 45 min after the addition was complete. The mixture was then poured into 300 ml of water and the aqueous solution was extracted with three 100-ml portions of ether. The combined ether extracts were washed with 5% aqueous HCl, water, and saturated aqueous NaCl and dried ($MgSO_4$). Evaporation of the ether *in vacuo* left a faintly brown oil which was distilled to give 11.6 g (93%) of colorless nitrile: bp 72° (0.9 mm); ir 2220 (m), 1880 cm^{-1} (w); nmr ($CDCl_3$) δ 0.97 (6 H, t), 1.55 (4 H, m), 1.68 (1 H, s), 2.43 (4 H, t).

Δ^2-2,3-Dipropylcyclopropenylcarbinylamine.—A solution of 14.9 g (0.1 mol) of 1-cyano-2,3-dipropylcycloprop-2-ene in 30 ml of dry ethyl ether was added dropwise over 0.5 hr to a rapidly stirred suspension of 4.5 g (0.12 mol) of $LiAlH_4$ in 90 ml of ether at 0°. After the addition was complete, the mixture was stirred at 0° for 5 hr. Excess hydride was decomposed by the dropwise addition of 10% NaOH solution. The white granular precipitate which formed was filtered off and washed with fresh ether. The combined ether solutions were washed with saturated aqueous NaCl and dried ($MgSO_4$). Evaporation of the ether *in vacuo* left a faintly brown oil which was distilled to give 12.1 g (79%) of amine: bp 82° (20 mm); ir 3360 (m), 3280 (m), 1860 cm^{-1} (w); nmr ($CDCl_3$) δ 0.97 (8 H, t + s), 1.55 (5 H, m), 2.43 (4 H, t), 2.63 (2 H, d). Treatment of the nmr sample with D_2O caused a two proton decrease in the integral at δ 0.97.

The amine was converted to its hydrochloride with HCl in ether; after three recrystallizations from ether–pentane it melted at 134–135°.

Anal. Calcd for $C_{10}H_{20}NCl$: C, 63.29; H, 10.62; N, 7.32. Found: C, 63.33; H, 10.47; N, 7.18.

Methyl *N*-(Δ^2-2,3-Dipropylcyclopropenylcarbinyl)urethane.—Excess methyl chloroformate (4 ml) was added dropwise over 10 min to a stirred solution of 3.33 g (22 mmol) of Δ^2-2,3-dipropylcyclopropenylcarbinylamine, 30 ml of benzene, and 5 ml of dry pyridine cooled in an ice bath. When the addition was complete, the ice bath was removed and the mixture was stirred for an additional 0.5 hr. The mixture was poured into ice water (100 ml) and the layers were separated. The aqueous solution was washed once with benzene. The combined organic layers were washed with cold 5% aqueous HCl, 10% aqueous $NaHCO_3$, water, and saturated aqueous NaCl and dried ($MgSO_4$). Evaporation of the benzene *in vacuo* left a brown oil which was distilled to yield 3.7 g (82%) of colorless urethane: bp 81–83° (0.4 mm); ir 3340 (s), 1850 (w), 1700 cm^{-1} (s); nmr ($CDCl_3$) δ 0.97 (6 H, t), 1.55 (5 H, m), 2.43 (4 H, t), 3.10 (2 H, t), 3.59 (3 H, s), 5.87 (1 H, bs).

Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02. Found: C, 67.86; H, 9.72.

Methyl *N*-(Δ^2-2,3-Dipropylcyclopropenylcarbinyl)-*N*-nitrosourethane (2).—Dinitrogen tetroxide (2 ml, 3 g) was condensed in a calibrated trap at −40°. The trap was then warmed to room temperature and the N_2O_4 was distilled into 100 ml of dry ether at −20° to give a *ca.* 0.32 *M* solution.

