ppm from TMS were absent. Absorptions for the 14 hydrogens of the molecule occurred at 1.4–2.3 ppm from TMS.

A glpc analysis (polyphenyl ether–Carbowax column) indicated that the 1,3,5-trimethylbenzene content of this reactant substrate was ~95%. The remaining material apparently consisted of other isomeric trimethylbenzenes. The product was resolved quantitatively on the above glpc column. A mass spectrometric analysis showed that the main product was 1,3,5-trimethylcyclohexene. No cyclic dienes were formed.

The product from the reduction of tetralin was resolved from tetralin by glpc with a 20-ft polyphenyl ether–Carbowax column at 250°. The mass spectrum of the product showed it to be octalin, $C_{10}H_{16}$. The infrared spectrum corresponded closely to that $\Delta^{9,10}$-octalin,[24] but weak bands at 10.8 and 11.5 μ and the enhancement of the 12.5-μ band might be due to minor amounts of $\Delta^{1,9}$-octalin. The 60-Mc/sec nmr spectrum indicated the product to be ~95% $\Delta^{9,10}$-octalin. That is, from the area under the absorption centered at δ ~5.3 ppm from TMS for vinylic hydrogens, the amount of $\Delta^{1,9}$-octalin must be ~5%. If the double bond were located in one of the other nonsymmetrical positions so that two vinylic hydrogens per double bond were present, the calculated amount of octalins other than $\Delta^{9,10}$-octalin would be even less than 5%.

1-*t*-Butylcyclohexene was resolved by glpc from the other olefin isomers and unreacted *t*-butylbenzene. Mass spectrometric, infrared, and nmr analyses confirmed assigned structures of the products. The 60-Mc/sec nmr spectrum of 1-*t*-butylcyclohexene showed absorption centered at 5.65 ppm from TMS for one vinylic hydrogen, at 2.2 ppm for four allylic hydrogens, at 1.78 ppm for four other hydrogens, and a singlet at 1.2 ppm for the nine equivalent *t*-butyl hydrogens.

(24) I. Moritani, S. Nishida, and M. Murakami, *J. Am. Chem. Soc.*, **81**, 3420 (1959).

Isomerization of 4-Methylcyclohexene.—According to the general procedure described above, 0.4 mole of potassium methylamide (isolated from a reaction of potassium with toluene in methylamine at 100°), 0.1 mole of 4-methylcyclohexene (Aldrich Chemical Co.), and 59 g of anhydrous methylamine were stirred in a 300-ml, stainless steel Magnadrive autoclave for 1.0 hr at 60°. In a second experiment, 4-methylcyclohexene was treated similarly with 0.4 mole of lithium methylamide (prepared in the same manner as potassium methylamide). Analyses (glpc) of the methylcyclohexene before and after treatment with the metal methylamides showed the compositions given in Table IV.

TABLE IV

	4-Methylcyclohexene, %	3-Methylcyclohexene, %	1-Methylcyclohexene, %
Olefin before isomerization	95		5
Olefin after CH_3NHK treatment		8[a]	92
Olefin after CH_3NHLi treatment		91.5[a]	8.5

[a] Sum of 4-methyl- and 3-methyl-cyclohexenes.

Registry No.—Potassium methylamide, 13427-02-6; 1-isopropylcyclohexene, 4292-04-0; 1,2-dimethylcyclohexene, 1674-10-8; 1-*t*-butylcyclohexene, 3419-66-7; $\Delta^{9,10}$-octalin, 493-03-8.

Acknowledgments.—We wish to thank G. W. Schoenthal for able technical assistance. Appreciation is expressed to R. E. Thorpe, J. Forbes, and R. W. Kearney for mass spectrometric, nmr, and infrared analyses, respectively.

