carbonyl oxide is proposed to exist in syn or anti forms. The barriers to syn–anti interconversion and to cyclization of the carbonyl oxide are shown to be substantial so that the chemistry observed in the ozonolysis reaction in solution is very likely that of the initial mixture of carbonyl oxides generated by cleavage of the primary ozonide. The 1,2-dioxocyclopropane is shown, however, to be more stable than the carbonyl oxide, in agreement with previous studies.

Thermochemical calculations are permissive for various fates of the carbonyl oxide including reduction via epoxidation and oxygen formation.

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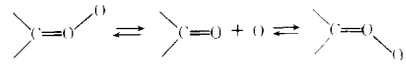
Registry No.—Formaldehyde carbonyl oxide, 62024-18-4; 1,2-dioxocyclopropane, 157-26-6.

References and Notes

(1) R. Criegee, *Rec. Chem. Progr.*, **18,** 11 (1957).
(2) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **14,** 745 (1975), and references therein.
(3) For example: R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Am. Chem. Soc.*, **88,** 3143 (1966); R. W. Murray, R. D. Youssefyeh, G. J. Williams, and P. R. Story, *Tetrahedron*, **24,** 4347 (1968); S. Fliszar and J. Charles, *Can. J. Chem.*, **47,** 3921 (1969).
(4) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Am. Chem. Soc.*, **90,** 1822 (1968).
(5) R. P. Lattimer, R. L. Kuczkowski, and C. W. Gillies, *J. Am. Chem. Soc.*, **96,** 348 (1974).
(6) I. T. Millar and H. D. Springall, "The Organic Chemistry of Nitrogen", Oxford University Press, London, 1966, p 316.
(7) J. Renard and S. Fliszar, *J. Am. Chem. Soc.*, **92,** 2628 (1970).
(8) S. Fliszar, J. Renard, and D. Z. Simon, J. Am. Chem. Soc., **93,** 6953 (1971).
(9) R. A. Rouse, *J. Am. Chem. Soc.*, **95,** 3460 (1973).
(10) T-K. Ha, H. Kuhne, S. Vaccani, and H. Gunthard, *Chem. Phys. Lett.*, **24,** 172 (1974).
(11) W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97,** 3004 (1975).
(12) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97,** 1285 (1975), and the following four articles.
(13) Available from Quantum Chemistry Program Exchange, Indiana University, and adapted for use at Union College on a Burroughs 5700 by L. Hull and R. P. Frosch.
(14) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **96,** 7578 (1974); M. Dewar and W. Thiel, *ibid.*, **97,** 3978 (1975); M. J. S. Dewar, A. C. Griffin, W. Thiel, and I. Turchi, **97,** *ibid,* 4439 (1975); M. J. S. Dewar, R. Haddon, W-K. Li, W. Thiel, and P. Werner, *ibid.*, **97,** 4540 (1975).
(15) R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **94,** 9107 (1972).
(16) L. E. Sutton, *Chem. Soc. Spec. Publ.*, **No. 18** (1965).
(17) T. A. Walter, J. J. Bufalini, and B. W. Gay, Jr., *Environ. Sci. Technol.*, **11,** 382 (1977).
(18) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97,** 1302 (1975).
(19) M. J. S. Dewar, A. C. Griffin, W. Thiel, and I. Turchi, *J. Am. Chem. Soc.*, **97,** 4439 (1975).
(20) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **68,** 279 (1968).
(21) Another route for syn–anti interconversion is via the carbonyl oxide dissociation and recombination as indicated below. The intermediacy, however, of an oxygen atom seems unlikely in the solution phase reactions.[2]



(22) W. C. Gardner, "Rates and Mechanisms of Chemical Reactions", W. H. Benjamin, Menlo Park, Calif., 1972, p 113.
(23) S. Fliszar and J. Renard, *Can. J. Chem.*, **48,** 3002 (1970).
(24) "JANAF Thermochemical Tables", Dow Chemical Co., Midland, Mich., 1965.
(25) R. Keay and G. Hamilton, *J. Am. Chem. Soc.*, **98,** 6578 (1976).
(26) S. Jackson and L. A. Hull, *J. Org. Chem.*, **41,** 3340 (1976).
(27) P. D. Bartlett and G. Guaraldi, *J. Am. Chem. Soc.*, **89,** 4799 (1967).

