Effects of Acid Strength on Schmidt Reactions of Alkyl Cyclopropyl Ketones and Alkyl Phenyl Ketones[1a]

Lewis E. Fikes and Harold Shechter*[1b]

Department of Chemistry and Physics, Erskine College, Due West, South Carolina 29639, and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received July 5, 1978

Alkyl cyclopropyl ketones undergo acid-catalyzed reactions with hydrazoic acid (Schmidt reactions) to give isomeric amides by competitive migration of alkyl and cyclopropyl groups. The ratios of isomeric amides formed from these ketones are markedly influenced by the acidity of the reaction medium. Evidence is presented that these Schmidt reactions occur via (1) decomposition of α-hydroxyhydrazidium ion intermediates in media of low acidities and (2) collapse of *syn*- and *anti*-iminodiazonium ions in strong acid environments. Schmidt reactions of alkyl phenyl ketones and cyclopropyl phenyl ketones also give amide pairs. The isomer ratios from these systems are not affected by the catalyst acidity, and it is presumed that these processes involve *syn*- and *anti*-iminodiazonium ions exclusively.

The acid-catalyzed reaction of an unsymmetrical ketone with hydrazoic acid (the Schmidt reaction[2]) yields as principal products two isomeric amides (eq 1), the ratio of which is profoundly influenced by the structure of the starting ketone. The Schmidt reaction has been postulated to proceed through α-hydroxyhydrazidium ion **1**—arising from nucleophilic attack of hydrazoic acid on the protonated ketone—by either of two mechanisms (Scheme I): (a) direct rearrangement of **1** with loss of nitrogen, or (b) dehydration of **1**, stereospecific trans rearrangement of iminodiazonium ions **6** and **7** with nitrogen expulsion, and hydration of **8** and **9**.[2] In the first mechanism, the ratio of isomeric amides produced will be strongly influenced by the inherent migratory abilities of R and R′ or/and the abilities of R and R′ as stationary groups to support positive charge. In the second mechanism, the ratio of amides can be determined by the relative populations of iminodiazonium ions **6** and **7**, which are a result of the different steric repulsions in the transition states for dehydration of **1** to **6** and **7**. Note, however, that if isomerization of **6** and **7** is appreciably faster than their rearrangement, then equilibration between **6** and **7** would be achieved continually while rearrangement is proceeding. Thus, the migratory and/or the stationary abilities of R and R′ will again affect the product proportions.

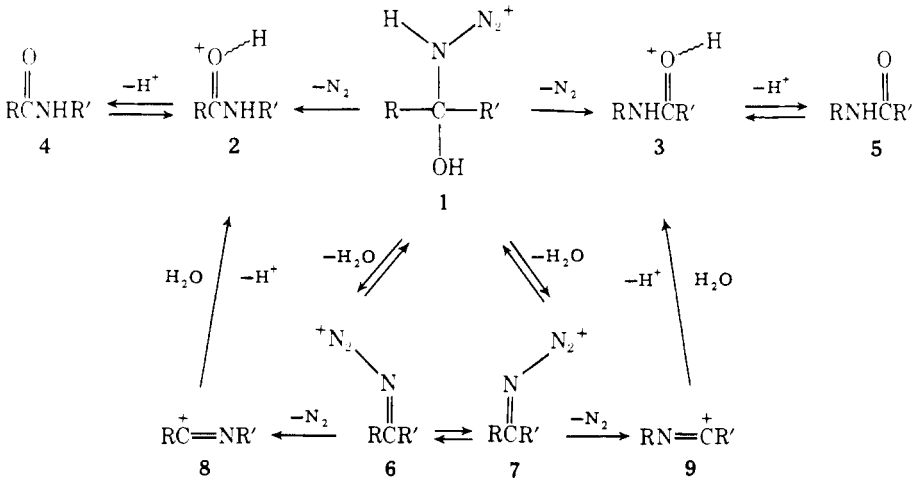
$$RC(=O)R' \xrightarrow[-N_2]{HN_3,\ H^+} RNHC(=O)R' + RC(=O)NHR' \qquad (1)$$

