Acid-Catalyzed Oxidative Dimerization of Formaldehyde Dimethylhydrazone to Glyoxal Bisdimethylhydrazone. A Mechanism Study

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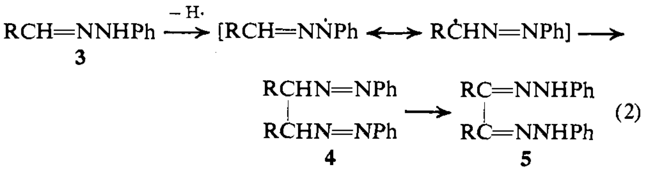
Abstract: Formaldehyde dimethylhydrazone (**1**) gives glyoxal bisdimethylhydrazone (**2**) when treated with acids, with or without a solvent. The reaction is accompanied by the formation of dimethylamine and tarry by-product. The transformation of **1** to **2** was also observed to take place slowly with water as a catalyst, and very slowly in pure, dry samples of **1** at room temperature, with no added catalyst. With acetic acid as catalyst, and 1,4-dioxane or 1-propanol as solvent, the yield of **2** approached 51.5%, or 77% of theory, with one-third of **1** undergoing reduction. When the reaction was carried out in the presence of 1,1-dimethylhydrazine, and 1,4-dioxane as solvent, polymer formation was reduced, and the yield of **2** approached 77%, or again 77% of theory, since the 1,1-dimethylhydrazine served as a replenisher of the **1** undergoing reduction. The reaction was shown to involve the formation of the simple head-to-head dimer of **1**, 2,2-dimethylhydrazinoacetaldehyde dimethylhydrazone (**8**). This intermediate was isolated and was shown to give **2** when heated with acetic acid. Following established pathways, **8** may undergo cleavage to dimethylamine and glyoxal dimethylhydrazone imine (**10**), which can give **2** by a transamination reaction with 1,1-dimethylhydrazine or, in its absence, by a transhydrazonation reaction with **1**.

During the course of work with hydrazines in this laboratory, a rapid, exothermic reaction of formaldehyde dimethylhydrazone (**1**) with acids was observed, resulting in the formation of a large amount of glyoxal bisdimethylhydrazone (**2**). In this paper

$$\underset{\mathbf{1}}{2\mathrm{Me_2NN{=}CH_2}} \xrightarrow{\mathrm{H^+}} \underset{\mathbf{2}}{\mathrm{Me_2NN{=}CHCH{=}NNMe_2}} + [2\mathrm{H}] \qquad (1)$$

are described results of experiments designed to shed light on the course and mechanism of this reaction.

The reaction bears superficial resemblance to the well-known oxidative dimerization of aldehyde phenylhydrazones,[2] eq 2. This is brought about by oxidizing agents, however, such as manganese dioxide, iodine, and ammoniacal silver nitrate.[2a] It takes place by a free-radical mechanism[2a,b] and gives a complex mixture of products, including *vic*-bisphenylazoalkanes (**4**) and osazones (**5**); the latter arise by tautomerization of the former, as in eq 2.



$$\underset{\mathbf{3}}{\mathrm{RCH{=}NNHPh}} \xrightarrow{-\mathrm{H}\cdot} [\mathrm{RCH{=}N\dot{N}Ph} \longleftrightarrow \mathrm{R\dot{C}HN{=}NPh}] \longrightarrow$$

$$\underset{\mathbf{4}}{\begin{matrix}\mathrm{RCHN{=}NPh}\\ |\\ \mathrm{RCHN{=}NPh}\end{matrix}} \longrightarrow \underset{\mathbf{5}}{\begin{matrix}\mathrm{RC{=}NNHPh}\\ |\\ \mathrm{RC{=}NNHPh}\end{matrix}} \qquad (2)$$

The free-radical pathway shown in eq 2 is not available to formaldehyde dimethylhydrazone because of the absence of hydrogen on nitrogen. Indeed, it has been shown that only N-monosubstituted hydrazones (like **3**) undergo oxidative dimerization to osazones (like **5**) by the free-radical mechanism[3] of eq 2.

An observation more closely related to that of eq 1 is the finding of glyoxal bisphenylhydrazone (**5**, R = H) among the products of reaction of formaldehyde and phenylhydrazine in the presence of acetic acid, in an early, unsuccessful attempt to prepare formaldehyde phenylhydrazone (**3**, R = H).[4] That reaction gives a complex mixture containing at least five nitrogen-containing compounds,[5] including a small amount of glyoxal bisphenylhydrazone.[4,5] The formation of glyoxal bisphenylhydrazone under these conditions was assumed[4b] to be a result of autoxidation like that described earlier.[2c] Our findings with formaldehyde dimethylhydrazone, however, suggest a different interpretation.

Results and Discussion

The transformation **1** → **2** (eq 1) was first observed when an attempt was made to purify a sample of **1** that was contaminated with about 20% 1,1-dimethylhydrazine, by treatment with phthalic anhydride in an amount sufficient to convert the 1,1-dimethylhydrazine to a nonvolatile hydrazide. After brief refluxing, the reaction mixture was distilled (oil bath to 135°) for recovery of **1**. Recovery was poor (about 50%), and the recovered material still contained about 10% 1,1-dimethylhydrazine. The nonvolatile residue was a dark brown mixture of liquid and gummy solid. The liquid portion was taken into ether and then distilled under reduced pressure. The product, **2**, was obtained as a yellow oil, bp 90–95° (4 mm), and was identified by comparison of its nmr, ir, and uv spectra with an authentic sample prepared by reaction of aqueous glyoxal with 1,1-dimethylhydrazine.[6]

In subsequent experiments, **2** was obtained in a small amount upon attempted reduction of **1** (to tri-

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[1] On leave from the Institute for Atomic Physics, Bucharest, Rumania.

