84%) was obtained, bp 116–117° (lit.[48] 114–116°). The acid chloride (1.0 ml) was added to 2,4-dinitrophenylhydrazine (1.0 g) in pyridine (30 ml) and the solution was heated at 100° for 5 min. On cooling the solution was poured on ice chips (50 g) and the hydrazide was precipitated, mp 165–170°. On crystallization from aqueous ethanol the same hydrazide was obtained as by method A above, mp 176–177°, with $[\alpha]^{25}_{578}$ +26.6° (*c* 1.0, acetone).

Bromination of Trimethylacetaldehyde N-Methyl-N-2,4-dinitrophenylhydrazone. A.—The hydrazone (1.0 g) was suspended as a slurry with acetic acid (3.0 ml) containing acetic anhydride (10%) and the mixture was rapidly stirred while bromine (0.2 ml) was added (over a period of 30 sec). The hydrazone dissolved and after 30–40 min the N-methyl-N-(2,4-dinitrophenyl)-C-(*t*-butyl)hydrazidic bromide precipitated, mp 103° (910 mg, 70%). Crystallization from acetic acid raised the melting point of the hydrazidic bromide to 108°.

Anal. Calcd for $C_{12}H_{15}BrN_4O_4$: C, 40.15; H, 4.21; Br, 22.26; N, 15.61. Found: C, 40.37; H, 4.18; Br, 21.93; N, 15.65.

The nmr spectrum is also consistent with the hydrazidic bromide structure. The peak at τ 3.09 ppm assigned to the methine proton, present in the starting hydrazone, is absent in the hydrazidic bromide.

B. With Excess Bromine.—The hydrazone (1.0 g) was stirred with glacial acetic acid (4.0 ml) and bromine (1.0 ml) in acetic acid (1.0 ml) was added. When the solution had stirred for 24 hr, a light yellow solid had precipitated, mp 168–170° (760 mg). After two recrystallizations from aqueous ethanol the melting point was raised to 176° and the compound was shown to be N-methyl-N-(2,4-dinitrophenyl)-C-(*t*-butyl)hydrazide which was also unambiguously prepared by the reaction of equimolar quantities of trimethyl acetyl chloride and N-methyl-N-2,4-dinitrophenylhydrazine in pyridine.

Anal. Calcd for $C_{12}H_{16}N_4O_5$: C, 48.64; H, 5.45; N, 18.93. Found: C, 48.76; H, 4.90; N, 19.60.

Registry No.—IIa, 15009-34-4; IIb, 14947-23-0; IIc, 14947-24-1; IId, 14947-25-2; IIe, 14947-26-3; IIf, 14947-27-4; IIg, 14947-28-5; IIh, 14947-29-6; IV-(Ar-2,4-$(NO_2)_2C_6H_3$), 5920-44-5; Table V, a, 15009-36-6; Table V, b, 14947-30-9; Table V, c, 14947-31-0; Table V, d, 14947-32-1; Table VI, a, 6561-63-3; Table VI, b, 7461-93-0; Table VI, c, 14947-35-4; Table VI, d, 14947-36-5; N-(2,4-dinitrophenyl)-N′-phenyl-C-(2′-butyl)amidiazone, 14947-37-6; N-(2,4-dinitrophenyl)-C-(2′-butyl)hydrazidic azides, 14947-38-7; N-(2,4-dinitrophenyl)-C-(2′-butyl)hydrazidine, 14947-39-8; N-(2,4-dinitrophenyl)-C-(2′-butyl)hydrazidine benzal derivative, 15077-12-0; N-methyl-N-(2,4-dinitrophenyl)-C-*t*-butyl)hydrazidic bromide, 14947-40-1; N-methyl-N-(2,4-dinitrophenyl)-C-(*t*-butyl)hydrazide, 14947-41-2; benzylidine - N - methyl - N - *p* - nitrophenylhydrazone, 14947-42-3.

Acknowledgment.—Financial assistance (to A. F. H.) from the Department of Education (State Maintenance Grant for Research 1964–1966) and the Commissioners for the Exhibition of 1851 (Overseas Research Fellow, 1967) is gratefully acknowledged.

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[48] K. B. Wiberg and T. W. Hutton, *J. Am. Chem. Soc.*, **78**, 1640 (1956).

Oxidation of Hydrazones. III. α,β-Unsaturated Monoalkylhydrazones[1,2]

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The oxidation of cinnamaldehyde monomethylhydrazone (**1**) with lead tetraacetate in methylene chloride yields N-acetylcinnamic acid methylhydrazide (**2**). When this oxidation is carried out in ether as solvent, acylation occurs to give N-acetylcinnamaldehyde methylhydrazone (**3**). The peracetic acid oxidation of **1** has been found to give the azoxy acetate **4**. The oxidation of isophorone monomethylhydrazone with either lead tetraacetate or peracetic acid has been found to yield an 8:1 ratio of azo acetates **6** and **7**. Also the oxidation of 3-methyl-2-cyclopenten-1-one monomethylhydrazone with either oxidant affords a 2.2:1 ratio of azo acetates **9** and **10**. In contrast, however, oxidation of 2-cyclohexen-1-one monomethylhydrazone with either reagent has been found to yield the azo acetate **12** exclusively.

