Cromer and Waber,[35] and these light atom scattering curves were taken from the tabulations of Hanson et al.[36] The effects of anomolous dispersion were included in the calculated structure factors with the values of $\Delta D'$ and $\Delta f''$ for Pd and Cl taken from the report of Cromer.[37] The data were reduced and the Patterson maps calculated on a Data General NOVA 1200 using programs written in this laboratory. All further calculations were done on the CDC 6400 at the University of Colorado using programs supplied by Dr. James Ibers.

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(36) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
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Attempted Synthesis of a Keto Diazene: Reactions of Propargylic Amines, Sulfamides, and Ureas

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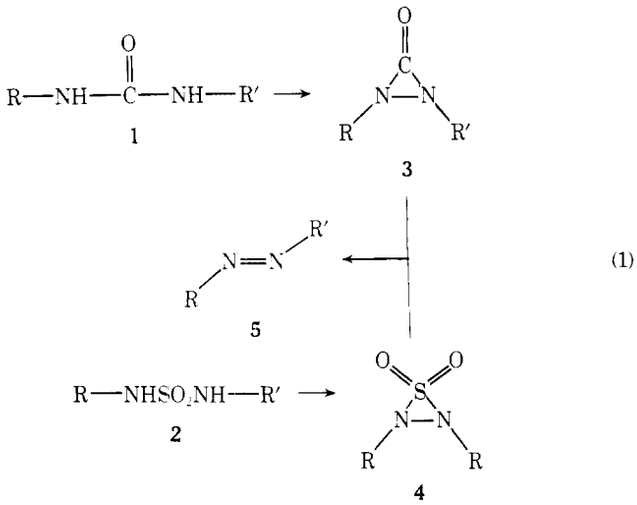
Several attempts to prepare bis(2-oxo-1,1-dimethylpropyl)diazene (**5e**) from propargylic derivatives led to a number of interesting cyclizations giving nitrogen heterocycles (isoxazole **11**, imidazolidinones **22**, and pyrazole **27**). One of these provides an alternate synthesis of hydantoins (imidazolidinediones **23**).

Ureas **1**,[1] sulfamides **2**,[2] diaziridinones **3**,[3,4] and thiadiaziridine 1,1-dioxides **4**[5,6] have been used as precursors to dialkyldiazenes (**5**, eq 1).[1] In a continuation[7] of our study of



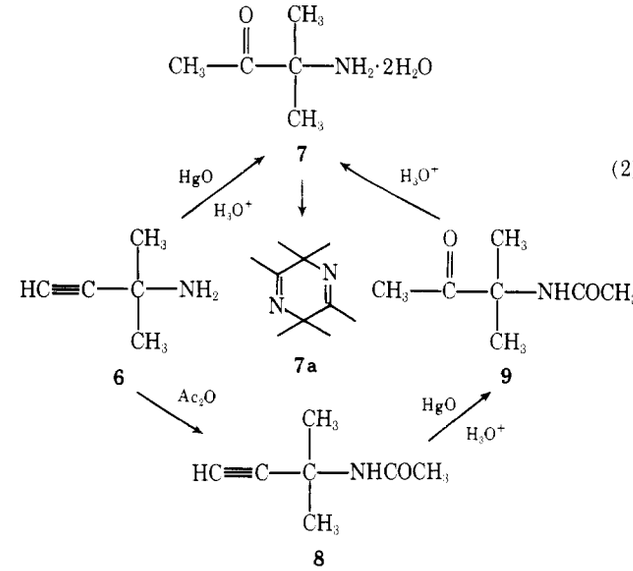
(1)

(a) R = $HC{\equiv}CC(CH_3)_2$—; R′ = $(CH_3)_3C$—
(b) R = R′ = $HC{\equiv}CC(CH_3)_2$—
(c) R = $CH_3COC(CH_3)_2$—, R′ = $(CH_3)_3C$—
(d) R = $HC{\equiv}CC(CH_3)_2$—, R′ = $CH_3COC(CH_3)_2$—
(e) R = R′ = $CH_3COC(CH_3)_2$—

diazenes as models of radical stabilities, we were interested in synthesizing a diazene with a β keto R group such as **5c** or **5e**. Since substituted acetylenes can be considered synthons of keto groups by hydration of the triple bond, we considered the four following methods as possible routes to ketodiazene **5c,e:** (a) hydration of 1,1-dimethylpropargylamine (**6**), (b) hydration of β-substituted propargylsulfamides **2a,b,** (c) hydration of propargyldiaziridinones **3a,b** or thiadiaziridine 1,1-dioxides **4a,b,** and (d) hydration of propargyldiazenes **5a,b.** These attempts have not been completely successful, but have led to some interesting chemistry described herein.

Results and Discussion

(a) Hydration of 1,1-Dimethylpropargylamine. 1,1-Dimethylpropargylamine (**6**) was considered as a precursor to 3-amino-3-methyl-2-butanone (**7**) so that the latter could be directly converted to diazene **5e** with IF_5[1,8] or first converted to urea **1e** or sulfamide **2e** and then to the diazene **5e.**[1] However, hydration of the propargylamine **6** proceeded in very low yield (<5%). Similarly, hydration of acetylated propargylamine **8** followed by acidic hydrolysis also gave unsatisfactory results (~13% overall from **6**, eq 2). While this amine



(2)

has been reported previously as the monomeric amine hydrochloride salt,[9] spectral data seem to indicate that in completely dehydrated form the "amine" appears to be dimeric (**7a,** see Experimental Section). An x-ray analysis is presently being attempted.