A 100-ml round-bottom flask, equipped with magnetic stirring, thermometer, and gas inlet extending to the bottom of the flask, was charged with 1.37 g (6 mmol) of methyl *N*-(Δ^2-2,3-dipropylcyclopropenylcarbinyl)urethane, 0.88 g (10 mmol) of anhydrous NaOAc, and 30 ml of dry ethyl ether. The mixture was cooled to −70° with a Dry Ice–acetone bath and argon was slowly bubbled into the solution. To this vigorously stirred mixture was added 30 ml (*ca.* 10 mmol) of the precooled N_2O_4 in ether solution by means of a syringe. The green solution which resulted was stirred under argon at −70° for 1.25 hr. The solution was then poured with stirring into 50 ml of 5% aqueous NH_4OH and the layers were separated. The organic layer was washed with 10% aqueous $NaHCO_3$, water, and saturated aqueous NaCl and dried ($MgSO_4$). Evaporation of the ether *in vacuo* at room temperature returned a green oil. The oil was taken up in a small volume of hexane and chromatographed on 45 g of silica gel. The column was eluted with 100 ml of hexane, then 300 ml of 5% ether in hexane. A distinctly yellow band separated and was collected. Evaporation of the solvent *in vacuo* gave 850 mg (58%) of the nitrosourethane as a yellow oil, homogeneous on tlc: ir 1870 (w), 1755 cm^{-1} (s); nmr ($CDCl_3$) δ 0.95 (6 H, t), 1.45 (5 H, m), 2.30 (4 H, t), 3.65 (2 H, d), 3.95 (3 H, s).

Δ^2-2,3-Dipropylcyclopropenylcarbinyl Alcohol (9).[4a]—A solution of 20.2 g (0.12 mol) of Δ^2-2,3-dipropylcyclopropenecarboxylic acid[10] in 50 ml of dry ethyl ether was added dropwise over 1.5 hr to a stirred suspension of 8.8 g (0.24 mol) of $LiAlH_4$ in 100 ml of ether at −40°. The solution was stirred at −40° for 1 hr after the addition was complete, and then allowed to warm to room temperature and stirred for 2.5 hr. Excess hydride was destroyed by the dropwise addition of 5% aqueous NaOH. The white, granular precipitate was filtered off and extracted with 100 ml of boiling ether. The combined ether layers were washed with 5% aqueous NaOH, water, and saturated aqueous NaCl. After drying ($MgSO_4$), the ether was removed *in vacuo*, leaving a faintly yellow oil. The oil was distilled to give 16.9 g (92%) of colorless alcohol: bp 74–75° (1.5 mm); ir 3360 (s), 1870 cm^{-1} (w); nmr ($CDCl_3$) δ 0.97 (6 H, t), 1.55 (5 H, m), 2.43 (4 H, t), 3.53 (2 H, d), 4.1 (1 H, bs).

Δ^2-2,3-Dipropylcyclopropenecarboxaldehyde (13).—A solution of 6.2 g (0.04 mol) of Δ^2-2,3-dipropylcyclopropenylcarbinyl alcohol in 50 ml of methylene chloride was added to 62 g of dipyridine chromium trioxide complex (Collins reagent)[16] in 650 ml of methylene chloride. After stirring for 0.75 hr at room temperature the mixture was filtered and concentrated *in vacuo* to a black oil. The oil was taken up in 200 ml of ethyl ether and filtered through a short column of silica gel. The filtrate was concentrated *in vacuo* to a yellow oil. Distillation afforded 4.2 g (70%) of product: bp 80–83° (3.5 mm); ir 2770 (m), 2690 (m), 1895 (w), 1690 cm^{-1} (s); nmr (neat) δ 0.97 (6 H, t), 1.53 (4 H, m), 2.12 (1 H, d) 2.65 (4 H, t), 8.75 (1 H, d). The compound rapidly turned yellow upon standing in air.

Methyl (Δ^2-2,3-Dipropylcyclopropenylcarbinyl) Carbonate (6).—To a solution of 2.31 g (15 mmol) of 9 and 5 ml of pyridine in 50 ml of benzene, cooled in an ice bath, was added over 20 min a solution of 5 ml of methyl chloroformate in 5 ml of benzene. After the addition was complete, the ice bath was removed and the mixture was stirred for an additional 30 min. The mixture was then poured into 100 ml of 5% aqueous HCl and the layers were separated. The benzene layer was washed with 10% aqueous $NaHCO_3$ and saturated aqueous NaCl. After drying ($MgSO_4$), the solution was concentrated *in vacuo* to an oil. Distillation of the oil through a 6-in. Pt gauze column gave 2.42 g (80%) of product: bp 50° (0.05 mm); ir 1870 (w), 1750 cm^{-1} (s); nmr ($CDCl_3$) δ 0.97 (6 H, t), 1.53 (5 H, m), 2.42 (4 H, t), 3.68 (3 H, s), 3.98 (2 H, d); mass spectrum *m/e* 212.