[2] (a) J. Buckingham, *Quart. Rev., Chem. Soc.*, **23**, 37 (1969), and references therein; (b) C. Wintner and J. Wiecko, *Tetrahedron Lett.*, 1595 (1969), and references therein; (c) the first to report such a reaction were F. R. Japp and F. Klingemann, *Justus Liebigs Ann. Chem.*, 247, 190 (1888).

[3] H. Minato, H. Tatena, and H. Yokokawa, *Bull. Chem. Soc. Jap.*, **39**, 2724 (1966).

[4] (a) H. von Pechmann, *Ber.*, 30, 2459 (1897); (b) *ibid.*, **31**, 2183 (1898).

[5] E. Schmitz and R. Ohme, *Justus Liebigs Ann. Chem.*, **635**, 82 (1960).

[6] R. H. Wiley, S. C. Slaymaker, and H. Kraus, *J. Org. Chem.*, **22**, 204 (1957).

Table I. Acid-Catalyzed Oxidative Dimerization of Formaldehyde Dimethylhydrazone (**1**)[a]

					Anal. yield (glpc), mol % **1**			Isolated **2**, mol %	
Run	Catalyst (mol/mol of **1**)	Solvent[b]	Time, hr	Temp, °C	Unreacted **1**	**8**	**2**[c]	Yield[c,d]	Purity (glpc)
1	AcOH (0.15)[e]	None[e]	1	110–135		0	26		
2	AcOH (0.60)	None	1.75	80–100	3	8	49.5		
3	*p*-TsOH (0.33)[f]	None	2.75	80–105	1.5	7.25	40		
4	AcOH (0.56)	MeOH	3.5	70–78	2	12.1	47		
5	AcOH (0.69)	*n*-PrOH	4.25	75–103	1	0.7	51	50	95.5
6	AcOH (0.69)	1,4-Dioxane	4.5	75–105	1	0.6	51.5	51	94.2

[a] Scale: 0.25 mol of **1**. [b] Where a solvent was used, the amount was 80 ml/mol of **1**. [c] Based on eq 1. [d] The yield is that of pure **2** in the isolated product. For example, in run 5, the isolated yield corresponded to a 52.5% yield of **2** of 95.5% purity. [e] Acetic anhydride, 0.25 mol/mol of **1**, was also present. [f] Upon mixing of the reagents, a solid salt appeared; upon being heated, it disappeared; then a new insoluble salt appeared.

methylhydrazine) with formic acid, and in about 35% yield from a reaction of **1** (containing about 2% each 1,1-dimethylhydrazine and water) with acetic anhydride in a molar ratio of 3:1. Presumably acetic acid was the catalyst in the latter experiment.

In a search for by-products that would account for the two hydrogens lost in the transformation **1** → **2** (eq 1), reaction mixtures were examined by gas–liquid partition chromatography (glpc). No trimethylhydrazine and no acettrimethylhydrazide were found (see below); but dimethylamine was identified by its retention time in glpc and by its nmr spectrum in ether solution. Also, when the reaction was carried out in the presence of acetic anhydride, N,N-dimethylacetamide was identified in the mixture by its retention time in glpc and by its nmr and ir spectra.

In addition, the reaction is accompanied by formation of some tarry, presumably polymeric, material, which is soluble in water, but only partially soluble in ether. Accordingly, the reaction of eq 1 can be written as a disproportionation, eq 3.

$$\underset{\mathbf{1}}{3\mathrm{Me_2NN{=}CH_2}} \xrightarrow{\mathrm{H^+}} \underset{\mathbf{2}}{\mathrm{Me_2NN{=}CHCH{=}NNMe_2}} + \mathrm{Me_2NH} + [\mathrm{H_2C{=}NH}]\ (\text{polymer}) \qquad (3)$$

The results to be presented indicate that this transformation takes place by a mechanism comprising at least the following two steps: (i) acid-catalyzed head-to-head dimerization of **1** to an isolable intermediate, 2,2-dimethylhydrazinoacetaldehyde dimethylhydrazone (**8**), pictured as in eq 4a-c; and (ii) dehydrogenation of **8**, with **1** serving as hydrogen acceptor, as shown in eq 5.

$$\underset{\mathbf{1}}{\mathrm{Me_2NN{=}CH_2}} + \mathrm{HA} \rightleftharpoons \underset{\mathbf{6}}{[\mathrm{Me_2N\overset{+}{N}H{=}CH_2} \longleftrightarrow \mathrm{Me_2NNH\overset{+}{C}H_2}]} + \mathrm{A^-} \qquad (4a)$$

$$\underset{\mathbf{6}}{\mathrm{Me_2NNH\overset{+}{C}H_2}} + \underset{\mathbf{1}}{\mathrm{CH_2{=}N{-}\ddot{N}Me_2}} \longrightarrow \underset{\mathbf{7}}{\mathrm{Me_2NNHCH_2CH_2N{=}\overset{+}{N}Me_2}} \qquad (4b)$$

$$\mathbf{7} + \mathrm{A^-} \rightleftharpoons \underset{\mathbf{8}}{\mathrm{Me_2NNHCH_2CH{=}NNMe_2}} + \mathrm{HA} \qquad (4c)$$

$$\mathbf{8} + \mathbf{1} \longrightarrow \mathbf{2} + \mathrm{Me_2NH} + [\mathrm{NH{=}CH_2}]\ (\text{polymer}) \qquad (5)$$

Evidence in support of this mechanism and some elaboration of its details are presented below.