The Ritter reaction of 3-hydroxyl-3-methyl-2-butanone (**10**) was selected as an alternative route to **7** by hydrolysis of the expected amide. However, our initial attempts employing the normal aqueous workup recovered only "unreacted" starting material. More careful low-temperature workup gave two products, 4-hydroxy-2,4,5,5-tetramethyl-2-oxazoline (**11,** 17% yield) and 3-oxo-2-methyl-2-butyl acetate (**12,** 22% yield). A reaction sequence explaining the recovery of starting material is illustrated in eq 3. Isolated oxazoline **11** was converted to ester **12** under mild hydrolytic conditions and **12** was converted back to **10** by hydrolysis of the ester under more rigorous conditions.

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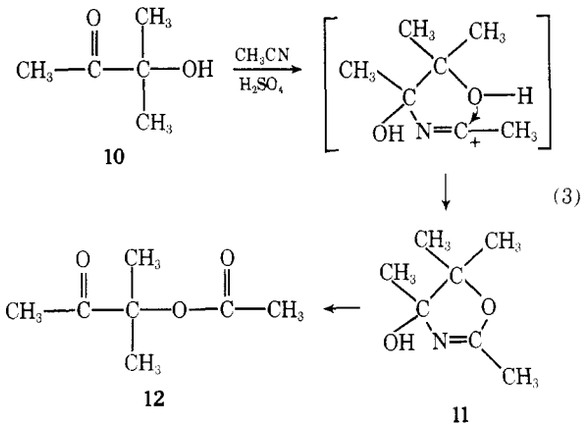
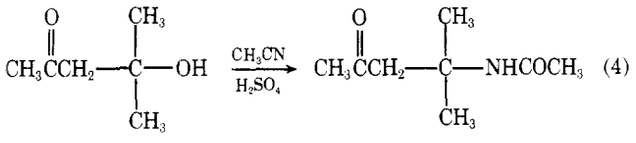


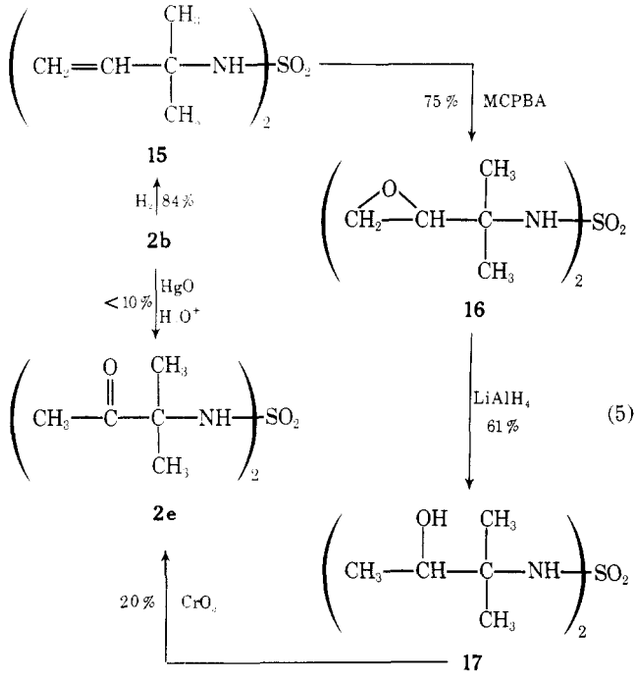
10 11 12 (3)

It is interesting to note that diacetone alcohol **13** (4-hydroxy-4-methyl-2-pentanone, **13**) gives the normal Ritter product amide **14**; undoubtedly, this reflects the difference between **10** and **13** in their respective cation stabilities.



13 14 (4)

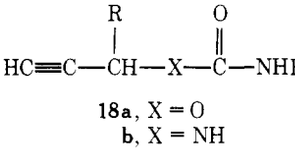
(b) Hydration of Sulfamides. Hydration of *N,N'*-bis(1,1-dimethylpropynyl)sulfamide (**2b**), prepared from the corresponding propargylamine with sulfuryl chloride according to Engel and Bishop,[10] was also a low-yield process (1%). Alternatively, we have prepared the bisketo sulfamide **2e** by the sequence shown in eq 5. Hydrogenation of **2b** to the



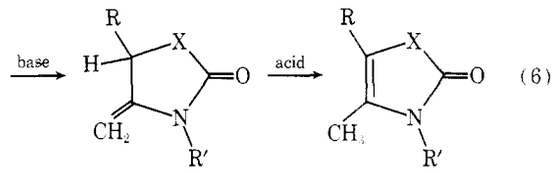
15 16 17 2b 2e (5)

bisallylic sulfamide **15** is known,[10] and compound **15** can be epoxidized to **16** (75%), reduced to alcohol **17** (61%), and oxidized to sulfamide **2e** (20%). However, neither the aqueous conversion (NaOCl, NaOH)[2] of **2e** to **5e** nor nonaqueous conversion of **2e** to **5e** (NaH, *t*-BuOCl)[5] was successful.

