3-proton singlets 0.80, 0.84, 1.02, 1.04 p.p.m. (C–Me); 2-proton doublets 5 42, 5.53 p.p.m. (J = 5.5 c.p.s.) (olefinic hydrogens).

Anal. Calcd. for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 88.26; H, 11.53.

Stachene (XIIIb).—Treatment of 100 mg. of stachenone (XIIIa)[22] in 5 ml. of aqueous methanol with a solution of semicarbazide hydrochloride–sodium acetate afforded 100 mg. of solid which after several crystallizations from methanol gave plates of stachenone semicarbazone (XIII, Y = NNHCONH₂), m.p. 220–222°.

Anal. Calcd. for $C_{21}H_{33}N_3O$: C, 73.42; H, 9.68; N, 12.23. Found: C, 73.34; H, 9.46; N, 12.44.

$$\overset{O}{\overset{\|}{}}$$

A mixture of 25 mg. of the semicarbazone (XIII, Y = NNHCNH₂) and *ca.* 30 mg. of sodium methoxide in 1 ml. of methanol was heated at 160° in a sealed tube for 4 hr. Isolation of the product by ether extraction gave 17 mg. of a clear mobile oil which was dissolved in hexane and passed through a short column of alumina. Gas chromatography of the oily filtrate, 12 mg., on a Carbowax column (20% w.w. on Chromosorb) at 250° showed a single peak which on collection gave pure stachene (XIIIb), m.p. 25–27°, [α]²³D +39° (*c* 2.0, CHCl₃); spectra: infrared, *gem*-dimethyl 7.16 (m) and 7.27 (m) μ, olefinic H bending 13.74 (s) μ; p.m.r., 3-proton singlets 0.90, 1.00, 1.03, 1.07 p.p.m. (C–Me); 2-proton doublets 5.42, 5.67 p.p.m. (J = 5.5 c.p.s.) (olefinic hydrogens).

Anal. Calcd. or $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 88.32; H, 11.85.

Ester XVIIb.—The acid XVIIa, obtained from the Jones oxidation of beyerol (XIX),[25] was dissolved in ether and treated with excess ethereal diazomethane. The crude ester was crystallized from methanol to afford an 85% yield of pure ester XVIIb (prisms), m.p. 138–140°; spectra: infrared (Nujol), C=O

5.78 (s), 5.82 (s), 5.90 (s) μ; p.m.r., 3-proton singlets 0.92, 1.28 p.p.m. (C–Me) and 3.68 p.p.m. (OMe); 2-proton singlet 5.86 p.p.m. (C_{15}- and C_{16}-hydrogens); 1-proton singlet 9.65 p.p.m. (aldehyde hydrogen).

Anal. Calcd. for $C_{21}H_{28}O_4$: C, 73.22; H, 8.19. Found: C, 73.08; H, 8.23.

Diol Ester XIVc.—A solution of 150 mg. of the ester XVIIb in 15 ml. of absolute methanol was cooled to 0° and 45 mg. of sodium borohydride added slowly with stirring. After being allowed to stand at 0° for 1 hr., the solution was evaporated *in vacuo* and the residue was treated with water and extracted with ether. Removal of the ether, after drying, left 135 mg. of gum which was dissolved in benzene and chromatographed on 1 g. of alumina (activity IV). Elution with benzene and 19:1 benzene–ether gave 80 mg. of solid which on successive crystallizations from ether–hexane and ether–methanol afforded needles of pure diol ester XIVc, m.p. 148–148.5°, [α]²⁰D +53° (*c* 1.6, 95% EtOH); spectra: infrared (CCl₄), OH 2.95 (w), C=O 5.78 (s) μ.

Anal. Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.85; H, 9.20.

Triester XVIIIb.—A mixture of 27 mg. of the diol ester XIVc and 10 mg. of anhydrous sodium acetate was refluxed in acetic anhydride for 2 hr. The solution was cooled, poured into water, and extracted with ether. The extract was worked up in the usual manner giving 21 mg. of product which on three crystallizations from hexane yielded 10 mg. of long prisms of the triester XVIIIb, m.p. 126–127.5°; spectra: infrared (CCl₄), C=O 5.75 (s) μ; p.m.r., 3-proton singlets 0.78, 1.03 p.p.m. (C—Me); 2.03, 2.05 p.p.m. (CH₃CO); 3.68 p.p.m. (OMe); 2-proton doublets 4.17, 4.35 p.p.m. (J = 7.5 c.p.s.) (acetoxymethyl); 1-proton multiplet 4.45–4.70 p.p.m. (C₃-H); 2-proton singlet 5.80 p.p.m. C_{15}- and C_{16}-hydrogens.

Anal. Calcd. for $C_{25}H_{34}O_6$: C, 69.74; H, 7.96. Found: C, 69.80; H, 8.39.

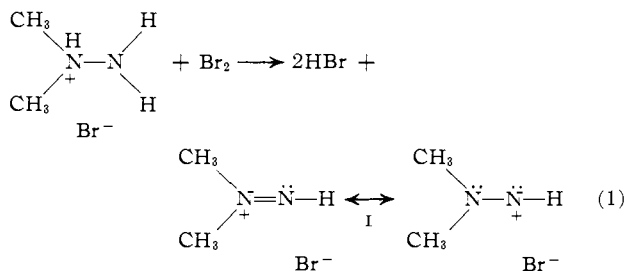# Electrophilic Addition Reactions of 1,1-Dimethyldiazenium Bromide with 1,3-Dienes and Styrenes[1]

By W. H. Urry, Peter Szecsi, C. Ikoku, and D. W. Moore

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1,1-Dimethyldiazenium bromide (I), prepared by the oxidation of 1,1-dimethylhydrazine with bromine in hydrobromic acid solution, reacts with conjugated olefins. For example, with 1,3-butadiene, a good yield of 1,1-dimethyl-Δ⁴-tetrahydropyridazinium bromide, and, with styrene, 1,1-dimethyl-2-(2-bromo-2-phenylethyl)-hydrazinium bromide (II) is obtained. Compound II dissolves in aqueous base to give 1,1-di methyl-4-phenyl-1,2-diazetidinium hydroxide (III), and immediate addition of sodium perchlorate gives its perchlorate IV. If the basic solution of III (pH above 8) is allowed to stand, it hydrolyzes to give 1,1-dimethyl-2-(2-hydroxy-2-phenylethyl)hydrazine (V). In weakly acidic solutions, V is also formed, but a competing decomposition of II gives styrene. With dilute acid, V gives an interesting fragmentation reaction to yield dimethylamine, ammonia, formaldehyde, and benzaldehyde, and hydrolyzes to give 1,1-dimethylhydrazine and phenylacetaldehyde.