A few ketones are presumed to react via direct rearrangement of 1,[3] but Schmidt reactions of most unsymmetrical ketones result in preferential migration of the bulkier substituent and have been postulated to occur via the nonequilibrating structures **6** and **7** of the second mechanism.[2] It appeared to us that—since the occurrence of the second mechanism requires dehydration of **1**—the mechanism of the Schmidt reaction might change as the acid strength is varied, resulting (in the case of some unsymmetrical ketones) in quite different amide ratios as a function of acid strength. Kinetic evidence has shown that for various meta- and para-substituted acetophenones the mechanism of the Schmidt reaction does change as acid strength is varied.[4] However, as yet there are no reported examples in which the ratios of amides from Schmidt reactions of unsymmetrical ketones are altered by acid strength. The present report is a study of the effects of acid strength on the mechanism and product distribution of Schmidt reactions of alkyl cyclopropyl ketones and alkyl phenyl ketones.[1]

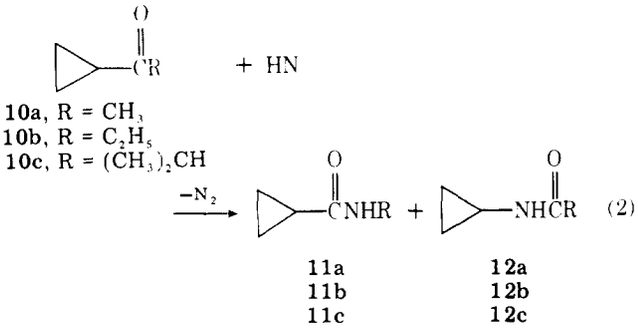
Results and Discussion

The data in Table I for reactions of cyclopropyl methyl ketone (**10a**), cyclopropyl ethyl ketone (**10b**), and cyclopropyl isopropyl ketone (**10c**) with hydrazoic acid (eq 2) reveal several significant features. Most significant is the dramatic dependence of the amide ratio upon acid strength. The proportions of amides **11a–c** and **12a–c** are essentially reversed in media of low acid strength (50% sulfuric acid or trichloroacetic acid) compared to high acid strength (83% sulfuric acid). Also noteworthy is the high proportion of cyclopropyl, rather than alkyl, migration that occurs at the higher acid strengths. Furthermore, at all concentrations of sulfuric acid, the mi-

Scheme I



0022-3263/79/1944-0741$01.00/0 © 1979 American Chemical Society



gration order for alkyl groups (relative to cyclopropyl) is Me > Et > *i*-Pr. Such an order has never been previously observed for Schmidt reactions of ketones; the usual migration order is *i*-Pr > Et > Me.[2]

In 83% sulfuric acid the percent cyclopropyl migration increases as the steric bulk of the alkyl group opposite it in the ketone (**10a–c**) increases, a result that is clearly contrary to the prediction that steric repulsions in the transition states leading to iminodiazonium ions **13** and **15** (Scheme II) are responsible for the observed amide ratios. However, in 83% sulfuric acid the reactions may proceed via **13** and **15** if they isomerize readily to one another, then allowing migration aptitudes to determine the amide ratios. The interconversions of **13** and **15** may occur rapidly because the double character of their imino linkages is greatly reduced as in **14** and **16** because of cyclopropylcarbinyl resonance. But the observed preferential cyclopropyl, rather than alkyl, migration is opposite to what is expected in view of the hybridization of the bonding orbitals of the migrating carbon in each case.[6] The migrating carbon in an alkyl group would use an sp^3 hybridized orbital, whereas the migrating carbon of a cyclopropyl group would use an orbital that is of higher s character than the alkyl carbon orbital, making the electron pair more tightly bound and less able to stabilize the partially positive nitrogen to which it is becoming bonded in the transition state. Clearly there must be some effect in Schmidt reactions of alkyl cyclopropyl ketones (**10a–c**) in 83% sulfuric acid that is overcoming this unfavorable hybridization of the cyclopropyl group and allowing (at high acid strength) cyclopropyl to migrate to a partially positive nitrogen to a greater extent than do alkyl groups.