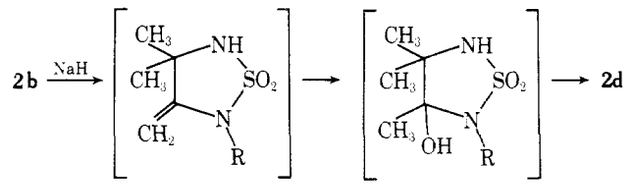
(c) Attempted Preparation of Propargyldiaziridinones and Thiadiaziridine 1,1-Dioxides. The preferred method of preparing thiadiaziridine 1,1-dioxides (**4**, eq 1) involves treating the sodium salt of the sulfamide (**2** + NaH) with *tert*-butyl hypochlorite.[6,11] However, it is known that propargylic urethanes[12] **18a** and ureas[13] **18b** cyclize with sodium methoxide, pyridine, or sodium acetate to give 5-methylene-2-oxazolidinones **19a** and imidazolidinones **19b.** We believe this same cyclization occurs with propargylic sulfamide **2b** with sodium hydride to give thiadiazolidine 1,1-dioxide (**21b**). However, because of the extreme lability its presence could only be conjectured from NMR data (see Experimental Section) and from the corresponding keto sulfamide **2d** isolated from the aqueous workup. The oxazolidinones **19a** and imidazolidinones **19b** previously obtained by this cyclization all contained hydrogen at C-4, and acid treatment resulted in tautomerization from the exocyclic isomer **19a,b** to the endocyclic isomer **20a,b**[14]. Because the thiadiazolidine dioxide **21b** was only presumed as an intermediate, the corresponding *N,N'*-bis(1,1-dimethylpropynyl)ureas were cyclized to imidazolidinones **22a,b** as further evidence of the intermediacy of **21b.** Even though unlikely, we had to establish that the keto sulfamide **2d** was not produced directly from basic hydration of the propargylsulfamide (**2b**). The cyclic ureas **22a,b** were more stable than the cyclic sulfamide and could be isolated in good yields. As expected, these imidazolidinones **22a,b** with two methyls at C-4 were blocked toward tautomerization, and hydrolysis to the keto ureas **1c** and **1d** resulted.



18a, X = O
b, X = NH



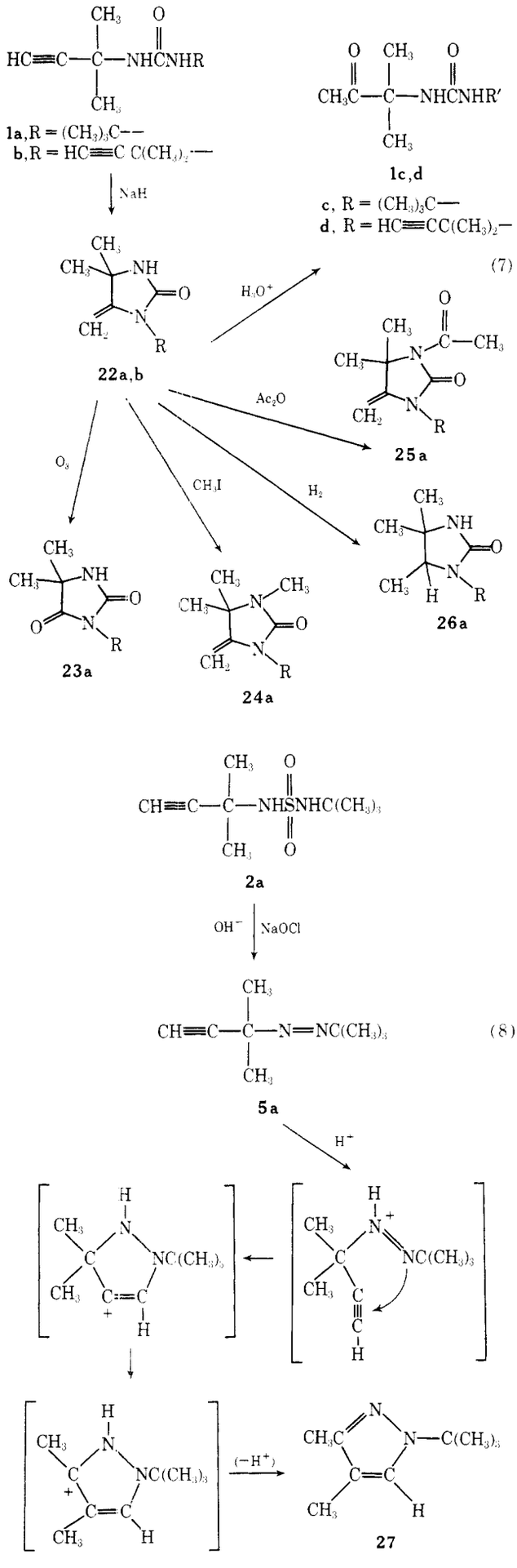
19a,b 20a,b (6)



21b 2d

The imidazolidinones can be alkylated (**24a**) or acetylated (**25a**) on nitrogen and the exocyclic double bond can be reduced to a methyl group (**26a**) or ozonolyzed to hydantoin (2,4-imidazolidinedione) **23a.** Hydantoins represent a class of compounds with an extensive history and find use as herbicides and antibacterial, antifungal, antiarrhythmatic, and anticonvulsant agents.[15,16] We are presently investigating this method as a procedure for making functionalized hydantoins which are difficult to obtain by other procedures.

(d) Attempted Hydration of Propargyldiazenes. Alkylsulfamides **2** are readily converted to alkyldiazenes **5** using aqueous base and hypochlorite.[2] Bis(1,1-dimethylpropynyl)-diazene has been prepared by Engel[10] using this procedure (**2b** to **5b**). Following this lead, sulfamide **2a** was converted to *N-tert*-butyl-*N'*-1,1-dimethylpropynyldiazene (**5a**) with aqueous hypochlorite and base. The NMR of the pentane extract showed signals expected for diazene **5a,** but the compound rapidly rearranged to 1-*tert*-butyl-3,4-dimethylpyrazole (**27**). The reaction appears to be acid catalyzed and yields up to 70% can be obtained by treating the pentane extract with



formic acid. The formation of pyrazole **27** can be rationalized as shown in eq 8 and clearly indicates that acid-catalyzed hydration of propargyldiazenes is not feasible.