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.76; H, 9.61.

Ethyl (Δ^2-2,3-Dipropylcyclopropenylcarbinyl) Carbonate (7).—

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[24] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 1180.

[25] T. L. Brown, D. W. Dicherhoof, and D. A. Bafus, *J. Amer. Chem. Soc.*, **84**, 1371 (1962).

[26] C. Ruechardt and H. Schwarzer, *Chem. Ber.*, **99**, 1871 (1966).

Using ethyl chloroformate, **7** was prepared in identical fashion as described above for the preparation of **6**. The product was obtained in 71% yield: bp 62-63° (0.5 mm); ir 1750 cm^{-1} (s); nmr ($CDCl_3$) δ 0.97 (6 H, t), 1.30 (3 H, t), 1.53 (5 H, m), 2.42 (4H, t), 4.03 (2 H, d), 4.20 (2 H, t), mass spectrum *m/e* 226.

Methyl (Δ^2-2,3-Dipropylcyclopropenylcarbinyl) Ether.—A solution of 1.54 g (10 mmol) of **9** in 30 ml of ether, cooled in a Dry Ice–isopropyl alcohol bath, was treated with a 1.8 *M* solution of methyllithium ether until gas evolution ceased. After the solution had warmed to room temperature, excess methyl iodide was added and the mixture was refluxed for 24 hr. After aqueous work-up, glpc at 160° showed a 70:30 mixture of two components. The components were collected by preparative glpc and the first was identified as the desired ether: ir 1860 (w), 1110 cm^{-1} (s); nmr ($CDCl_3$) δ 0.97 (6 H, t), 1.50 (5 H, m), 2.42 (4 H, t), 3.27 (2 H, d), 3.33 (3 H, s). The second component was identified as the starting alcohol.

Δ^2-2,3-Dipropylcyclopropenylcarbinyl Acetate (12).[4a]—A solution of 250 mg (1.4 mmol) of **9** in 10 ml of pyridine was treated with 2 ml of acetic anhydride over 10 min. The solution was stirred for a few minutes and then poured into 50 ml of 5% aqueous HCl. The aqueous solution was extracted twice with 50 ml of ether. The combined ether extracts were washed with water and saturated aqueous NaCl. After drying ($MgSO_4$), the ether was removed *in vacuo* to give 230 mg of an oil, homogeneous on glpc: ir 1860 (w), 1740 cm^{-1} (s); nmr (CCl_4) δ 0.97 (6 H, t), 1.52 (5 H, m), 1.90 (3 H, s), 2.35 (4 H, t), 3.80 (2 H, d).

Methyl (Δ^2-2,3-Dipropylcyclopropenyl) Ketone (14).—Modifying the published procedure,[17] 32 ml of a 2.0 *M* solution of methyllithium in ether was added over 1 hr to an ice-cold solution of 5 g (30 mmol) of Δ^2-2,3-dipropylcyclopropenecarboxylic acid in 30 ml of ether. After the addition was complete, the solution was stirred at 0° for 1 hr, then poured with stirring into 30 ml of cold water. The layers were separated and the ether solution was washed with 5% aqueous NaOH, water, and saturated aqueous NaCl. After drying ($MgSO_4$), the ether was removed *in vacuo*. Distillation of the remaining oil gave 4.1 g (83%) of colorless ketone, bp 50-51° (0.45 mm) [lit.[17] bp 63-64° (1.4 mm)], 2,4-DNP mp 147.5-148° (EtOH).