The oxidation of saturated monoalkylhydrazones with lead tetraacetate or peracetic acid has been investigated by many workers.[3] We wished to add to the research in this area by studying the lead tetraacetate and peracetic acid oxidations of α,β-unsaturated aldehyde and ketone monoalkylhydrazones.

Cinnamaldehyde monomethylhydrazone was prepared by the reaction of cinnamaldehyde and monomethylhydrazine in diethyl ether. The crude product obtained after removal of the solvent was used without any further purification since attempted distillation resulted in extensive cyclization to 1-methyl-2-phenyl-Δ⁴-pyrazoline.[4] The hydrazone was estimated to be about 85% pure by comparison of its ultraviolet maximum and molar absorptivity with that of a pure sample of cinnamaldehyde dimethylhydrazone. Infrared and nmr spectral data also showed the crude hydrazone to be about 85% pure. The yields obtained in the oxidations of this hydrazone were calculated on the basis of 85% purity of the crude hydrazone.

When cinnamaldehyde monomethylhydrazone (**1**) is oxidized with lead tetraacetate in methylene chloride a 44% yield of N-acetylcinnamic acid methylhydrazide (**2**) is obtained. Assignment of this structure is made on the basis of infrared, ultraviolet, and nmr spectral data and microanalysis. On the contrary, when the oxidation is carried out in diethyl ether as solvent, acylation occurs giving rise to N-acetylcinnamaldehyde monomethylhydrazone (**3**).

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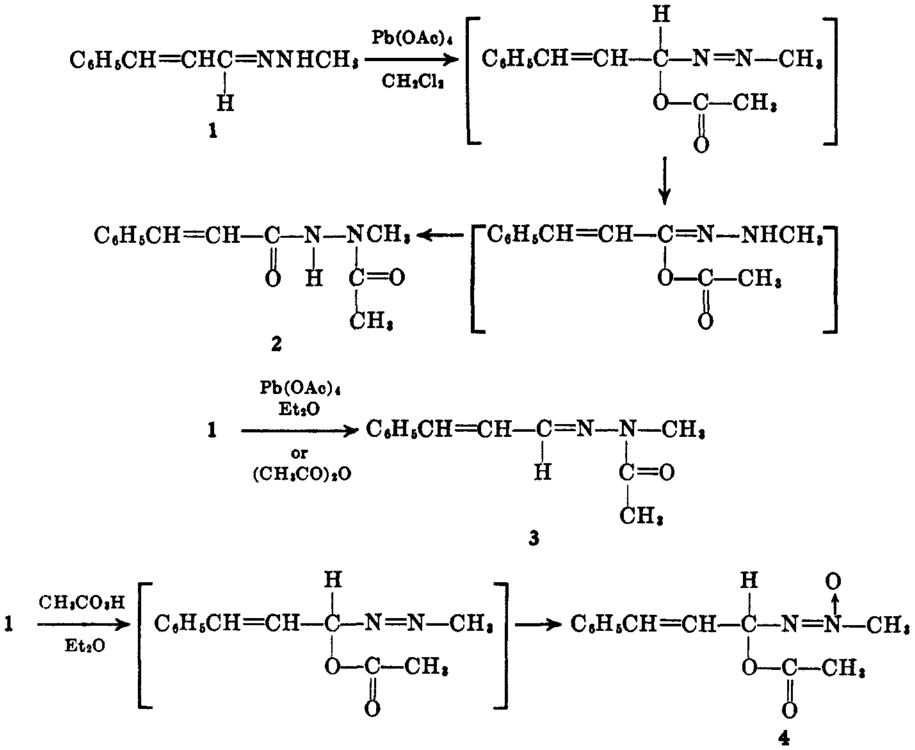
[1] This investigation was supported by Public Health Service Grant AI-02923 from the National Institute of Allergy and Infectious Diseases.

[2] For the preceding publication in this series, see ref. 3e.

[3] (a) D. C. Iffland, L. Salisbury, and W. R. Schafer, *J. Am. Chem. Soc.*, **83**, 747 (1961); (b) W. A. F. Gladstone and R. C. Norman, *J. Chem. Soc.*, 3048, 5177 (1965); (c) F. L. Scott and R. N. Butler, *ibid.*, 1202 (1966); (d) B. T. Gillis and K. F. Schimmel, *J. Org. Chem.*, **27**, 413 (1962); (e) B. T. Gillis and K. F. Schimmel, *ibid.*, **32**, 2865 (1967); (f) J. P. Freeman, *ibid.*, **28**, 2508 (1963).

[4] von K. v. Auwers and P. Heimke, *Ann.*, **458**, 211 (1927).

SCHEME I



This same product is obtained in 85% yield by the reaction of 1 with acetic anhydride. (See Scheme I.) Again the structure of 3 was confirmed by its spectral properties and microanalysis.