Summary

Attempts to prepare β-ketodiazenes **5c,e** have uncovered a number of interesting side reactions. In particular, one of these, the closure of propargylureas **1** followed by ozonolysis could provide a useful synthetic route to hydantoins **23.**

Experimental Section

3-Amino-3-methyl-2-butanone Hydrate (7). To a stirred solution of 0.83 g (3.8 mmol) of red mercuric oxide in 60 mL of 10% H_2SO_4 heated to 70 °C was added dropwise 5.58 g (67 mmol) of 1,1-dimethylpropargylamine (Aldrich). After stirring for 1 h at room temperature, ether was added and the aqueous solution was neutralized with 5 M KOH. The ether layer was dried over $MgSO_4$ and distilled. The crude amine was sublimed to yield colorless cubic crystals of 3-amino-3-methyl-2-butanone dihydrate (**7,** 0.03 g, 0.5%), mp 77–84 °C, or **7a** hexahydrate: NMR (CCl_4 solution dried over Na_2SO_4) δ 1.22 (s, 3 H) and 1.95 ppm (s, 1 H); IR (CCl_4 solution dried) 3291, 2971, 1655, 1368, 1357 and 1161 cm^{-1}; mass spectrum *m/e* 166.

Anal. Calcd for $C_5H_{11}NO{\cdot}2H_2O$ or $C_{10}H_{18}N_2{\cdot}6H_2O$: C, 43.77; H, 11.04; N, 10.21. Found: C, 44.05; H, 11.04; N, 10.30.

***N*-1,1-Dimethyl-2-propynylacetamide (8).** To a solution of 4 g (0.048 mol) of 1,1-dimethylpropargylamine in 50 mL of ether cooled to 0 °C was added dropwise 6 g (0.058 mol) of acetic anhydride. The mixture was stirred at reflux overnight. The etheral solution was washed with several portions of 5% $NaHCO_3$ and combined with several chloroform extracts of the aqueous layer. The organic extracts were dried ($MgSO_4$), concentrated, and recrystallized from $CHCl_3$–hexane to give 4.1 g (68%) of white crystals: mp 104.5–106 °C; NMR ($CDCl_3$) δ 1.64 (s, 6 H), 1.95 (s, 3 H), 2.32 (s, 2 H) and 5.60 ppm (br s, ~1 H); IR ($CHCl_3$) 3441, 3302, and 1692 cm^{-1}.

Anal. Calcd for $C_7H_{11}NO$: C, 67.21; H, 8.80; N, 11.20. Found: C, 67.34; H, 9.02; N, 11.16.

2-Methyl-3-oxo-2-butylacetamide (9). *N*-1,1-Dimethyl-2-propynylacetamide (**8,** 6.0 g, 48 mmol) and red mercuric oxide (1 g, 5.0 mmol) were dissolved in 130 mL of 24% H_2SO_4 and stirred overnight at room temperature. The solution was neutralized with K_2CO_3 and continuously extracted with $CHCl_3$ for 24 h. The $CHCl_3$ extract was dried ($MgSO_4$) and concentrated. The crude product was recrystallized from $CHCl_3$–hexane to give 4.0 g (70%) of white needles: mp 109–111 °C; IR ($CHCl_3$) 3395, 3440, 1725 and 1665 cm^{-1}; NMR ($CDCl_3$) δ 1.50 (s, 6 H), 1.98 (s, 3 H), and 6.4 ppm (br s, ~1 H); mass spectrum *m/e* 143.

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.75; H, 9.09; N, 9.79. Found: C, 58.94; H, 9.18; N, 9.80.

3-Amino-3-methyl-2-butanone (7). 2-Methyl-3-oxo-2-butylacetamide (**9,** 3.3 g, 0.023 mol) in 40 mL of 20% HCl was heated to reflux for 12 h. The solution was neutralized with K_2CO_3 and continuously extracted with $CHCl_3$ for 60 h. After drying the $CHCl_3$ extract ($MgSO_4$) and distilling off the $CHCl_3$, a yellow oil remained which was recrystallized from pentane at −80 °C to give 0.65 g (28%) of white needles, mp 82–85 °C, identical with material (**7**) obtained as above.

***N,N'*-Bis(1,1-dimethyl-2,3-epoxypropyl)sulfamide (16).** To a refluxing solution of 21.0 g (0.09 mol) of *N,N'*-bis(1,1-dimethylallyl)sulfamide (**15**)[10] in 250 mL of CH_2Cl_2 was added 55.1 g (0.226 mol) of *m*-chloroperbenzoic acid (85%, Aldrich) in 200 mL of CH_2Cl_2 at a rate sufficient to maintain reflux. The solution was heated at reflux for 20 h at which time a white solid had formed. The excess peracid was destroyed by washing twice with 100-mL portions of 10% $NaHSO_3$. The solution was washed with two portions of 100 mL of 5% $NaHCO_3$, followed by water and a saturated NaCl solution. The organic layer was dried ($MgSO_4$) and concentrated to give 18.0 g (0.068 mol, 75% crude) of a viscous yellow oil which could not be crystallized and was used in the subsequent steps without further purification: NMR ($CDCl_3$) δ 1.40 (q, 6 H), 2.78 (d, 2 H), 3.08 (t, 1 H), and 4.5 ppm (br s, 1 H); IR ($CHCl_3$) 3683, 3375, 3050, 3040, 1370, 1270, and 1122 cm^{-1}.

