Chemistry of Dicyclopropylcarbene and Related Intermediates in Dimethyl Sulfoxide

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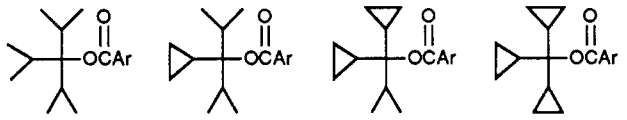
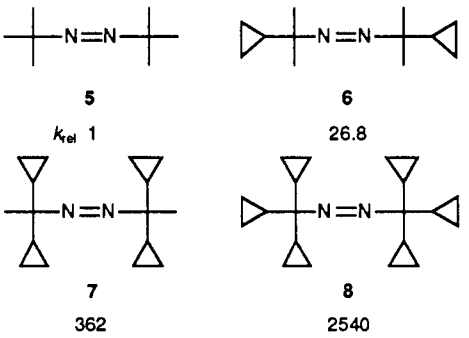
The potassium salts of the anions of (phenylsulfonyl)hydrazones of diisopropyl, isopropyl cyclopropyl, and dicyclopropyl ketone were decomposed in dimethyl sulfoxide in the temperature range of 110–130 °C. The diisopropyl phenylsulfonyl anion decomposes to form 2,4-dimethyl-2-pentene and diisopropyl ketone. Similar decomposition of the isopropyl cyclopropyl substrate forms 1-cyclopropyl-2-methylpropene, 1-isopropylcyclobutene, and isopropyl cyclopropyl ketone, while thermal decomposition of the dicyclopropyl ketone (phenylsulfonyl)-hydrazone anion forms cyclopropylcyclobutene and dicyclopropyl ketone. The rate constants for the first and second steps of the consecutive first-order decomposition of the (phenylsulfonyl)hydrazone anions were determined over the temperature range of 110–130 °C. The activation parameters $\Delta H^{\ddagger}$ (kcal/mol), $\Delta S^{\ddagger}$ (eu), and $\Delta G^{\ddagger}$ (kcal/mol) were calculated for the diazo compound to carbene step (k_2) for the diisopropyl (15.6 ± 1.1, −30.9 ± 2.8, and 27.7 ± 1.6), the isopropyl cyclopropyl (27.7 ± 2.0, 3.3 ± 5.1, and 26.4 ± 2.8), and the dicyclopropyl (36.8 ± 1.8, 28.4 ± 4.6, 25.6 ± 2.5). These results are discussed in terms of two factors: interaction of the cyclopropane ring with the functional group and orientation of the polar solvent.

The role of the cyclopropyl group in stabilizing reactive intermediates has been an important theme in the development of modern physical organic chemistry. The studies of Roberts and co-workers on the solvolytic reactions of cyclopropylcarbinyl systems led to the suggestion of the bicyclobutonium ion.[1] Schleyer and co-workers measured rates of solvolysis of methylated cyclopropylcarbinyl 3,5-dinitrobenzoates and proposed a symmetrical bisected cyclopropylcarbinyl cation.[2] Hart and co-workers analyzed the solvolyses of the *p*-nitrobenzoate (benzoate) esters in the series triisopropylcarbinyl through tricyclopropylcarbinyl and observed the rate enhancements listed (**1**–**4**).[3] Overall, the cyclopropyl group is more effective at stabilizing an adjacent carbocation center than is phenyl or vinyl.[3,4]



	1	2	3	4
k_{rel}^{OPNB}	1	246	23 500	
$k_{rel}^{O_2CPh}$			1	1080

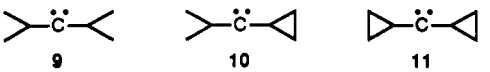
Cyclopropyl groups are also quite effective at stabilizing free radical intermediates[5] as revealed, for example, in the enhanced rate for decomposition of cyclopropaneacetyl peroxide relative to cyclohexaneacetyl peroxide.[6] Martin and Timberlake measured the rates of decomposition of the dialkyl azo substrates **5**–**8** and observed a monotonic increase with increasing cyclopropyl substitution analogous to the carbocation case.[7] Recent studies of cyclopropyl-



	5	6	7	8
k_{rel}	1	26.8	362	2540

carbene species have focused on intermolecular reactivity,[8a] the mechanism of ring expansion,[8b] the stereochemistry of fragmentation,[8c] and the syntheses of novel strained systems.[8d]

With use of the carbocation studies of Hart and coworkers as a model plan of attack, the goal of the present study was to characterize the nature of cyclopropylcarbenes by measuring the rate of formation of diisopropylcarbene (**9**), isopropylcyclopropylcarbene (**10**), and dicyclopropylcarbene (**11**) and identifying the products generated.