Recent research[2–4] has shown that in the oxidation of 1,1-dialkylhydrazines in cold (0°) aqueous acidic solutions 2 equivalents of oxidizing agent (I₂, Br₂, Cl₂, and NaBrO₃) are consumed, and a moderately stable oxidation intermediate, the 1,1-dialkyldiazenium salt, is obtained.

The unusual structure I is supported by its unique nuclear magnetic resonance spectrum. This n.m.r. absorption (methyl singlet, 4.78 δ) appears when bromine is added to a solution of 1,1-dimethylhydrazine in hydrobromic acid (D₂O, 0°, methyl singlet of hydrazinium ion, 3.39 δ; and broad singlet due to all exchangeable hydrogen, DOH–NH, 5.92 δ). The latter absorp-

(1) Presented in part at the Combined Regional Meeting of the Southwest and Southeast Regions of the American Chemical Society, New Orleans, La., Dec. 7–9, 1961.
(2) W. R. McBride and H. W. Kruse, *J. Am. Chem. Soc.*, **79**, 572 (1957).
(3) W. H. Urry, H. W. Kruse, and W. R. McBride, *ibid.*, **79**, 6568 (1957).
(4) W. R. McBride and E. M. Bens, *ibid.*, **81**, 5546 (1959).

tion shifts to higher δ-values as the hydrobromic acid concentration of the sample is increased. The absorptions of I and the 1,1-dimethylhydrazinium ion, however, are quite independent of their concentrations and the acidity of the solution. When 1,1-dimethylhydrazine in deuteriotrifluoroacetic acid is oxidized with bromine, the same type of spectrum is observed (n.m.r. in deuteriotrifluoroacetic acid with TMS; hydrazinium

methyl singlet, 3.04 δ; methyl singlet of I, 4.42 δ; and singlet of exchangeable hydrogen species, 10.01 δ).

When the acidic solutions of oxidation intermediates such as I are made basic, tetralkyltetrazenes are formed in quantitative yield (n.m.r. of tetramethyltetrazene in D_2O–HBr: methyl singlet, 2.86 δ; DOH–singlet, 4.80 δ; n.m.r. in CCl_4: methyl singlet, 2.75 δ). Recently, mixtures of these diazenium salts have been made basic, and a statistical distribution of all possible tetralkyltetrazenes is obtained.[4] Further, reaction of I with acetaldehyde gave 1,1-dimethylhydrazine and acetic acid (see Experimental).

A preliminary communication[3] reported that the reaction of I with isoprene gives 1,1,4-trimethyl-Δ^4-tetrahydropyridazinium bromide (84%) and the dimethylhydrazone of trans-2-methylbut-2-enal (12%). Similarly, when a hydrobromic acid solution of I was stirred with 1,3-butadiene at −10° for 6 hr., 1,1-dimethyl-Δ^4-tetrahydropyridazinium bromide (73%) was obtained. No dimethylhydrazone of trans-but-2-enal was observed. Catalytic hydrogenation of this pyridazinium bromide gave 1-amino-4-dimethylaminobutane (2 moles of hydrogen absorbed). This diamine was identical with that prepared by the reduction with lithium aluminum hydride of γ-dimethylaminobutyronitrile (prepared from dimethylamine with γ-bromobutyronitrile, obtained from the reaction of 1,3-dibromopropane with potassium cyanide).

When a mixture of styrene with a solution of I in hydrobromic acid at 0° is vigorously stirred, crystalline II(76%) precipitates.
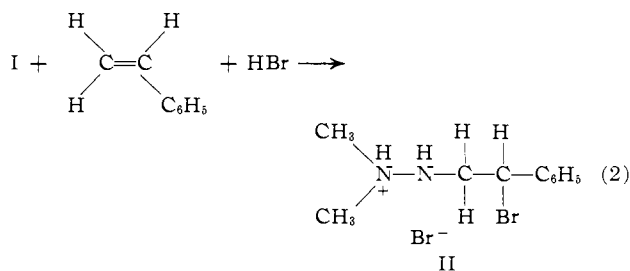
Compound II was identified with its n.m.r. spectrum (in dimethylformamide at 80°: N–methyl peak, 3.15 δ; methylene doublet, 3.91 δ; and benzylic hydrogen triplet, 5.60 δ, J = 7.5 c.p.s.; and phenyl multiplet, 7.45 δ), and its hydrogenation to give 2-phenylethylamine (76%), 1,1-dimethyl-2-(2-phenylethyl)hydrazine (15%), and dimethylamine.
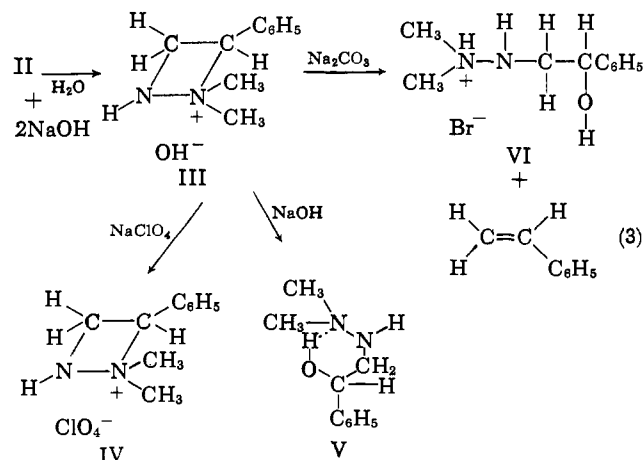
Compound II appears to dissolve in dilute aqueous alkaline solutions. This interesting phenomenon has been shown to be due to cyclization of the intermediate hydrazinobromide to give III.

Treatment of II with dilute sodium carbonate solution and then with sodium perchlorate solution gave 1,1-dimethyl-4-phenyl-1,2-diazetidinium perchlorate (IV, n.m.r. in D_2O: two methyl peaks, 2.91 and 3.62 δ; methylene triplets, 4.26 and 4.71 δ; NH–DOH, 4.82 δ, change with concentration; benzylic triplet, 6.27 δ; and a singlet phenyl peak at 7.74 δ; areas, 2.9:3.0:1.1:-0.95:5.1; spectrum same with change of concentration of IV and pH). A solution of the diazetidinium salt in aqueous acetic acid gave this n.m.r. spectrum that was unchanged after 48 hr. at room temperature. Accordingly, its hydrogenation under these conditions gave 2-dimethylamino-2-phenylethylamine (identical with that prepared by the method of Hauser).[5,6]

When II is dissolved in solutions of sodium hydroxide in deuterium oxide, the n.m.r. spectrum indicates that III is first formed, but this spectrum disappears as that of V develops (approximate half-life with 4 N NaOH in D_2O, 15 min.; that with 1.16 N NaOH in D_2O, 2.5 hr.). However, when excess II is added to sodium carbonate solution (0.36 N in D_2O), as the initial spectrum III fades that of VI develops (over 24 hr., final solution acidic), and styrene (n.m.r. spectrum of a carbon tetrachloride extract identical with known) separates as an upper layer. These results suggest that the basic hydrolysis of III is a displacement reaction by hydroxide ion. Precise kinetic studies are in progress. When this hydrolysis is slow as a consequence of low hydroxide ion concentration, decomposition of II to give styrene and I occurs.