***N,N'*-Bis(3-hydroxy-2-methyl-2-butyl)sulfamide (17).** To a solution of 10.6 g (0.04 mol) of the epoxide **16** in 100 mL of anhydrous ether was added 3.1 g (0.08 mol) of $LiAlH_4$. The mixture was stirred at reflux overnight. A saturated Na_2SO_4 solution was added to destroy the excess $LiAlH_4$. Enough $MgSO_4$ was added to contain the aqueous layer. The dry ether layer was concentrated to yield 5.62 g (0.021 mol, 54% crude) of a light-yellow oil which could not be crystallized and

was used in the next step without further purification: NMR ($CDCl_3$) δ 1.34 (m, 9 H), 3.45 (q, 1 H), and 5.0 ppm (br exchangable protons); IR ($CHCl_3$) 3492, 3380, 1369, and 1138 cm^{-1}.

***N,N'*-Bis(2-methyl-3-oxo-2-butyl)sulfamide (2e) by Oxidation of 17.** To a solution of *N,N'*-bis(2-methyl-3-oxo-2-butyl)sulfamide (**17**, 5.6 g, 0.02 mol) in 100 mL of acetone cooled to 0 °C was added dropwise 33 mL of a Jones reagent solution prepared by dissolving 7.0 g of CrO_3 in 10 mL of water followed by the addition of 6.1 mL of concentrated H_2SO_4 followed by 20 mL of water. The mixture was stirred for 3 h at room temperature. Solid $NaHSO_3$ was added until the brown color disappeared. The ether extract was washed successively with 100-mL portions of saturated NaCl, 5% $NaHCO_3$, saturated NaCl solutions, and dried over $MgSO_4$. Concentration yielded a semisolid which was purified by chromatography on neutral alumina and recrystallized from $CHCl_3$–hexane to yield 1.0 g (3.38 mmol, 18%) of white solid, mp 147–149 °C. This compound was identical in every respect with the keto sulfamide prepared below.

***N,N'*-Bis(2-methyl-3-oxo-2-butyl)sulfamide (2e) by Hydration of 2b.** *N,N'*-bis(1,1-dimethylpropynyl)sulfamide[10] (**2b**, 5g, 22 mmol) was combined with 0.1 g (4.6 mmol) of red mercuric oxide and 60 mL of 25% H_2SO_4. After stirring for 24 h, the solution was extracted with $CHCl_3$, dried ($MgSO_4$), and concentrated to give a brown oil which was crystallized from ether at −78 °C to yield 0.05 g (1%) of white crystals: mp 149–151 °C; NMR ($CDCl_3$) δ 1.56 (s, 6 H), 2.25 (s, 3 H), and 5.34 ppm (br s, 1 H); IR ($CHCl_3$) 3333, 1710, 1325 and 1147 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}N_2O_4S$: C, 45.42; H, 7.62; N, 10.63. Found: C, 45.20; H, 7.57; N, 10.49.

Ritter Reaction of 3-Hydroxy-3-methyl-2-butanone (10). To a 250-mL flask equipped with an overhead stirrer and cooled to 0 °C was added 16 g (0.14 mol) of acetonitrile, 25 mL of concentrated H_2SO_4, and 50 mL of glacial acetic acid. To this mixture was added 10 g (0.102 mol) of 3-hydroxy-3-methyl-2-butanone (Aldrich). The solution was stirred for 24 h. In rapid succession the mixture was poured over ice, rapidly neutralized with K_2CO_3, and extracted with $CHCl_3$. The $CHCl_3$ extract was dried ($MgSO_4$) and concentrated to give a thick yellow liquid which afforded 3.2 g (22%) of 2-methyl-3-oxo-2-butyl acetate (**12**) with vacuum distillation: bp 28 °C/0.1 mm; NMR ($CDCl_3$) δ 1.47 (s, 6 H), 2.08 (s, 3 H) and 2.11 ppm (s, 3 H); IR ($CHCl_3$) 1734, 1719, and 1252 cm^{-1}; mass spectrum *m/e* 144.

Anal. Calcd for $C_7H_{12}O_3$: C, 58.33; H, 8.33. Found: C, 58.11; H, 8.59.

The crude solid which remained was recrystallized from pentane to give 2.5 g (17%) of 4,5-dihydro-2,4,5,5-tetramethyl-4-hydroxyoxazole (**11**) as white needles: mp 93–94 °C; NMR ($CDCl_3$) δ 1.27 (s, 3 H), 1.41 (s, 6 H), 1.96 (s, 3 H), and 2.96 ppm (s, 1 H); IR ($CHCl_3$) 3605, 3160, 1655, and 1140 cm^{-1}; mass spectrum *m/e* 143.

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.75; H, 9.09; N, 9.79. Found: C, 58.61; H, 9.20; N, 9.69.

Oxazole (**11**) was hydrolyzed in 15 mL of 5% HCl to a mixture of 2-methyl-3-oxo-2-butyl acetate (**12**) and 3-methyl-3-hydroxy-2-butanone (**10**) as determined by NMR. Refluxing the oxazole in 5% HCl showed only keto alcohol **10** as the product.