9 **10** **11**

Our initial plan called for the use of the consecutive unimolecular two-step tosylhydrazone salt decomposition (eq 1) and the determination of the rate constants for both steps (k_1 and k_2). Since alkali-metal salts of tosyl-

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(2) Buss, V.; Gleiter, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3927. Ree, B. R.; Martin, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 1660. Schleyer, P. v. R.; Van Dine, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 2321.

(3) Hart, H.; Saundri, J. M. *J. Am. Chem. Soc.* **1959**, *81*, 320. Hart, H.; Law, P. A. *J. Am. Chem. Soc.* **1964**, *86*, 1957.

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(6) Hart, H.; Wyman, D. P. *J. Am. Chem. Soc.* **1959**, *81*, 4891. Hart, H.; Cipriani, R. A. *J. Am. Chem. Soc.* **1962**, *84*, 3697–700.

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(8) (a) Moss, R. A.; Vezza, M.; Guo, W.; Munjal, R. C.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1979**, *101*, 5088. Moss, R. A.; Fantina, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 6788. Békhazi, M.; Risbood, P. A.; Warkentin, J. *J. Am. Chem. Soc.* **1983**, *105*, 5675. (b) Schoeller, W. W. *J. Org. Chem.* **1980**, *45*, 2161. (c) Olin, S. S.; Venable, R. M. *J. Chem. Soc., Chem. Commun.* **1974**, 273. (d) Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E.; Dailey, W. P.; Burgmaier, G. J.; Bailey, W. F.; Warner, P. *Tetrahedron* **1986**, *42*, 1895. Komatsu, K.; Tomioka, I.; Okamoto, K. *Tetrahedron Lett.* **1980**, 947. Teraji, T.; Moritani, I.; Tsuda, E. *J. Chem. Soc. C* **1971**, 3252. For earlier references, see: Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; pp 32–36.

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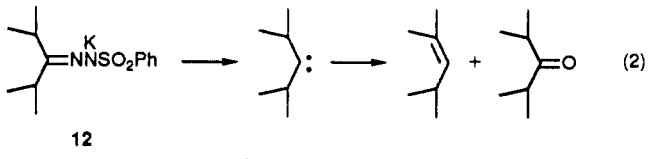
$$R_2C{=}N\overset{M}{N}Ts \xrightarrow{k_1} \underset{M^+Ts^-}{R_2C{=}N_2} \xrightarrow{k_2} R_2C: + N_2 \quad (1)$$

hydrazones of ketones are insufficiently soluble in diglyme, the traditional solvent, potassium salts of the tosylhydrazones of diisopropyl, isopropyl cyclopropyl, and dicyclopropyl ketone were prepared by treatment with potassium hydride and their solubilities tested in diglyme in the presence of complexing agent 18-crown-6. The resulting solubilities, however, were not improved adequately for our kinetic analyses. At this point two changes were made. The solvent was changed to dimethyl sulfoxide, in which the potassium salts were sufficiently soluble, without crown ether, and the leaving group was changed to benzenesulfinate by switching to (phenylsulfonyl)hydrazones. The latter change was employed to speed up the first step in order to achieve a better curve fit in the kinetic analyses.

With the optimized conditions established, characterization of the product arrays generated for each substrate was undertaken. The (phenylsulfonyl)hydrazones were each converted to their corresponding potassium salts by treatment with potassium hydride in dry THF. The potassium salts were isolated and then allowed to decompose in dry dimethyl sulfoxide in the temperature range of 110–130 °C. The products generated in the decomposition of the potassium salt of the (phenylsulfonyl)hydrazone of diisopropyl ketone are 2,4-dimethyl-2-pentene and diisopropyl ketone in an isolated yield of 60% in a ratio of 42:18 (eq 2). Similar treatment of the potassium salt of the



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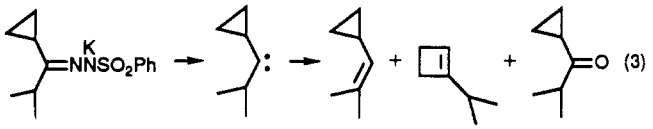