1,2-Diazetidine Conformation. Double Nitrogen Inversion[1,2]

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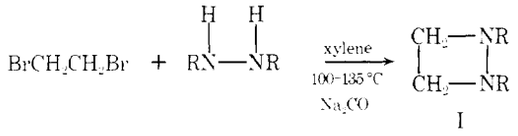
Several 1,2-dialkyl-1,2-diazetidines have been synthesized and their NMR spectra examined as a function of temperature. The methylene protons exhibited an AA'BB' pattern at temperatures below 0 °C, but as the temperature was raised, the AA'BB' pattern broadened, and then coalesced into a singlet. Line-shape analysis as a function of temperature gave ΔH^* values in the range 14.9–18.9 kcal mol^{-1} and ΔS^* values in the range +1 to −7 cal deg^{-1} mol^{-1}. The effect of *N*-alkyl substituents on the rate of double nitrogen inversion and on the 1,2-diazetidine ring conformation is discussed. Mass spectral data of 1,2-diazetidines are presented.

Conformational studies on saturated ring systems containing two adjacent nitrogen atoms have been the subject of a number of reports during the last several years.[3–19] However, there appears to have been only a few reports on the 1,2-diazetidine ring system.[8,16–19] We would like to report the synthesis of several 1,2-dialkyl-1,2-diazetidines and the results of a proton magnetic resonance study on these interesting compounds.

The 1,2-dialkyl-1,2-diazetidines used in this study were prepared by direct reaction of 1,2-dibromoethane and the corresponding 1,2-dialkylhydrazine in hot xylene in the presence of anhydrous sodium carbonate.



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This procedure was reported by Horwitz[20] in a patent. However, we were not able to prepare 1,2-dimethyl-1,2-diazetidine in a useful yield using the procedure in the patent. It was found that the yields could be increased substantially by using a large excess of ethylene bromide (a considerable amount is lost during the reaction by undergoing elimination) and adding it dropwise to the 1,2-dialkylhydrazine and sodium carbonate in a large volume of xylene over a period of several hours. This high dilution technique gave yields as follows (R's, yield): CH_3, 32%; C_2H_5, 28%; $(CH_3)_2CH$, 60%; $(CH_3)_3C$, 2.3%.

The 1,2-dimethyl-1,2-diazetidine prepared by the above method was contaminated by an impurity (ca. 10%) which could not be removed, but it did not interfere with the NMR study. The 1,2-di-*tert*-butyl-1,2-diazetidine was prepared only once in 2.3% yield. In spite of several attempts, we were never able to isolate it a second time. Other dibromides can be used. Reaction of 1,2-dibromopropane with 1,2-diethylhydrazine

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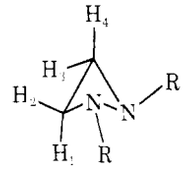
Table I. 60 MHz NMR Parameters of the Methylene Hydrogens in 1,2-Dialkyl-1,2-diazetidines



Compd	Registry no.	Substituents R's	Chemical shift, Hz		Coupling constants, Hz			
			$H_1 = H_4$	$H_2 = H_3$	J_{14}	$J_{12} = J_{34}$	$J_{13} = J_{24}$	J_{23}
I	52433-27-9	CH_3[b]	173.41	207.16	10.14	−6.27	7.90	2.76
II	66303-57-9	CH_3CH_2[c]	178.24	208.42	9.85	−6.50	8.54	3.17
III	66303-58-0	$(CH_3)_2CH$[d]	180.23	201.14	8.79	−7.24	9.26	4.57
IV	66303-59-1	$(CH_3)_3C$[e]	192.70	222.80	9.80	−9.04	9.10	4.61
V	66303-60-4	1,2-Diisopropyl-3-phenyl-1,2-diazetidine[a,f]						
		$H_1 = 175$, $H_2 = 225$, $H_4 = 254$			$J_{12} = -6.7$, $J_{14} = 8.6$, $J_{24} = 8.6$			

[a] Same numbering as above with phenyl in place of H_3. [b] CH_3, 2.36 ppm. [c] CH_3, 0.87 ppm; CH_2, 2.55 ppm. [d] CH_3, 0.91 ppm; CH, 2.82 ppm. [e] CH_3, 0.83 ppm. [f] CH_3, 0.95 ppm; CH of isopropyl groups, 2.90 ppm.