I. The Acidic Catalysis. Presented in Table I are data from experiments seeking to determine the optimum conditions for production of **2** from **1**. While acetic acid was the catalyst in most of those experiments, *p*-toluenesulfonic acid was also effective (run 3), and the use of formic acid and phthalic acid (or its acid hydrazide) was mentioned above.

The possibility that the reaction is thermally induced is eliminated by the fact that it took place as well in methanol (run 4), at a temperature at which pure **1** distilled unchanged after being heated at reflux for a similar time.

The use of a solvent had little influence on the yield of **2**, but it helped to control the temperature, as the reaction is vigorous and exothermic, once started. The yield of 51–51.5%, achieved in runs 5 and 6, with 1-propanol or 1,4-dioxane as solvent, corresponds to 76–77% of theory, with one-third of **1** undergoing reduction, as in eq 3.

In Figure 1 is shown the rate of formation of **2** from **1** at room temperature in the presence of various quantities of acetic acid (runs T1, T2, and T3), in the presence of various quantities of water (runs T4 and T5), in pure **1** without added catalyst (run T6), and in pure **1** stored on solid sodium hydroxide (run T7) or calcium hydride (run T8). The rate is clearly dependent on the concentration of acetic acid (runs T1–T3) or water (runs T4 and T5), which would be expected to behave as a weak acid in solution in **1**.

Runs T6–T8 show that **2** is produced from **1** at a very slow, nearly constant rate in purified samples of **1** (run T6) and in samples of **1** stored on solid sodium hydroxide or calcium hydride (runs T7 and T8, respectively). This slow formation of **2** cannot be ascribed to the presence of traces of water, because the rates were essentially the same, while it is unlikely the concentrations of water were the same, in the three samples. It may be the result of autoxidation or a base-catalyzed process with a mechanism involving anions as intermediates.[7]

II. The Dimerization Step. The head-to-head dimerization of **1** to **8** contrasts with the behavior of formaldehyde imines, which ordinarily undergo head-to-tail polymerization and give hexahydro-*s*-triazines.[8] As pictured in eq 4, of the three potentially nucleophilic centers in the hydrazone, namely, dimethylamino nitrogen, imino nitrogen, and methylenic carbon,[9] the

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(7) J. S. Walia, H. Singh, M. S. Chatta, and M. Satyanarayana, *Tetrahedron Lett.*, 1959 (1969).

(8) J. Graymore, *J. Chem. Soc.*, 1490 (1931).

(9) S. F. Nelsen, *J. Org. Chem.*, 34, 2248 (1969).

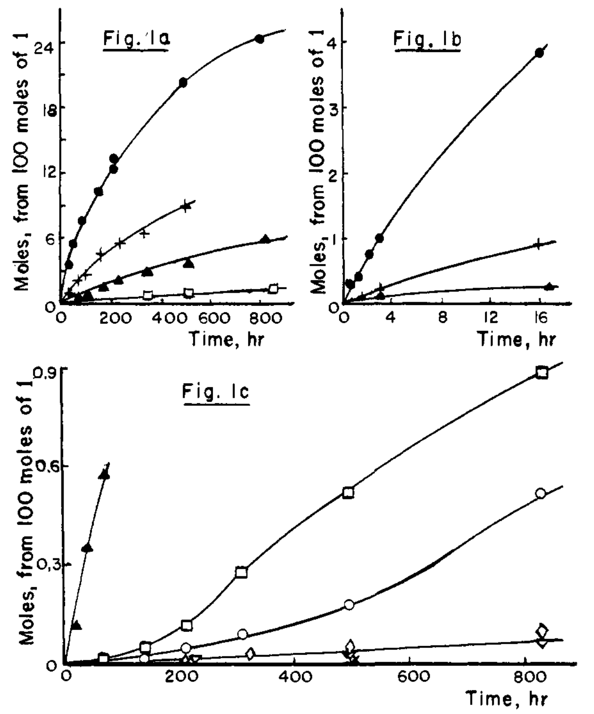

Figure 1. Rate of formation of **2** from 100 mol of **1**: run T1, with 19.44 mol of AcOH (●); T2, with 9.61 mol of AcOH (+); T3, with 5.1 mol of AcOH (▲); T4, with 20.25 mol of H_2O (□); T5, with 10.21 mol of H_2O (○); T6, without catalyst (▽); T7, stored on solid NaOH (×); T8, stored on calcium hydride (◇).

imino nitrogen is involved in protonation (eq 4a) and the methylenic carbon in dimerization (eq 4b). The result appears to be a consequence of two factors: (i) protonation at carbon[10] gives a substance, $Me_2N^+{=}NCH_3$, which is a poor electrophile; and (ii) electrophilic attack of **6** on **1** at the methylenic carbon is aided by electron release by the dimethylamino group as shown in eq 4b. The behavior is consistent with that observed with other hydrazones, which undergo attack at methylenic carbon by electrophiles,[2a] such as diazonium ions,[11] chlorosulfonyl isocyanates,[12a] and Vilsmeier reagent.[12b]

Although increasing acidity promoted the dimerization (data of Figure 1), it is noteworthy that **1** gives a stable hydrobromide, which can be purified at ambient temperatures without alteration.[13] The dimerization clearly requires the presence of both **1** and **6** in the reaction mixture.