The peracetic acid oxidation of 1 in diethyl ether gives a 21% yield of the azoxy acetate 4 along with a considerable amount of cinnamaldehyde.

Isophorone monomethylhydrazone 5 was prepared in 62% yield by the reaction of isophorone with monomethylhydrazine. The hydrazone was oxidized with lead tetraacetate and distillation afforded a 60% yield of a yellow liquid which was shown by an nmr spectrum to be an 8:1 mixture of azo acetates 6 and 7 (Figure 1). The ultraviolet spectrum of the mixture had an azo peak at 340 mμ attributable to 6 and 7 and a peak at 235 mμ due to 7. The infrared spectrum of the mixture had strong acetate bands at 1750 and 1250 cm^{-1} and trisubstituted double bond peaks at 1670, 840, and 800 cm^{-1}.

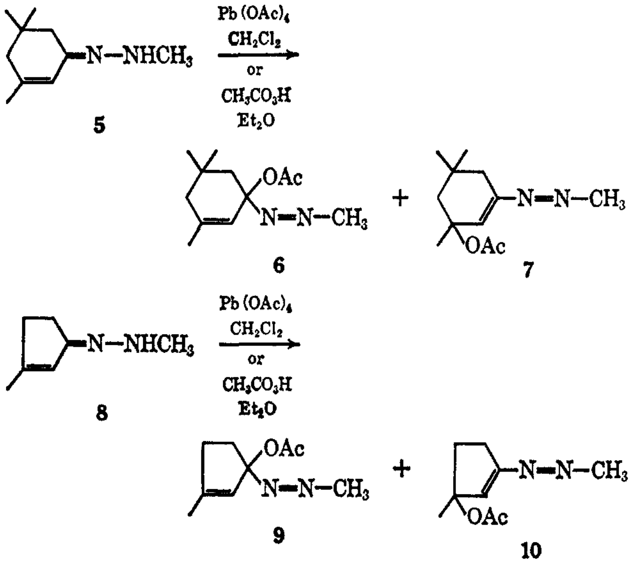
When hydrazone 5 is oxidized with peracetic acid in ether, distillation affords a mixture of 6 and 7 identical in composition with that obtained in the lead tetraacetate oxidation of 5.

In view of the fact that the lead tetraacetate oxidation of cinnamaldehyde monomethylhydrazone gave different products when methylene chloride and ether were used as solvents, the oxidation of 5 with lead tetraacetate was repeated in ether. In this case, however, the change in solvent did not alter the course of the reaction.

The monomethylhydrazone of 3-methyl-2-cyclopenten-1-one 8 was prepared in 29% yield by the reaction of the ketone with monomethylhydrazine in ether. An analytical sample of 8 could not be obtained due to its extremely rapid decomposition in air. However, infrared, ultraviolet, and nmr spectral data left little doubt as to its structure.

Oxidation of 8 with lead tetraacetate in methylene chloride gave a 55% yield of a mixture of azo acetates 9 and 10. The nmr spectrum (Figure 2) showed this to be a 2.2:1 mixture of 9 and 10, respectively. The ultraviolet spectrum of the mixture had a peak at 334 mμ due to 9 and 10 and a peak at 248 mμ due to 10.

Oxidation of 8 with peracetic acid in ether again afforded a 2.2:1 ratio of isomers 9 and 10; however, the over-all yield was somewhat lower.



In contrast to the above results, the oxidation of 2-cyclohexen-1-one monomethylhydrazone 11 with either lead tetraacetate or peracetic acid afforded only the azo acetate 12 in 70% yield. The structure of 12 was assigned on the basis of infrared, ultraviolet, and nmr spectral data and microanalysis.

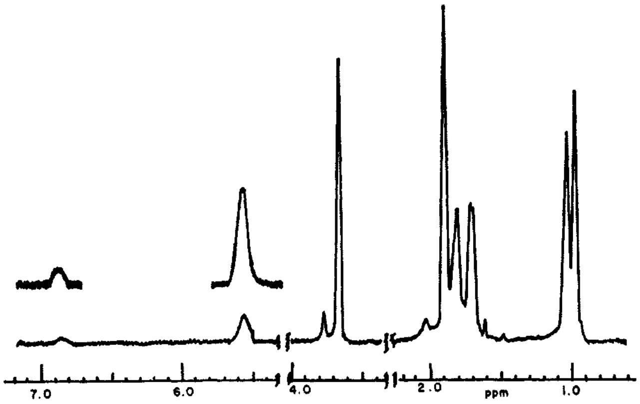


Figure 1.—Nmr spectrum of oxidation products from **5**.