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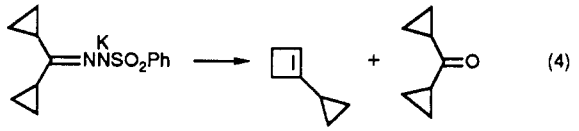

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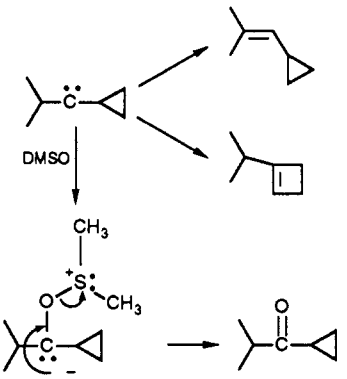
(phenylsulfonyl)hydrazone of cyclopropyl isopropyl ketone formed 1-cyclopropyl-2-methyl-1-propene, 1-isopropylcyclobutene, and cyclopropyl isopropyl ketone in an isolated yield of 56% in a ratio of 21:16:19 (eq 3), while the thermal decomposition of the potassium salt of the (phenylsulfonyl)hydrazone of dicyclopropyl ketone resulted in an isolated yield of 58% of 1-cyclopropylcyclobutene and dicyclopropyl ketone in 28:30 ratio (eq 4).

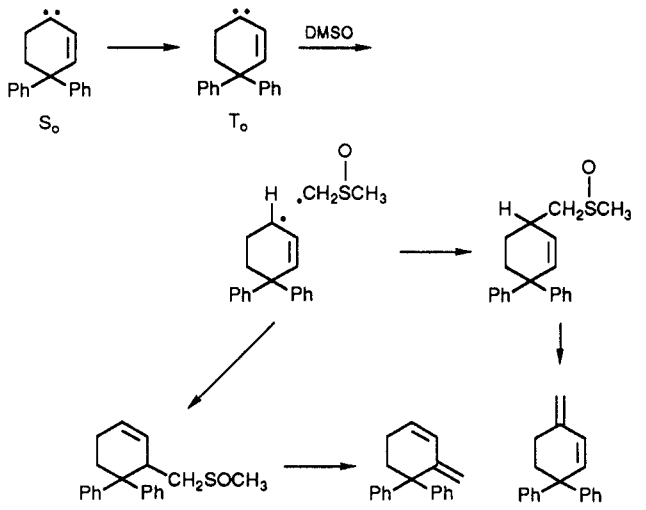
The reactions of isopropylcyclopropylcarbene illustrate all pathways for the series: hydride migration to form 1-cyclopropyl-2-methylpropene, cyclopropyl to cyclobutyl ring expansion, and oxygen abstraction from the solvent (Scheme I). Oxygen abstraction is viewed as proceeding through the zwitterion pictured in Scheme I.[9] γ-insertion is not observed in any of the three decompositions, in contrast to the γ-insertion found for isopropylcarbene, which exhibits a ratio of γ-insertion/hydride migration of 33:67. This may be explained in terms of a more rapid hydride migration in the case of diisopropylcarbene, since

(9) Oda, R.; Meino, M.; Hayashi, Y. *Tetrahedron Lett.* **1967**, *25*, 2363.

Scheme I



Scheme II



this leads to a trialkylated alkene rather than to isobutylene, a disubstituted terminal alkene. In the case of isopropylcyclopropylcarbene, no γ-insertion is observed and hydride migration occurs only in the direction that forms an unstrained double bond. Dicyclopropylcarbene reacts exclusively by ring expansion and oxygen abstraction. Hydride migration would produce a strained methylenecyclopropane derivative, whereas γ-insertion would form a strained bicyclobutane ring system. The results for isopropylcyclopropylcarbene and dicyclopropylcarbene are consistent with those of Friedman and Shechter,[10] who found that cyclopropylmethylcarbene underwent ring expansion and hydride migration to vinylcyclopropane in a 92:1 ratio, with no evidence for hydride migration to form a strained methylenecyclopropane derivative. In a similar vein, Bēkhazi et al. have found that dicyclopropylcarbene undergoes ring expansion in benzene or chlorine atom abstraction in CCl_4 or intermolecular C–H insertion in $CHCl_3$.[8a] It seems reasonable to view all these processes as singlet-state processes;[8,11] no evidence was uncovered for triplet-state hydrogen abstraction processes similar to those found for 4,4-diphenylcyclohexenylidene and related carbenes[12] (Scheme II).