Peracetic Acid Oxidation of Hydrazones. II. Aliphatic Ketone and Aldehyde Alkylhydrazones[1-3]

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The oxidation of aliphatic ketone monoalkylhydrazones $R_1R_2C{=}NNHR_3$ with peracetic acid furnished azoacetates and azoxyacetates of the types $R_1R_2C(O_2CCH_3)N{=}NR_3$ (1) and $R_1R_2C(O_2CCH_3)N(O){=}NR_3$ (2), respectively. The latter compounds were shown by an independent synthesis to be formed in the reaction by the peracetic acid oxidation of the corresponding 1. The aliphatic aldehyde monoalkylhydrazones $R_1CH{=}NNHR_3$ were oxidized by peracetic acid to acetylalkylhydrazides of the type $R_1CONHN(COCH_3)R_3$ (6). These products were postulated to form by an O → N acyl migration in an intermediate hydrazimino anhydride, the tautomer of an azoacetate of type 1, where R_2 = H. The type-2 compounds were found labile to acid, liberating nitrogen, $R_1R_2C{=}O$, and R_3OH.

The peracetic acid oxidation of aromatic aldehyde monoalkylhydrazones had been investigated previously and reported to yield simple azoxy compounds.[3] The present investigation was undertaken in an attempt to extend this reaction to aliphatic ketone and aldehyde monoalkylhydrazones.

When cyclohexanone methylhydrazone was oxidized with peracetic acid using a 1:1 ratio, two products, 1-(methylazo)cyclohexanol acetate (**1a**) and 1-(methylazoxy)cyclohexanol acetate (**2a**)[4] were isolated in 41 and 15% yield, respectively. When a 2:1 ratio of peracetic acid to hydrazone was used, a greater amount of decomposition was noticed from which a 17.5% yield of **2a** was obtained and no **1a** was isolated. These results were undoubtedly due to the complete oxidation of **1a** by peracetic acid and to the labile nature of **2a** toward acid. The structures of **1a** and **2a** were demonstrated by independent synthesis and spectral studies. Oxidation of cyclohexanone methylhydrazone by the method of Iffland, *et al.*,[5] using lead tetraacetate furnished authentic **1a**. This material was then oxidized with peracetic acid to yield authentic **2a** in 55% yield (Scheme I).

Oxidation of cyclohexanone phenylhydrazone with 1 equiv of peracetic acid yielded 29% of 1-(phenylazo)-cyclohexanol acetate (**1b**) and 6% of 1-(phenylazoxy)-cyclohexanol acetate[4] (**2b**). When a 2:1 ratio of per acid to hydrazone was used, the large amount of

(1) This work was supported by Research Grant E-2923 from the National Institute of Allergy and Infectious Diseases, National Institute of Health.

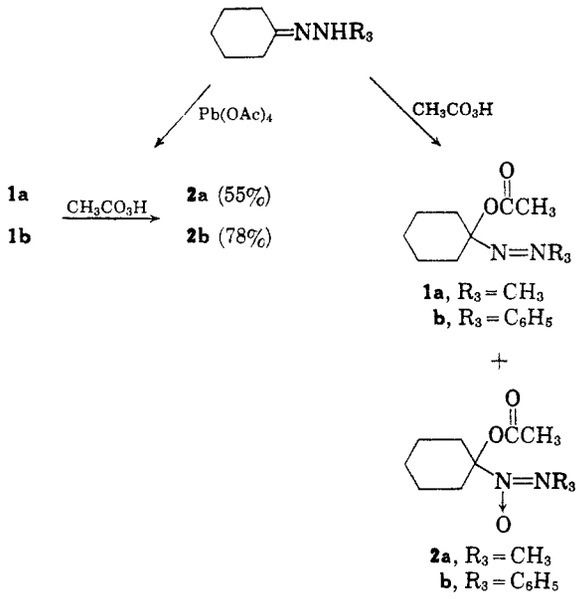
(2) Abstracted from the Ph.D. Dissertation of K. F. Schimmel, Duquesne University, 1961.

(3) Previous paper: B. T. Gillis and K. F. Schimmel, *J. Org. Chem.*, **27**, 413 (1962).

(4) The nomenclature used herein is consistent with that used in ref 3.

