and $AgNO_3$, collecting the precipitate of AgCl, and weighing it. The ir spectra were determined with a Beckman IR-8 spectrometer and the nmr spectra were determined with a Varian HA-100 spectrometer. Hydrolysis equivalents, neutralization equivalents, and titration curves were determined by titrating the samples with standard base with the aid of a Sargent Model D recording titrator.

Monoethyl 2-Ethoxyvinylphosphonochloridate (4).—Thionyl chloride (82.5 g, 0.8 mol) was added dropwise with stirring to diethyl phosphonoacetaldehyde diethyl acetal[5] (**3**) (50.8 g, 0.2 mol), the addition being at a rate to maintain a reaction temperature of 40°. The solution was heated under reflux for 12 hr and was distilled, giving 12.2 g (30%) of crude **4**: bp 90–95° (1 mm); ir (neat), 6.2 (vinyl ether), 8.0 (P=O), 9.8 μ (P–O–C); nmr (neat), δ 1.32 (m, CH_3), 4.10 (m, CH_2), 5.20 (d of d, J_{HH} = 13 cps, J_{PH} = 15 cps, PCH), and 7.34 (t, $J_{HH} = J_{PH}$ = 13 cps, CHOR). *Anal.* Calcd for $C_6H_{12}ClO_3P$: Cl, 17.85; hydrolysis equiv, 99.3. Found: Cl, 17.9; hydrolysis equiv, 106. The hydrolysis equiv was determined by dissolving a weighed sample in water, allowing the solution to stand for 30 min, followed by titrating with standard base. It was assumed that **4** was converted to **5**. The analyses indicate that this compound was not analytically pure. However, the thermal instability of **4** prevented its careful fractional distillation. It was necessary to distil it without a column and preferably at a temperature below 100°. Above 100° decomposition seemed to increase rapidly and a violent decomposition occurred once at 115–120°.

Monoethyl Phosphonoacetaldehyde 2,4-Dinitrophenylhydrazone.—Crude **4** (2.45 g, 0.0125 mol) was added to 20 ml of water. The mixture was stirred to effect complete solution (about 5 min), it was added to 2.50 g (0.0126 mol) of 2,4-dinitrophenylhydrazine in 95 ml of water–ethanol–sulfuric acid (20:60:15 by vol), the solution was allowed to stand for 30 min, water was added to cause a cloudy solution, and the mixture was allowed to stand 12 hr longer. The resulting orange precipitate was collected and recrystallized from water–ethanol to give 3.70 g (89%) of the DNP derivative, mp 192–193° dec. *Anal.* Calcd for $C_{10}H_{13}N_4O_7P$: N, 16.87; P, 9.33; neut equiv, 332. Found: N, 16.86, 17.08; P, 9.37, 9.25; neut equiv, 328, 333.

2-Acetoxy-2-chloroethylphosphonyl Dichloride (6).—By following the procedure of Lutsenko and Kirilov,[6] **6** was prepared in 76% yield, bp 83° (0.3 mm), $n^{25}D$ 1.4861 (lit.[6] bp 99–100° (1.5 mm), $n^{20}D$ 1.4855).

Phosphonoacetaldehyde (2).—Five grams (0.021 mol) of **6** was dissolved in 50 ml of tetrahydrofuran and 1.2 g (0.067 mol) of water was added dropwise with stirring so that the temperature did not rise above 30°. The reaction flask was stoppered and allowed to stand for 4 days at room temperature. After the solvent was removed with a water aspirator, the residue was placed in a vacuum desiccator over solid KOH–$CaCl_2$ and at 1 mm pressure for 6 hr. The resulting residue was a viscous, slightly yellow oil, weighing 2.7 g (theor 2.6 g). No further purification of **2** was attempted.