It is then conceivable that cyclopropyl, rather than alkyl, migration to positive nitrogen might occur because the cyclopropyl group in **15** can stabilize the transition state leading to cyclopropyl migration by delocalization of the σ bonds of the ring which are high in p character. Such stabilization might

Scheme II

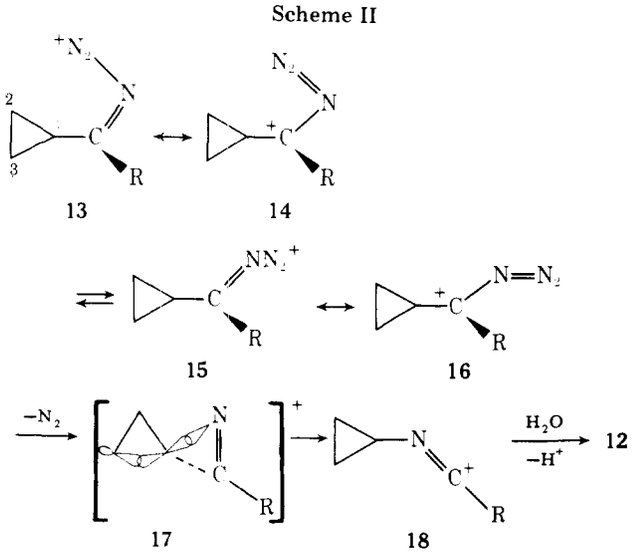


Table I. Alkyl/Cyclopropyl Migration Ratios in Schmidt Reactions of Alkyl Cyclopropyl Ketones (10a–c)[a]

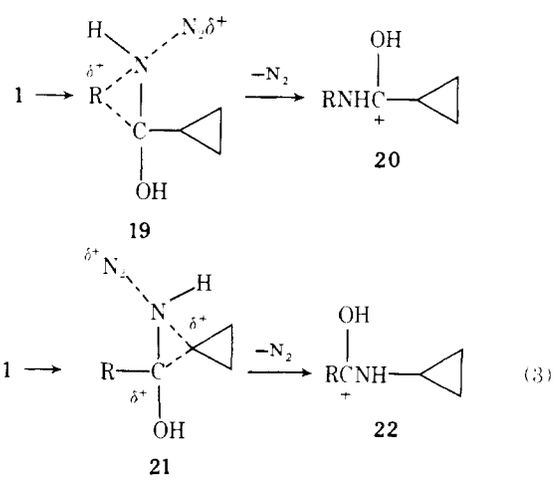
acid catalyst	R/cyclopropyl migration ratio (11/12)[b] R = Me	R = Et	R = *i*-Pr
89% H_2SO_4[c]	27:73		
83% H_2SO_4	26:74	18:82	8:92
69% H_2SO_4	56:44	18:82	4:96
50% H_2SO_4	90:10	74:26	18:82
CCl_3CO_2H	73:27	74:26	52:48

[a] Yields of crude solid ranged from 88 to 100% (usually >95%), except in 50% H_2SO_4 where large amounts of unreacted ketone were present. [b] By VPC and NMR analysis of the crude amide mixture, using authentic samples of the individual amides for comparison. All reactions were run at least twice, and the data were reproducible within ±1%. [c] In 89% H_2SO_4 hydrolysis of *N*-cyclopropylacetamide to propanal and acetamide occurs. Schmidt reactions of cyclopropyl ethyl ketone and cyclopropyl isopropyl ketone in H_2SO_4 concentrations greater than 83% thus were not investigated.[5]

come about in either of two ways, by ring-edge participation or perhaps more favorably by participation of the back lobes of the cyclopropyl ring orbitals (C-1,2 and C-1,3) as in transition state **17**.[6]

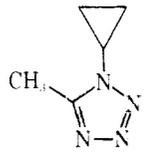
The surprising migration order (relative to cyclopropyl) of Me > Et > *i*-Pr in 83% sulfuric acid may be a result of some combination of several factors: (1) increasing stability of **17** arising from inductive electron release by R in the expected order *i*-Pr > Et > Me, (2) greater hyperconjugative stabilization of the transition states for migration of the less highly branched alkyl groups in **13**[7] and (3) sterically accelerated cyclopropyl migration from **15** when R is *i*-Pr (and to a lesser extent, Et). It is very difficult to distinguish among these factors, but future work in this area may help to clarify the matter.