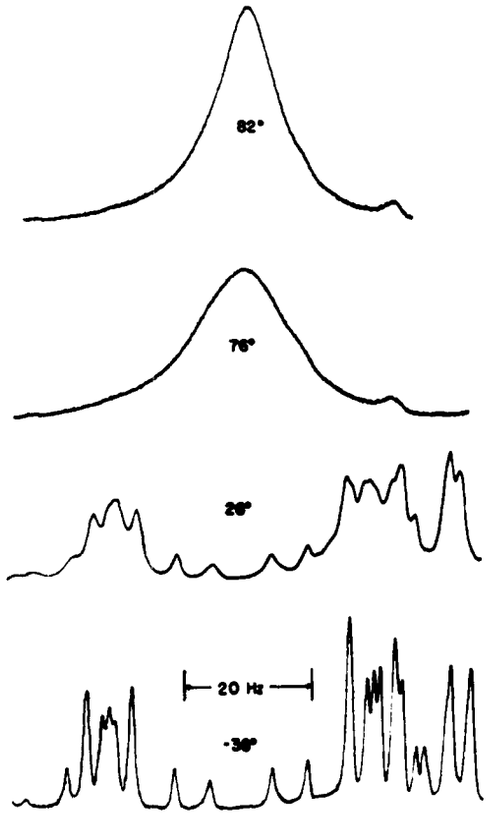


Figure 1. NMR spectra of 1,2-diethyl-1,2-diazetidine. The right side of the spectrum shows part of the ethyl CH_2 quartet and the peak due to $CHCl_3$.

gave a 24% yield of the 1,2-diethyl-3-methyl-1,2-diazetidine. However, GLC indicated that it was contaminated with an impurity and it was not investigated further. Reaction of 1-phenyl-1,2-dibromoethane with 1,2-diisopropylhydrazine gave only a 2% yield of the 1,2-diazetidine.

The 1,2-dialkyl-1,2-diazetidines are very stable compounds. For example, 1,2-di-*tert*-butyl-1,2-diazetidine survived distillation at 155 °C. 1,2-Diethyl-1,2-diazetidine was recovered after treatment with sodium amide at room temperature for 2 weeks. Butyllithium had no effect on 1,2-diisopropyl-1,2-diazetidine, nor did concentrated hydrochloric or 98% sulfuric acid at room temperature. Catalytic hydrogenation (50 psi) of 1,2-diisopropyl-1,2-diazetidine over platinum on charcoal failed to cleave the N–N bond.

The NMR spectra of the 1,2-dialkyl-1,2-diazetidines showed the methylene hydrogens as a well-defined AA'BB' pattern at temperatures below 0 °C. A typical set of spectra are given in Figure 1. Using the LAOCN3 computer program,[18] the chemical shifts and coupling constants were assigned as given in Table I.

Examination of the coupling constants in Table I reveals a very large difference in J_{14} and J_{23}. This large difference indicates clearly that the 1,2-diazetidine must be highly puckered.

We have assigned the larger of the coupling constants, $J_{1,4}$, to the diaxial hydrogens and the smaller of the two to the equatorial hydrogens in line with the anticipated effect of a larger dihedral angle for the diaxial hydrogens. Using a modified Karplus relationship[19] we estimated the dihedral angle between H_1 and H_4 to be 166, 161, 152, and 159° for the dimethyl, diethyl, diisopropyl, and di-*tert*-butyl groups, respectively. Although such calculations are not very reliable, the difference between J_{14} and J_{23} (10.14 and 2.76) for the 1,2-dimethyl-1,2-diazetidine is so large that it is difficult to rationalize the data without assuming a dihedral angle of this magnitude. Rademacher[16] estimated the dihedral angle between the nonbonded electron pairs on nitrogen in 1,2-dimethyl-1,2-diazetidine as 145°. This is difficult to compare with our data without making assumptions as to the bond angles around the nitrogen, but the numbers are at least of the right order of magnitude.