Crude **2** (1.55 g, 0.0125 mol) in 10 ml of water was added to 2.5 g (0.0126 mol) of 2,4-dinitrophenylhydrazine in 95 ml of water–ethanol–sulfuric acid (20:60:15 by vol). The solution was allowed to stand overnight at room temperature, during which time a yellow-orange precipitate formed. After the solution was cooled to 5°, the solid was collected and recrystallized from water to give 3.1 g (81%) of yellow-orange crystals, mp 177–178° dec. *Anal.* Calcd for $C_8H_9O_7N_4P$: N, 18.42; P, 10.18; neut equiv, 304. Found: N, 18.38; P, 10.48; neut equiv, 305. The titration curve had two distinct breaks at pH 5.2 and pH 9.9.

The crude **2** from the hydrolysis of 1.0 g of **6** was dissolved in 200 ml of 0.1 *M* acetate buffer (pH 5). The solution was heated at 90° for 8 hr while a slow stream of nitrogen was passed through the solution and then through 200 ml of a saturated solution of 2,4-dinitrophenylhydrazine in 2 *M* HCl. In about 1 hr a precipitate began to separate from the HCl solution. After 8 hr, the solid was collected and recrystallized from ethanol–water to give 0.62 g (66%) of acetaldehyde dinitrophenylhydrazone, mp 147–148°. Authentic acetaldehyde dinitrophenylhydrazone and a mixture of the two solids showed the same melting point.

The acetate buffer solution was made alkaline by the addition of concentrated NH_4OH. To the alkaline solution was added 25 ml of "magnesia reagent" (0.246 *M* magnesium chloride and 1.87 *M* ammonium chloride) and the solution was chilled overnight in a refrigerator. The resulting white solid was collected and washed successively with dilute NH_4OH, 95% ethanol, and ether. The solid, assumed to be magnesium ammonium phosphate hexahydrate, was dried by pulling air through it, 0.985 g (98%).

One gram of crude **2** in 10 ml of water was cooled to 10° and was made basic to pH 10 by the addition of 6 *N* NaOH. A 5% aqueous solution of $KMnO_4$ was added dropwise with stirring until the characteristic permanganate color persisted; filtration removed MnO_2. To the filtrate, 5% aqueous $NaHSO_3$ was added until the solution was colorless and completely clear. The solution was evaporated to dryness, the residue was dissolved in a small amount of water, and the solution was passed through a column of Dowex 50 (H^+) ion-exchange resin. The strongly acidic eluate was collected and evaporated to dryness, leaving 0.85 g of a viscous oil that slowly crystallized. Recrystallization from glacial acetic acid gave 0.77 g (68%) of white crystals, mp 138–139°. A sample of authentic phosphonoacetic acid was prepared by the hydrolysis of triethyl phosphonoacetate[9] and was shown to melt also at 138–139°, as did a mixture of the two solids.

Conversion of Diethyl Phosphonoacetaldehyde (7) to 2-Aminoethylphosphonic Acid (1).—A 5-g quantity of **7**[6] was added to a solution of 5 g of hydroxylamine hydrochloride in 25 ml of absolute ethanol and 25 ml of anhydrous pyridine. After the solution was allowed to stand for 48 hr at room temperature, it was evaporated to dryness *in vacuo*. The residue was dissolved in 50 ml of acetic anhydride and 150 ml of glacial acetic acid, 1 g of 5% Pd–C was added, and the mixture was shaken with 60 psi H_2 for 24 hr. The solution was filtered and the filtrate was evaporated to dryness, leaving a residue which was heated under reflux for 48 hr with 100 ml of 6 *N* HCl. Evaporation of the hydrolysate to dryness and boiling the residue in 100 ml of 2 *N* NaOH removed volatile basic impurities. Excess HCl was added, the solution was evaporated to dryness, and the solid residue was extracted with three 50-ml portions of hot ethyl alcohol–concentrated HCl (5:1 by vol). The extracts were evaporated to dryness, the residue was dissolved in 25 ml of water, and the resulting solution was passed through a column of Dowex 50 (H^+) ion-exchange resin. A strongly acidic eluate was discarded, followed some time later by a ninhydrin-positive eluate, which was evaporated to dryness. Recrystallization of the residue from water–ethanol gave 1.5 g (43%) of 2-aminoethylphosphonic acid (**1**). The **1** prepared in this manner had neut equiv 124.7 (calcd 125.1) and an ir spectrum identical with that reported for the metastable α form.[10]

Registry No.—**2**, 16051-76-6; **4**, 5607-01-2; monoethyl phosphonoacetaldehyde 2,4-dinitrophenylhydrazone, 18916-92-2; **2** 2,4-dinitrophenylhydrazone, 18910-31-1.