(5) D. C. Iffland, L. Salisbury, and W. R. Schaffer, *J. Am. Chem. Soc.*, **83**, 747 (1961).

SCHEME I

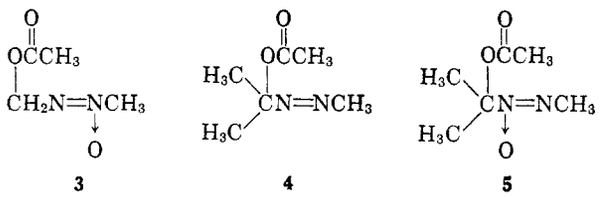


tarry material which formed prevented isolation of any significant amount of products. Compounds **1b** and **2b** were independently synthesized by the same procedures as were **1a** and **2a**. The peracetic acid oxidation of **1b** furnished 78% yield of the azoxyacetate **2b**. The infrared spectra of both **1a** and **1b** showed normal acetate–carbonyl and C–O stretch absorptions at 1730 and 1250 cm^{-1} indicating no unusual interaction of the carbonyl with the azo nitrogen which might have a directive effect on forming the N-oxide bond in a subsequent oxidation step.

The infrared spectra of **2a** and **2b** both showed the characteristic strong azoxy absorptions[6] at 1490–1500 and 1320–1280 cm^{-1}. Comparison of the spectra of **1a** and **1b** with that of **2a** and **2b** was especially revealing of the relatively minor change in the molecule, other than N-oxide formation. The assignment of the N-oxide position in **2a** and therefore in **2b** was possible from nuclear magnetic resonance studies carried out by Freeman.[7] The compound **2a** exhibited two sharp singlets in the nmr spectrum at 2.17 and 3.15 ppm and two broad bands due to the ring protons. The ultraviolet spectrum of **2a** exhibited a maximum at 218.5 $m\mu$ (ϵ 5880) which was consistent with the maximum of aliphatic azoxy compounds, while the spectrum of **2b** showed maxima at 221 $m\mu$ (ϵ 7261) and 287.5 (9580), the latter absorption confirming the placement of the N-oxide in **2b**.

When either **2a** or **2b** were warmed with aqueous acetic acid, nitrogen was smoothly evolved and cyclohexanone was formed which was characterized by formation of its semicarbazone derivative. In addition, phenol was liberated from **2b** and isolated as its 2,4,6-tribromo derivative. This decomposition facilitated by acid could occur by several plausible mechanistic pathways, two of which would be hydrolysis of the acetoxy group followed by decomposition or heterolysis of the cyclohexylazoxy bond followed by collapse. It was of interest that *no* acid isomerization to a hydrazide derivative was observed for **2a**, in contrast to that undergone by benzylazoxy groups.[3] The lower acidity of the methyl hydrogens, together with the presence of the acetate group, apparently make evolution of nitrogen the favored reaction path.

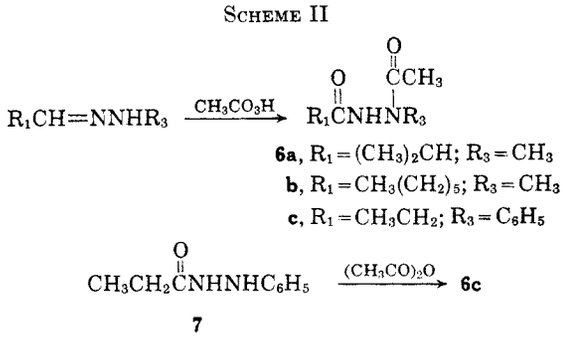
The simplest compounds in the series of azo and azoxy acetates derived from ketones were also prepared. The latter would be more closely related to, but isomeric, in respect to the N-oxide bond, with the acetylated aglycone moiety (**3**) from the plant poisons Macrozamin[8] and Cycasin.[9a] Acetone methylhydrazone was prepared and oxidized by lead tetraacetate to the azo acetate (**4**) in 55% yield. Further oxidation of **4** using 40% peracetic acid in ether gave a 50% yield of the azoxy acetate (**5**). Both **3** and **5** are presumed capable



of forming diazomethane or serving as an alkylating agent *in vivo*,[9b] thus accounting for their mutual toxicity.