III. The Intermediate. Close examination of the curves in Figure 1 shows that some of them (those showing the very early stages of the reaction) exhibit a point of inflection, which suggests that **2** arises from an intermediate. In fact glpc analysis showed the presence of six compounds with retention times between those of **1** and **2** at various times in the reaction mixtures. These are designated for convenience A–F, in order of increasing retention time in gas chromatography. Of these, C was the one present in highest concentration throughout most of the reaction (Figures 2 and 3). The same compound was found in significant amounts in the preparative runs conducted for short times or at low temperatures (Table I, **8**).

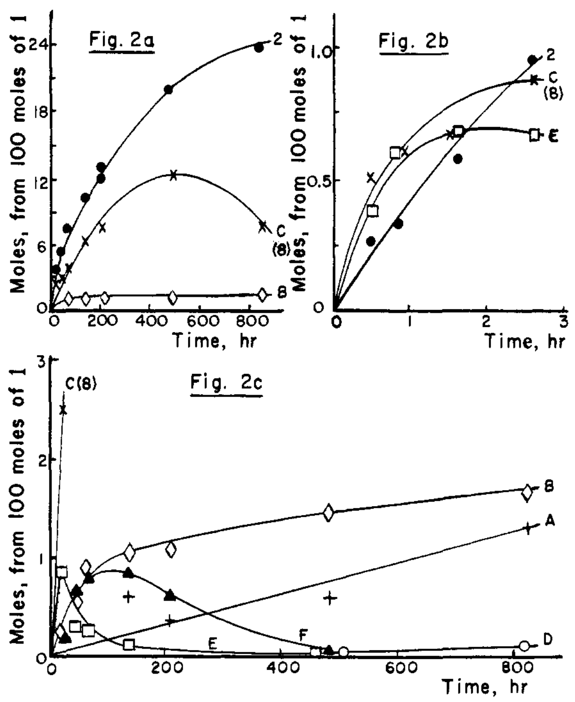

Figure 2. Rates of formation of products from 100 mol of **1** with 19.44 mol of AcOH (run T1).

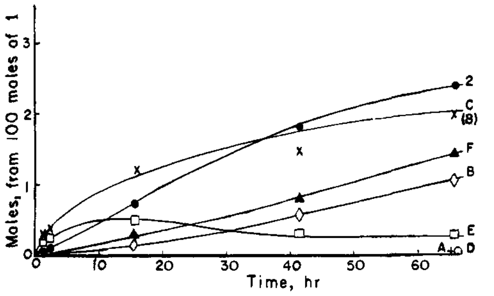

Figure 3. Rates of formation of products from 100 mol of **1** with 9.61 mol of AcOH (run T2).

As shown in Figures 2 and 3, the concentration of C rose faster than that of **2** in the initial stages of the reaction, reached a maximum, and decreased rapidly during the last stages of the reaction. This is the behavior that would be expected if C were an intermediate to **2**.[14,15] The substance C was isolated by preparative glpc and was shown to be **8**.

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[10] Probably all three sites are protonated reversibly in varying degrees; *cf.* G. J. Karabatsos, F. M. Vane, R. A. Taller, and N. Hsi, *J. Amer. Chem. Soc.*, **86**, 3351 (1964).

[11] A. F. Hegarty and F. L. Scott, *Chem. Commun.*, 622 (1966); *J. Org. Chem.*, **32**, 1957 (1967); F. A. Neugebauer and H. Trischmann, *Justus Liebigs Ann. Chem.*, **706**, 107 (1967).

[12] (a) R. Brehme and H. J. Nikolajevski, *Tetrahedron*, **25**, 1159 (1969); (b) *Z. Chem.*, **8**, 226 (1968).

[13] S. Wawzonek and W. McKillip, *J. Org. Chem.*, **27**, 3946 (1962).

[14] Of the other components of the reaction mixture, only E accumulated faster than **2** in the early stages of the reaction and therefore could be considered a precursor of **2** (Figures 2b, 3). E accumulated more slowly than C, as it would if it were an intermediate *subsequent* to C. It disappeared completely from the reaction mixture, however, while the concentration of C was still increasing (Figure 2c), as it might if it were an intermediate *preceding* C. Furthermore, in the runs at low acidity (water as catalyst), E developed later than the final product, **2**. (This is not shown by the figures given.) It is concluded, therefore, that E is an intermediate in a side reaction. The same appears to be true of the other components, A, B, D, and F. The small concentrations of these minor components precluded their isolation and identification.

[15] Of the runs from Figure 1, only runs T1 and T2 are presented in detail in Figures 2 and 3. The other runs gave curves with a similar pattern.