As one increases the bulk of the groups from methyl to ethyl to isopropyl a regular increase in J_{23} and a decrease in J_{14} is noted, suggesting that the ring is flattening out somewhat. A similar result has been observed in 1-alkylazetidines,[23] where variation of the alkyl group from methyl to ethyl to isopropyl to *tert*-butyl causes flattening of the ring.

Examination of the coupling constants and chemical shifts for 1,2-di-*tert*-butyl-1,2-diazetidine suggest that it may have a somewhat different conformation. For example, when the substituent increases in size from methyl to isopropyl, there is a regular decrease in J_{14} but as you go to the *tert*-butyl group, J_{14} increases again. There is also a significant downfield shift of both H_1 and H_4 in the di-*tert*-butyl compound. If one builds models of the di-*tert*-butyl compound and assumes a

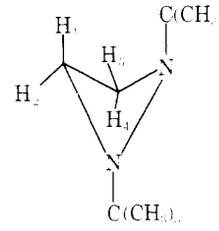


Table II. Rate Constants for Nitrogen Double Inversion in 1,2-Diazetidines

1,2-Dimethyl		1,2-Diethyl		1,2-Diisopropyl		1,2-Di-*tert*-butyl	
T, °C	k, s^{-1}	T, °C	k, s^{-1}	T, °C	k, s^{-1}	T, °C	k, s^{-1}
18.0	5.0	26	6.0	22	2.2	120	8.0
25.5	8.0	29	8.0	25	3.0	143	30
37.0	20.0	34	12.0	29	4.0	148	40
43.0	38.0	40	20.0	35	8.5	155	66
46.0	50.0	47	45.0	38	11		
55.0	74.0	54	70.0	44	22		
53.0	86.0	59	100	48	30		
57.0	121	63	130	49	35		
59.5	143	66	154	53	40		
67.0	196	71	220	56	50		
72.0	300	75	312	66	100		
		79	380				
		82	500				
		85	600				

Table III. Activation Parameters for Nitrogen Inversion in 1,2-Diazetidines

Compd	R's	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
I	CH_3	14.9 ± 0.8	−4.4 ± 2.4
II	C_2H_5	15.9 ± 0.5	−1.9 ± 1.5
III	$(CH_3)_2CH$	17.1 ± 1.0	+1.1 ± 3.0
IV	$(CH_3)_3C$	18.9 ± 1.2	−6.9 ± 2.8

dihedral angle of 150–160°, one comes to the conclusion that the more stable conformation in this case is probably the one with the *tert*-butyl groups diaxial.

The effect of the di-*tert*-butyl groups is noted in the coalescence temperature of the methylene hydrogens; whereas the coalescence temperatures of the dimethyl, diethyl, and diisopropyl compounds are in the 60–70 °C range (Figure 1), the coalescence temperature of the di-*tert*-butyl compound is about 155°. The di-*tert*-butyl compound still exhibits a sharp AA′BB′ spectrum even at a temperature of 72 °C.

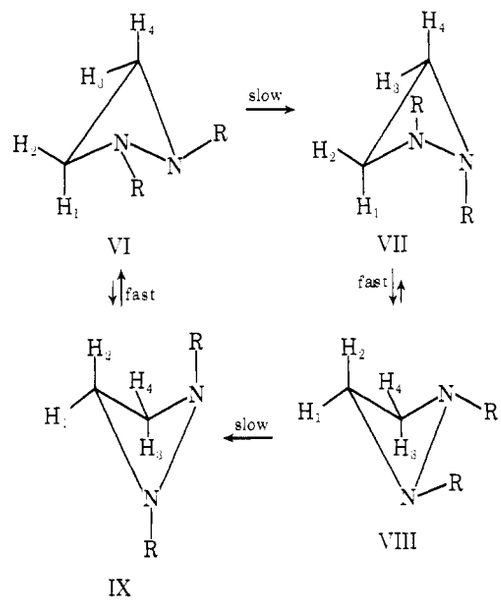
In order to obtain more quantitative information, the changes in the NMR spectra of compounds I–IV were studied as a function of temperature and the rate of nitrogen inversion was determined by comparison of the line shapes of the experimental spectra with those calculated using the DNMR program.[24] The rate constants obtained are listed in Table II.