The treatment of aliphatic aldehyde monoalkylhydrazones with peracetic acid gave hydrazide derivatives. Isobutyraldehyde methylhydrazone when oxidized with peracetic acid furnished N′-acetylisobutyric acid methylhydrazide (**6a**). Similarly, heptaldehyde methylhydrazone upon oxidation gave N′-acetylheptanoic acid methylhydrazide (**6b**). Propionaldehyde phenylhydrazone by oxidation yielded N′-acetylpropionic acid phenylhydrazide (**6c**). The structures **6a–c** for the products were established by chemical and spectral properties, together with the independent synthesis of **6c** from propionic acid phenylhydrazide (**7**) (Scheme II).

SCHEME II



The mechanism for the formation of **1a**, **1b**, **6a**, **6b**, and **6c** must differ at least slightly from the mechanism that results in the formation of azoxy compounds from aromatic aldehyde monoalkylhydrazones.[3] Whereas an aromatic group would cause stabilization of a carbanion, cation, or free radical, this would not be so with aliphatic groups. Acetic acid anion or radical may attack an intermediate to form the azoacetate **1**. The azoacetate **1** can tautomerize when R_2 is H to the hydrazimino anhydride intermediate by path 3 of Scheme

(6) J. N. Brough, B. Lythgoe, and P. Waterhouse (*J. Chem. Soc.*, 4069 (1954)) reported 1460–1500 and 1280–1320 cm^{-1} as the azoxy group absorption.

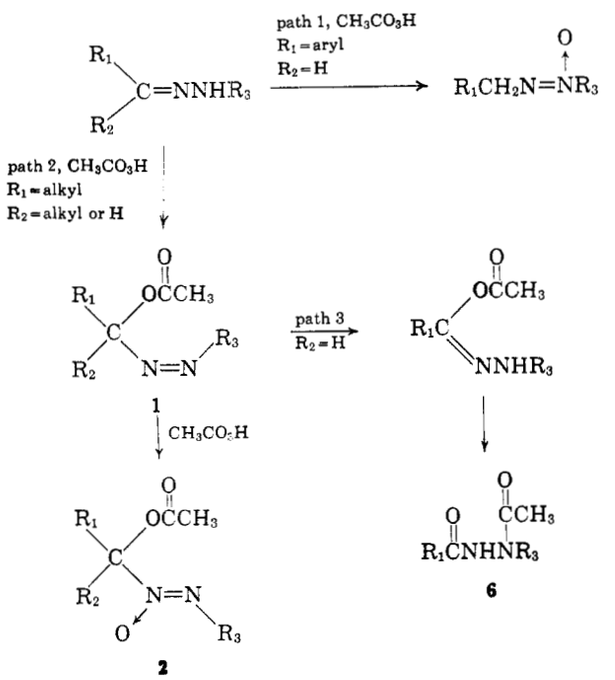
(7) J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).

(8) B. W. Langley, B. Lythgoe, and L. S. Rayner, *J. Chem. Soc.*, 4191 (1952).

(9) (a) A. Kobayashi and H. Matsumoto, *Arch. Biochem. Biophys.*, **110**, 373 (1965), and references therein; (b) J. A. Miller and E. C. Miller, *Cancer Res.*, **25**, 1292 (1965), and references therein.

III. An O → N acyl migration subsequently furnishes **6**. Some evidence for the O → N acyl migration was gleaned from close inspection of the various distillation fractions of **6c**. Comparison of spectra of a small early fraction and later fractions were indicative of this migration. The phenylhydrazone products were much slower in the migration as expected owing to the lower basicity of the nitrogen attached to phenyl. Indeed, some propionic acid phenylhydrazide (**7**) was also isolated after an aqueous work-up of the peracetic acid oxidation of propionaldehyde phenylhydrazone.