Table II. Acid-Catalyzed Oxidative Dimerization of Formaldehyde Dimethylhydrazone (**1**) in the Presence of Other Hydrazine Derivatives[a]

			Added hydrazine deriv				Anal. yield (glpc), mol % **1**			Isolated **2**, mol %	
Run	Mol of AcOH/mol of **1**	Solvent[b]	Formula	Mol/mol of **1**	Time, hr	Temp, °C	Unreacted **1**	**8**	**2**[c]	Yield[c,d]	Purity (glpc)
7	1.12	None	$Me_2NN{=}CMe_2$	1.0	3.5	75–85	12	4.7	33.3		
8	1.12	None	$Me_2NN{=}CMe_2$	1.0	3.75	75–100	6.5	1.75	45.2	44.3	92.5
9	1.12	None	$Me_2NN{=}CMe_2$	0.6	4	75–102	2.8	0.66	48.1	47.6	92.4
10	1.70	1,4-Dioxane	$Me_2N{-}NMe_2$	1.0	6	75–105	1	0.2	46	46	99
11[e]	1.38	1,4-Dioxane	$Me_2N{-}NH_2$	1.0	4	75–102	≥20	5	57.5	56.8	90.5
12[e]	1.68	1,4-Dioxane	$Me_2N{-}NH_2$	1.0	5.5	75–103	12	1.5	71	68.2	93.6
13[e]	1.70	1,4-Dioxane	$Me_2N{-}NH_2$	1.0	6	75–105	6	0.4	77	75	93.4

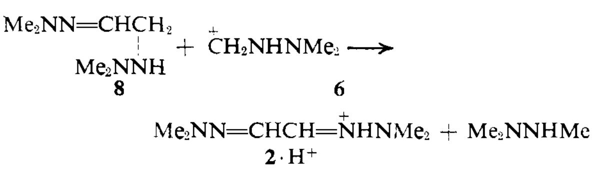
[a] See Table I, footnote *a*. [b] See Table I, footnote *b*. See Table I, footnote *c*. [d] See Table I, footnote *d*. [e] The reaction mixture in these runs was dark yellow or light brown and transparent; in all the others, it was black.

The nmr spectrum of C (δ 2.27, singlet, 6 H; 2.78, singlet, 6 H; 3.07, doublet, 2 H; and 6.63 ppm, triplet, 1 H, J = 5.5 cps, in $CDCl_3$ with internal TMS) and its ir spectrum were in agreement with structure **8**. The substance C was identical in all respects with a specimen of **8** synthesized by reaction of 1,1-dimethylhydrazine with chloroacetaldehyde, eq 6, a method previously used for similar compounds.[16] Finally, C was transformed into **2** (although in low yield) by treatment with acetic acid under conditions similar to those used for the conversion of **1** to **2** (see Experimental Section).

$$3Me_2NNH_2 + ClCH_2CHO \longrightarrow \underset{\mathbf{8}}{Me_2NNHCH_2CH{=}NNMe_2} + Me_2NNH_3^+Cl^- + H_2O \quad (6)$$

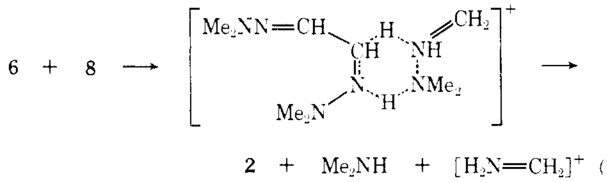
IV. **The Dehydrogenation.** For conversion of **8** to the final product **2**, several paths were considered, even though the step is like a corresponding step in osazone formation.[17]

a. A mechanism involving hydride transfer from **8** to **6**, as in eq 7, appears to be ruled out by the fact that no trimethylhydrazine was found in any run, nor was acettrimethylhydrazide found when the reaction was conducted in the presence of acetic anhydride. Furthermore, such a mechanism does not readily account for the formation of dimethylamine.



$$\underset{\mathbf{8}}{\begin{matrix}Me_2NN{=}CHCH_2\\ \vdots\\ Me_2NNH\end{matrix}} + \underset{\mathbf{6}}{\overset{+}{C}H_2NHNMe_2} \longrightarrow \underset{\mathbf{2}\cdot H^+}{Me_2NN{=}CHCH{=}\overset{+}{N}HNMe_2} + Me_2NNHMe \quad (7)$$

b. An intermolecular transfer of hydrogen between **6** and **8** as in eq 8, like that considered[18] and rejected[17] for the formation of osazones, also seems to be ruled out by the results of experiments in which other hydrazine derivatives were tested as hydrogen acceptors. These results are presented in Table II.

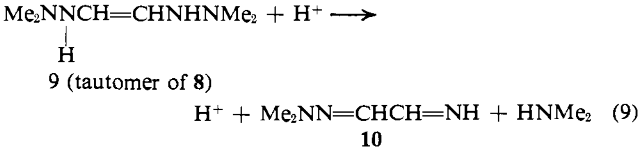


(8)

Comparison of the data in Tables I and II shows that no improvement in the yield of **2** was effected by carrying out the conversion of **1** to **2** in the presence of tetramethylhydrazine or acetone dimethylhydrazone, which are conceivable hydrogen acceptors in a process like that of eq 8. A considerable improvement in yield was obtained, however, with 1,1-dimethylhydrazine.