Methyl (Δ^2-2,3-Dipropylcyclopropenyl) Ketohydrazone (3).—A solution of 1.4 g (8.5 mmol) of **14** and 1.3 g (40 mmol) of 85% hydrazine in 40 ml of methanol was stirred at room temperature for 48 hr. Methanol and most of the excess hydrazine were removed *in vacuo* at room temperature, leaving a faintly yellow oil. The oil was taken up in ether, washed with water and saturated aqueous NaCl, and dried ($MgSO_4$). Evaporation of the ether *in vacuo* left a colorless oil (1.5 g): ir 3360 (s), 3210 (m), 1880 (w), 1620 cm^{-1} (s); nmr ($CDCl_3$) δ 0.97 (6 H, t), 1.40 (3 H, s), 1.57 (4 H, m), 2.17 (1 H, s), 2.42 (4 H, t), 4.50 (2 H, bs). The hydrazone was used without further purification; it was stored in methylene chloride solution at −5°.

Methyl (Δ^2-2,3-Dipropylcyclopropenyl)carbinyl Acetate (15).—A solution of 1.7 g (10 mmol) of **14** in 20 ml of ether was added over 0.25 hr to a suspension of 0.38 g (10 mmol) of $LiAlH_4$ in ether at −70°. After addition was complete the mixture was stirred for 1 hr at −70° and then for 2 hr at room temperature. Destruction of the excess $LiAlH_4$ with 5% aqueous NaOH, followed by the usual work-up, gave 1.4 g (84%) of colorless alcohol: ir 3400 (s), 1860 cm^{-1} (w); nmr (neat) δ 0.95 (6 H, t), 1.08 (3 H, d), 1.53 (5 H, m), 2.42 (4 H, t), 3.53 (1 H, dq), 3.62 (1 H, bs).

Without further purification, 0.7 g of the alcohol was stirred overnight with 1 ml of acetic anhydride in 15 ml of pyridine. The solution was concentrated *in vacuo*, leaving a brown oil. Distillation of the oil through an 8-in spinning band column afforded 0.6 g (73%) of colorless acetate: bp 70-71° (2.1 mm); ir 1860 (w), 1740 cm^{-1} (s); nmr (neat) δ 0.95 (6 H, t), 1.10 (3 H, d), 1.50 (5 H, m), 1.88 (3 H, s), 2.38 (4 H, t), 4.58 (1 H, dq).

Attempted Thermal Decomposition of 2.—A solution of 0.425 g of **2** in 30 ml of cyclohexane was refluxed for 24 hr. No gas evolution was detected. The solution was cooled and the cyclohexane was removed *in vacuo*. Nmr of the recovered material (0.410 g) indicated it to be essentially pure **2**.

Potassium *tert*-Butoxide Decomposition of 2.—A solution of 0.82 g (3.4 mmol) of **2** in 10 ml of ether was added to a cold (−30°) suspension of 0.78 g (7 mmol) of potassium *tert*-butoxide in ether. No gas evolution was detected. After the solution was stirred for 20 min, 5 ml of water was injected into the mixture, resulting in a vigorous evolution of gas. The layers were separated and the colorless ether layer was washed with saturated aqueous NaCl. After drying ($MgSO_4$) the solution was concentrated *in vacuo* to a pale yellow oil (0.89 g). Glpc of the oil (160°) showed components with retention times of 4 and 10 min, which were identified by Moss as 3-propyl-1,3,4-heptatriene and 2-propyl-3-methyl-2-hexenal, respectively. No peaks with a longer retention time were observed.

Lithium Ethoxide Decomposition of 2.—To a stirred suspension of 0.42 g (8 mmol) of anhydrous lithium ethoxide in 30 ml of ether was rapidly added 0.97 g (4 mmol) of **2** in 20 ml of ether. A gradual evolution of 68 ml (75%) of N_2 occurred over 0.5 hr accompanied by fading of the yellow nitrosourethane color. After the solution was stirred for 3 hr at room temperature, 10 ml of water was added. The layers were separated and the ether layer was washed with saturated aqueous NaCl. After drying ($MgSO_4$), the ether solution was concentrated *in vacuo* to a brown oil (0.67 g). Nmr of the oil showed no trace of the starting nitrosourethane (absence of singlet at 3.95 ppm).