While diazetidinium salts such as IV have not been observed previously, an interesting chemistry of this ring system exists. Examples are: (1) the reactions of azobenzenes with diarylketenes to give 1,2,3,3-tetraaryl-1,2-diazetid-4-ones[7–11]; (2) photolysis of cis-azobenzene and ketene in hexane to give 1,2-diphenyl-1,2-diazetidone-3[12]; (3) reactions illustrated by that of tetrafluoroethylene with methyl azodiformate to give dimethyl 3,3,4,4-tetrafluoro-1,2-diazetidine-1,2-dicarboxylate[13–17]; (4) formation of 1,2-bis(2-pyridyl)-1,2-diazetidine from the reaction of 2,2'-azodipyridine with diazomethane[18–20]; (5) reactions of 4-substituted-1,2-diaryl-3,5-dioxopyrazolidines with sodium hypochlorite in sodium hydroxide solution to give 3-substituted 1,2-diphenyl-3-carboxy-1,2-diazetid-4-ones[21,22];

(5) G. F. Morris and C. R. Hauser, J. Org. Chem., 26, 4741 (1961).

(6) G. F. Morris and C. R. Hauser, ibid., 27, 465 (1962).

(7) D. K. Ingold and S. D. Weaver, J. Chem. Soc., 127, 378 (1925).

(8) A. H. Cook and D. G. Jones, ibid., 184 (1941).

(9) L. Horner, D. Spietschka, and A. Gross, Ann., 573, 17 (1951).

(10) D. Y. Curtin and J. L. Tveten, J. Org. Chem., 26, 1764 (1961).

(11) M. Colonna and A. Risaliti, Gazz. chim. ital., 90, 1165 (1960).

(12) G. O. Schenck and N. Engelhard, Angew. Chem., 68, 71 (1956).

(13) R. D. Cramer, U. S. Patent 2,456,176 (Dec. 14, 1948).

(14) J. C. Kauer, U. S. Patent 2,860,154 (Nov. 11, 1958).

(15) J. C. Kauer and A. K. Schneider, J. Am. Chem. Soc., 82, 852 (1960).

(16) W. H. Knoth, Jr., and D. D. Coffman, ibid., 82, 3873 (1960).

(17) J. L. Anderson, R. E. Putnam, and W. H. Sharkey, ibid., 83, 386 (1961).

(18) M. Colonna, Atti. accad. nazl. Lincei Rend. Classe sci. fis. mat. nat., 26, 248 (1959).

(19) M. Colonna and A. Risaliti, Gazz. chim. ital., 89, 2493 (1959).

(20) A. Risaliti and A. Monti, ibid., 90, 397 (1960).

(21) R. Pfister and F. Hafliger, U. S. Patent 2,859,211 (Nov. 4, 1958).

(22) J. R. Geigy Akt.-Ges., British Patent 813,474 (May 21, 1959).

and (6) the action of phenylhydrazine on ω-haloaceto-phenones to give 1,3-diphenyl-1,2-Δ²-diazetine.[23]

Of special interest is the preparation of 3,3,4,4-tetra-fluoro-1,2-Δ¹-diazetine in 80% yield by passing cyano-gen over argentic fluoride at 105°.[24] The claim by Curtius[25] of the preparation of dimethyl-1,2-diazete has not been challenged hitherto. His product (prepared from 2,3-butanedione and hydrazine in aqueous acid, m.p. over 270°, insoluble in benzene, alcohol, or water) probably was polymeric.

When II was treated with aqueous sodium hydroxide solution (10%) on a larger scale, V was isolated (43%). Treatment of V with aqueous acidic solutions gives two simultaneous reactions: (1) fragmentation to give benzaldehyde, formaldehyde, dimethylamine, and am-monia; and (2) dehydration and hydrolysis to give phenylacetaldehyde and 1,1-dimethylhydrazine. The former reaction is an intramolecular oxidation–reduc-tion assisted by the weak nitrogen–nitrogen link of V.

The reaction of I under the same conditions with the more reactive 2-phenylpropene occurs with lower con-version (66%). No solid addition product precipi-tates; but when the reaction mixture is made basic, 1,1-dimethyl-2-(2-hydroxy-2-phenylpropyl)hy-drazine (VII, 93% yield, based on olefin consumed) is obtained. Unreacted 2-phenylpropene (34%) was recovered, and tetramethyltetrazene (76% yield, based upon I not consumed in the formation of the addition product) was also isolated.

Compound VII also undergoes fragmentation with acid to give acetophenone, formaldehyde, dimethyl-amine, and ammonia; and dehydration–hydrolysis to 2-phenylpropanal and 1,1-dimethylhydrazine.

The reaction (time, 7 hr.) of I with indene at 0–5° gave the crystalline 1,1-dimethyl-2-(1-bromo-2-in-danyl)hydrazinium bromide (58% yield, based on in-dene consumed). Indene (58%) was recovered, and when the aqueous acid solution was neutralized, tetra-methyltetrazene (85% yield) was obtained. In an-other experiment the above hydrazinium bromide was not isolated; and as stirring was continued (reaction time, 15 hr.), the solid product vanished to give a reac-tion mixture of two liquid phases. The latter was neutralized with base to give the 1,1-dimethyl-2-(1-hydroxy-2-indanyl)hydrazines (62% yield, two prod-ucts, presumably cis and trans), and unreacted indene (32%) was recovered. Catalytic hydrogenation of the 1,1-dimethyl-2-(1-bromo-2-indanyl)hydrazinium bromide gave 2-aminoindane, 1,1-dimethyl-2-(2-in-danyl)hydrazine, and dimethylamine. The identity of this hydrazine product was confirmed by its oxidation to the dimethylhydrazone of 2-indanone (not isolated) that was converted to its 2,4-dinitrophenylhydrazone.

These additions of I to the olefins used seem to at-tain equilibrium, and the separation of the addition

(23) J. van Alphen, Rec. trav. chim., 65, 112, 117 (1946).