[9] P. Nylen, *Ber.*, **57**, 1023 (1924).

[10] M. Horiguchi and M. Kandatsu, *Agr. Biol. Chem.* (Tokyo), **28**, 408 (1964).

Monohydrazones of Thiocarbohydrazide. The Occurrence of 1,4,5,6-Tetrahydro-3(2H)-s-tetrazinethione Structures

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Thiocarbohydrazide and its bishydrazones have been known for some time.[1-4] Examples of monohydrazones

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[1] R. Stollé and R. E. Bowles, *Ber.*, **41**, 1099 (1908).

[2] P. C. Guha and S. C. Dey, *Quart. J. Ind. Chem. Soc.*, **2**, 225 (1925).

[3] H. W. Stephen and F. J. Wilson, *J. Chem. Soc.*, 2531 (1926).

[4] W. Reid and G. Oertel, *Ann.*, **590**, 136 (1954).

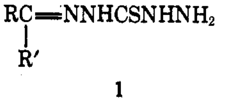
TABLE I

MONOHYDRAZONES OF THIOCARBOHYDRAZIDE

Carbonyl compound	Yield,[a] %	Mp, °C[b,c]	Formula	Calcd, %				Found, %				λ_{max}	$\epsilon \times 10^{-3}$
				C	H	N	S	C	H	N	S		
Propionaldehyde	76	161–162[d] dec	$C_4H_{10}N_4S$	32.9	6.9	38.3	21.9	32.6	7.2	38.0	21.6	251	12.7
Isovaleraldehyde	98	178–179[d] dec	$C_6H_{14}N_4S$	41.4	8.1	32.2	18.4	41.6	8.1	32.2	18.6	250	12.4
n-Heptaldehyde	84	159–160 dec	$C_8H_{18}N_4S$	47.5	9.0	27.7	15.9	47.3	9.0	28.0	15.8	250	12.6
Phenylacetaldehyde	60	168–170 dec	$C_9H_{12}N_4S$	51.9	5.8	26.9	15.4	51.6	6.1	26.9	15.6	252	12.8
Benzaldehyde	98	193–194[e] dec	$C_8H_{10}N_4S$									313	27.4
Pivalaldehyde	90	168–169 dec	$C_6H_{14}N_4S$	41.4	8.1	32.2	18.4	41.3	8.4	32.6	18.3	249[f]	12.4
Cyclohexanone	89	166–167[g] dec	$C_7H_{14}N_4S$									250[f,h]	13.4
Pinacolone	78[i]	140–142	$C_7H_{16}N_4S$	44.7	8.6	29.8	17.0	44.7	8.4	30.0	17.1	267	23.6
Cyclopentanone	91	179–180 dec	$C_6H_{12}N_4S$	41.8	7.0	32.5	18.6	41.8	7.1	32.6	18.4	250[f]	13.3
2-Butanone	84	131–134	$C_5H_{12}N_4S$	37.5	7.6	35.0	20.0	37.3	7.2	34.7	20.3	249[f]	13.1
3-Methyl-2-butanone	74	. . .[j]	$C_6H_{14}N_4S$	41.4	8.1	32.2	18.4	41.3	8.3	32.2	18.5	249[f]	12.8
Acetone	88	197–198[k] dec											