In the presence of 1 mol of 1,1-dimethylhydrazine, up to 77% **1** is converted to **2** (Table II, runs 11–13). Clearly some of the added dimethylhydrazine is taking the place of **1** as a hydrogen acceptor, for if it were not, and leaving out the possibility of acceptance of more than 1 mol of hydrogen by 1 mol of **1** under these new conditions, only 66²/₃% **1**, at most, could be converted to **2**, according to eq 3.

c. A mechanism consistent with our findings involves a protolytic cleavage of the tautomer, **9**, of **8** to give dimethylamine and glyoxal dimethylhydrazone imine, **10** (eq 9). Such a cleavage is well established for similar compounds.[17,19] The iminohydrazone **10** could give **2** by an acid-catalyzed transhydrazonation reaction[20] with **1**, eq 10, conceivably by way of a cyclic intermediate or transition state.[21]



$$\underset{\text{9 (tautomer of 8)}}{Me_2N\underset{\underset{H}{|}}{N}CH{=}CHNHNMe_2} + H^+ \longrightarrow H^+ + \underset{\mathbf{10}}{Me_2NN{=}CHCH{=}NH} + HNMe_2 \quad (9)$$

$$\underset{\mathbf{10}}{Me_2NN{=}CHCH{=}NH} + \underset{\mathbf{1}}{Me_2NN{=}CH_2} \xrightarrow{H^+} \underset{\mathbf{2}}{Me_2NN{=}CHCH{=}NNMe_2} + HN{=}CH_2 \quad (10)$$

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(16) H. Simon, G. Heubach, and H. Wacker, *Chem. Ber.*, **100**, 3101 (1967).

(17) H. Simon, G. Heubach, and H. Wacker, *ibid.*, **100**, 3106 (1967); H. Simon and W. Moldenhauer, *ibid.*, **102**, 1191 (1969).

(18) G. J. Bloink and K. H. Pausacker, *J. Chem. Soc.*, 661 (1952).

(19) L. Cagliotti, G. Rosini, and F. Rossi, *J. Amer. Chem. Soc.*, **88**, 3865 (1966).

(20) A. E. Arbuzov and Yu. P. Kitaev, *Tr. Kazan. Khim. Tekhnol. Inst.*, **23**, 60 (1957); *Chem. Abstr.*, **52**, 9980 (1958).

(21) While it is also possible that **10** may give **2** by a transamination reaction with 1,1-dimethylhydazine produced from part of **1** by solvolysis or acetolysis, it should be noted that the conversion of **1** to **2** was shown to take place in the presence of acetic anhydride (run 1, Table I) or with *p*-toluenesulfonic acid as catalyst (run 3). Under these conditions, the formation of free 1,1-dimethylhydrazine from **1** is unlikely, and a direct reaction of **10** with **1** must be admitted, conceivably involving a four-center transition state or an unstable hexahydro-*s*-triazine as intermediate. In the experiment in which the isolated intermediate C (**8**) was transformed into **2** by treatment with acetic acid, the low yield (27%, see Experimental Section) may be attributed in part to the small size of the sample used, but also in part to the need for part of **8** to take the place of **1** in this *trans*-hydrazonation reaction with **10**. The apparent inability of acetone dimethylhydrazone to compete with **1** in such a process (runs 7–9, Table II) may be ascribed to steric or electronic factors, or both.

With 1,1-dimethylhydrazine, **10** may be converted to **2** by an acid-catalyzed transamination reaction. Alternatively, the added 1,1-dimethylhydrazine may take part in a transamination reaction with formaldehyde imine produced as in eq 10, thus regenerating **1**. In either case, polymer formation, which is ascribed in part to formaldehyde imine or its equivalent,[22] would be reduced (footnote *e*, Table II), and the stoichiometry of the reaction would approach that shown in eq 11.

$$\underset{\mathbf{1}}{2\mathrm{Me_2NN{=}CH_2}} + \mathrm{Me_2NNH_2} \longrightarrow \underset{\mathbf{2}}{\mathrm{Me_2NN{=}CHCH{=}NNMe_2}} + \mathrm{Me_2NH} + \mathrm{NH_3} \quad (11)$$

In any case, since the iminohydrazone **10** was not detected in any reaction mixture, its conversion to **2** must be rapid compared to its formation from **8**.

Experimental Section

Nmr spectra were obtained on a Varian A-60 instrument, ir spectra on a Perkin-Elmer 137 spectrometer, and glpc analyses were made on a Varian Aerograph Model 90P gas chromatograph, with a column, 1.5 m × 6 mm diameter, filled with silicone SE-30, 20% on Chromosorb W (pretreated with DCMS), and with helium as carrier gas.

Reagents used in syntheses or as standards for ir, nmr, or glpc analyses were commercial pure grade materials and were used without prior treatment unless otherwise stated.

The 1,1-dimethylhydrazine was a practical grade obtained from Matheson Coleman and Bell. It was used as such for the preparation of **1**, but for use in reactions of **1** with acetic acid and in a reaction with chloroacetaldehyde for the preparation of 2,2-dimethylhydrazinoacetaldehyde dimethylhydrazone, it was dried for several days with calcium hydride and then distilled from calcium hydride.

1,4-Dioxane was dried for several days with calcium hydride and distilled from calcium hydride before use.

Glacial acetic acid was heated just before use with 2–3% acetic anhydride to remove traces of water.

Anhydrous *p*-toluenesulfonic and oxalic acids were prepared from their hydrated forms just before use, by azeotropic distillation of water with benzene.