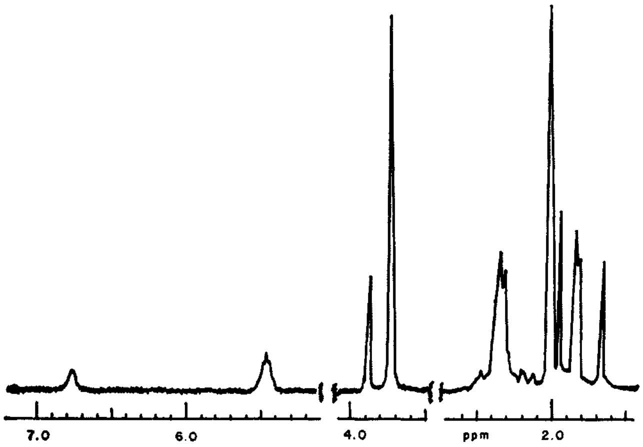
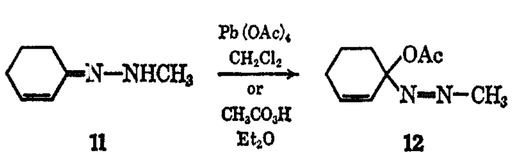
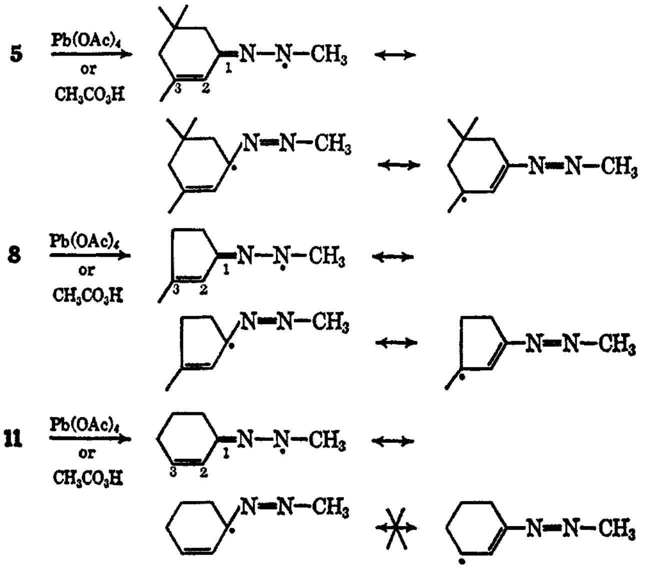


Figure 2.—Nmr spectrum of oxidation products from **8**.



The above results are consistent with the free-radical mechanism proposed by Iffland, *et al.*,[3a] and suggests that peracetic acid also reacts with ketone monoalkylhydrazones *via* a similar mechanism. In the case of hydrazones **5** and **8** the radical produced *via* the abstraction of a hydrogen atom by an acetate radical can resonate to carbons 1 and 3 thus giving rise to the azo acetates **6**, **7**, **9**, and **10**. In the case of 2-cyclohexen-1-one monomethylhydrazone **11**, however, the radical formed would not likely resonate out to carbon 3 (a less substituted carbon atom) and would give rise to acetate attack at carbon atom 1 exclusively.



Experimental Section[5]

Cinnamaldehyde Dimethylhydrazone.—To 20.0 g (0.15 mole) of *trans*-cinnamaldehyde in 200 ml of anhydrous ether was added with cooling 10.0 g (0.17 mole) of *asym*-dimethylhydrazine. The reaction mixture was removed from the ice bath after the addition of the hydrazine was completed and was allowed to sit at room temperature over anhydrous magnesium sulfate overnight. The solution was then filtered and the ether was removed under reduced pressure. The residual yellow liquid was then distilled under vacuum to give 20.0 g (77%) of a yellow liquid, bp 114–118° (0.26–0.22 mm). Redistillation of this material afforded an analytical sample of the hydrazone, bp 106° (0.42 mm), $\lambda_{\max}^{\mathrm{EtOH}}$ 324 mμ (ε 32,800) and 237 mμ (ε 8080).

Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.64; H, 8.30; N, 16.22.

Cinnamaldehyde Monomethylhydrazone (1).—To a solution of 99.0 g (0.75 mole) of *trans*-cinnamaldehyde in 400 ml of anhydrous ether was added with cooling 36.0 g (0.78 mole) of monomethylhydrazine. The mixture was allowed to sit at room temperature for 48 hr over anhydrous magnesium sulfate. The solution was then filtered and the ether was removed under reduced pressure to give 109 g (88%) of a yellow liquid, **1**. The ultraviolet spectrum of this crude product had $\lambda_{\max}^{\mathrm{EtOH}}$ 318 mμ (ε 26,600) and 233 mμ (ε 7200). The purity of this crude hydrazone was estimated to be about 85% by comparison of its ultraviolet molar absorptivities with those of cinnamaldehyde dimethylhydrazone. The infrared spectrum of **1** showed a strong N-H peak at 3370 cm^{-1} and a strong *trans*-olefin peak at 970 cm^{-1}. There was no peak at 880 cm^{-1} where 1-methyl-2-phenyl-Δ^4-pyrazoline (the product formed upon cyclization of the hydrazone) shows a strong absorption. The nmr spectrum of **1** had a complex pattern between 7.3 and 6.4 ppm, a broad N-H peak at 5.45 ppm, and two N-methyl singlets at 2.85 and 2.75 ppm, with relative intensities of 6:1, attributed to *syn* and *anti* isomers of the hydrazone. The relative intensities were 9:1:3.