Examination of the data in Table II reveals that the relative rates of nitrogen inversion at 66° are 1:0.78:0.51:0.74 × 10^{-3}. The results indicate only small differences in rates of inversion in the dimethyl, diethyl, and diisopropyl compounds but a very restricted inversion in the di-*tert*-butyl compound. These results contrast with those on 1-alkylaziridines, where steric acceleration has been reported.[25,26] The activation parameters, ΔH^* and ΔS^*, are listed in Table III.

The enthalpy of activation increases systematically with increasing size of the alkyl group. In the dimethyl, diethyl, and diisopropyl cases the increasing enthalpy of activation is offset by an increasing entropy of activation so that the total rate and ΔG^* is not affected greatly. In the di-*tert*-butyl case the entropy swings back negative, suggesting a high degree of steric crowding in the transition state.

The free energy of activation for 1,2-dimethyl-1,2-diazetidine (16.4 kcal/mol) is much larger than that reported by Ogden[8] for the perfluoro derivative (7.25 kcal/mol). The free energy is also much larger than that reported by Anderson[7] for 1,2-dimethylpyridazine (11.7 kcal/mol) or by Junge and Staab[6] for the corresponding benzopyridazine (12.0 kcal/mol). Mannschreck and co-workers[4] examined the NMR spectra of some 1,2-dialkyldiaziridines and found that the rate of nitrogen inversion was slow. They calculated the barrier to inversion in 1-isopropyl-3,3-dimethyl-1,2-diaziridine to be 23 kcal/mol, a value higher than those in Table III. Fahr and co-workers examined 1,2-diaryl-1,2-diazetidinones and reported ΔG^* values of 13–16 kcal/mol based on coalescence temperatures.[19] Philips reported an E_a of 8.0 kcal/mol for 1,2-dicarboethoxy-3,3,4,4-tetrafluoro-1,2-diazetidine apparently based on coalescence temperature.[17] However, these data are in doubt because Carlson, Schapp, and Raban have shown that the kinetic process observed for 1,1-dicarboethoxy-3,3,4,4-tetramethoxy-1,2-diazetidine is due to restricted rotation of the carboethoxy groups around the C–N bond, a process which has a ΔG^* of 13.6 kcal/mol.[18]

The NMR data presented can best be rationalized by the following conformational changes:



If the inversion at nitrogen is slow compared to ring inversion, the rate of the exchange process (VI to VIII) would be controlled by the rate of inversion at nitrogen (VI to VII or VIII to IX). At low temperature the AA′BB′ spectrum observed would be that of VI (or VIII), since the concentration of VII (or IX) would be expected to be low for the dimethyl, diethyl, and diisopropyl cases due to 1,3 interactions. Apparently what little steric interaction there is between the alkyl groups on the adjacent nitrogens leads only to flattening of the ring with little effect on nitrogen inversion. In the di-*tert*-butyl case, the rates may be reversed with VII and IX being the more stable structures and the rate-determining step in the ex-

change process would then be conversion of VII to VI (or IX to VIII).

In this rationalization, the possibility of an axial-equatorial isomer has been ignored since no evidence was found requiring its postulation. Anderson and Lehn[5] have argued that nitrogen inversion in such compounds should be consecutive rather than simultaneous, since simultaneous inversion requires eclipsing of the *N*-alkyl groups. This possibility cannot be excluded in the diazetidines, but one must assume that one of the inversions is fast compared to the other. If this were not the case, one would expect to see peaks due to an axial-equatorial isomer.

Experimental Section

The NMR spectra were recorded on a Varian 56/60 using deuterated chloroform as solvent and Me_4Si as internal standard. All frequencies were calibrated using standard sidebanding techniques. The variable temperature probe was calibrated with methanol at temperatures below 40 °C and with ethylene glycol above 40 °C. Mass spectra were run on a CEC Model 21-104 at 70 eV. Decoupling experiments were done on an HA 100. Boiling points are uncorrected. The IR and far-IR spectra of the described 1,2-diazetidines have been determined as have the pK_b values.[2] These results will be the subject of a separate paper.