(24) H. J. Eméleus and G. L. Hurst, J. Chem. Soc., 3276 (1962).

(25) Th. Curtius and K. Thun, J. prakt. Chem., [2] 44, 175 (1891).

products as a second phase (either solid or liquid) drives the reactions to higher conversion (see Table I). With styrene (compare Table Ia and Ib), the conversion to II was limited by the small amount of bromide present when sulfuric acid was used in preparing the solution of I and no other addition product was obtained. With indene when methanol was used (Table If) only limited conversion to its addition product (20%) oc-curred in a homogeneous reaction mixture.

TABLE I

YIELDS AND CONVERSIONS IN THE REACTION OF I
WITH STYRENES AND INDENE

	Olefin	Time, hr.	Conver-sion,[a] %	Yield,[b] %	Yield of TMT,[c] %
(a)	Styrene	5	100	76	[f]
(b)	Styrene[d]	4	42	44	40
(c)	2-Phenylpropene	6	66[e]	93	65
(d)	Indene	15	68	62	[f]
(e)	Indene	7	46	75	75
(f)	Indene[g]	5	20	52	85

[a] Based upon recovered olefin. [b] Of addition product of I to olefin, based upon olefin consumed. [c] Tetramethyltetrazene, based on that part of I not used in the formation of addition product, obtained after reaction mixture is made basic. [d] In reaction with a solution of I (1.34 M) in sulfuric acid (5.0 N) and hydrobromic acid (1.34 N). [e] 2-Phenylpropene (17%) recovered and remainder (17%) converted to dimers. [f] Not measured. [g] Methanol (250 ml.) added to reaction mixture of I with indene (0.20 mole).

The weak electrophilic reactivity of I under the condi-tions is indicated by three observations: (1) the limited conversions in the above reactions; (2) it does not react with 1-phenylpropene or trans-stilbene[26]; and (3) attempts to achieve aromatic substitution with I and phenol or dimethylaniline[26] failed. The reactivity of I may be decreased by the water in the two-phase reaction mixture used. It is obvious, however, that under these reaction conditions I is more reactive than hydrobromic acid since none of the organic bromide from addition of the latter to the olefin was observed. Indications that II decomposes to give I and styrene permits the hope that further electrophilic substitution and addition reactions may be achieved with II in organic media.

Experimental

The Reaction of I with 1,3-Butadiene.—The general prepara-tion of I involved the addition with vigorous stirring of a solution containing bromine (32 g., 0.20 mole), hydrobromic acid (Baker and Adamson, 48%, 75 ml.), and water (100 ml.) to a solution of 1,1-dimethylhydrazine (Westvaco, 12 g., 0.20 mole, b.p. 63°, n^{20}D 1.4088) in hydrobromic acid (48%, 50 ml.) and water (100 ml.) held at 0°. This solution (350 ml.) contained I (0.57 M) in hydrobromic acid (3.75 N).

The two-phase reaction mixture of this solution with butadiene (Matheson, 40 g., 0.74 mole) was stirred for 4 hr. at −10°. Evaporation (Rinco) of the resulting mixture at 40° gave a brown residue (37.5 g.). Several repetitions of addition of anhydrous ethanol to the residue, and then its evaporation, gave crystalline material. This product (28 g., 73% yield, m.p. 201–202° after 3 recrystallizations from anhydrous 2-propanol) was shown to be 1,1-dimethyl-Δ⁴-tetrahydropyridazinium bromide.

Anal. Calcd. for $C_6H_{13}N_2Br$: C, 37.3; H, 6.8; Br, 41.4. Found: C, 37.3; H, 6.9; Br, 41.4.

Another experiment with the same quantities of reagents and conditions was carried out to study volatile products. The reac-tion mixture was made basic with sodium hydroxide solution (20%), and was extracted with ether (400 ml., dried Na₂SO₄). Distillation gave tetramethyltetrazene (0.9 g., 0.008 mole, 8% yield, infrared identical with known), and no dimethylhydrazone of crotonaldehyde was detected.

(26) P. Szecsi, Ph.D. Thesis, University of Chicago, 1961.

The 1,1-dimethyl-Δ^4-tetrahydropyridazinium bromide (42.0 g., 0.22 mole) in ethanol (95%, 500 ml.) was hydrogenated in a Parr apparatus at room temperature (pressure 40–50 p.s.i.; Adams catalyst, 0.3 g.; hydrogen, 0.36 mole, absorbed). Then, the reaction mixture was filtered, and the filtrate was evaporated (Rinco). The residual product salt was made basic with sodium hydroxide solution (10%, 50 ml.), and the resulting mixture was extracted with chloroform (four 50-ml. portions). Fractional distillation of the chloroform solution (dried over Na_2SO_4) gave 1-amino-4-dimethylaminobutane (6.21 g., 28%, b.p. 50–53° at 42 mm., $n^{20}D$ 1.4210). With a saturated solution of oxalic acid in ether, it gave its dioxalate (m.p. 123–125° from 95% ethanol).

Anal. Calcd. for $C_{10}H_{20}N_2O_8$: C, 40.5; H, 6.8; N, 9.5. Found: C, 40.7; H, 6.9; N, 9.3.

The authentic diamine was prepared by the following preparative sequence. 1-Bromo-3-cyanopropane (13 g., 0.088 mole, 35% yield, b.p. 101–103° at 21 mm.) and recovered 1,3-dibromopropane (Eastman, 57.5 g., 0.284 mole, b.p. 165°) were obtained in the reaction of 1,3-dibromopropane (101 g., 0.50 mole) with potassium cyanide (16.25 g., 0.25 mole) in anhydrous methanol (300 ml., reflux 7 hr.).[27] The 1-bromo-3-cyanopropane (13.0 g., 0.080 mole) and an aqueous solution of dimethylamine (40%, 100 g., 0.88 mole) was held at reflux (7 hr., Dry Ice condenser)[28] to give 1-cyano-3-dimethylaminopropane (2.5 g., 0.032 mole, 25%, b.p. 75–76° at 18 mm., $n^{20}D$ 1.4271).[29] Reduction of this nitrile (2.5 g., 0.022 mole) with a solution of lithium aluminum hydride (3.8 g., 0.10 mole)[30] gave 1-amino-4-dimethylamino butane (2.0 g., 0.017 mole, 80%, b.p. 52° at 45 mm., $n^{20}D$ 1.4196). The infrared spectrum of this diamine was identical with that obtained by the hydrogenation of 1,1-dimethyl-Δ^4-tetrahydropyridazinium bromide. Its dioxalate (m.p. 125–126°, mixture m.p. 125–126°) was prepared.