Oxidation of 1 with Lead Tetraacetate in Methylene Chloride.—To a solution of 10.0 g of crude **1** in 200 ml of methylene chloride was added slowly with cooling in an ice water bath 32.0 g (1 equiv) of lead tetraacetate (85% active). The reaction mixture was then allowed to sit at ambient temperature for 2 hr. The lead diacetate was then filtered and the filtrate was washed several times with aqueous bicarbonate solution. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to give 13 g of a red-orange oil. A solid shortly formed and this was slurried in benzene and filtered to give 5.0 g (44%) of N-acetylcinnamic acid methylhydrazide **2**. Recrystallization from hexane afforded an analytical sample, mp 167–168°, $\lambda_{\max}^{\mathrm{EtOH}}$ 280 mμ (ε 20,900). The infrared spectrum of **2** showed an N-H peak at 3300 and two carbonyl peaks at 1690 and 1650 cm^{-1}. The nmr spectrum of **2** showed an amide-type N-H at 10.0, a typical cinnamyl pattern between 7.9 and 6.6, an N-methyl singlet at 3.24, and an acetyl methyl singlet at 2.1 ppm. The relative intensities were 1:7:3:3, respectively.

Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.02; H, 6.46; N, 12.84. Found: C, 66.15; H, 6.66; N, 12.92.

Oxidation of 1 with Lead Tetraacetate in Diethyl Ether.—To 10.0 g of crude hydrazone in 300 ml of diethyl ether was added slowly with cooling in an ice water bath 32 g (1 equiv) of lead tetraacetate. The mixture was allowed to stir at room temperature for 24 hr. The lead diacetate was then filtered and the ether was washed several times with aqueous bicarbonate solution. The ether was then dried over sodium sulfate

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[5] Boiling points and melting points are uncorrected. Microanalyses were performed by A. Bernhardt, Mulheim, Germany, and H. Galbraith, Knoxville, Tenn. The spectra were measured on a Cary Model 14 ultraviolet-visible spectrophotometer and a Perkin-Elmer Model 137 double beam infrared spectrophotometer. The nmr spectra were measured on a Varian Model A-60 spectrophotometer at 60 MHz with tetramethylsilane as an internal standard.

and the solvent was removed on the aspirator. A pale yellow solid crystallized out of solution toward the end of the removal of the ether. This solid was filtered to give 4.5 g (43%) of N-acetylcinnamaldehyde methylhydrazone (**3**). Recrystallization from ethanol afforded an analytical sample (mp 144–145°, λ_{max}^{EtOH} 310 mμ (ϵ 38,200)). The infrared spectrum of **3** showed no N–H band but had an amide-type carbonyl peak at 1670 cm^{-1}. The nmr spectrum of **3** showed a multiplet of peaks between 7.5 and 6.8, an N-methyl singlet at 3.25 and an acetylmethyl singlet at 2.3 ppm.

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.34; H, 7.09; N, 13.79.

Reaction of 1 with Acetic Anhydride.—To a solution of 50 ml of acetic anhydride in 200 ml of 5% aqueous hydrochloric acid was added slowly with cooling 4.5 g of crude **1**. The reaction mixture was allowed to stir at 5° for 2.5 hr. Acylated hydrazone (4 g, 84%) was obtained upon filtration of the solution. The solid was recrystallized from ethanol to afford a pure sample of **3**, mp 144–145°. The infrared spectrum of this material was identical with that of the product obtained *via* the oxidation of **1** with lead tetraacetate in diethyl ether.

Oxidation of 1 with Peracetic Acid.—To 10.0 g of crude **1** in 200 ml of ether was added with stirring and cooling in an ice water bath 30.0 g (2 equiv) of 40% peracetic acid. The solution was then allowed to stir at ambient temperature for 2 hr. Work-up similar to those previously described afforded an oil which had a strong odor of cinnamaldehyde. This oil was dissolved in ethanol and allowed to sit in the cold overnight. The crystals thus obtained were filtered to yield 2.6 g (21%) of **4**, a pale yellow solid. Recrystallization from ethanol afforded an analytical sample (mp 98–99°, λ_{max}^{EtOH} 252 mμ (ϵ 15,200) and 217 mμ (ϵ 17,600)). The infrared spectrum of **4** had strong acetate peaks at 1750 and 1250 and azoxy peaks at 1310 and 1460 cm^{-1}. The nmr spectrum of **4** had a phenyl multiplet at 7.24, a doublet centered at 7.0 (J_{AB} = 10 Hz), a doublet of doublets centered at 6.15 (J_{AB} = 10 Hz, J_{BC} = 6 Hz), a singlet at 6.8, a singlet at 4.1, and a singlet at 2.1 ppm. The relative intensities were 5:1:1:1:3:3, respectively.

Anal. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.53; H, 6.02; N, 11.96. Found: C, 61.71; H, 6.09; N, 11.77.