The rate constants for diazo compound formation from (phenylsulfonyl)hydrazone salt (BH) (k_1) and carbene formation from diazo compound (k_2) (eq 1) were determined by measuring the nitrogen evolved versus time and

(10) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002.
(11) Sohn, M. B.; Jones, M., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 8280. Moritani, I.; Yamanoto, Y.; Murahashi, S.-I. *Tetrahedron Lett.* **1968**, 5697. Jones, M., Jr.; Ando, W. *J. Am. Chem. Soc.* **1968**, *90*, 2200.
(12) Freeman, P. K.; Tafesh, A. M.; Clapp, G. E. *J. Org. Chem.* **1989**, *54*, 782.

Table I. Rate Constants for the First and Second Steps in the Decompositions of the Potassium Salts of Ketone (Phenylsulfonyl)hydrazones 12, 13, and 14

temp (°C)	10^3k_1	10^3k_2
Potassium Salt of Diisopropyl Ketone (Phenylsulfonyl)hydrazone (12)		
110	0.687	1.92
115	1.09	2.70
120	1.99 ± 0.03	3.18 ± 0.2
125	3.10	4.14
130	4.32	5.92
Potassium Salt of Cyclopropyl Isopropyl Ketone (Phenylsulfonyl)hydrazone (13)		
110	1.20 ± 0.06	6.52 ± 1.0
115	1.78 ± 0.02	11.9 ± 2.7
120	2.90 ± 0.04	18.4 ± 0.8
125	4.23 ± 0.05	24.1 ± 1.9
130	6.13 ± 0.19	47.0 ± 2.4
Potassium Salt of Dicyclopropyl Ketone (Phenylsulfonyl)hydrazone (14)		
110	0.578	12.9
115	0.699	28.2
120	1.52 ± 0.0	48.9 ± 3.2
125	2.17	97.3
130	3.03	150.0

Table II. Activation Parameters for the Decomposition of the Potassium Salts of Ketone (Phenylsulfonyl)hydrazones

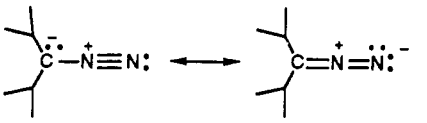
reaction	E_a	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
diisopropyl				
step 1	28.9 ± 1.4	28.1 ± 1.4	0.0 ± 3.6	28.1 ± 2.0
step 2	16.4 ± 1.1	15.6 ± 1.1	−30.9 ± 2.8	27.7 ± 1.6
cyclopropyl isopropyl				
step 1	25.2 ± 0.6	24.5 ± 0.6	−8.6 ± 1.5	24.7 ± 0.8
step 2	28.5 ± 2.0	27.7 ± 2.0	3.3 ± 5.1	26.4 ± 2.8
dicyclopropyl				
step 1	27.2 ± 2.9	26.4 ± 2.9	−4.9 ± 7.3	28.3 ± 4.0
step 2	37.6 ± 1.8	36.8 ± 1.8	28.4 ± 4.6	25.6 ± 2.5

fitting the data obtained to the integrated rate equation (eq 5) using a nonlinear least-squares curve fitting program (PCNONLIN).

$$[N_2] = \frac{[BH]_0}{k_2 - k_1}[k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})] \qquad (5)$$

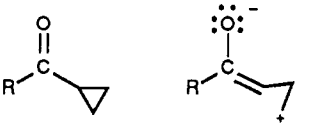
The rate constants obtained are listed in Table I and the activation parameters for the first and second steps in Table II. It is the rate constant for the second step (k_2) that is of paramount importance, since it governs the rate of carbene formation. The integrated rate expression (eq 5) is, however, symmetrical (k_1 and k_2 may be switched without changing the value of the expression), so that it is necessary to establish which constant pertains to the first step. Rate constants for the disappearance of starting (phenylsulfonyl)hydrazone salt of isopropyl cyclopropyl ketone (k_1) were determined independently by HPLC at 110 °C, (1.24 ± 0.12) × 10^{-3} s^{-1}, and 130 °C, (6.26 ± 0.35) × 10^{-3} s^{-1}. A similar analysis of k_1 for dicyclopropyl ketone (phenylsulfonyl)hydrazone at 130 °C provided a value of (1.97 ± 0.07) × 10^{-3} s^{-1}. The slow step in these two cases is clearly the first step. With these results as a guide, the activation parameters for the diisopropyl ketone (phenylsulfonyl)hydrazone were calculated from the data in Table I, assuming the slow step represents the first step. That this assumption is correct was verified by independently determining the activation parameters for the conversion of diisopropyl ketone (phenylsulfonyl)-hydrazone to diazo compound (k_1) by HPLC: E_a = 27.5 ± 1.2 kcal/mol, $\Delta H^\ddagger$ = 26.7 ± 1.2, and $\Delta S^\ddagger$ = 3.3 ± 3.1 eu. Thus the first step is insensitive to structural change.