The profound increase in alkyl migration as acid strength is reduced (Table I) suggests that in 50% sulfuric acid and in trichloroacetic acid reactions occur predominantly by direct rearrangement of **1**. In transition states **19** and **21** (eq 3), due

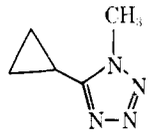


to the presence of both the OH and the cyclopropyl groups, considerable positive charge may reside on the migration origin, so that **19** and **21** would resemble products **20** and **22**, respectively. Thus, methyl or ethyl migration, rather than cyclopropyl, may arise from stabilization of **19** (R = Me, Et) by cyclopropylcarbinyl resonance.[8] In contrast, at high acid strengths in which dehydration to **13** and **15** is likely, there presumably is considerable positive charge at the migration terminus, which might be stabilized by cyclopropyl migration as in **17**.

The proposal that at reduced acid strengths rearrangement takes place via 1 is consistent with suppositions that (1) ions analogous to **8** and **9** (which, with excess hydrazoic acid, can be trapped as tetrazoles[2]) are formed only at high acid concentrations, since **23** and **24** were obtained when the Schmidt



23

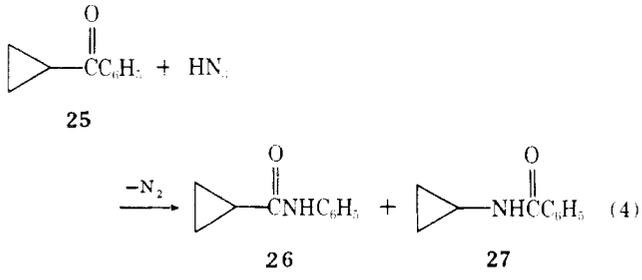


24

reaction of cyclopropyl methyl ketone (**10a**) was carried out in 83% sulfuric acid and a 10 molar excess of hydrazoic acid, but not when effected in 50% sulfuric acid or trichloroacetic acid and a 10 molar excess of hydrazoic acid, and (2) dehydration of **1** to **6** and **7** should be less likely in the poorer dehydrating media of 50% sulfuric acid or trichloroacetic acid. The present data, however, for cyclopropyl isopropyl ketone (**10c**) suggest that dehydration of its azidohydrinium ion (**1**, R = *i*-Pr) is facile even in 50% sulfuric acid, possibly because of relief of steric strain. When R = *i*-Pr, perhaps only in CCl_3CO_2H is dehydration of **1** retarded, allowing direct rearrangement to **2** and **3**.

The migration order (relative to cyclopropyl) of Me > Et > *i*-Pr observed at the lower acid strengths could result from the increasing stability of **21** arising from inductive electron release by R in the expected order *i*-Pr > Et > Me, and/or from greater hyperconjugative stabilization of the transition states for migration of the less highly branched alkyl groups in **19**.

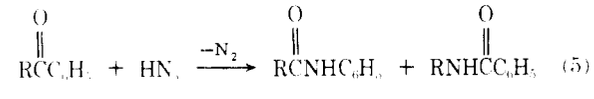
The ratio of isomeric amides **26** and **27** (eq 4) obtained in the Schmidt reaction of cyclopropyl phenyl ketone (**25**) is



25

26 **27** (4)

unaffected by changes in acid catalyst strength, giving a phenyl/cyclopropyl ratio of 93:7 (±2) in all catalysts used: 69–99% sulfuric acid and trichloroacetic acid. Reaction did not occur in 50% sulfuric acid. It is postulated that in all these acids Schmidt reactions of **25** proceed via analogues of **6** and **7** since dehydration to these conjugated ions should be so facile. This postulate is supported by observations that the ratios of isomeric amides produced in Schmidt reactions (eq 5) of ethyl phenyl ketone (**28**) and isopropyl phenyl ketone



(5)

28, R = C_2H_5 **29**, 85% **30**, 15%
31, R = $(CH_3)_2CH$ **32**, 35% **33**, 65%

(**31**) are similarly unaffected by changes in acid catalyst strength, giving a phenyl/ethyl migration ratio of 85:15 (±1) and a phenyl/isopropyl migration ratio of 35:65 (±1), respectively, in 69–93% sulfuric acid and in trichloroacetic acid. These results strongly suggest that in Schmidt reactions of alkyl phenyl ketones **28** and **31** dehydration of **1** to conjugated ions **6** and **7** (R = phenyl) is facile even in media of low acid strength.