2-Methyl-4-oxo-2-pentylacetamide (14). To 7.15 g (0.174 mol) of acetonitrile, 20 mL of concentrated H_2SO_4, and 40 mL of glacial acetic acid was added 13.5 g (0.116 mol) of diacetone alcohol (4-methyl-4-hydroxy-2-pentanone, Aldrich). After stirring for 24 h, the mixture was poured over ice, neutralized with K_2CO_3, and extracted with $CHCl_3$. The dried $CHCl_3$ extract ($MgSO_4$) was concentrated to give an orange-red liquid. Distillation gave a yellow liquid (bp 115–118 °C/~1 mm) which crystallized from pentane at −78 °C to give 9.1 g (50%) of amide **14** which was recrystallized from pentane to give pure 2-methyl-4-oxo-2-pentylacetamide (**14**): mp 44–45 °C (lit. 46 °C);[17] NMR ($CDCl_3$) δ 1.42 (s, 6 H), 1.96 (s, 3 H), 2.18 (s, 3 H) and 3.0 ppm (s, 2 H); IR ($CHCl_3$) 3440, 1746, 1710, and 1658 cm^{-1}.

Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.30; H, 9.55; N, 8.93.

***N*-*tert*-Butyl-*N'*-1,1-dimethylpropynylurea (1a).** To a solution of 39 g (0.47 mol) of 1,1-dimethylpropargylamine in 150 mL of purified hexane at 0 °C under a nitrogen atmosphere was added 46.5 g (0.47 mol) of freshly distilled *tert*-butyl isocyanate. The mixture was stirred for 2 h at room temperature. The solid which formed was filtered and recrystallized from ethanol–water to yield 73.6 g (87%) of *N*-*tert*-butyl-*N'*-1,1-dimethylpropynylurea: mp 202–203 °C; NMR ($CDCl_3$) δ 1.38 (s, 9 H), 1.58 (s, 6 H), 2.46 (s, 1 H), 4.30 (br s, 1 H), and 5.10 ppm (br s, 1 H); IR ($CHCl_3$) 3406, 3297, 2285, and 1662 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}N_2O$: C, 65.88; H, 9.97; N, 15.37. Found: C, 65.81; H, 10.12; N, 15.30.

***N,N'*-Bis(1,1-dimethylpropynyl)urea (1b).** To 45.8 g (0.55 mol) of 1,1-dimethylpropargylamine and 55.7 g (0.55 mol) of triethylamine in 250 mL of dry benzene in a flask cooled in an ice bath was added 27.3 g (0.27 mol) of phosgene in 200 mL of dry benzene. The mixture was stirred for 2 h followed by the careful addition of 200 mL of 5% $NaHCO_3$ solution. The solid formed was filtered, redissolved in $CHCl_3$, dried ($MgSO_4$), concentrated, and recrystallized from ethanol–H_2O to give 35 g (66%) of urea **1b**: mp 189–190 °C; NMR ($CDCl_3$) δ 1.60 (s, 6 H), 2.40 (s, 1 H), and 5.20 ppm (br s, 1 H); IR ($CHCl_3$) 3394, 3300, 2111, and 1670 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}N_2O$: C, 68.70; H, 8.40; N, 14.57. Found: C, 68.75; H, 8.31; N, 14.51.

1-*tert*-Butyl-5-methylene-4,4-dimethyl-2-imidazolidinone (22a). To 2.0 g of sodium hydride dispersion washed with dry THF (~42 mmol) suspended in 50 mL of THF was added 1 g (5.5 mmol) of *N*-*tert*-butyl-*N'*-1,1-dimethylpropynylurea. The mixture was heated to reflux for 3 h followed by the careful addition of 50 mL of water. After stirring 1 h at room temperature, the THF was removed in vacuo. Extraction with ether, drying over K_2CO_3, and removal of the ether left a white solid which was recrystallized from pentane to yield 0.5 g (50%) of 1-*tert*-butyl-5-methylene-4,4-dimethyl-2-imidazolidinone (**22a**): mp 104–105 °C; ^1H NMR ($CDCl_3$) δ 1.30 (s, 6 H), 1.59 (s, 9 H), 4.02 (d, 1 H, J = 3 Hz) and 4.32 ppm (d, 1 H, J = 3 Hz); ^{13}C NMR ($CDCl_3$ relative to Me_4Si) δ 28.8 [$(C^*H_3)_2C$–], 29.6 [$(C^*H_3)_3C$–], 55.2 [$(CH_3)_2C^*$–], 55.9 [$(CH_3)_3C^*$–], 82.8[H_2C^*=C], 154.0 [H_2C=C^*], and 158.8 ppm [C^*=O]; mass spectrum *m/e* 182; IR ($CHCl_3$) 3445, 1710, and 1664 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}N_2O$: C, 65.88; H, 9.97; N, 15.37. Found: C, 65.93; H, 9.89; N, 15.17.

1-(1,1-Dimethylpropynyl)-5-methylene-4,4-dimethyl-2-imidazolidinone (22b). To 5.5 g (~90 mmol) of sodium hydride suspension washed with THF suspended in 150 mL of THF was added 18.0 g (94 mmol) of *N,N'*-bis(1,1-dimethylpropynyl)urea (**1b**). After stirring for 24 h the solution was filtered and the THF removed in vacuo. The yellow solid was recrystallized four times from hexane to yield 14 g (78%) of 1-(1,1-dimethylpropynyl)-5-methylene-4,4-dimethyl-2-imidazolidinone (**22b**): mp 110–111 °C; NMR ($CDCl_3$) δ 1.32 (s, 6 H), 1.77 (s, 1 H), 1.88 (s, 6 H), 2.45 (s, 1 H), 4.17 (d, 1 H, J = 3 Hz), and 4.82 ppm (d, 1 H, J = 3 Hz); IR ($CHCl_3$) 3410, 3395, 3300, 1710, and 1665 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}N_2O$: C, 68.70; H, 8.39; N, 14.57. Found: C, 68.57; H, 8.50; N, 14.60.