Formaldehyde dimethylhydrazone (1) was prepared as described in the literature.[23] After distillation from solid sodium hydroxide, it was dried with calcium hydride at least three days, and then distilled from calcium hydride, bp 71–73° (lit.[23] bp 72° (730 mm)).

Acetone dimethylhydrazone was prepared as described[6,24] and was purified in the same manner as **1**.

The following compounds were prepared as described in the literature references given: **trimethylhydrazine**, bp 59–60° (lit.[23] bp 60° (735 mm)); **tetramethylhydrazine**, bp 73–74.5° (lit.[25] bp 71–72°); **acet-2,2-dimethylhydrazide**, bp 109–113° (24 mm) (lit.[26] bp 98–99° (16 mm)).

Acettrimethylhydrazide was prepared similarly to acet-2,2-dimethylhydrazide from trimethylhydrazine and acetic anhydride, bp 79–81° (21 mm) (lit.[27] bp 63–64° (8 mm)).

Oxidative Dimerization of 1. For the systematic study of reaction 1, the reagents were mixed in the proportions given in Tables I and II and heated in a flask equipped with a reflux condenser to about 70°, when an exothermic reaction began. The heat was removed and the temperature was maintained at about 70°, by cooling if necessary. After cessation of the exothermic reaction, the temperature was slowly raised to the maximum indicated in the tables and maintained at that temperature for the remainder of the time reported there. In those experiments where a solvent was used, the maximum temperature reported is the final reflux temperature of the mixture.

In some experiments, gases issuing from the top of the condenser were led to a trap containing ether and cooled in a Dry Ice–acetone mixture. The contents of the trap were analyzed by use of glpc and of nmr spectroscopy. Dimethylamine was identified as a product of the reaction in this way.

The reaction mixtures became black, except for those obtained in the presence of added 1,1-dimethylhydrazine, which were dark yellow or light brown, and transparent. After standing overnight at room temperature, the reaction mixture was cooled in ice and treated with 50% sodium hydroxide to pH 11. Water was added if necessary to dissolve solid salts, and the mixture was thoroughly extracted with ether. The ether extract was dried with solid sodium hydroxide 2 days, filtered, and distilled at atmospheric pressure for removal of the ether. Other solvents and volatile components were removed by distillation at 40–55° (25 mm) and collected in a Dry Ice–cooled trap. These two volatile fractions were weighed and analyzed by glpc for unreacted **1**. Dimethylamine was also found in the ether fraction.

The residue was worked up in one of two ways. (i) For analysis, it was distilled under vacuum as completely as possible and collected in a receiver cooled in Dry Ice–acetone. This distillate was weighed and analyzed by glpc. (ii) For preparation and isolation of **2**, it was distilled under vacuum, and a forerun to about 90° (4 mm) was separated. The product (**2**) was collected at 90–100° (4–6 mm) (lit.[6] bp 105° (10 mm)) in a receiver cooled in Dry Ice–acetone. It crystallized in the cold receiver and liquefied only after several hours at room temperature. Its purity was determined by glpc analysis.

The ir and uv spectra of **2** were identical with those of a standard prepared[6] from glyoxal and 1,1-dimethylhydrazine; the nmr spectrum (δ 2.81, 12 H, and 6.99 ppm, 2 H, singlets, in $\mathrm{CCl_4}$ with internal TMS) was the same for the two preparations.

Time Study Experiments. For a time study of the reaction of **1** with various quantities of acid, a mixture of **1** with quinaldine (integration standard for glpc analysis), in a 100:1 molar ratio, was prepared. Carefully measured portions of this mixture (2.5 ml, 2.057 g) were mixed with accurately weighed portions of acetic acid or water in glass-capped weighing bottles. (The proportions are given with Figure 1). In run T1, where the portion of acetic acid was so large as to cause an exothermic reaction on mixing, it was frozen at −10° before addition of **1**. It was brought to room temperature quickly and turned yellow immediately. In the other runs, the reagents were mixed at room temperature, very little or no heating was observed, and the yellow color developed much more slowly.

The mixtures were kept in the glass-capped bottles at room temperature (27 ± 2°), and samples were withdrawn at intervals and analyzed by glpc. In run 1, after 210 hr, the mixture was diluted with 0.6 part by weight of methanol, as it had become too viscous to be sampled otherwise.

The samples were injected into the gas chromatograph without prior treatment, the hydrazone acetates being instantly decomposed at the temperature of the injection port (200°). The validity of the procedure was demonstrated by analyzing a synthetic mixture of **2** with quinaldine (5:1 molar ratio) in the absence and in the presence of an excess of acetic acid (20 mol).

The composition of each sample was determined by measuring areas of peaks in the gas chromatograms, the molar ratio of components being assumed to be equal to the ratio of the corresponding peak areas. The points given in the figures are based on at least two chromatograms, excepting those corresponding to reaction times of less than 3 hr, for a glpc analysis required about 15 min.

Reaction of 2,2-Dimethylhydrazinoacetaldehyde Dimethylhydrazone (8) with Acetic Acid. Component C (**8** 350 mg) (isolated by preparative glpc from the reaction of **1** with acetic acid in methanol, run 4, Table I) was treated with 0.15 ml of acetic acid at 90–100° for 1 hr, then left overnight. The black reaction mixture was treated with NaOH solution and then extracted with ether. After drying and evaporation of the ether, there remained a 175-mg residue. Distillation of this under vacuum afforded 110 mg of distillate, which was shown by glpc analysis to consist of 85% **2**.