The Reaction of I with Styrene.—A mixture of styrene (Matheson Coleman and Bell, 21.0 g., 0.20 mole, b.p. 43–45° at 15 mm., $n^{20}D$ 1.5471) with the above diazenium bromide solution was stirred vigorously for 5 hr. at 0°. The white crystalline product 1,1-dimethyl-2-(2-bromo-2-phenylethyl)hydrazinium bromide (II, 49.0 g., 76% yield, m.p. 130° from anhydrous 2-propanol) that precipitated was removed on a filter.

Anal. Calcd. for $C_{10}H_{16}N_2Br_2$: C, 37.1; H, 5.0; N, 8.6; Br, 49.3. Found: C, 37.2; H, 5.0; N, 8.7; Br, 49.5.

The filtrate was evaporated to dryness (Rinco) to give a semicrystalline dark residue (20 g.). Attempts to isolate further product from this residue failed.

1,1-Dimethylhydrazine (12.0 g., 0.20 mole) in a solution of sulfuric acid (20 ml.) in water (100 ml.) was oxidized with bromine (32 g., 0.20 mole). The styrene (21 g., 0.20 mole) was added to it, and the mixture was stirred for 4 hr. at 0°. Compound II (12 g., 18%, m.p. 126–129°) was recovered by filtration, and after the filtrate was made basic it was extracted with ether. Distillation gave recovered styrene (12.1 g.) and tetramethyltetrazene (4.7 g.).

This addition product II (35.0 g., 0.108 mole) in ethanol (95%, 500 ml.) with Adams platinum oxide catalyst (0.3 g.) was hydrogenated (Parr, pressure 40–50 p.s.i., 25°; after 7 hr., 0.23 mole of H_2 absorbed). The reaction mixture was filtered, and hydrobromic acid (48%, 10 ml.) was added to it. Evaporation (Rinco, 10 mm.) gave a residue that was treated with sodium hydroxide solution (10%, 100 ml.) and was then extracted with ether (six 50-ml. portions, dried Na_2SO_4). Fractional distillation gave 2-phenylethylamine (10.0 g., 76%, b.p. 65–66° at 8 mm., $n^{20}D$ 1.5200), and 1,1-dimethyl-2-(2-phenylethyl)hydrazine (2.85 g., 15% yield, b.p. 85–87° at 8 mm., $n^{20}D$ 1.5006). The amine gave its known oxalate (m.p. 212–213°),[31] benzoyl derivative (m.p. 116–117°),[32] and picrate (m.p. 167–168° from ethanol).[33]

The hydrazine reduced alcoholic silver nitrate solution to give metallic silver and gave a positive Jamieson test. With oxalic acid in ether, it gave 1,1-dimethyl-2-(2-phenylethyl)hydrazinium oxalate (m.p. 125–126° from 95% ethanol).

Anal. Calcd. for $C_{12}H_{18}N_2O_4$: C, 56.7; H, 7.1; N, 11.0. Found: C, 56.8; H, 7.7; N, 10.6.

Ether from the above distillation contained dimethylamine that was identified by conversion to dimethylammonium oxalate (m.p. 149–151°)[34] with oxalic acid. With picric acid, dimethylammonium picrate (m.p. 159–160°,[35] mixture m.p. 158–159°) was prepared.

In another experiment, the 1,1-dimethyl-2-(2-bromo-2-phenylethyl)hydrazinium bromide (18.0 g., 0.05 mole) was again hydrogenated as above to give 2-phenylethylamine (3.5 g., 60%, 0.03 mole), and dimethylammonium oxalate (4.15 g., 60%, 0.03 mole, m.p. 149–150°) was obtained by treatment of the volatile products with oxalic acid.

The Reaction of II with Sodium Hydroxide Solution.—A suspension of II (26.0 g., 0.08 mole) was stirred in water (50 ml.), and sodium hydroxide solution (20%, 50 ml.) was added at 0°. The reaction mixture, on standing overnight, separated into two phases. It was extracted with ether (four 50-ml. portions, dried Na_2SO_4). Distillation gave V (6.2 g., 43%, b.p. 100–101° at 2 mm., $n^{20}D$ 1.5308). An intractable residue (4 g.) remained. Compound V (m.p. 45–47° from 90° petroleum ether) solidified on cooling in a Dry Ice bath.

Anal. Calcd. for $C_{10}H_{16}N_2O$: C, 66.6; H, 8.9; N, 15.5. Found: C, 66.4; H, 8.7; N, 15.7.

The structure V is confirmed by its n.m.r. spectrum (in CCl_4 with TMS; methyl singlet, 2.44 δ; methylene quadruplet, 2.70, 2.75, 2.78, and 2.83 δ; hydroxyl singlet, 3.34 δ (changed with concentration); benzylic quadruplet, 4.67, 4.73, 4.80, and 4.86 δ; and phenyl doublet, 7.24 δ; areas, 6.1:2.0:1.1:1.0:5.1. The phenyl doublet and the typical ABX spectrum of the methylene and benzylic hydrogens suggest the indicated hydrogen bonding. The oxalate of V (structure VI) has the typical methylenic doublet and benzylic triplet (below).

Reaction of V with oxalic acid in ether gave 1,1-dimethyl-2-(2-hydroxy-2-phenylethyl)hydrazinium oxalate (m.p. 122–123.5° from absolute ethanol). The n.m.r. spectrum of this oxalate (hydrazinium oxalate in D_2O; TMS external standard; methyl singlet, 3.28 δ; methylene doublet, 3.52 δ; benzylic triplet, 5.13 δ; and phenyl singlet, 7.65 δ; areas, 6.0:2.0:1.1:5.1) showed that it was in equilibrium with the free base (its methyl singlet, 2.44 δ, decreased when oxalic acid was added).

Anal. Calcd. for $C_{12}H_{18}N_2O_5$: C, 53.3; H, 6.7; N, 10.4. Found: C, 53.8; H, 7.0; N, 10.3.