SCHEME III



Experimental Section[10]

Peracetic Acid Oxidation of Cyclohexanone Methylhydrazone (1:1).—To 12.6 g (0.1 mole) of cyclohexanone methylhydrazone[11] in 50 ml of methylene chloride was slowly added at ice-bath temperature 20 g of a 40% peracetic acid in acetic acid solution. After the addition was complete, the solution was allowed to stir for 3 hr and then was extracted with water until the aqueous phase showed no reaction toward a bicarbonate solution. The organic phase was dried over anhydrous sodium sulfate, filtered, and vacuum concentrated. The concentrate was vacuum distilled and 7.6 g (41.2%) of 1-(methylazo)cyclohexanol acetate (**1a**), bp 78° (5 mm), n^{25}D 1.4559,[12] d^{25} 0.977, was obtained. The distillation residue was subjected to an evaporative distillation and 3 g (15%) of 1-(methylazoxy)cyclohexanol acetate (**2a**), bp 65° (0.05 mm), n^{25}D 1.4720, d^{25} 1.0624, λ_{max}^{EtOH} 218.5 mμ (ε 5580), was obtained.

Anal. Calcd for $C_9H_{16}N_2O_3$: C, 53.98; H, 8.05; N, 18.89. Found: C, 54.15; H, 8.12; N, 13.98.

Independent Synthesis of 2a.—To 18.4 g (0.1 mole) of 1-(methylazo)cyclohexanol acetate[13] (**1a**) in 50 ml of methylene chloride was slowly added with stirring 20 g of a 40% peracetic acid solution. The extraction of the solution with water until the aqueous phase showed no reaction with a bicarbonate solution was followed by drying the organic phase over anhydrous sodium sulfate, filtration, and vacuum concentration. The concentrate was subjected to an evaporative distillation. A total of 11 g (55%) of **2a**, bp 60° (0.05 mm), n^{26}D 1.4722, d^{25} 1.0629, was obtained, whose infrared spectrum was superimposable with that of material obtained in low yield from the peracetic acid oxidation of cyclohexanone methylhydrazone.

Peracetic Acid Oxidation of Cyclohexanone Methylhydrazone (2:1).—To 12.6 g (0.1 mole) of cyclohexanone methylhydrazone in 50 ml of methylene chloride was slowly added at ice-bath temperature with stirring 40 g of a 40% peracetic acid solution. The mixture was allowed to stir 3 hr and then was worked up in the same manner as the experiment using a 1:1 ratio of reactants. Upon evaporative distillation 3.8 g (17.4%) of **2a**, bp 62° (0.05 mm), n^{26}D 1.4720, was obtained.

Peracetic Acid Oxidation of Cyclohexanone Phenylhydrazone (1:1).—The same procedure as used for oxidation (1:1) of the cyclohexanone methylhydrazone was followed on 18 g (0.1 mole) of cyclohexanone phenylhydrazone. The vacuum distillation of the resultant concentrate gave 7 g (29%) of 1-(phenylazo)-cyclohexanol acetate (**1b**), bp 137° (1.0 mm), n^{25}D 1.5363.[14] The residue was subjected to an evaporative distillation and furnished 1.5 g (6%) of 1-(phenylazoxy)cyclohexanol acetate (**2b**), bp 45° (0.01 mm), n^{26}D 1.5444.

Anal. Calcd for $C_{14}H_{18}N_2O_3$: C, 64.10; H, 6.92; N, 10.68. Found: C, 64.00; H, 6.70; N, 10.81.