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(22) The near equality of the maximum yields of **2** observed in runs with and without added 1,1-dimethylhydrazine (77% of theory) suggests that about 23% **1** is consumed in a side reaction that is competitive with the head-to-head dimerization leading to **2**. This could be a head-to-tail polymerization accounting for part of the tarry by-product. Hexamethylenetetramine was not found in these mixtures. This is not surprising, however, for its formation from formaldehyde and ammonia presumably requires the presence of free formaldehyde to react with hexahydro-*s*-triazine, the cyclic trimer of formaldehyde imine, if indeed the latter is an intermediate. It need not be, for the various hydroxymethylamines would serve as well.

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Synthesis of 2,2-Dimethylhydrazinoacetaldehyde Dimethylhydrazone (8). Chloroacetaldehyde (7.85 g, 0.1 mol) (prepared from the acetal and anhydrous oxalic acid[28]) was cooled to −20° and 29 g (0.4 mol) of 1,1-dimethylhydrazine, previously dried several days with calcium hydride, was added. An exothermic reaction was observed on mixing the reagents. The mixture was kept for 14 hr at 0° and for 4 hr at room temperature. It was then cooled in ice and treated with concentrated sodium hydroxide solution and ether. A stable three-layer system was produced. The ether layer was separated and the remainder was thoroughly extracted with ether. The ether extract was dried with sodium hydroxide and the ether was removed by evaporation at room temperature. The residue (7.63 g) consisted (glpc) of 80% of a mixture of **8** and **2** in a molar ratio of 1:1.66 and 20% of a mixture of starting materials and several minor components. That is, the yields were 15.9% **8** and 26.4% **2**, which presumably arose from **8** during the process. Both **8** and **2** were isolated by preparative glpc.

The product **8**, a colorless liquid, was unstable and darkened on standing. Combustion analysis was considered impractical. Its nmr spectrum was identical with that of the product C isolated from the reaction of **1** with acids (see Results and Discussion). The ir spectrum (also identical with that of C) showed the bands expected for the assigned structure:[6,24] 3380 (w, broad), 2937 (s), 2850 (s), 2810 (s), 2760 (s), 1609 (mw), 1554 (vw), 1467 (s), 1452 (s), 1402 (vw), 1370 (w), 1325 (m), 1260 (s), 1179 (m), 1164 (mw), 1137 (m), 1111 (w), 1094 (mw), 1041 (s), 1013 (vs), 961 (vw), 882 (mw), 834 (mw), and 814 (ms) cm^{-1} (neat, film between NaCl plates).

A mass spectrum of **8**, direct from the gas chromatograph, was obtained with a Varian MAT-CH5 instrument, coupled with an Aerograph 1700 gas chromatograph. The spectrum, obtained at 70 eV, did not exhibit the molecular ion, but showed principal peaks at *m/e*: 129 (8%, M − CH_3?), 86 (22%), 85 (27%), 84 (7%), 83 (14%), 71 (10%), 58 (100%, base, Me_2N_2?), 57 (6%), 46 (7%), 44 (33%, Me_2N?), 43 (11%), 42 (47%), 30 (9%), 28 (7%), 27 (5%). The spectrum at *m/e* below 55 was very similar to that of **2**.

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The Palladium Chloride Catalyzed Cyclodimerization of 1-Methylcyclopropene

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Abstract: 1-Methylcyclopropene undergoes a thermal oligomerization in the presence or absence of free-radical inhibitors. The dimeric products of this reaction are shown to be those expected from an "ene" reaction. In the presence of a variety of palladium compounds, a facile cyclodimerization predominates, yielding a mixture of dimethyltricyclo[3.1.0.0^{2,4}]hexanes. The latter reaction is also shown by 1,3,3-trimethylcyclopropene, but not by 1,2-dimethylcyclopropene, cyclobutene, norbornadiene, or *trans*-cyclooctane. The mechanistic implications of the catalyzed cyclodimerizations are discussed.

Transition metal catalyzed cycloadditions are an interesting and important branch of organometallic chemistry.[1] The number of catalyzed reactions of simple olefins which yield four-membered rings, however, is quite limited, and the examples known apparently arise from diverse mechanisms. Butadiene gives 1,2-divinylcyclobutane with a bis(cyclooctadiene)-nickel–tris(*o*-phenylphenyl) phosphite catalyst by way of a bis-π-allylnickel intermediate which can close to either a four-, six-, or eight-membered ring.[2] Norbornadienes give pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradecanes with a wide variety of transition-metal catalysts.[3] Allene is dimerized to dimethylenecyclobutanes by nickel phosphine catalysts.[4]

Acetylenes can be catalytically dimerized to cyclobutadienes, trimerized to benzenes, or tetramerized to cyclooctatetraenes depending on the exact nature of the system.[5]

Four-membered ring intermediates have been suggested for the metathesis of both olefins[6,7] and acetylenes[8] using tungsten catalysts. It has been suggested that bond reorganization leads to an excited state of the cyclobutane which can revert to either of the two pairs of isomeric olefins or acetylenes. No cyclobutanes have actually been isolated from these reactions however.

The action of Lewis acids on 2-butyne leads to the

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