1,2-Dimethyl-1,2-diazetidine. Into a flask equipped with a mechanical stirrer, a nitrogen atmosphere, a dry ice condenser, and a dropping funnel were placed 53 g (0.5 mol) of anhydrous sodium carbonate, 100 mL of anhydrous xylene, and 10.2 g (0.17 mol) of 1,2-dimethylhydrazine. The temperature was raised to 100 °C and a solution of 33.5 g (0.18 mol) of 1,2-dibromoethane in 50 mL of anhydrous xylene was added dropwise with stirring over a 4-h period. Heating was continued for an additional 8 h. The reaction mixture was distilled until the temperature reached 110 °C, yielding a two-phase distillate. The top phase was redistilled to give 4.7 g (32%) of the diazetidine: bp 70–72 °C (lit.[20] 70–71 °C); mass spectrum (rel intensity) 86 (100), 71 (30), 56 (15).

1,2-Diethyl-1,2-diazetidine. Using a procedure similar to that above, to 100 g of anhydrous sodium carbonate, 200 mL of anhydrous xylene, and 30 g (0.34 mol) of 1,2-diethylhydrazine[23] at 120 °C was added dropwise with stirring 100 g (1.06 mol) of 1,2-dibromoethane over a period of 8 h. The insoluble salts were removed by filtration and the solution was extracted with 4 N hydrochloric acid. The acid extracts were made basic and the organic layer was extracted with ether. The ether extract was dried over magnesium sulfate and then distilled to give 10.5 g (28%) of the 1,2-diazetidine: bp 119–120 °C; mass spectrum *m/e* (rel intensity) 114 (9), 99 (26), 85 (27), 56 (100).

Anal. Calcd for $C_5H_{14}N_2$: C, 63.11; H, 12.36; N, 24.53. Found: C, 62.89; H, 12.42; N, 24.79.

1,2-Diisopropyl-1,2-diazetidine. The same procedure as for the diethyl compound was used except for a temperature of 130 °C, a 20-h addition time, and a tenfold excess of ethylene bromide. Workup as with the diethyl compound gave 25.2 g (60%) of the diazetidine: bp 37 °C (7 mm) and 154–155 °C (atmospheric pressure) from 34.2 g of 1,2-diisopropylhydrazine;[24] mass spectrum *m/e* (rel intensity) 142 (4), 127 (1), 99 (11), 56 (100).

Anal. Calcd for $C_8H_{18}N_2$: C, 67.55; H, 12.76; N, 19.69. Found: C, 67.79; H, 12.73; N, 19.51.

1,2-Di-*tert*-butyl-1,2-diazetidine. The same procedure was used as for the diethyl compound, except for a reaction temperature of 135 °C, an addition time of 16 h, and a tenfold excess of ethylene bromide. Workup as with the diethyl compound gave 1.1 g (2.3%) of the diazetidine: bp 30–31 °C (4.7 mm) from 40 g of 1,2-di-*tert*-butylhydrazine;[25] mass spectrum *m/e* (rel intensity) 170 (2), 155 (0.2), 113 (1), 56 (100).

1,2-Diisopropyl-3-phenyl-1,2-diazetidine. To 28.5 g (0.25 mol) of 1,2-diisopropylhydrazine, 200 g of anhydrous sodium carbonate, and 650 mL of xylene at 130 °C was added dropwise with stirring a solution of 66 g (0.25 mole) of 1-phenyl-1,2-dibromoethane in 300 mL of anhydrous xylene over a period of 72 h. Workup as with the diethyl compound gave 1.5 g (2.9%) of the diazetidine: bp 105 °C (1 mm); mass spectrum *m/e* (rel intensity) 218 (8), 203 (2), 175 (4), 132 (100).

1,2-Diethyl-3-methyl-1,2-diazetidine. The same procedure as with the diethyl compound was used except that a temperature of 120 °C, an addition time of 16 h, and a threefold excess of 1,2-dibromopropane was used. A yield of 16.5 g (24%) of the diazetidine, bp 25 °C (9 mm), was obtained from 47.3 g of 1,2-diethylhydrazine. The elemental analysis was not satisfactory. Gas chromatography indicated the presence of an impurity. Mass spectrum *m/e* (rel intensity) 128 (58), 113 (18), 99 (88), 70 (100).