If the Schmidt reaction of cyclopropyl phenyl ketone (**25**) is indeed proceeding via analogues of **6** and **7**, then the small percent of cyclopropyl migration is at first glance surprising since the larger cyclopropyl group gives less migration (~7%) than does the smaller ethyl group (15% migration) in the Schmidt reaction of ethyl phenyl ketone (**28**). However, this may indicate—as has been postulated above for Schmidt reactions of alkyl cyclopropyl ketones (**10a–c**)—that the cyclopropyl group promotes isomerization of **6** and **7** (R = phenyl, R′ = cyclopropyl) to one another at a rate that is faster than their rearrangement, so that the observed migration ratio is not simply a result of the relative steric bulk of R and R′, but is influenced by migration aptitudes also. Thus, the Schmidt reaction of cyclopropyl phenyl ketone (**25**) might be expected, as observed, to produce nearly exclusive phenyl migration since phenyl has a very high migratory aptitude.[2,7]

It is conceivable that in the Schmidt reactions of alkyl phenyl ketones (**28** and **31**) isomerization between iminodiazonium ions **6** and **7** (R = phenyl, R′ = alkyl) could also occur. However, the observed order of alkyl migration (relative to phenyl) *i*-Pr > Et > Me is opposite to that found in the Schmidt reactions of alkyl cyclopropyl ketones (**10a–c**). This suggests that in the case of alkyl phenyl ketones (**28** and **31**) rearrangement of **6** and **7** is faster than their isomerization, thereby allowing the ratio of isomeric amides to be determined by the relative populations of **6** and **7**. These result from the different steric repulsions in the transition states for dehydration of **1** to **6** and **7** and would follow the order *i*-Pr > Et > Me.

Further study of the effects of acid strength on Schmidt reactions of unsymmetrical ketones is in progress.

Experimental Section

General. All melting points are uncorrected. Nuclear magnetic resonance spectra were determined on a Varian A-60-A spectrophotometer using deuteriochloroform as solvent and Me_4Si as an internal standard. Analytical vapor phase chromatography of products was performed on an Aerograph Hy-Fi Model 600-D gas chromatograph using a hydrogen flame ionization detector. The column used was either a 10 ft × ⅛ in. column of 20% Carbowax 20M on Chrom W (oven temperature = 200 °C) or a 5 ft × ⅛ in. column of 15% XF-1150 on Chrom W (oven temperature = 170 °C). Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., or by Micro-Analysis, Inc., Wilmington, Del.

Materials. Cyclopropyl phenyl ketone (**25**) and cyclopropyl methyl ketone (**10a**) were purchased from Aldrich and used as supplied. Cyclopropyl ethyl ketone (**10b**) and cyclopropyl isopropyl ketone (**10c**) were prepared according to Bruylants.[9] All ketones were at least 99% pure by VPC. Analytical grade sodium azide was supplied by Fisher, and analytical grade chloroform and sulfuric acid were supplied by Baker.

General Schmidt Reaction Procedure. The reactions were conducted in a 100-mL, three-neck flask equipped with a magnetic stirrer, a thermometer, and a vial for sodium azide addition. One neck of the flask was connected to an inverted water-filled graduated cylinder for semiquantitative measurement of the progress of the reaction by the volume of nitrogen evolved. When chloroform was the solvent, it was added to the ketone, followed by addition of the sulfuric acid catalyst. While stirring and at room temperature, a 10% molar excess of sodium azide was added to the ketone solution in small quantities in 0.3–0.5 h, keeping the reaction temperature at 23 ± 3 °C. When trichloroacetic acid was used both as a solvent and catalyst, the reaction was maintained at 63 ± 1 °C. Reactions were generally complete within 15–24 h or less, except in 50% sulfuric acid where reaction was incomplete even after 5–7 days. The product was worked up by pouring the reaction mixture into 150 mL of water. The reaction flask was rinsed with water and chloroform, and the washings were combined with the aqueous mixture, which was then extracted with chloroform (3 × 100 mL for higher molecular weight amides and 6–9 × 100 mL for lower molecular weight amides). The chloroform extracts were combined and filtered through anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator. Yields of crude solids were near quantitative, except in 50% (and sometimes 69%) sulfuric acid where considerable unreacted ketone was present. The crude product mixtures were then analyzed by VPC and/or NMR to determine the amide ratios. Assignments were made by comparing

VPC retention times or NMR absorptions with those of authentic samples of the individual amides.