Independent Synthesis of 2b.—To 18.2 g (0.074 mole) of **1b**[13] in 150 ml of methylene chloride at ice-bath temperature was slowly added with stirring 14 g (0.074 mole) of 40% peracetic acid dissolved in 100 ml of methylene chloride. The same procedure as used for isolation of **2a** was followed. Upon evaporative distillation at 45° (0.01 mm), 15 g (78%) of 1-(phenylazoxy)-cyclohexanol acetate (**2b**), n^{26}D 1.5470, d^{25} 1.204, was obtained. An infrared spectrum of this sample was superimposable with that of the sample of **2b** obtained directly from the per acid oxidation of the phenylhydrazone: $\lambda_{max}^{95\%\ EtOH}$ 221 mμ (ε 7261) and 287.5 (9588).

Acid Hydrolysis of 1-(Methylazoxy)cyclohexanol Acetate.—To 6 g of the title compound (**2a**) was added 25 ml of a 50% acetic acid solution. The mixture was warmed and nitrogen was evolved. The mixture was then refluxed 3 hr, cooled, and extracted with methylene chloride. The methylene chloride extracts were combined, washed with aqueous sodium hydroxide, and concentrated on a steam bath to an oil. The oil was dissolved in ethanol and semicarbazide hydrochloride was added. Cyclohexanone semicarbazone (4 g, 86%) was obtained: mp 165–166°.[15] A mixture melting point determination with this derivative and an authentic sample showed no depression in melting point.

Acid Hydrolysis of 1-(Phenylazoxy)cyclohexanol Acetate.—To 4 g of the title compound (**2b**) was added 25 ml of a 50% acetic acid solution. The mixture evolved nitrogen upon warming. After 3 hr at 50° the solution was cooled and extracted with methylene chloride. The methylene chloride extracts were combined and washed with 5% sodium bicarbonate solution to remove acetic acid. The organic solution was then extracted with 10% sodium hydroxide solution. Concentration of the methylene chloride layer yielded an oil which was placed in ethanol and treated with semicarbazide hydrochloride to furnish 1.71 g (73%) of cyclohexanone semicarbazone, mp 165–166°.[15] A mixture melting point determination with this sample and authentic material showed no depression. The sodium hydroxide extract was acidified and treated with bromine to give 3.8 g (76%) of 2,4,6-tribromophenol, mp 94–95°,[15] whose structure was also confirmed by the mixture melting point method.

Acetone Methylhydrazone.—To 400 g of distilled acetone was added slowly with stirring 92 g of methylhydrazine. The solution was stirred for 2 hr and then dried over anhydrous sodium sulfate. Upon filtration, the solvent was removed by distillation and 93 g (54%) of acetone methylhydrazone was collected: bp 116–118°, n^{25}D 1.4458, d^{25} 0.8407.

Anal. Calcd for $C_4H_{10}N_2$: C, 55.77; H, 11.70; N, 32.53. Found: C, 55.38; H, 11.55; N, 32.30.

(10) Melting points and boiling points are uncorrected. Spectra were determined on a Beckman DU ultraviolet spectrophotometer and a Perkin-Elmer Model 137 double-beam infrared spectrophotometer. Microanalyses were performed by A. Bernhardt, Mülheim (Ruhr), Germany, and H. W. Galbraith, Knoxville, Tenn. The nmr spectra were determined on a Varian A-60 with tetramethylsilane as an internal standard.

(11) Prepared by the method of R. H. Wiley and G. Irick, *J. Org. Chem.*, **24**, 1925 (1959).

(12) Iffland, *et al.*,[5] reported bp 78° (5 mm), n^{25}D 1.4560.

(13) Prepared by the lead tetraacetate oxidation of cyclohexanone alkylhydrazone following the procedure of Iffland, *et al.*[5]

(14) Iffland, *et al.*,[5] reported bp 137° (1.0 mm), n^{25}D 1.5361, for compound **1b**.

(15) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1957, pp 316 (mp 166° for cyclohexanone semicarbazone), 325 (mp 95° for 2,4,6-tribromophenol).