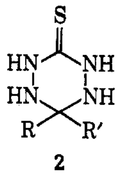
[a] Crude, from neutral solution unless otherwise indicated. [b] Uncorrected, determined using recrystallized material unless otherwise indicated. [c] Recrystallized from methanol unless otherwise indicated. [d] Recrystallized from ethanol. [e] Lit.[5] mp 193° dec. [f] Determined using crude material. [g] Lit.[6] mp 166–167° dec. [h] Lit.[6] uv max 250 mμ (ϵ 12,600). [i] Yield obtained from 1 *N* acetic acid. [j] See footnote 12. [k] Lit.[6] mp 194–195° dec; extremely insoluble substance.

have also been prepared and studied.[5,6] The latter derivatives were depicted as true hydrazones, *i.e.*, 1-alkylidene- or -benzylidene-3-thiocarbohydrazide (**1**). In the present work, the monohydrazones of a number of simple aldehydes and ketones were prepared. The nmr spectra of these materials confirmed the presence of either **1** or the corresponding 1,4,5,6-tetrahydro-3(2H)-*s*-tetrazinethione (**2**), or a mixture of the two forms. This duality of structure is analogous to that recently shown for hydrazones of simple aliphatic aldehydes.[7]



$$\underset{R'}{RC}{=}NNHCSNHNH_2$$

1



2

The derivatives prepared from aliphatic aldehydes without α branching (see Table I) gave nmr spectra consistent with the pure cyclic form **2** (R = alkyl; R′ = H). No signals were present to indicate CH═N or CH adjacent to that grouping. A one-proton multiplet was observed in each case at δ 3.4–3.5, as was a two-proton doublet at δ 4.7–4.8 and a two-proton singlet at δ 9.1–9.2, corresponding to H-6 and the pair of protons at N-1 and N-5 and those at N-2 and N-4 of the cyclic form, respectively.[8] Assignment of the NH signals was confirmed by deuterium exchange. Treatment of the propionaldehyde derivative with deuterium oxide also caused the resolution of the δ 3.4 signal to a broad triplet. The coupling of H-6 and adjacent NH was further confirmed by double-resonance studies on the isovaleraldehyde and *n*-heptaldehyde samples (J = 9–11 Hz). Benzaldehyde with thiocarbohydrazide yielded the true monohydrazone (**1**, R = C_6H_5; R′ = H). The phenyl proton signals appeared as an A_3B_2 pattern at δ 7.5 and 7.9 and the signal due to the CH═N proton at δ 8.15. Singlets due to NH appeared at δ 4.97 (NH_2), 9.8, and 11.5.[9]

The pivalaldehyde derivative gave signals corresponding to structure **2** (R = *t*-butyl; R′ = H), *i.e.*, a singlet at δ 0.95, a triplet at δ 3.20, a doublet at δ 4.65, and a singlet at δ 9.12. Peaks due to the linear isomer were also observed at δ 1.07 and 1.10 (*t*-butyl groups of *syn* and *anti* isomers) and 7.35 (CH═N). The relative amount of linear isomer in solution increased on standing, from 0–25%, initially observed, to 45–70% after standing overnight. Standing in DMSO for 36 hr, followed by dilution with water, yielded the unchanged solid pivalaldehyde derivative in 86% recovery.

The product obtained from cyclohexanone and thiocarbohydrazide gave the very simple nmr spectrum expected for **2** [RR′ = $(CH_2)_5$]. Single peaks were observed for cyclohexane ring protons at δ 1.41 and NH protons at δ 4.60 and 8.9. Recrystallization appeared to introduce a small amount of the linear form.

The spectrum of the pinacolone derivative conformed

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(5) R. Stollé and E. Gaertner, *J. Prakt. Chem.*, [2] **132,** 209 (1931).

(6) J. Sandström, *Acta Chem. Scand.*, **14,** 1037 (1960).

(7) W. Skorianetz and E. Sz. Kovats, *Tetrahedron Lett.*, 5067 (1966).

(8) The phenylacetaldehyde derivative showed an analogous set of signals at δ 3.8, 5.0, and 9.3.