If one focuses attention on the diazo compound to carbene fission step (k_2), it is noteworthy that replacement of isopropyl with cyclopropyl results in an increase in rate and E_a and $\Delta H^\ddagger$. The increases in E_a and $\Delta H^\ddagger$ are counterbalanced by a favorable trend in entropy of activation, which increases dramatically, bringing the free energies of activation into agreement (within experimental error). The negative entropy of activation for diisopropylcarbene formation can be understood in terms of the change in dipole moment. The starting diazo compound can be represented as a resonance hybrid of forms A and B, which are nearly equally balanced in importance (B slightly more important). The C–N fission, which leads to the transition state, would be expected to disconnect the p π bonding before the C_{sp^2}–N_{sp} bonding due to the more extensive σ overlap of carbon sp hybrids relative to p π overlap.[13] To the extent that the disconnection of the p π system is predominant, resonance form A will be predominant and may lead to an increased dipole moment, increased orientation of the polar dimethyl sulfoxide solvent and, thus, a negative entropy of activation.



A B

In contrast to the diisopropyl case, the entropy of activation for isopropylcyclopropyl is neutral, while that for dicyclopropyl is highly favorable (28.4 eu). It appears that the trend in entropy of activation is the result of the effect of cyclopropyl upon the polarity of starting diazo compound. The dramatic effect that cyclopropyl groups have upon the polarity of the closely related carbonyl group is nicely illustrated by the retention times observed for diisopropyl (10.9 min), isopropyl cyclopropyl (20.9 min), and dicyclopropyl ketone (56.0 min) on a Carbowax gas chromatographic column. The enhanced polarities for cyclopropyl ketones may be rationalized by invoking an additional charged separated resonance form (D) illustrated in the resonance hybrid (C ↔ D).

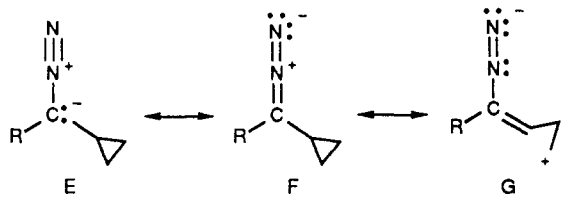


C D

In a similar manner, an additional charge-separated form may contribute to a ground-state cyclopropyldiazomethane species as illustrated in E ↔ F ↔ G. In the carbene generation step, therefore, as the C–N bond distance is increased, the participation of the cyclopropane is reduced, and the dipole moment is reduced, thus leading to less ordering of the solvent and a positive entropy of activation. This also explains the ordering of enthalpies of activation. As isopropyl groups are replaced by cyclopropyl groups, the dipole moment of the ground state is increased, leading to greater stabilization by solvent and a larger enthalpy of activation.

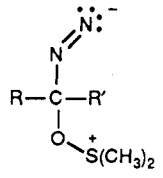
Since oxygen is transferred in the process under consideration, one could reconsider the mechanism for the decomposition (eq 1). Perhaps solvent participation (k_3) competes with diazoalkane decomposition (k_2), with solvent participation leading to ketone. If this were the case, one would expect $\Delta S^\ddagger$ to decrease as the ratio k_3/k_2 increases. This is not the case, however, as $\Delta S^\ddagger$ increases

(13) Roberts, J. D. *Notes on Molecular Orbital Calculations*; Benjamin: New York, 1961; pp 29–30.
(14) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.