The fragmentation reaction of V with dilute sulfuric acid was most convenient in the presence of 2,4-dinitrophenylhydrazine since products are aldehydes. A solution containing 2,4-dinitrophenylhydrazine (2 g., 0.01 mole), sulfuric acid (7 ml.), water (12 ml.), and ethanol (95%, 30 ml.) was added to a solution of V (0.9 g., 0.005 mole) in ethanol (95%, 5 ml.). Hydrazones precipitated immediately, but the mixture was allowed to stand (25°, 24 hr.). The precipitate (1.33 g.) was isolated on a filter. A sample of it (0.08 g.) was analyzed by column chromatography (2 × 10 cm., packed with 2:1 silicic acid and Super-Cel; activated 24 hr. at 200°; sample added in chloroform, 10 ml.). Development (9:1 petroleum ether, 30°, and ethyl ether) eluted the first band, the 2,4-dinitrophenylhydrazone of phenylacetaldehyde (0.014 g., 17.5%, m.p. 119–122°, mixture m.p. 119–122°). The second (eluted 1:1 petroleum ether and ethyl ether) and third bands (eluted 1:1 ethyl ether and ethyl acetate) contained the 2,4-dinitrophenylhydrazones of formaldehyde (0.02 g., 25%, m.p. 166–169°) and benzaldehyde (0.03 g., 38%, m.p. 236–238°, mixture m.p.'s not depressed, chromatography recovery 81%). Hydrolysis of V with dilute sulfuric acid in the absence of the hydrazine gave essentially the same results. After the aldehydes had been removed by steam distillation, the residual solution was made basic. Further distillation gave dimethylamine (oxalate, m.p. 150–151°) and ammonia.

Preparation of IV.—Compound II (1.0 g., 0.0031 mole) was dissolved in a solution of sodium carbonate in water (0.36 N, 10 ml., 0°), and a saturated solution of sodium perchlorate in water (10 ml.) was added. This reaction mixture was allowed to stand (3 hr.) and white crystalline 1,1-dimethyl-4-phenyl-1,2-diazetidinium perchlorate (IV, 0.52 g., 0.002 mole, 65%, m.p. 82–83° from anhydrous ethanol) precipitated. The n.m.r. spectrum confirming structure IV is described above. An unusual feature of this spectrum is that splitting constants (J = 8.5 c.p.s.) for each of the methylene hydrogens and the benzyl hydrogen atom are equal with the result that triplets are observed for each one.

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Anal. Calcd. for $C_{10}H_{15}N_2O_4Cl$: C, 45.7; H, 5.8; N, 10.7; Cl, 13.5. Found: C, 45.6; H, 5.6; N, 10.5; Cl, 13.4.

Hydrogenation of basic solutions of III (PtO₂, rhodium-on-alumina, or palladium-on-charcoal) was too slow to compete with its hydrolysis. However, the n.m.r. spectrum (acetic acid methyl, 2.10δ ; 2.90, 3.60, 4.25, 4.69, 6.29, and 7.74 δ) of a solution prepared by dissolving II in sodium carbonate solution (D₂O) and then adding excess acetic acid was the same as that of IV, and the spectrum remained unchanged after 48 hr.

Accordingly, II (16.5 g., 0.051 mole) was dissolved in sodium carbonate solution (0.36 N, 275 ml., styrene odor observed) held at 0°. Glacial acetic acid (37.5 ml.) and palladium-on-charcoal (2.13 g.) were then added to the cold reaction mixture. Hydrogenation (pressure ~760 mm., 25°; hydrogen, 1238 ml., standard conditions, 0.055 mole absorbed) was complete in 28 hr.

The reaction mixture was filtered (Celite) and the filtrate (310 ml.) was evaporated (Rinco) to 25 ml. Sodium hydroxide pellets were added at 0°. The strongly basic mixture then was filtered and the filtrate was extracted with ether (six 125-ml. portions). Distillation gave 2-dimethylamino-2-phenylethylamine (3.0 g., 36% yield, b.p. 68–70° at 1 mm., n^{25}D 1.5256). The infrared spectrum of this product was identical with that prepared by Hauser with lithium aluminum hydride reduction of α-dimethylaminophenylacetonitrile from the reaction of the sodium bisulfite-benzaldehyde addition product with dimethylamine and sodium cyanide. Reaction of this diamine with phenyl isothiocyanate gave 1-(2-dimethylamino-2-phenylethyl)-3-phenyl-2-thiourea (m.p. 140–142°, mixture m.p. 141–142°).

Anal. Calcd. for $C_{17}H_{21}N_3S$: C, 68.2; H, 7.0; N, 14.0; S, 10.7. Found: C, 68.0; H, 7.0; N, 13.9; S, 10.8.

N.m.r. Studies of I and II.—1,1-Dimethylhydrazine was dissolved in hydrobromic acid (n.m.r. in D₂O: methyl singlet, 3.33 δ and DOH–NH singlet, 5.18 δ). Bromine was added to the n.m.r. tube (n.m.r., 0°, stirring: $(CH_3)_2NHNH_2Br$ methyl singlet, 3.39 δ; singlet methyl of I, 4.78 δ; and DOH–NH singlet, 5.92 δ) and relative areas of two methyl peaks showed that the mole fraction of I was 0.26.

With successive additions of bromine, the methyl peak of I (4.78 δ) and that of singlet peak due to DOH–NH increased in area and the latter shifted to higher δ-values (n.m.r.: mole fraction of I of 0.36 and 1.0, excess Br₂, gave 6.25 and 7.27 δ, respectively) as that of the hydrazinium methyl decreased at the same δ. Reverse trends were observed with subsequent successive additions of the initial solution of 1,1-dimethylhydrazinium bromide in hydrobromic acid (n.m.r.: peaks of DOH–NH at 7.12, 6.91, and 6.42 δ when mole fractions of I were 0.96, 0.71, and 0.43, respectively). In all of these experiments, the chemical shift of the methyl peak of I (4.78 δ) and that of the 1,1-dimethylhydrazinium ion (3.39 δ) did not change with changes in concentration of the ions and in acid concentration. A careful n.m.r. scan to 16.0 δ revealed no other absorption peaks. Apparently, exchange of hydrogen attached to nitrogen occurs so rapidly between I or the hydrazinium ion and DOH that only one peak is observed.

With changes in concentration (0.2008 and 0.3654 molal in D₂O) and acidity (0.3654 molal in IV and 0.3641 molal in oxalic acid) of solutions of IV, its n.m.r. spectrum remained the same as that given above.

When II is dissolved in concentrated sodium hydroxide solution (15% in D₂O), reaction to give III and its basic hydrolysis is so rapid that the n.m.r. spectrum taken immediately is a composite of that of IV and the methyl (2.44 δ) and the phenyl peaks (7.24 δ) of V. With subsequent spectra, the peaks of III diminish and then disappear (after 30 min.) while the two dominant peaks of V reach a limited height, and an oil layer accumulates above the aqueous solution. When carbon tetrachloride (containing tetramethylsilane) is added to the n.m.r. tube, the n.m.r. spectrum of this extract (lower phase) is identical with that of V above. Observations were the same with 1.16 N sodium hydroxide solution in D₂O, except that a longer time (~12 hr.) elapsed before the n.m.r. spectrum of III disappeared.