Registry No.—1,2-Diethyl-3-methyl-1,2-diazetidine, 66303-61-5; 1,2-dimethylhydrazine, 540-73-8; 1,2-dibromoethane, 106-93-4; 1,2-diethylhydrazine, 1615-80-1; 1,2-diisopropylhydrazine, 3711-34-0; 1,2-di-*tert*-butylhydrazine, 13952-69-7; 1-phenyl-1,2-dibromoethane, 93-52-7; 1,2-dibromopropane, 78-75-1.

References and Notes

(1) Presented in part before the 2nd International Heterocyclic Congress, Montpellier, France, June 1969.
(2) This work is from the thesis of William S. Bigard which was submitted in partial fulfillment of the Ph.D. requirements at Southern Illinois University August 15, 1970.
(3) E. Lustig and R. M. Moriarty, *J. Am. Chem. Soc.*, **87**, 3252 (1965).
(4) A. Mannschreck, R. Radeglia, E. Grundemann, and R. Ohme, *Chem. Ber.*, **100**, 1778 (1967).
(5) J. E. Anderson and J. M. Lehn, *J. Am. Chem. Soc.*, **89**, 81 (1967).
(6) B. Junge and H. A. Staab, *Tetrahedron Lett.*, 709 (1967).
(7) J. E. Anderson, *J. Am. Chem. Soc.*, **91**, 6374 (1969).
(8) P. Ogden, *Chem. Commun.*, 1084 (1969).
(9) Y. Nomura, N. Masai, and Y. Takeuchi, *Chem. Commun.*, 288 (1974).
(10) E. L. Alred, C. L. Anderson, R. L. Miller, and A. L. Johnson, *Tetrahedron Lett.*, 1535 (1967).
(11) S. E. Nelson and G. R. Weisman, *J. Am. Chem. Soc.*, **96**, 7111 (1974).
(12) R. A. Y. Jones, A. R. Katritzky, D. L. Ostercamp, K. A. F. Record, and A. C. Richards, *Chem. Commun.*, 644 (1971).
(13) R. A. Y. Jones, A. R. Katritzky, and R. Scattergood, *Chem. Commun.*, 644 (1971).
(14) R. A. Y. Jones, A. R. Katritzky, D. L. Ostercamp, K. A. F. Record, and A. C. Richards, *J. Chem. Soc., Perkin Trans. 2*, 34 (1972).
(15) R. A. Y. Jones, A. R. Katritzky, K. A. F. Record, and R. Scattergood, *J. Chem. Soc., Perkin Trans. 2*, 406 (1974).
(16) P. Rademacher, *Tetrahedron Lett.*, **1**, 83 (1974).
(17) W. D. Phillips in "Determination of Organic Structure by Physical Methods", Vol. 2, Academic Press, New York, N.Y., 1962, p 452.
(18) E. H. Carlson, A. P. Schapp, and M. Raban, *J. Org. Chem.*, **38**, 1605 (1973).
(19) E. Fahr, W. Fischer, A. Jung, and L. Sauer, *Tetrahedron Lett.*, 161 (1967).
(20) D. Horwitz, U.S. Patent 3129215 (1964).
(21) LAOCN3 by A. A. Bothner-By and S. Castellano, available from Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
(22) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959). The equation used was in the form $J = A + C \cos 2\theta$; the *B* term in the original equation was assumed to be small.
(23) E. Doomes and N. H. Cromwell, *J. Org. Chem.*, **34**, 310 (1969).
(24) DNMR by G. Binsch and D. A. Kleier, available from Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
(25) S. J. Brois, *J. Am. Chem. Soc.*, **89**, 4242 (1967).
(26) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958).
(27) H. H. Hatt, "Organic Synthesis", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 208.
(28) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1945).
(29) H. L. Lochte, J. R. Bailey, and W. A. Noyes, *J. Am. Chem. Soc.*, **43**, 2597 (1921).
(30) J. C. Stowell, *J. Org. Chem.*, **32**, 2360 (1967).