Hydrolysis of 1-(1,1-Dimethylpropynyl)-5-methylene-4,4-dimethyl-2-imidazolidinone (22b). To 4.1 g (0.021 mol) of 3-(1,1-dimethylpropynyl)-5-methylene-4,4-dimethyl-2-imidazolidinone (**22b**) was added 80 mL of 6% H_2SO_4. The mixture was stirred for 15 min, extracted with $CHCl_3$, dried ($MgSO_4$), and concentrated to give 3.6 g (82%) of crude yellow solid. The solid was chromatographed on a Florisil column and eluted with $CHCl_3$. After decolorizing with Norite, and recrystallizing from $CHCl_3$–hexane, there was obtained *N*-2-methyl-3-oxo-2-butyl-*N'*-1,1-dimethylpropynylurea (**1d**) as white needles: mp 174–177 °C; NMR ($CDCl_3$) δ 1.46 (s, 6 H), 1.60 (s, 6 H), 2.22 (s, 3 H), 2.46 (s, 1 H), and 4.87 ppm (br s, 2 H); IR ($CHCl_3$) 3392, 3295, 1708 and 1664 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}N_2O$: C, 62.86; H, 8.57; N, 13.33. Found: C, 62.65; H, 8.54; N, 12.95.

Hydrolysis of 1-*tert*-Butyl-5-methylene-4,4-dimethyl-2-imidazolidinone (22a). A mixture of 0.5 g (2.8 mmol) of imidazolidinone **22a** and 50 mL of 5% hydrochloric acid was stirred for 12 h at room temperature. The solution was extracted with $CHCl_3$, dried ($MgSO_4$), and concentrated, and the solid was recrystallized from hexane to give 0.2 g (36%) of *N*-*tert*-butyl-*N'*-2-methyl-3-oxo-2-butylurea (**2c**): mp 201–202 °C; NMR ($CDCl_3$) δ 1.32 (s, 9 H), 1.41 (s, 6 H), 2.21 (s, 3 H), 4.50 (br s, 1 H) and 5.10 ppm (br s, 1 H); IR ($CHCl_3$) 3431, 1711, and 1680 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}N_2O_2$: C, 59.97; H, 10.07; N, 13.99. Found: C, 59.80; H, 10.11; N, 13.80.

3-*tert*-Butyl-5,5-dimethyl-2,4-imidazolidinedione (Hydantoin 23a). Ozone was passed through a solution of 1 g (5.5 mmol) of 1-*tert*-butyl-5-methylene-4,4-dimethyl-2-imidazolidinone (**22a**) in 100 mL of $CHCl_3$ maintained at 0 °C for 1 h. Water (50 mL) was added to the mixture which was stirred at room temperature for 2 h. The organic layer was separated, dried ($MgSO_4$), and concentrated. The residual white solid was recrystallized from $CHCl_3$–hexane to give 0.43 g (45%) of 3-*tert*-butyl-5,5-dimethyl-2,4-imidazolidinedione (**23a**): mp 147–148 °C; NMR ($CDCl_3$) δ 1.34 (s, 6 H), 1.60 (s, 9 H), and 5.60 ppm (br s, 1 H); IR ($CHCl_3$) 3665, 1769, and 1702 cm^{-1}.

Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.77; H, 8.94; N, 15.17.

3-Acyl-1-*tert*-butyl-5-methylene-4,4-dimethyl-2-imidazolidinone (25a). To 2.0 g (~42 mmol) of sodium hydride dispersion in 50 mL of THF was added 1.0 g (5.5 mmol) of 1-*tert*-butyl-5-

methylene-4,4-dimethyl-2-imidazolidinone (**22a**). The solution was heated to reflux for 2 h and cooled to room temperature, and 0.60 g (5.8 mmol) of acetic anhydrite was added. After stirring for 1 h, 50 mL of water was cautiously added and the THF was removed in vacuo. An ether extract was dried ($MgSO_4$) and the solid concentrate was recrystallized from pentane to give 0.99 g (50%) of the acylated product (**25a**); mp 64–65 °C; NMR ($CDCl_3$) δ 1.60 (s, 6 H), 1.62 (s, 9 H), 2.45 (s, 3 H), 4.02 (d, 1 H, J = 2.5 Hz), and 4.32 ppm (d, 1 H, J = 2.5 Hz).

Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.26; H, 8.99; N, 12.49. Found: C, 64.30; H, 9.00; N, 12.50.

3-Methyl-1-*tert*-butyl-5-methylene-4,4-dimethyl-2-imidazolidinone (24a). Following the procedure outlined above, a THF solution of 2.0 g of sodium hydride dispersion and 1.0 g of imidazolidinone **22a** was heated to reflux for 2 h. After cooling to room temperature, 0.78 g (5.5 mmol) of iodomethane was added, Workup and distillation, 137 °C/35 mm, gave a liquid tentatively identified as the methylated imidazolidinone by lack of a N–H stretch: NMR ($CDCl_3$) δ 1.25 (s, 6 H), 1.57 (s, 9 H), 2.72 (s, 3 H), 4.04 (d, 1 H J = 3 Hz) and 4.32 ppm (d, 1 H, J = 3 Hz); mass spectrum m/e 196.

The compound was somewhat unstable and was analyzed as the hydantoin derivative, mp 81-82 °C, obtained by ozonolysis of **24a.**

Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.49; H, 9.04; N, 13.95.