(9) The areas of the NH signals were low compared with the areas of the signals for protons on carbon in the spectra of the benzaldehyde and pinacolone derivatives.

with nearly pure 1 (R = *t*-butyl; R' = CH_3). Signals were observed for *t*-butyl (δ 1.10), α-methyl (1.87), and NH (4.7, 8.8, and 9.7).[9] Very weak signals at δ 0.95 and 1.21 were probably due to the presence of cyclic isomer.

The nmr spectra of other ketone derivatives were determined with crude and recrystallized samples. The observed mixtures contained 55–95% cyclic isomer, the remainder being the linear form.

As seen in Table I, consistencies in the ultraviolet (uv) spectra supported cyclic structures for all derivatives shown except those of pinacolone and benzaldehyde.[10] The spectra of the latter two closely resembled those of propionaldehyde and benzaldehyde thiosemicarbazone, respectively (see Experimental Section).

An infrared (ir) band at 6.15 μ was present in the spectrum of the pinancolone derivative, resulting from NH_2 in-plane bending as well as C=N stretching. The benzaldehyde analog produced a band of similar shape and intensity at 6.21 μ, although phenyl ring absorption is also expected in this region. Surprisingly, the acetone derivative gave a band at 6.08 μ.[11] Similar bands were absent in the spectra of other derivatives, an observation consistent with the cyclic structure.[12]

Experimental Section

General.—The nmr spectra were determined in DMSO-d_6 on a Varian A-60 instrument. Double-resonance experiments were carried out on a Varian HA-100 spectrometer. Ir spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer using KBr disks. Band positions given in the text were confirmed with a Baird-Atomic NK-1 instrument. Uv spectra were determined in methanol on a Perkin-Elmer Model 202 spectrophotometer.

Monoisovaleraldehyde Thiocarbohydrazone, *i.e.*, 1,4,5,6-Tetrahydro-6-isobutyl-3(2H)-*s*-tetrazinethione.—Thiocarbohydrazide (10.6 g, 0.10 mol) was dissolved in 200 ml of hot water. The solution was stirred magnetically without further heating and treated dropwise over 15 min with 8.6 g (0.10 mol) of isovaleraldehyde in 30 ml of ethanol. The product began to precipitate during the course of addition. The mixture was allowed to stand overnight and then was filtered. After the product was washed with dilute ethanol and air dried, it weighed 17.1 g, mp 178–179° dec.

Other derivatives were similarly prepared. Less soluble carbonyl compounds required higher dilutions and longer addition times. The *n*-heptaldehyde derivative was prepared at steam-bath temperature with vigorous mechanical stirring. The use of 1 *N* acetic acid in place of water improved the yield and the appearance of the crude material in some cases, especially that of the pinacolone derivative, but did not alter the structure of the products.

Thiosemicarbazones of Propionaldehyde and Benzaldehyde.—Thiosemicarbazide was heated in ethanol containing an excess of the aldehyde until solution was complete. The products crystallized on cooling and were purified by recrystallization from ethanol. The propionaldehyde derivative had mp 158–159° (lit.[13] mp 159°), uv max (methanol) 270 mμ (ϵ 22,400). The benzaldehyde derivative had mp 162–163° (lit.[14] mp 160°), uv max (methanol) 311 mμ (ϵ 32,800).

Registry No.—1 (R = $PhCH_2$; R' = H), 18801-46-2; 1 (R = Ph; R' = H), 5351-58-6; 1 (R = *t*-Bu; R' = H; *syn*), 18801-48-4; 1 (R = *t*-Bu; R' = H; *anti*), 18801-49-5; 1 (R = *t*-Bu; R' = Me), 18801-50-8; 1 [RR' = $-(CH_2)_4-$], 18801-51-9; 1 (R = Et; R' = Me), 18801-52-0; 1 (R = *i*-Pr; R' = Me), 18801-53-1; 2 (R = Et; R' = H), 18801-54-2; 2 (R = *i*-Bu; R' = H), 18801-55-3; 2 (R = *n*-hexyl; R' = H), 18801-56-4; 2 (R = $PhCH_2$; R' = H), 18801-57-5; 2 (R = *t*-Bu; R' = H), 18801-58-6; 2 [RR' = $-(CH_2)_5-$], 18801-59-7; 2 [RR' = $-(CH_2)_4-$], 18801-60-0; 2 (R = Et; R' = Me) 18801-61-1; 2 (R = *i*-Pr; R' = Me), 18801-62-2.