Isophorone Monomethylhydrazone (5).—To 138 g (1 mole) of isophorone in 200 ml of ether was added slowly with stirring 46 g (1 mole) of monomethylhydrazine. The solution was refluxed in the presence of anhydrous sodium sulfate overnight. The solution was then filtered and the ether was removed on an aspirator. The yellow residual liquid was then distilled *in vacuo*. Unreacted isophorone (40 g) was recovered. A yellow liquid (**5**) was then collected, bp 77–78° (1.3 mm). The yield was 70 g (62%) based on unrecovered ketone. The ultraviolet spectrum of **5** had a λ_{max}^{EtOH} 273mμ (ϵ 10,900) and 235 mμ (ϵ 8200). The infrared spectrum of **5** showed a strong N–H peak at 3320 and strong C=C and C=N peaks at 1665 and 1630 cm^{-1}, respectively. The nmr spectrum of **5** had olefinic hydrogen signals at 6.20 and 5.95, and N-methyl singlets at 2.95 and 2.90 corresponding to *syn* and *anti* forms of the hydrazone, a broad N–H peak at 4.65, a cyclohexyl multiplet at 2.2–1.8, and two methyl singlets at 1.0 ppm. The relative intensities were 1:1:3:7:6. The nmr spectrum indicated a ratio of *syn* to *anti* forms of the hydrazone of 11:4.

Anal. Calcd for $C_{10}H_{18}N_2$: C, 72.24; H, 10.90; N, 16.85. Found: C, 72.22; H, 10.85; N, 16.64.

Oxidation of Isophorone Monomethylhydrazone with Lead Tetraacetate.—To 10.0 g (0.06 mole) of **5** dissolved in 200 ml of methylene chloride was added slowly with cooling in an ice water bath 31.5 g (0.06 mole) of lead tetraacetate. The solution was allowed to stir at ambient temperature for 2 hr. Filtration of the lead diacetate followed by the usual work-up afforded a reddish brown residual liquid which on distillation under reduced pressure yielded 8.0 g (60%) of crude product, bp 73–76° (0.55–0.45 mm). Redistillation of this material afforded an analytical sample, bp 64–64.5° (0.26 mm), n^{25}D 1.4714. Spectral data showed this liquid to be an 8:1 mixture of 1-(methylazo)-3,5,5-trimethyl-2-cyclohexen-1-ol acetate (**6**) and 1-(methylazo)-3,5,5-trimethylcyclohexen-3-ol acetate (**7**). The ultraviolet spectrum of this liquid mixture had λ_{max}^{EtOH} 340 mμ (ϵ 46) and 235 mμ (ϵ 3650). The infrared spectrum of the mixture had strong acetate peaks at 1750 and 1250 and a C=C band at 1675 cm^{-1}. An nmr spectrum of the mixture had an olefin peak at 6.85 and an N-methyl singlet at 3.75 both due to **7**, an olefin peak at 5.55 and an N-methyl singlet at 3.65 both due to (**6**), in addition to an acetate methyl singlet at 2.0, a cyclohexyl methylene signal at 2.05–1.6, an olefinic methyl signal at 1.85, and two methyl singlets at 1.02 and 0.95 ppm. The ratio of **6** to **7** was shown by the spectrum to be 8:1.

Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.28; H, 8.99; N, 12.49. Found: C, 64.52; H, 8.92; N, 12.83.

Oxidation of Isophorone Monomethylhydrazone with Peracetic Acid.—To 15.0 g (0.09 mole) of **5** dissolved in 200 ml of anhydrous ether was added slowly with cooling in an ice water bath 20.0 g (0.10 mole) of 40% peracetic acid. The solution was then stirred at ambient temperature for 2 hr. The usual work-up followed by distillation of the residual liquid afforded 8.9 g (42%) of a mixture of **6** and **7**, bp 70° (0.4 mm), n^{25}D 1.4725. The infrared and nmr spectra of this liquid were identical with those of the product obtained *via* the oxidation of **5** with lead tetraacetate in methylene chloride.

3-Methyl-2-cyclopenten-1-one Monomethylhydrazone (8).—To 100 g (1.04 moles) of 3-methyl-2-cyclopenten-1-one[6] in 250 ml of anhydrous ether in the presence of anhydrous magnesium sulfate was added 51 g (1.1 moles) of monomethylhydrazine. The solution was stirred at reflux overnight. The solution was then filtered and the solvent was removed on an aspirator. The yellow residual liquid was then fractionally distilled. Unreacted ketone (45 g) was recovered. Thirty-five grams (29% based on unrecovered ketone) of a yellow liquid (**8**), bp 111–115° (6 mm), was collected. Redistillation of this liquid afforded a pure sample of **8**, bp 54–55° (0.22 mm), n^{26}D 1.5430. The ultraviolet spectrum of **8** had λ_{max}^{EtOH} 265 mμ (ϵ 11,700), and 225 mμ (ϵ 7450). The infrared spectrum of **8** had no C=O band but had a strong N–H peak at 3300 and a strong C=N peak at 1625 cm^{-1}. The nmr spectrum of **8** had olefin peaks at 6.15 and 5.75 and two N-methyl singlets at 2.80 and 2.75 attributed to *syn* and *anti* isomers of the hydrazone, along with a broad N–H peak at 4.6, a broad peak at 2.3, and a singlet at 1.85 ppm. Compound **8** was very unstable in air giving rise to a very dark liquid. It was for this reason that an analysis could not be obtained on this hydrazone. We do believe, however, that the spectral evidence presented herein leaves no doubt as to the structure of the compound.