Product Analyses of Schmidt Reactions of Alkyl Cyclopropyl Ketones (10a–c). NMR analyses of Schmidt reactions of cyclopropyl methyl ketone (**10a**) used the methyl protons (τ 8.05, s) of *N*-cyclopropylacetamide (**11a**)[10] and the methyl protons (τ 7.20, d) of *N*-methylcyclopropanecarboxamide (**12a**).[11] Analyses of Schmidt reactions of cyclopropyl ethyl ketone (**10b**) by NMR used the methylene protons (τ 6.35–7.00, m) of *N*-cyclopropylpropionamide (**12b**). Schmidt reactions of cyclopropyl isopropyl ketone (**10c**) were analyzed using the methine proton (τ 5.60–6.22, m) of *N*-isopropylcyclopropanecarboxamide (**11c**) and the methine proton (τ 7.3–7.8, m) and cyclopropyl proton (τ 7.1–7.5, m) of *N*-cyclopropylisobutyramide (**12c**). VPC analyses confirmed the ratio of amides found by NMR.

Product Analyses of Schmidt Reactions of Cyclopropyl Phenyl Ketone (25). By column chromatography (on silica gel, using 9:1 benzene–ethyl acetate as eluent) of the crude reaction mixture it was possible to isolate the individual amides.[12] Also isolated were *N*-cyclopropyl-*N'*-phenylurea (5–10%; depending upon the acid concentration), arising from reaction of analogues of **8** and **9** with hydrazoic acid and water, and benzamide (1–3%), resulting from acid-catalyzed ring opening of *N*-cyclopropylbenzamide (**25**). In calculating the percent cyclopropyl migration, the amount of **25** lost by hydrolysis to benzamide and propanal was included. Results of column chromatography were verified by VPC analysis. *N*-Cyclopropyl-*N*-phenylurea isolated from the Schmidt reaction of **25** had the following properties: mp 164.5–165.5 °C; IR (KBr) 3300 (N–H) and 1635 (C=O) cm^{-1}; NMR τ 2.70 (m, 5, aromatic), 7.45 (m, 1, cyclopropyl), 9.35 (m, 4, cyclopropyl); mass spectrum, *m/e* 176 (parent peak). Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.89. Found: C, 68.18; H, 6.87; N, 15.94.

Product Analyses of Schmidt Reactions of Isopropyl Phenyl Ketone (31). NMR analyses of the products used the methine proton (τ 5.4–6.1, m) of *N*-isopropylbenzamide (**33**)[13] and the methine proton (τ 7.1–7.9, m) of isobutyranilide (**32**).[14] These results agreed with the VPC analyses of the product mixtures. In addition, by using column chromatography (silica gel, 9:1 benzene–ethyl acetate as eluent), *N*-isopropyl-*N'*-phenylurea, comprising 5–10% of the reaction mixture, could be isolated: mp 155.5–156.5 °C; IR (KBr) 3300 (NH) and 1640 (C=O) cm^{-1}; NMR τ 2.80 (m, 5, aromatic), 6.07 (m, 1, $\mathbf{CH}(CH_3)_2$), 8.92 (d, 6, $CH(\mathbf{CH_3})_2$); mass spectrum, *m/e* 178 (parent peak). Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.71. Found: C, 67.42; H, 7.83; N, 15.26.

Product Analyses of Schmidt Reactions of Ethyl Phenyl Ketone (28). NMR analyses of the products used the methylene protons (τ 7.4–7.9, q) of *N*-phenylpropionamide (**29**)[15] and the methylene protons (τ 6.2–6.9, m) of *N*-ethylbenzamide (**30**).[16] Minor amounts of *N*-ethyl-*N'*-phenylurea in the crude product mixture were indicated by thin-layer chromatography and mass spectroscopy, but no attempt was made to isolate and characterize the urea.