E F G

as the fraction of ketone increases. Alternatively, one might consider attack of solvent nucleophile upon the starting (phenylsulfonyl)hydrazone anion. This is most easily visualized as an S_N2' process generating intermediate **15**. Such a process should proceed, however, more readily



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with the neutral parent (phenylsulfonyl)hydrazone. The (phenylsulfonyl)hydrazones of diisopropyl, cyclopropyl isopropyl, and dicyclopropyl ketone were tested under the reaction conditions at 120 °C and found to be completely unreactive, thus suggesting that the simplest and preferable mechanism is the classic one illustrated in eq 1.

Experimental Section

General. The melting points reported were determined on a Büchi melting point apparatus. Melting and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer 727B spectrometer. The spectra of solids were obtained by using KBr pellets and those of liquids were obtained in CCl_4 solution using NaCl plates. Proton NMR spectra were recorded on a Varian Associates FT-80 and a Brüker AM-400 spectrometer (80 and 400 MHz). ^{13}C NMR spectra were recorded on the FT-80 spectrometer at 20 MHz. The GC–mass spectra were obtained on a Finnigan 4023 mass spectrometer equipped with a 9610 Finnigan gas chromatograph. Elemental analyses were carried out by Mic Anal Organic Microanalysis (Tucson, AZ). Vapor-phase chromatography analyses were carried out on a Hewlett-Packard F & M Scientific 700 Laboratory chromatograph, using a thermal conductivity detector and a 20 ft × 0.25 in. aluminum column containing 10% Carbowax 20M on Chromosorb P, 60/80 mesh.

Preparation of Diisopropyl Ketone (Phenylsulfonyl)-hydrazone. A mixture of 8.6 g (0.05 mol) of (phenylsulfonyl)-hydrazine and 5.7 g (0.05 mol) of diisopropyl ketone dissolved in 50 mL of 95% ethanol with two drops of concentrated HCl was allowed to reflux for 3 h. The reaction mixture was cooled to room temperature and then refrigerated. The crystals formed were recrystallized from 95% ethanol to yield 9.1 g (0.034 mol, 69%) of a white crystalline product, which has the following spectral characteristics that are consistent with the proposed structure: ^1H NMR (DMSO-d_6) 1.1 (two doublets, 12 H, methyl protons of isopropyl groups), 2.4–2.9 (m, 2 H, tertiary isopropyl hydrogens), 7.4–8.0 (m, 5 H, aromatic protons); IR (KBr pellet) 3200 cm^{-1} (strong, N–H stretch), 2930 (strong), 1460 (medium), 1340 (strong), 1180 (strong), 1020 (medium), 940 (medium). Anal. Calcd for $C_{13}H_{20}N_2O_2S$: C, 58.18; H, 7.51. Found: C, 58.15; H, 7.59.

Preparation of Cyclopropyl Isopropyl Ketone (Phenylsulfonyl)hydrazone. A mixture of 8.6 g (0.05 mol) of (phenylsulfonyl)hydrazine and 5.6 g (0.05 mol) of cyclopropyl isopropyl ketone dissolved in 50 mL of 95% ethanol was allowed to reflux for 12 h. The reaction mixture was cooled to room temperature and then refrigerated. The crystals formed were recrystallized from 95% ethanol to yield 8.6 g (0.032 mol, 65%) of a white crystalline product, which has the following spectral characteristics that are consistent with the proposed structure: ^1H NMR (DMSO-d_6) 0.3–0.8 (m, 4 H, cyclopropyl ring protons), 1.0 (d, J = 10 Hz, 6 H, methyls of isopropyl group), 1.3–1.5 (1 H, m, cyclopropyl ring proton adjacent to carbonyl group), 1.9–2.3 (m, J = 10 Hz, 1 H, tertiary isopropyl hydrogen), 7.4–8.0 (m, 5 H, aromatic protons); IR (KBr pellet) 3200 cm^{-1} (strong, N–H stretch), 2970 (medium), 1630 (weak), 1460 (medium), 1410 (medium), 1350 (strong), 1180 (strong), 1100 (medium), 1010 (medium), 960 (medium). Anal. Calcd for $C_{13}H_{18}N_2O_2S$: C, 58.55; H, 6.89. Found: C, 58.62; H, 6.81.