When an excess of II is added to sodium carbonate solution (0.36 N in D₂O; undissolved II still suspended in sample), the initial n.m.r. spectrum is a composition of that of IV and that of V in acid solutions (methyl, 3.28 δ; phenyl, 7.65 δ) and another peak (3.37 δ; probably that of the methyl of dissolved II). Nuclear magnetic resonance spectra taken after various periods of reaction time show the successive decrease of peaks due to III and II and an increase of a spectrum identical with that of the oxalate of V given above (phenyl peaks of III and V of equal area

after 3 hr.). When the spectrum of III has disappeared (8 hr.), that of the acid form of V remains, and an upper oil layer had separated. Its extract in carbon tetrachloride gave an n.m.r. spectrum identical with that of styrene.

The dimethylhydrazone of phenylacetaldehyde (n.m.r. in CCl₄ with TMS: methyl, 2.69 δ; methylene doublet, 3.46 δ; aldehydic triplet, 6.49 δ; and phenyl singlet, 7.15 δ) apparently is not a product in these reactions.

The Reaction of I with 2-Phenylpropene.—A mixture of 2-phenylpropene (23.6 g., 0.20 mole) and the standard solution of I was stirred at 0° for 6 hr. No solid precipitated and two liquid phases were observed throughout the reaction. The organic phase was taken up in chloroform, and the aqueous solution remaining was extracted with more chloroform (200 ml., dried Na₂SO₄). Distillation gave recovered 2-phenylpropene (4 g., b.p. 44–46° at 7 mm., n^{20}D 1.5385). A residue (4 g., 2-phenylpropene dimers) remained.

Sodium carbonate (106 g., 1 mole) was added to the aqueous phase, and near neutrality it became purple-red in color to become colorless again on further addition. An organic phase separated and the mixture was extracted with ether (eight 50-ml. portions, dried Na₂SO₄). Its distillation gave tetramethyltetrazene (3.0 g., b.p. 48.5–49° at 32 mm., n^{20}D 1.4651, 65% yield based upon I not used in reaction with 2-phenylpropene), and 1,1-dimethyl-2-(2-hydroxy-2-phenylpropyl)hydrazine (23.5 g., b.p. 113–114° at 5 mm., n^{20}D 1.5195, 93% yield based on 2-phenylpropene consumed).

Anal. Calcd. for $C_{11}H_{18}N_2O$: C, 68.0; H, 9.3; N, 14.4. Found: C, 67.8; H, 9.3; N, 14.2.

A residue (1.2 g.) was left in the distilling flask.

This hydrazino alcohol was treated with a saturated solution of oxalic acid in ether to give its oxalate (two crystalline forms: m.p. 120–121°, rapid cooling from anhydrous ethanol; m.p. 130–130.5°, slow cooling from ethanol; interconverted).

Anal. Calcd. for $C_{13}H_{20}N_2O_5$: C, 54.9; H, 7.1; N, 9.9. Found (m.p. 120–121°): C, 55.4; H, 7.2; N, 10.0. Found (m.p. 130–131.5°): C, 54.9; H, 7.2; N, 9.7.

The identity of this hydrazino alcohol was confirmed by its fragmentation reaction in acid. 1,1-Dimethyl-2-(2-hydroxy-2-phenylpropyl)hydrazine (1.0 g., 0.005 mole) in ethanol (95%, 5 ml.) was added to a solution containing 2,4-dinitrophenylhydrazine (2.0 g., 0.01 mole), sulfuric acid (concentrated 7 ml.), water (10 ml.), and ethanol (95%, 30 ml.; reaction time, 72 hr.) The crystalline hydrazone mixture (0.2 g.) was collected on a filter. A sample (0.07 g.) in chloroform (10 ml.) was added to the chromatographic column previously described. Development (9:1 petroleum ether, 30°, and ethyl ether) gave three bands. Elution of the first band with the developing mixture gave the 2,4-dinitrophenylhydrazone of formaldehyde (0.01 g., 14% yield, m.p. 166–168°). The second band was 2,4-dinitrophenylhydrazone of 2-phenylpropanal (eluted, ethyl ether; 0.03 g., 43% yield, m.p. 136–138°, mixture m.p. same). The third band was the 2,4-dinitrophenylhydrazone of acetophenone (eluted, ethyl acetate; 0.02 g., 29% yield, m.p. 244–248°, mixture m.p. not depressed).

The Reaction of I with Indene.—These reactants were brought into reaction under three different conditions with differing results. The usual solution of I and redistilled indene (Eastman, 23.2 g., 0.20 mole, b.p. 75–76° at 22 mm., n^{20}D 1.5592) were stirred for 4.5 hr. at 0°. A white solid precipitated from the reaction mixture; but when it was stirred overnight at room temperature, the crystalline material disappeared leaving two liquid phases. No reprecipitation of it occurred when the mixture was stirred for 5 hr. more at 0°.

The reaction mixture was extracted with ether (200 ml.) and the ether extract was washed with sodium carbonate solution (10%, 100 ml., dried Na₂SO₄). Distillation gave indene (7.48 g., 32% recovered, b.p. 72–73° at 20 mm., n^{20}D 1.5412; infrared identical with starting indene). A distillation residue (3.0 g.) remained.

The aqueous phase of the reaction mixture was made basic with a solution of potassium hydroxide (95 g., in 350 ml. of water), and an oil separated. The mixture was extracted with ether (four 100-ml. portions, dried Na₂SO₄). Evaporation gave a mixture of the racemic *cis* and *trans* forms of 1,1-dimethyl-2-(1-hydroxy-2-indanyl)hydrazine (16.0 g., 62% yield based on indene used, m.p. 87–88°); the second isomer (0.05 g., m.p. 114–117°) was isolated from the recrystallization filtrate. Recrystallization from petroleum ether (90°) gave the major product.

Anal. Calcd. for $C_{11}H_{16}N_2O$: C, 68.7; H, 8.4; mol. wt., 192. Found (major product): C, 68.3; H, 8.1; mol. wt., 195. Found (minor product): C, 68.6; H, 8.3.

The minor product was not investigated further.

The major product gave a positive Jamieson test as did its oxalate (m.p. 135–137° from ethanol).

Anal. Calcd. for $C_{24}H_{34}N_4O_6$: C, 60.7; H, 7.2. Found: C, 60.4; H, 7.2.

This hydrazino alcohol gave a different oxalate (1:1; m.p. 108–109° from ethanol–ether) when it was treated with an excess of oxalic acid in ether.

Anal. Calcd. for $C_{13}H_{18}N_2O_5$: C, 55.3; H, 6.4. Found: C, 55.1; H, 6.4.