Synthesis of *N*-Ethylcyclopropanecarboxamide (11b) and *N*-Cyclopropylpropionamide (12b). To a stirred mixture of ethylamine (1.35 g, 30 mmol), chloroform (25 mL), and 20% aqueous sodium hydroxide (25 mL) was slowly added cyclopropanecarboxylic acid chloride (3.1 g, 30 mmol). The aqueous layer was extracted with chloroform, the chloroform layers were combined and dried (sodium sulfate), and the solvent was removed under reduced pressure. The crude white solid was recrystallized from petroleum ether (60–110 °C) at −70 °C to give **11b** (2.7 g, 80%) as a white powder: mp 59.0–60.0 °C; IR (KBr) 3300 (NH) and 1625 (C=O) cm^{-1}; NMR τ 6.72 (m, 2, $NHCH_2CH_3$), 8.48 (m, 1, cyclopropyl), 8.85 (t, 3, $CH_2\mathbf{CH_3}$), 9.15 (m, 4, cyclopropyl); mass spectrum, *m/e* 113 (parent peak). The procedure used to prepare **11b** was employed to obtain **12b** as a white powder (2.4 g, 70%) upon recrystallization from petroleum ether (60–110 °C) at −70 °C; mp 42.5–43.5 °C; IR (KBr) 3300 (NH) and 1625 (C=O) cm^{-1}; NMR τ 7.28 (m, 1, cyclopropyl), 7.77 (q, 2, $-\mathbf{CH_2}CH_3$), 8.85 (t, 3, $CH_2\mathbf{CH_3}$), 9.35 (m, 4, cyclopropyl); mass spectrum, *m/e* 113 (parent peak).

Synthesis of *N*-Cyclopropylisobutyramide (12c) and *N*-Isopropylcyclopropanecarboxamide (11c). The same general procedure as above was used to prepare these amides. *N*-Cyclopropylisobutyramide (**12c**) was obtained in 88% yield as white crystals: mp 91.6–92.0 °C; IR (KBr) 3300 (NH) and 1640 (C=O) cm^{-1}; NMR τ 5.90 (m, 1, $\mathbf{CH}(CH_3)_2$), 8.88 (d, 6, $CH(\mathbf{CH_3})_2$), 9.40 (m, 4, cyclopropyl); mass spectrum, *m/e* 127 (parent peak). *N*-Isopropylcyclopropanecarboxamide (**11c**) was isolated in 83% yield as white crystals: mp 90.0–90.5 °C; IR (KBr) 3300 (NH) and 1640 (C=O) cm^{-1}; NMR τ 5.90 (m, 1, $\mathbf{CH}(CH_3)_2$), 8.58 (m, 1, cyclopropyl), 8.84 (d, 6, $CH(\mathbf{CH_3})_2$), 9.21 (m, 4, cyclopropyl); mass spectrum, *m/e* 127 (parent peak).

Isolation of 1-Cyclopropyl-5-methyltetrazole (23) and 5-Cyclopropyl-1-methyltetrazole (24). The mixture from reaction of cyclopropyl methyl ketone (**10a**) in 83% sulfuric acid and a 10-fold excess of sodium azide was subjected to preparative VPC using a 6 ft × 0.25 in. column of 20% SE-30 on Chrom W at 175 °C. Tetrazoles **23** and **24**, which constituted about 40% (NMR) of the mixture, were collected as a mixture: IR (KBr) 1525 and 1550 cm^{-1} (N=N and C=N); NMR τ 5.85 (s, $>NCH_3$), 6.42 (m, $\overline{CH_2CH_2CH}N$), 7.35 (s, $-C(=N)CH_3$), 8.70 (m, cyclopropyl); the mass spectral fragmentation pattern was similar to that of other tetrazoles.[17] Anal. Calcd for $C_5H_8N_4$: C, 48.37; H, 6.49; N, 45.13. Found: C, 48.16; H, 6.26; N, 45.09.

Acknowledgment. The authors are indebted to the National Science Foundation for support of this research.

Registry No.—**10a**, 765-43-5; **10b**, 6704-19-4; **10c**, 6704-20-7; **11a**, 7108-40-9; **11b**, 26389-61-7; **11c**, 26389-62-8; **12a**, 29512-07-0; **12b**, 68437-52-5; **12c**, 68437-53-6; **23**, 68437-54-7; **24**, 68437-55-8; **25**, 3481-02-5; **26**, 2759-52-6; **27**, 15205-35-3; **28**, 93-55-0; **29**, 620-71-3; **30**, 614-17-5; **31**, 611-70-1; **32**, 4406-41-1; **33**, 5440-69-7; hydrazoic acid, 7782-79-8; *N*-cyclopropyl-*N'*-phenylurea, 13140-86-8; benzamide, 55-21-0.