The oil was chromatographed on 20 g of silica gel. Progress of the chromatograph was monitored by glpc (160°). Elution with hexane (100 ml) afforded 30 mg (5%) of an oil with glpc retention time of 4 min. Its nmr and ir spectra were comparable with the data reported for 3-propyl-1,3,4-heptatriene.[4a]

Elution with 5% ether in hexane (250 ml) afforded 380 mg of an oil. Glpc showed it to be a mixture of two major components in a 2:3 ratio with retention times of 22 and 32.5 min, respectively, plus trace amounts of two overlapping peaks (9 and 10 min). The major components were isolated by preparative glpc and identified as the methyl carbonate **6** and the ethyl carbonate **7** by comparison of their spectral properties with those of authentic samples. The two trace components had the retention times of Δ^2-2,3-dipropylcyclopropenylcarbinyl alcohol (**9**) and *cis*- and *trans*-2-propyl-3-methyl-2-hexenal (**5**). Nmr of the components collected together showed aldehyde protons at 10.00 and 10.08 ppm and a doublet at 3.53 ppm characteristic of **9**. Treatment of the mixture with 2,4-DNP reagent afforded a derivative, mp 144–150° (CH_3OH).

Continued elution of the column with 500 ml of ether afforded 170 mg (25%) of a single component oil (glpc retention time 36.5 min) identified as 3,4-dipropylpyridazine (**8**): ir 3050 (w), 1580 (m), 1560 cm^{-1} (m); nmr ($CDCl_3$) δ 1.03 (6 H, t), 1.72 (4 H, m), 2.67 (2 H, t), 3.00 (2 H, t), 7.27 (1 H, d, J = 5.2 Hz), 8.92 (1 H, d, J = 5.2 Hz); mass spectrum *m/e* 164, 136; uv $\lambda_{\max}^{\text{pentane}}$ 254 mμ (log ϵ 2.9), 258 (2.9), 334 (2.2). Preparative glpc afforded an analytical sample.

Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.12; H, 9.83; N, 17.05. Found: C, 73.15; H, 9.85; N, 16.95.

Reaction of 6 with Lithium Ethoxide.—A solution of **6** (100 mg) and lithium ethoxide (100 mg) in ether (20 ml) was stirred at room temperature for 3 hr. The reaction was quenched with 20 ml of water and the layers were separated. Glpc of the ether solution revealed virtually complete conversion of **6** to a mixture of the ethyl carbonate **7** (85%) and alcohol **9** (15%).

Sodium Ethoxide Decomposition of 2. A.—A solution of 2.1 g (9 mmol) of **2** and 2 drops of methanol in 30 ml of ether was rapidly added to a stirred suspension of 1.2 g (22 mmol) of anhydrous sodium methoxide in 20 ml of ether. Within 5 min, 105 ml (52%) of gas was collected and the solution turned a faint pink. After the solution was stirred for 4 hr at room temperature, the pink color had faded with little further gas evolution. An aliquot of the mixture was removed and examined by glpc (80°) for the presence of 4-octyne and dimethyl carbonate. By comparing the glpc traces of the reaction mixture and appropriate calibration mixtures, the yields of 4-octyne (<1.4%) and dimethyl carbonate (12%) could be estimated.

The rest of the mixture was quenched with 20 ml of water. After the mixture was stirred for a few minutes, the layers were separated and the organic layer was washed with saturated aqueous NaCl. After drying ($MgSO_4$), the ether solution was concentrated *in vacuo* to a brown oil (1.4 g). Nmr of the oil showed no trace of **2** (absence of 3 H singlet at 3.95 ppm). Glpc of the mixture (160°) showed a mixture of *ca.* ten products; addition of small amounts of methyl (Δ^2-2,3-dipropylcyclopropenylcarbinyl) ether to the reaction mixture followed by glpc demonstrated that none of the peaks corresponded to the ether.