2-(Methylazoxy)-2-propanol Acetate (5).—To 41 g (0.477 mole) of acetone methylhydrazone in 75 ml of methylene chloride was added slowly with stirring a solution of 218 g (0.5 mole) of lead tetraacetate in 550 ml of methylene chloride over a period of 2 hr. An exothermic reaction occurred and the reaction mixture was stirred an additional 6 hr. The reaction solution was then washed successively with three 200-ml portions of water, three 200-ml portions of 5% sodium bicarbonate, and three 200-ml portions of water. The methylene chloride solution was then dried over anhydrous sodium sulfate and filtered. The methylene chloride was removed from the solution under vacuum and the residue was distilled to give 37.2 g (55%) of 2-(methylazo)-1-propanol acetate (4), bp 60–65° (60 mm), n^{29}D 1.4132.

The oxidation of 35 g (0.243 mole) of 4 in 100 ml of dry ether was carried out by the slow addition of 50 ml of 40% peracetic acid in acetic acid dissolved in 100 ml of dry ether with agitation. After stirring 3 hr the solution was washed with three 50-ml portions of water, three 50-ml portions of 5% sodium bicarbonate, and was dried over magnesium sulfate. The ether was evaporated from the solution after filtration and the residue was vacuum distilled to furnish 19 g (50%) of 2-(methylazoxy)-2-propanol acetate (5), bp 84–87° (20 mm), n^{28}D 1.4362.

Anal. Calcd for $C_6H_{12}N_2O_3$: C, 44.98; H, 7.49; N, 17.49. Found: C, 45.06; H, 7.35; N, 17.70.

Peracetic Acid Oxidation of Isobutyraldehyde Methylhydrazone.—To 10 g (0.1 mole) of isobutyraldehyde methylhydrazone[11] in 50 ml of methylene chloride was slowly added with stirring 20 g of a 40% peracetic acid solution in acetic acid. The solution was allowed to stir for 3 hr after the addition was completed. The solution was then rinsed with water until the aqueous phase gave no reaction with sodium bicarbonate. The methylene chloride was then dried over anhydrous sodium sulfate, filtered, and vacuum concentrated. The concentrate was then evaporatively distilled to give 10.4 g (66%) of N′-acetylisobutyric acid methylhydrazide (6a), bp 75° (0.02 mm), n^{26}D 1.4655, d^{25} 1.009, whose infrared spectrum showed an NH peak at 3.18 μ and two carbonyl peaks at 5.88 and 6.25 μ, respectively. The distillate slowly crystallized to a low-melting hydroscopic solid, which could be sublimed and kept crystalline under a dry nitrogen atmosphere or in a drybox.

Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.15; H, 8.92; N, 17.71. Found: C, 53.00; H, 9.13; N, 17.66.

Peracetic Acid Oxidation of Heptaldehyde Methylhydrazone.—To 14.2 g (0.1 mole) of heptaldehyde methylhydrazone[11] in 50 ml of anhydrous ethyl ether was slowly added 20 g of 40% peracetic acid in acetic acid with stirring. After 3 hr of additional stirring, the ether solution was washed with three 50-ml portions of water, three 50-ml portions of 10% sodium bicarbonate solution, and it was then dried over anhydrous sodium sulfate. Upon filtration of the drying agent, the solution was concentrated and 14 g of crude material was obtained. The distillation of this residue gave 11 g (55%) of N′-acetylheptanoic acid methylhydrazide (6b), bp 75° (0.1 mm), n^{25}D 1.4580, d^{25} 0.901. An nmr spectrum of this material showed singlets at 11.75 ppm (NH), 3.05 (NCH_3), 1.97 ($NCOCH_3$), triplets at 2.25 (CH_2CO) and 0.90 ppm (CH_3), and a broad band at 1.35 ppm (CH_2) at the respectively integrated intensities of 1:3:3:3:3:8.

Anal. Calcd for $C_{10}H_{20}N_2O_2$: C, 59.97; H, 10.07; N, 13.99. Found: C, 59.87; H, 10.20; N, 14.26.