Preparation of Dicyclopropyl Ketone (Phenylsulfonyl)-hydrazone. A mixture of 8.6 g (0.05 mol) of (phenylsulfonyl)-hydrazine and 5.5 g (0.05 mol) of dicyclopropyl ketone dissolved in 50 mL of 95% ethanol was allowed to reflux for 12 h. The reaction mixture was cooled to room temperature and then was refrigerated. The crystals formed were recrystallized from 95% ethanol to yield 6.9 g (0.026 mol, 51%) of a white crystalline product, which exhibits the following spectral characteristics that are consistent with the proposed structure: ^1H NMR (DMSO-d_6) 0.5–1.0 (m, 8 H, cyclopropyl ring protons), 1.0–1.6 (m, 2 H, cyclopropyl ring protons adjacent to C=N), 7.4–8.0 (m, 5 H, aromatic protons); IR (KBr pellet) 3170 cm^{-1} (strong, N–H stretch), 3000 cm^{-1} (weak), 1620 (medium), 1460 (medium), 1420 (medium), 1320 (strong), 1260 (medium), 1160 (strong), 1100 (medium), 1060 (medium), 1000 (medium), 950 (medium). Anal. Calcd for $C_{13}H_{16}N_2O_2S$: C, 59.07; H, 6.10. Found: C, 58.94; H, 6.09.

Preparation of the Potassium Salts of the Ketone (Phenylsulfonyl)hydrazones 12–14. Each of the three ketone (phenylsulfonyl)hydrazones prepared was converted into its corresponding potassium salt (**12**, **13**, or **14**) by using the following general procedure: 2.0 g of 35% wt/wt KH in mineral oil (0.70 g of KH, 0.0175 mol) was washed 4 times with dry THF and the KH allowed to react with approximately 0.0175 mol (4.6–4.7 g) of the ketone (phenylsulfonyl)hydrazone dissolved in 20 mL of dry THF. The THF solvent was removed under vacuum in a desiccator and the solid product washed with dry THF and redried under vacuum. In each case the product was obtained in greater than 90% yield and was not characterized.

Thermolyses of the Potassium Salts of the Ketone (Phenylsulfonyl)hydrazones 12–14. The oil in an oil bath was first brought up to the desired temperature and then 30 mL of dry DMSO was transferred to a round-bottom flask in the bath via syringe and the stopper quickly put into place. The DMSO in the flask was allowed to stand for 45 min in order to reach thermal equilibrium with the oil in the oil bath. A sample of potassium salt **12**, **13**, or **14** was then added quickly to the DMSO in the flask. The approximate sample sizes used were 0.3 g for **12** and **13** and 0.5 g for **14**. The nitrogen gas evolved was collected in a burette over diethyl phthalate and the volume of nitrogen gas evolved versus time was recorded.

Workup of the Products from the Thermolyses for Product Identification. The following general procedure was used for each (phenylsulfonyl)hydrazone potassium salt: Approximately 1.00 g of the salt was allowed to undergo thermolysis in 70 mL of dry DMSO at 120 °C. A weighed amount of an internal standard (dodecane for thermolysis of **12**, decane for **13** and **14**) was also present in the reaction system. Upon completion, the reaction mixture was mixed with 100 mL of distilled water and the resulting solution extracted with two 100-mL aliquots of pentane. The pentane extracts were combined and washed with two 100-mL aliquots each of 10% H_2SO_4 (aq), saturated $NaHCO_3$ (aq), and distilled water. The pentane extract was dried over $MgSO_4$ and then most of the solvent removed by distillation through a Vigreux column. The remaining liquid residue in each case was subjected to gas–liquid chromatography for analysis.

Identification of the Products Obtained from the Thermolysis of the Potassium Salt of Diisopropyl Ketone (Phenylsulfonyl)hydrazone (12). The GC analysis of the reaction mixture of the thermolysis of **12** after the workup described above shows that the mixture contains two components (other than residual solvent and dodecane internal standard). The yields of these two products were determined by comparing their peak areas to that of the dodecane (retention time = 25.9 min) and adjusting the areas to take into account that the product components have different molecular weights.[15] The first peak, which

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had a retention time of 4.4 min, was identified as 2,4-dimethyl-2-pentene (42% yield). The GC–mass spectral data show that this peak corresponds to a compound with a molecular weight of 98 amu. After collection by preparative GC, the ^{1}H NMR spectrum proved to be identical with that found for 2,4-dimethyl-2-pentene in the literature.[16] The second peak, which has a retention time of 10.9 min, was identified as diisopropyl ketone (18% yield). The retention time and mass and ^{1}H NMR spectra of this component are identical with those of an authentic sample.