1-*tert*-Butyl-4,4,5-trimethyl-2-imidazolidinone (26a). To a solution of 2.0 g (11 mmol) of 1-*tert*-butyl-5-methylene-4,4-dimethyl-2-imidazolidinone in 50 mL of ethanol was hydrogenated at room temperature for 3 h at 50 psi with 1.5 g of 10% Pd/C catalyst. The solution was filtered and the residue after solvent removal was recrystallized from hexane to give 1.62 g (80%) of 1-*tert*-butyl-4,4,5-trimethyl-2-imidazolidinone (**26a**): mp 138–139 °C; NMR ($CDCl_3$) δ 1.13 (s, 4.5 H), 1.23 (s, 4.5 H), 1.42 (s, 9 H), 3.37 (q, 1 H, J = 6 Hz), and 4.48 ppm (br s, 1 H). The peaks at 1.13 and 1.23 (4.5 H each) are the result of coincidental equivalence of the chemical-shift difference of the C-4 diastereotopic methyl groups and the coupling constant (J = 6 Hz) between the methyl at C-3 and the ring hydrogen: NMR (C_6H_6) δ 0.78 (s, 1.5 H), 0.88 (s, 4.5 H), 1.37 (s, 9 H), and 2.88 (q, 1 H, J = 6 Hz); IR ($CHCl_3$) 3425 and 1691 cm^{-1}; mass spectrum (relative intensity) 184 (41), 168 (100), 126 (71), 112 (73), 57 (71), 56 (50), and 40 (61).

Anal. Calcd for $C_{10}H_{20}N_2O$: C, 65.18; H, 10.94; N, 15.20. Found: C, 65.21; H, 11.09; N, 15.33.

Conversion of *N,N'*-Bis(1,1-dimethylpropynyl)sulfamide (2b) to *N*-1,1-Dimethylpropynyl-*N'*-2-methyl-3-oxo-2-butylsulfamide (2d) Via 2-(1,1-Dimethylpropynyl)-4,4-dimethyl-3-methylene-1,2,5-thiadiazolidine *S,S*-Dioxide (21b). To 50 mL of dry THF were added 2.0 g (~35 mmol) of NaH dispersion washed with THF and 5.0 g (22 mmol) of sulfamide **2b**.[10] The solution was allowed to reflux for 10 h. The deep-brown solution was cooled to 0 °C and treated with just enough water to destroy the excess NaH. A small portion removed for spectral analysis showed the following NMR peaks: δ 1.52 (s, ~6 H), 1.89 (s, ~6 H), 2.55 (s, ~1 H), 4.30 (d, ~1 H, J = 3 Hz) and 4.85 ppm (d, ~1 H, J = 3 Hz), consistent with **21b.** A number of smaller extraneous peaks were also present. An additional 20 mL of water was added to the remaining solution which was allowed to stir overnight. The addition of 50 mL of a saturated NaCl solution caused the THF layer to separate. This organic layer was dried and concentrated to give 4.8 g of a viscous yellow oil. The NMR indicated the major component to be *N*-1,1-dimethylpropynyl-*N'*-2-methyl-3-oxo-2-butylsulfamide (**2d**). A small sample of pure **2d** was obtained by extracting the oil with ether and cooling the ether to −78 °C. Recrystallization from $CHCl_3$–hexane gave pure **2d:** mp 125–125.5; NMR δ 1.55 (s, 6 H), 1.62 (s, 6 H), 2.27 (s, 3 H), 2.50 (s, 1 H), 4.55 (br s, 1 H) and 5.60 ppm (br s, 1 H); IR ($CHCl_3$) 3392, 3295, 1708, and 1664 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}N_2SO_3$: C, 48.76; H, 7.36; N, 11.37. Found: C, 48.60; H, 7.48; N, 11.30.

1-*tert*-Butyl-3,4-dimethylpyrazole (27). To 100 mL of commercial bleach, 5 g of NaOH and 100 mL of pentane cooled at 0 °C was added 1.2 g (5.5 mmol) of *N*-*tert*-butyl-*N'*-1,1-dimethylpropynylsulfamide.[10] The mixture was stirred for 3 h at 0 °C. A portion of the pentane layer concentrated in vacuo at 0 °C and dissolved in $CDCl_3$ showed NMR signals consistent with *tert*-butyl-1,1-dimethylpropynyldiazene (**5a**): δ 1.41 (s, 6 H), 1.18 (s, 9 H), and 2.20 ppm (s, 1 H). For example, di-*tert*-butyldiazene, δ 1.12 ppm, and bis(1,1-dimethylpropynyl)diazene, δ 1.46 (s, 12 H) and 2.43 ppm (s, 2 H).

To the remaining pentane layer was added 3 mL of *tert*-butyl alcohol and 1 mL of HCO_2H. After stirring for 1 h at 0 °C, the pentane layer was dried over K_2CO_3 and concentrated to ~10 mL. Preparative GLC from a 9 ft 10% SE-30/Chromosorb P column at 100 °C with a 170 mL/min flow rate yielded 0.61 g (73%) of pure 1-*tert*-butyl-3,4-dimethylpyrazole: NMR (CCl_4) δ 1.42 (s, 9 H), 1.92 (s, 3 H), 2.07 (s, 3 H), and 6.96 ppm (s, 1 H); ^{13}C NMR (rel Me_4Si) δ 8.4 and 11.6 (2 CH_3), 29.9 [$(C^*H_3)_3C$–], 57.3 [$(CH_3)_3C^*$–], 112.9 [CH_3–C^*=CH], 124.8 [C^*H=C], and 146.3 ppm [CH_3–C^*=N]; mass spectrum m/e 152 (53%, parent ion), 137 (100%, –CH_3), and 95 [89%, –$C(CH_3)_3$].

Anal. Calcd for $C_9H_{16}N_2$: C, 71.05; H, 10.53; N, 18.42. Found: C, 71.28; H, 10.64; N, 18.18.

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