Peracetic Acid Oxidation of Propionaldehyde Phenylhydrazone.—To 14.8 g (0.1 mole) of propionaldehyde phenylhydrazone in 100 ml of methylene chloride was added slowly with stirring at ice-bath temperature 20 g of a 40% peracetic acid solution in acetic acid. After the addition was completed, the solution was stirred for 3 hr. The solution was then rinsed with water until the aqueous phase gave no reaction with a bicarbonate solution. The methylene chloride was then dried over anhydrous sodium sulfate, filtered, and vacuum concentrated. The concentrate was subjected to an evaporative distillation whereby 8 g (49%) of N′-acetylpropionic acid phenylhydrazide (6c), bp 80° (0.04 mm), n^{26}D 1.5342, d^{25} 1.175, was obtained. The infrared spectrum of this compound exhibited double carbonyl peaks at 5.8 and 5.95 μ and were identical with the infrared spectrum of material obtained in 75% yield by the action of acetic anhydride on N′-phenylpropionic acid hydrazide and which exhibited the same physical constants. The nmr spectrum of this material showed peaks at 0.92 (CH_3), 1.9 ($CH_3C{=}O$), 2.23 ($CH_2C{=}O$), and 7.13 ppm (C_6H_5) in ratios of 3:3:2:5, respectively.

Anal. Calcd for $C_{11}H_{14}N_2O_2$: N, 13.58. Found: N, 13.06.

Registry No.—1a, 13369-61-4; 1b, 13369-62-5; 2a, 13369-63-6; 2b, 13369-64-7; 4, 13369-65-8; 5, 13395-57-8; 6a, 13369-66-9; 6b, 13369-67-0; 6c, 13369-68-1; peracetic acid, 79-21-0; acetone methylhydrazone, 5771-02-8.

The Oxidation of Aliphatic Secondary Alcohols by Chromium(VI) in Concentrated Sulfuric Acid Solutions[1]

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Received March 22, 1967

A study of the rates of oxidation of 2-propanol, 1,1,1-trifluoro-2-propanol, and 1,1,1,3,3,3-hexafluoro-2-propanol by chromium(VI) in concentrated sulfuric acid solutions has been made and the results have been explained on the basis of a chromate ester mechanism. When 1,1,1-trifluoro-2-propanol was oxidized in very concentrated acid solutions, a reaction intermediate (or a species in equilibrium with it) was observed spectrophotometrically and the primary kinetic hydrogen isotope effect was found to be markedly decreased. These results suggest that under strongly acid conditions the rate-determining step in the oxidation of this compound is ester formation.

There is good evidence that chromic acid oxidizes alcohols *via* a chromate ester which undergoes a rate-determining decomposition by cleavage at the α-carbon–hydrogen bond[2] (eq 1 and 2).

$$R_2CHOH + H_2CrO_4 \underset{}{\overset{\text{fast}}{\rightleftharpoons}} R_2CHOCrO_2OH + H_2O \quad (1)$$

$$R_2CHOCrO_2OH \xrightarrow{\text{slow}} R_2C{=}O + H_2CrO_3 \quad (2)$$

We have previously reported kinetic results which indicate that the rate of oxidation of 2-propanol by chromium(VI) in aqueous acid is dependent not only on the acidity of the solution, but also on the identity of anions present.[3] The results were satisfactorily explained by assuming that the anions become intimately associated with the oxidant in moderately con-

(1) From part of the Ph.D. thesis of D. G. Lee, University of British Columbia, 1963. Presented at the 48th Conference of the Chemical Institute of Canada, Montreal, 1965.

(2) (a) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949); (b) R. Brownell, A. Leo, Y. W. Chang, and F. H. Westheimer, *J. Am. Chem. Soc.*, **82**, 406 (1960); (c) J. Rocek, F. H. Westheimer, A. Eschenmoser, L. Moldovanyi, and J. Schreiber, *Helv. Chem. Acta*, **45**, 2554 (1962); (d) K. B. Wiberg in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, p 142 ff; (e) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, pp 37–48.

(3) D. G. Lee and R. Stewart, *J. Am. Chem. Soc.*, **86**, 3051 (1964).