Identification of the Products Obtained from the Thermolysis of the Potassium Salt of Cyclopropyl Isopropyl Ketone (Phenylsulfonyl)hydrazone (13). the GC analysis of the reaction mixture obtained from the thermolysis of **13** after workup showed that the mixture contains three components (other than residual solvent or decane internal standard). Percent yields of the products were determined by using decane (retention time = 11.1 min) as the internal standard and following the procedure described above for product identification for the thermolysis of **12**. The first product peak, which had a retention time of 5.3 min, was identified as 1-isopropylcyclobutene (16% yield). The GC–mass spectral data show that this peak corresponds to a compound with a molecular weight of 96 amu; preparative GC provided an ^{1}H NMR spectrum consistent with the proposed structure: 0.95 (d, J = 12 Hz, 6 H, methyl protons of isopropyl group), 2.2–2.4 (m, 5 H, methylene protons of cyclobutene ring plus center proton of isopropyl group), 5.3 (s, 1 H, vinylic proton). This compound has been previously isolated.[17] The second product peak, which had a retention time of 7.3 min, was identified as 1-cyclopropyl-2-methyl-1-propene (21% yield). The GC–mass spectral data show that this peak corresponds to a compound with a molecular weight of 96 amu. Preparative GC followed by ^{1}H NMR analysis provided a spectrum identical with that described for 1-cyclopropyl-2-methyl-1-propene in the literature.[18] The third product peak, which had a retention time of 20.9 min, was identified as cyclopropyl isopropyl ketone (19% yield). The retention time and mass and ^{1}H NMR spectra of this component were identical with those of an authentic sample of cyclopropyl isopropyl ketone.

Identification of the Products Obtained from the Thermolysis of the Potassium Salt of Dicyclopropyl Ketone (Phenylsulfonyl)hydrazone (14). The GC analysis of the reaction mixture obtained from the thermolysis of **14** after workup showed that the mixture contained two components (other than residual solvent and decane internal standard). The percent yields of the products were determined as outlined above. The first product peak, which had a retention time of 9.6 min, was identified as 1-cyclopropylcyclobutene (28% yield). The GC–mass spectral data show that this peak corresponds to a compound with a molecular weight of 94 amu. The compound was collected by preparative GC and exhibits a ^{1}H NMR spectrum identical with that described in the literature.[19] The second product component, which had a retention time of 56.0 min, was identified as dicyclopropyl ketone (30% yield), by comparison of retention time and mass and ^{1}H NMR spectra with those of an authentic sample.

Independent Determination of k_1. The following procedure was performed for the thermal decomposition of the potassium salt of cyclopropyl isopropyl ketone (phenylsulfonyl)hydrazone (**13**) at 110 °C and 130 °C: The thermolysis procedure was identical with that described above except that one drop (approximately 0.02 g (2×10^{-4} mol)) of *N,N*-dimethylaniline was added to the dimethyl sulfoxide solvent prior to the potassium salt to serve as an internal standard. After the potassium salt had dissolved completely, 1-mL aliquots were withdrawn at 0, 50, 100, 150, 200, and 300 s and transferred to test tubes in an ice bath. Two drops of glacial acetic acid were added to each aliquot to convert the potassium salt present into the corresponding (phenylsulfonyl)hydrazone. Each aliquot was then analyzed by HPLC, using a Waters Associates liquid chromatograph equipped with a reversed liquid phase column (Hamilton PRP-1, 150 mm × 4.1 mm) and a Waters Associates Model 440 absorbance detector. Absorbance was measured at 254 nm. The solvent used was 58% acetonitrile in water at a flow rate of 2.0 mL/min. The retention times of cyclopropyl isopropyl ketone (phenylsulfonyl)hydrazone and *N,N*-dimethylaniline were 8.4 min and 12.0 min, respectively.

Registry No. **12**, 126063-48-7; **12**·K, 126063-51-2; **13**, 126063-49-8; **13**·K, 126063-52-3; **14**, 126063-50-1; **14**·K, 126063-53-4; NH_2NHSO_2Ph, 80-17-1; $Me_2CHC(O)CHMe_2$, 565-80-0; $Me_2CHCH{=}CMe_2$, 625-65-0; cyclopropyl isopropyl ketone, 6704-20-7; dicyclopropyl ketone, 1121-37-5; 1-isopropylcyclobutene, 22693-16-9; 1-cyclopropyl-2-methyl-1-propene, 1003-33-4; 1-cyclopropylcyclobutene, 22693-18-1.

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