A mixture of the solution of I with indene (25.0 g., 0.207 mole) was stirred for 7 hr. at 0°. The white solid that precipitated was removed upon a filter and was washed with cold acetone to give 1,1-dimethyl-2-(1-bromo-2-indanyl)hydrazinium bromide (18.0 g., 56% based on indene used, m.p. 125° dec.).

Anal. Calcd. for $C_{11}H_{16}N_2Br_2$: C, 39.3; H, 4.8; Br, 47.6. Found: C, 39.4; H, 4.8; Br, 47.0.

The two-phase filtrate was extracted with ether (200 ml.) and the ether solution was washed with sodium carbonate solution (5%) and water (extract dried Na_2SO_4). Its distillation gave indene (13.5 g., 54% recovered, b.p. 69–70° at 16 mm., $n^{20}D$ 1.5592).

The aqueous phase was made alkaline with sodium hydroxide solution (20%) and it was stirred overnight. The upper organic phase that had separated was extracted with ether (four 100-ml. portions, dried Na_2SO_4). Evaporation gave 1,1-dimethyl-2-(1-hydroxy-2-indanyl)hydrazine (3.5 g., 19% yield, m.p. 83–85° from ligroin).

Distillation of the ether solution that had been removed in the evaporation gave tetramethyltetrazene (5.43 g., 75% based upon I not used in the formation of other two products, b.p. 48.5–49° at 32 mm., $n^{20}D$ 1.46 49).

The usual solution of I and indene (23.2 g., 0.20 mole) in methanol (250 ml.) was stirred for 5 hr. at 0°. 1,1-Dimethyl-2-(1-bromo-2-indanyl)hydrazinium bromide (7.0 g., 0.021 mole, 52% based on indene used) precipitated. Indene (18.5 g., 0.16 mole, 80% recovery, b.p. 69–70° at 16 mm., $n^{20}D$ 1.5588) was obtained by distillation of a benzene extract of the reaction mixture.

The reaction mixture was made basic and was extracted with ether. Distillation gave tetramethyltetrazene (7.0 g., 0.068 mole, 85% yield).

The 1,1-dimethyl-2-(1-bromo-2-indanyl)hydrazinium bromide (38.0 g., 0.113 mole) in ethanol (95%, 340 ml.) was hydrogenated (Parr, 25°, Adams catalyst, 0.4 g.; hydrogen, 0.16 mole,

absorbed). The reaction mixture was filtered and then evaporated (Rinco). The residue was treated with a sodium hydroxide solution (10 g. in 50 ml. of H_2O; strong amine odor). The mixture was extracted with ether (350 ml., dried Na_2SO_4). Distillation gave an ether solution that was treated with excess oxalic acid to give dimethylammonium oxalate (3.0 g., 0.022 mole, m.p. 148–150° from ethanol,[34] 20%), 2-amino-indane (0.9 g., b.p. 43–46° at 1 mm., $n^{20}D$ 1.5352, 6%; benzoyl derivative, m.p. 152–155°,[36] oxalate m.p. 214–216° dec.), and 1,1-dimethyl-2-(2-indanyl)hydrazine (8.6 g., 0.049 mole, b.p. 65–69° at 1 mm., $n^{20}D$ 1.5310, 43%). This hydrazine gave an oxalate (m.p. 143–146° from ethanol).

Anal. Calcd. for $C_{13}H_{18}N_2O_4$: C, 58.6; H, 6.8; N, 10.5. Found: C, 58.6; H, 5.4; N, 10.2.

To confirm further the identity of this hydrazine its oxalate was dissolved in hydrochloric acid, and it was oxidized with potassium iodate solution. The residue from evaporation of an ether extract of this reaction mixture gave the 2,4-dinitrophenylhydrazone of 2-indanone (m.p. 194–196° dec. from 95% ethanol).[37]

The Reaction of I with Acetaldehyde.—A reaction mixture containing I and acetaldehyde (8.8 g., 0.20 mole) was stirred for 4 hr. at 0°. It was then made basic with sodium hydroxide solution, and it was extracted with ether (four 100-ml. portions). The ether solution (dried Na_2SO_4) was distilled to give tetramethyltetrazene (2.8 g., 0.024 mole, 24%; infrared identical with that of known). The ether distillate was treated with oxalic acid, and 1,1-dimethylhydrazinium oxalate (1.0 g., 0.006 mole, m.p. 142–143° from ethanol, positive Jamieson test) was obtained.

The distillate (300 ml.) from steam distillation of the basic aqueous solution until volatile base ceased to codistil contained 1,1-dimethylhydrazine (8.3 g., 0.138 mole, 72%; by titration of aliquot portions with standard potassium iodate solution in acid).

The aqueous solution remaining in the distilling flask was made acidic with sulfuric acid. It was then distilled until no more acid codistilled. Titration of the distillate with standard sodium hydroxide solution showed that it contained acetic acid (7.2 g., 0.12 mole, 60% yield). The distillate was then made basic and evaporated to dryness. The residual salt was treated in ethanol–water with *p*-nitrobenzyl chloride, and *p*-nitrobenzyl acetate (m.p. 76–77° from 95% ethanol) was obtained.

The same products as well as acetaldehyde and 1-butanol were obtained in the reaction of I with an equimolar amount of butyl vinyl ether. Apparently, in the acidic reaction mixture this ether was hydrolyzed to give the butanol and acetaldehyde that was then in part oxidized to acetic acid.

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Transition State Characterization for the Permanganate Oxidation of Fluoral Hydrate

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Rate data for the four kinetically distinct mechanisms for permanganate oxidation of fluoral hydrate have been analyzed to assign upper and lower limits to bond breaking and bond making in the four transition states. For the first time in this type of analysis, both upper and lower limits have been assigned for a single transition state. The data are shown to be interpreted easily by this approach if the reactions are assumed to proceed with hydride transfer from fluoral hydrate to permanganate in the rate-determining step. The data are shown to be inconsistent with this analysis if a hydrogen atom transfer mechanism is assumed.

It recently has been shown[2] that rate data for corresponding catalyzed and uncatalyzed reactions may be analyzed to obtain the thermodynamic parameters for the virtual dissociation of the catalyst from the transition state of the catalyzed reaction to yield the transition state of the uncatalyzed reaction. Such parameters may then be used to characterize the structures of the two transitions states.

A set of related reactions which are particularly well suited to such an analysis is found in the oxidation of fluoral hydrate to trifluoroacetic acid by permanganate.[3] For this reaction, the rates of four kinetically distinct processes have been determined. The kinetic terms differ only in the extent of protonation of the reactants, so that three successive pK_a's can be calculated corresponding to virtual equilibria between the four transition states. For reaction in aqueous solution

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