Acknowledgment.—The author is indebted to Dr. T. H. Regan and Mr. R. L. Young for nmr spectra and to Dr. T. H. Regan for helpful discussions throughout the course of this work.

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[10] On standing, the very dilute solutions used for uv determinations often showed such changes as broadening, shifting, and diminution of maxima. The tendency to shift toward a 267-mμ limit paralleled the tendency to exist as isomeric mixtures, as shown by nmr. The observed changes in the uv spectra were probably caused by isomerization and decomposition.

[11] The material was insoluble in DMSO-d_6. A solution was obtained by warming in DMSO-d_6-D_2O and the nmr spectrum was then recorded. A signal was observed at δ 1.08 (methyl groups of **2**, R = R' = CH_3). Two weaker signals at δ 1.81 and 1.89 were ascribed to **1**, indicating an isomeric mixture containing *ca.* 80% **2**. Signals at δ 1.20 and 2.05, one-fourth the area of the adjacent methyl signals, indicated the introduction of other products during solution of the sample.

[12] The crude 3-methyl-2-butanone derivative had mp 114–116°. Rapid recrystallization from ethanol (ice bath) gave material of varying melting point in poor recovery. The ir spectra of the original crude product and recovered material differed significantly, the latter showing, in particular, a weak but distinct band at 6.15 μ. The recovered material had uv max 264 mμ (ϵ *ca.* 16,000). A sample softening at 117° and melting at 139–141° gave analytical values shown in Table I. The nmr spectrum of this sample showed 55% **2**.

[13] Staff of Hopkin and Williams Research Laboratories, "Organic Reagents for Organic Analysis," Chemical Publishing Co., Brooklyn, N. Y., 1946, p 123.

[14] Reference 13, p 121.

Radical Coupling in the Photoreduction of an Aromatic Nitro Compound in Ether

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Photochemical excitation of nitroaromatic compounds frequently leads to products derived from hydrogen abstraction by an oxygen of the nitro group.[2] Such abstractions may be intramolecular from an *ortho* substituent, as in many well known photochromic and related systems, or it may be intermolecular, usually from the solvent. Several studies of the latter type of reaction have appeared recently.[3–5] Mechanistic studies[3,5] indicate that these reductions involve both photochemical and thermal steps; the first of these is hydrogen abstraction, probably by the $n \rightarrow \pi^*$ triplet state of the nitro compound. Nitrobenzene is photoreduced to phenylhydroxylamine[3] in isopropyl alcohol, and the resulting acetone has been identified; in

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[1] A National Science Foundation Undergraduate Summer Research Participant, 1967.

[2] Other processes, such as the nitro → nitrite rearrangement, are also possible; see O. L. Chapman, D. C. Heckert, D. W. Reasoner, and S. P. Thackaberry, *J. Amer. Chem. Soc.*, **88**, 5550 (1966). For leading references to other nitroaromatic photochemistry, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 477. For preparative uses, see A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, Inc., New York, N. Y., 1968, p 266.

[3] R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88**, 4330 (1966); R. Hurley and A. C. Testa, *ibid.*, **89**, 6917 (1967).

[4] R. A. Finnegan and D. Knutson, *ibid.*, **90**, 1670 (1968).

[5] J. A. Barltrop, N. J. Bunce, and A. Thomson, *J. Chem. Soc.*, *C*, 1142 (1967); J. A. Barltrop and N. J. Bunce, *ibid.*, 1467 (1968).