References and Notes

(1) (a) Abstracted in part from the Ph.D. Thesis of L. E. Fikes, The Ohio State University, Columbus, Ohio, 1972. For a preliminary communication of this work, see L. E. Fikes and H. Shechter, *Tetrahedron Lett.*, 2525 (1976). (b) Address correspondence to author at the Ohio State University.

(2) P. A. S. Smith in "Molecular Rearrangements", P. deMayo, Ed., Wiley, New York, N.Y., 1963, Chapter 8.

(3) (a) G. Gimaio and V. Permutti, *Tetrahedron*, **22**, 2059 (1966); (b) V. T. Bhalerao and G. Thyagarajan, *Can. J. Chem.*, **46**, 3367 (1968); (c) T. Sasaki, S. Equichi, and T. Toru, *J. Org. Chem.*, **35**, 4109 (1970).

(4) (a) M. J. Maximovich, M.S. Thesis, Kent State University, Kent, Ohio, 1964; (b) D. L. Fishel and M. J. Maximovich, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1964, p 855.

(5) S. C. Bunce and J. B. Cloke, *J. Am. Chem. Soc.*, **76**, 2244 (1954), report a methyl/cyclopropyl migration ratio of 77:33 in the Schmidt reaction of methyl cyclopropyl ketone (**10a**). We believe this is an error since we observed that their reaction conditions (96% H_2SO_4, 25–38 °C, 12 h) cause hydrolytic ring opening of *N*-cyclopropylacetamide (**12a**), which they did not take into account in determining the migration ratio.

(6) Y. E. Rhodes and T. Takino, *J. Am. Chem. Soc.*, **92**, 5270 (1970).

(7) (a) H. O. House, E. J. Grubbs, and W. F. Gannon, *J. Am. Chem. Soc.*, **82**, 4099 (1960); (b) S. Flisar, J. Renard, and D. Z. Simon, *ibid.*, **93**, 6953 (1971).

(8) (a) Such stabilization by cyclopropylcarbinyl resonance presumably also occurs in a related reaction: acid-catalyzed rearrangement of *n*-butyldicyclopropylcarbinyl azide, where 95% of the products arise by *n*-butyl migration.[8b] However, cyclopropylcarbinyl resonance is not significant in solvolyses of 2-cyclopropyl-2-methylpropyl brosylate[6] or in the Baeyer–Villiger reaction of cyclopropyl methyl ketone,[8c] for in both cases nearly exclusive cyclopropyl (rather than methyl) migration occurs. It may be significant though that migration in the latter two cases occurs to carbon and oxygen, respectively, rather than to nitrogen. (b) G. H. Potter, Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, N.Y., 1958. (c) R. B. Sauers and R. W. Uebersax, *J. Org. Chem.*, **30**, 3939 (1965).

(9) M. P. Bruylants, *Bull. Soc. Chim. Belg.*, **36**, 519 (1925).

(10) L. A. Paquette, J. R. Malpass, and G. R. Krow, *J. Am. Chem. Soc.*, **92**, 1980 (1970).

(11) J. P. Hopkins, R. P. Neighbors, and L. V. Phillipa, *J. Agric. Food. Chem.*, **15**, 501 (1967).

(12) (a) *N*-Cyclopropylbenzamide (**27**) was prepared according to the procedure of N. Kishner, *Chem. Zentralbl.*, **76**, 1704 (1905). (b) Cyclopropanecarboxanilide (**26**) was prepared by the method of L. I. Smith and S. McKenzie, Jr., *J. Org. Chem.*, **15**, 74 (1950).

(13) H. M. Kissman and J. Williams, *J. Am. Chem. Soc.*, **72**, 5323 (1950).

(14) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 893 (1921).

(15) J. B. Tingle and F. C. Blank, *J. Am. Chem. Soc.*, **30**, 1408 (1908).

(16) P. Van Romburgh, *Recl. Trav. Chim. Pays-Bas*, **4**, 384 (1885).

(17) D. M. Forkey and W. R. Carpenter, *Org. Mass Spectrom.*, **2**, 433 (1969).