The mixture was chromatographed on 40 g of silica gel as described above. Elution with hexane afforded 60 mg (5%) of 3-propyl-1,3,4-heptatriene (**4**). Elution with 20% ether in hexane afforded 710 mg of oil containing six minor compounds

(60%) (glpc retention times of 4.5–14 min) and one major component (40%) (time 22 min). Isolation by preparative glpc afforded the major component methyl (Δ^2-2,3-dipropylcyclopropenylcarbinyl) carbonate **6**. Two of the minor components were identified as Δ^2-2,3-dipropylcyclopropenylcarbinyl alcohol (**9**) and *cis*- and *trans*-2-propyl-3-methyl-2-hexenal (**5**) as described above. Elution with ether then afforded 200 mg (15%) of 3,4-dipropylpyridazine (**8**).

B.—A 5-min-old slurry of 200 mg (3.7 mmol) of sodium methoxide, 425 mg (1.7 mmol) of **2**, and 1 drop of methanol in 30 ml of ether was quenched by the addition of 4 ml of glacial acetic acid, resulting in vigorous gas evolution. The mixture was poured into 50 ml of water and the layers were separated. The ether layer was washed with water, 10% aqueous $NaHCO_3$, and saturated aqueous NaCl. After drying ($MgSO_4$), the solution was concentrated *in vacuo* to an oil (300 mg). Nmr showed no absorption at 3.95 ppm. Molecular distillation of the oil at 100° (0.05 mm) left no residue. Glpc (160°) showed a group of seven peaks with retention times of 4 to 14 min (38%), and two major peaks with retention times of 15.5 (38%) and 22 min (24%) (percentage by disk integration of peak areas). The peak with retention time of 22 min corresponded to the methyl carbonate **6**; none of the pyridazine **8** (retention time 36.5 min) could be detected. The peak with a retention time of 15.5 min was collected by preparative glpc and identified as Δ^2-2,3-dipropylcyclopropenylcarbinyl acetate (**12**) by spectral comparison with an authentic sample.

By comparison, a mixture of 1.14 g (4.8 mmol) of **2** and 0.59 g (11 mmol) of $NaOCH_3$ when decomposed as in part A afforded only 0.4 g of oil when subjected to molecular distillation at 100° (0.05 mm), leaving *ca.* 100 mg of nonvolatile residue which showed an infrared band at 1640 cm^{-1}. Glpc of the oil (160°) showed the group of seven peaks with retention times of 4 to 14 min (33%), and peaks with retention times of 22 (27%) and 36.5 min (20%). The latter two corresponded to the previously identified methyl carbonate **6** and pyridazine **8**. (Glpc percentages total 80%; the remaining 20% of the reaction mixture is the nonvolatile material removed by distillation.)

C.—A 5-min-old slurry of 270 mg (5 mmol) of sodium methoxide, 600 mg (2.5 mmol) of **2**, and 1 drop of methanol in 10 ml of ether was filtered in an inert atmosphere. An aliquot of the pink filtrate was transferred *via* syringe to an infrared cell. The infrared spectrum showed a strong diazo band at 2040 cm^{-1}.

Reaction of 6 with Sodium Methoxide.—A solution of 200 mg of **6** in 10 ml of ether was treated with 600 mg of sodium methoxide. After the solution was stirred for 3.5 hr at room temperature, 10 ml of water was added and the layers were separated. The ether layer was washed with saturated aqueous NaCl and dried ($MgSO_4$). Glpc (160°) showed a mixture of 15% of Δ^2-2,3-dipropylcyclopropenylcarbinyl alcohol and 85% of **6**.

Lead Tetraacetate Oxidation of 3.—A solution of 2.7 g (15 mmol) of **3** in 40 ml of methylene chloride was added over 1.5 hr to an ice-cold solution of 9.8 g (22 mmol) of lead tetraacetate in 80 ml of methylene chloride. Nitrogen evolution was evident during the addition and a white precipitate of lead acetate formed. After the addition was complete, the mixture was allowed to warm to room temperature for 0.5 hr. The mixture was poured into 30 ml of water and the layers were separated. The organic phase was washed with 10% aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated *in vacuo* to an oil (3.3 g). The oil (2 g) was chromatographed on 30 g of silica gel. Elution with hexane (100 ml) afforded 0.197 g of an unidentified unsaturated acetate, ir 3040 (m), 1740 (s), 1630 cm^{-1} (w), no cyclopropene C=C. Elution with 25% ether in hexane afforded 1.0 g (51%) of methyl (Δ^2-2,3-dipropylcyclopropenyl)carbinyl acetate (**15**), identical with an authentic sample.