Oxidation of 3-Methyl-2-cyclopenten-1-one Monomethylhydrazone with Lead Tetraacetate.—To 10.0 g (0.08 mole) of **8** in 200 ml of methylene chloride was added slowly with cooling 42.0 g (0.08 mole) of lead tetraacetate. The solution was allowed to stir under nitrogen at ambient temperature for 2 hr. Work-up in the usual manner followed by distillation of the residual liquid yielded 8.1 g (57%) of a yellow liquid, bp 78–81° (3.6 mm). Redistillation of this liquid afforded an analytical sample, bp 79.5° (3.7 mm). Spectral data of this material showed it to be a 2.2:1 mixture of 1-(methylazo)-3-methyl-2-cyclopenten-1-ol acetate (**9**) and 1-(methylazo)-3-methylcyclopenten-3-ol acetate (**10**). The ultraviolet spectrum of this liquid mixture had λ_{max}^{EtOH} 336 mμ (ϵ 118) and 248 mμ (ϵ 3600). The infrared spectrum of the liquid had an olefin peak at 5.45 and an N-methyl singlet at 3.65 both due to **9**, and an olefin peak at 6.75 and an N-methyl singlet at 3.82 both due to **10**, along with a broad multiplet at 2.3, two acetate signals at 2.00 and 1.96, and two C-methyl singlets at 1.8 and 1.6 ppm, again due to isomers **9** and **10**. The spectrum indicated the ratio of **9**–**10** to be 2.2:1.

Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.31; H, 7.68; N, 15.60.

Oxidation of 3-Methyl-2-cyclopenten-1-one Monomethylhydrazone with Peracetic Acid.—To 10.0 g (0.08 mole) of **8** dissolved in 125 ml of anhydrous ether was added slowly with cooling 15.4 g (0.08 mole) of 40% peracetic acid. The reaction mixture was allowed to stir at ambient temperature for 1.5 hr. The usual work-up followed by distillation of the residual liquid yielded 3.3 g (23%) of a yellow liquid, bp 78–82° (3.7 mm). The infrared and nmr spectra of this material were identical with those of the mixture of **9** and **10** obtained *via* the oxidation of **8** with lead tetraacetate.

2-Cyclohexen-1-one Monomethylhydrazone (11).—To 10.0 g (0.11 mole) of 2-cyclohexen-1-one in 50 ml of benzene was added with stirring 4.80 g (0.12 mole) of monomethylhydrazine. The solution was refluxed overnight and the water was removed azeotropically by means of a Dean-Stark trap. The solvent

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(6) R. M. Acheson and R. Robinson, *J. Chem. Soc.*, 1131 (1952).

was then removed and the residual liquid was distilled under reduced pressure to give 9.0 g (70%) of a yellow liquid (**11**): bp 78–79° (3.6 mm); $n^{27}\mathrm{D}$ 1.5552; $\lambda_{\max}^{\mathrm{EtOH}}$ 271 mμ (ε 11,600) and 230 mμ (ε 6250). The infrared spectrum of **11** had an N–H peak at 3300, a C=N peak at 1625, and a C–N stretch at 1125 cm^{-1}. Its nmr spectrum showed a multiplet of olefin peaks centered at 5.9, an N-methyl singlet at 2.9, and a cyclohexyl multiplet between 2.4 and 1.6 ppm.

Anal. Calcd for $C_7H_{12}N_2$: C, 67.26; H, 10.32; N, 22.41. Found: C, 66.84; H, 9.88; N, 22.60.

Oxidation of 2-Cyclohexen-1-one Monomethylhydrazone with Lead Tetraacetate.—To 10.0 g (0.08 mole) of **11** dissolved in 200 ml of methylene chloride was added slowly with stirring and cooling 42.4 g (0.08 mole) of lead tetraacetate. The solution was allowed to stir at ambient temperature for 2 hr. Work-up in the manner previously described followed by distillation of the residual liquid afforded 9.7 g (70%) of a yellow liquid (**12**): bp 81–81.5° (3.5 mm); $n^{28}\mathrm{D}$ 1.4739; $\lambda_{\max}^{\mathrm{EtOH}}$ 356 mμ (ε 27). The infrared spectrum of **12** had no N–H peak but had strong acetate peaks at 1750 and 1240 cm^{-1}. The nmr spectrum of **12** had an olefinic signal at 5.95, an N-methyl singlet at 3.75, an acetyl methyl singlet at 2.0, and a methylene multiplet at 2.2–1.6 ppm. The relative intensities were 2:3:3:6, respectively.

Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.17; H, 7.63; N, 15.45.

Oxidation of 2-Cyclohexen-1-one Monomethylhydrazone with Peracetic Acid.—To 10.0 g (0.08 mole) of **11** dissolved in 200 ml of anhydrous ether was added with stirring and cooling in an ice water bath 15.5 g (0.08 mole) of 40% peracetic acid. The solution was stirred at ambient temperature for 2 hr. The usual work-up followed by distillation of the residual liquid afforded 4.75 g (35%) of 1-(methylazo)-2-cyclohexen-1-ol acetate (**12**), bp 82.5° (3.7 mm). The ultraviolet, infrared, and nmr spectra of this product were identical with those of **12** prepared by the oxidation of **11** with lead tetraacetate. Back extraction of the first two aqueous bicarbonate washes with methylene chloride afforded 2.1 g of a liquid whose infrared spectrum showed it to be mainly 2-cyclohexen-1-one.

Registry No.—**1** (*syn*), 15023-24-2; **1** (*anti*), 15023-25-3; **2**, 15023-26-4; **3**, 15023-27-5; **4**, 15023-28-6; **5** (*syn*), 15023-29-7; **5** (*anti*), 15026-11-6; **6**, 15023-30-0; **7**, 15023-31-1; **8** (*syn*), 15023-32-2; **8** (*anti*), 15023-33-3; **9**, 15023-34-4; **10**, 15023-35-5; **11**, 15023-36-6; **12**, 15023-37-7; *trans*-cinnamaldehyde dimethylhydrazone, 15023-38-8.

Pseudo-Halogens. X. Effect of Some Electronic or Steric Factors on the Addition of N,N-Dichlorourethan to Unsaturated Compounds[1,2]

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The addition of N,N-dichlorourethan (DCU) to unsaturated compounds with special electronic or steric factors has been investigated. Yields of β-chlorocarbamates range from 35 to 80%. Electron-withdrawing groups slow down the addition reaction; extensive electron withdrawal completely arrests it. Perfluorocyclohexene, ethyl vinyl sulfone, and diethyl maleate do not react. Addition of DCU to substituted alkenes is subject to steric retardation and is also complicated by allylic chlorination. With 2,3-dimethyl-2-butene allylic chlorination is the exclusive process. DCU adds to all terminally unsaturated compounds studied in anti-Markownikow fashion. Nmr and chemical evidence have been used to prove the structures of the adducts. By controlled pyrolysis of methyl β-(N-carboethoxyamino)-α-chloropropionate and N-(2-chloro-2-cyanoethyl)carbamate, 5-carbomethoxy- and 5-cyano-2-oxazolidones, respectively, have been obtained in 65 and 35% yields. These oxazolidones are difficult to obtain by the usual alkali-catalyzed ring-closure methods.

Study of the scope, limitations, and mechanisms of the addition of pseudo-halogens (iodine isocyanate, nitrosyl acylates, N,N-dichlorourethan) to unsaturated compounds is of considerable interest in our laboratory.[1,3] In an earlier paper,[3a] we described the addition of N,N-dichlorourethan (DCU) to a series of monoolefinic compounds and showed that the reaction has many of the characteristics of a free-radical addition reaction. The initial group of unsaturated compounds studied comprised straight-chain terminal olefins ($RCH=CH_2$), internal olefins ($RCH=CHR$), a branched-chain terminal olefin ($RC(R)=CH_2$), an unsaturated compound with an electron-withdrawing group attached to the double bond (methyl acrylate) and two cyclic olefins (cyclohexene and norbornene). In most cases addition was rapid; the reaction provides a facile, one-step synthesis of compounds containing the carbon–nitrogen bond from monounsaturated compounds.

DCU is an unusual pseudo-halogen. Although it is extremely reactive, it can be distilled under vacuum and stored for long periods in the dark without excessive decomposition. Redistillation just before use provides the pure pseudo-halogen. This combination of properties makes DCU an attractive halogenoid reagent for chemical investigations.

In the present paper we are reporting (a) the reaction of DCU with selected unsaturated compounds having special electronic or steric features and (b) proof of structure of the addition products. When pure β-chlorocarbamates could be isolated, their pyrolysis and reaction with base were also studied in attempts to prepare unusual 2-oxazolidones and aziridines, respectively. Table I lists the β-chlorocarbamates prepared.

Addition of DCU to Unsaturated Compounds with Polar Substituents.—In all cases shown, yields of analytically pure, isolated β-chlorocarbamates are fair to good (35–80%) whether electron-donating or certain electron-withdrawing groups (–CN, $-CO_2C_2H_5$, $-CO_2CH_3$, Cl_2, $-COCH_3$) are attached to the double bond. This result is consistent with the generally

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(3) (a) T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3625 (1966), and references therein; (b) H. C. Hamann and D. Swern, *Tetrahedron Letters*, 3303 (1966).