Mercuric Oxide Oxidation of 3.—A solution of 2.3 g (13 mmol) of **3** in 20 ml of petroleum ether (bp 30–60°) was added over 10 min to a suspension of 6.1 g (26 mmol) of mercuric oxide (yellow powder) in 200 ml of petroleum ether. The mixture was stirred at high speed in a 500-ml Morton flask at room temperature for 24 hr.

The mixture was filtered through a bed of $MgSO_4$ and the filtrate was concentrated *in vacuo* to a brown oil (2.2 g). The oil was chromatographed on 50 g of silica gel. Elution with 600 ml of 1:3 ether–hexane afforded a dark multicomponent oil which was not investigated further. Elution with 450 ml of 3:1 ether–hexane afforded 1.35 g (58%) of a single-component oil by glpc, identified as 3,4-dipropyl-6-methylpyridazine (**17**): ir 3030 (w), 1590 (s), 1540 cm^{-1} (w); nmr ($CDCl_3$) δ 1.00 (6 H, t), 1.78 (4 H, m), 2.58 (2 H, t), 2.62 (3 H, s), 2.95 (2 H, t), 7.10 (1 H, s); uv $\lambda_{\max}^{\text{pet ether}}$ 262 mμ (log ϵ 3.3), 334 (2.5); mass spectrum *m/e* 178, 163, 150, 135. An analytical sample was obtained by preparative glpc as a colorless oil.

Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18. Found: C, 74.30; H, 10.26.

Thermal Stability of 3.—A solution of 3 (0.7 g) in 50 ml of absolute ethanol was refluxed for 18 hr. The ethanol was removed *in vacuo* at room temperature. The nmr and ir spectra of the residue were identical with those from freshly prepared **3**.

A solution of **3** (150 mg) in 0.5 ml of $CDCl_3$ was placed in a sealed nmr tube. The nmr spectrum showed an 18:2 integral ratio of CH (δ 0.95–2.42) to NH protons (δ 4.50). After 24 hr at room temperature the ratio was 18:1.3, consistent with gradual azine formation. No changes were observed in the CH portion of the spectrum.

Registry No.—**2,** 35890-03-0; **6,** 35890-04-1; **7,** 35890-05-2; **8,** 35890-06-3; **9,** 35890-07-4; **13,** 35890-08-5; **15,** 35890-09-6; **17,** 35890-10-9; 1-cyano-2,3-dipropylcycloprop-2-ene, 7525-49-7; Δ^2-2,3-dipropylcyclopropenylcarbinylamine, 35890-12-1; Δ^2-2,3-dipropylcyclopropenylcarbinylamine hydrochloride, 35890-13-2; methyl *N*-(Δ^2-2,3-dipropylcyclopropenylcarbinyl)urethane, 7572-55-6.

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Photolysis of Phenyl- and Diphenyldiazomethanes in Alkyl and Allylic Sulfides

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Photolysis of phenyl- and diphenyldiazomethanes in dimethyl sulfide gives ortho-substituted sulfur compounds through the sulfonium ylide intermediate. Photodecomposition of phenyldiazomethane in benzyl methyl sulfide gives the insertion product of phenylcarbene into benzyl hydrogen, presumably by ylide rearrangement of the benzyl group. The reaction in allylic sulfides gave allyl(alkylthio)arylmethanes together with some cyclopropane derivatives. Thermal decomposition of phenyldiazomethane gives only addition product, but diphenyldiazomethane gives both addition and insertion products.

Dialkyl sulfides give stable sulfur ylides by addition of singlet carbenes containing strongly electron-withdrawing substituents. Bis(phenylsulfonyl)carbene could be trapped with di-*n*-butyl sulfide to give the ylide.[1] The photoinduced reaction of diazo biscar-

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[1] J. Diekmann, *J. Org. Chem.*, **28**, 2933 (1963); **30**, 2272 (1965).