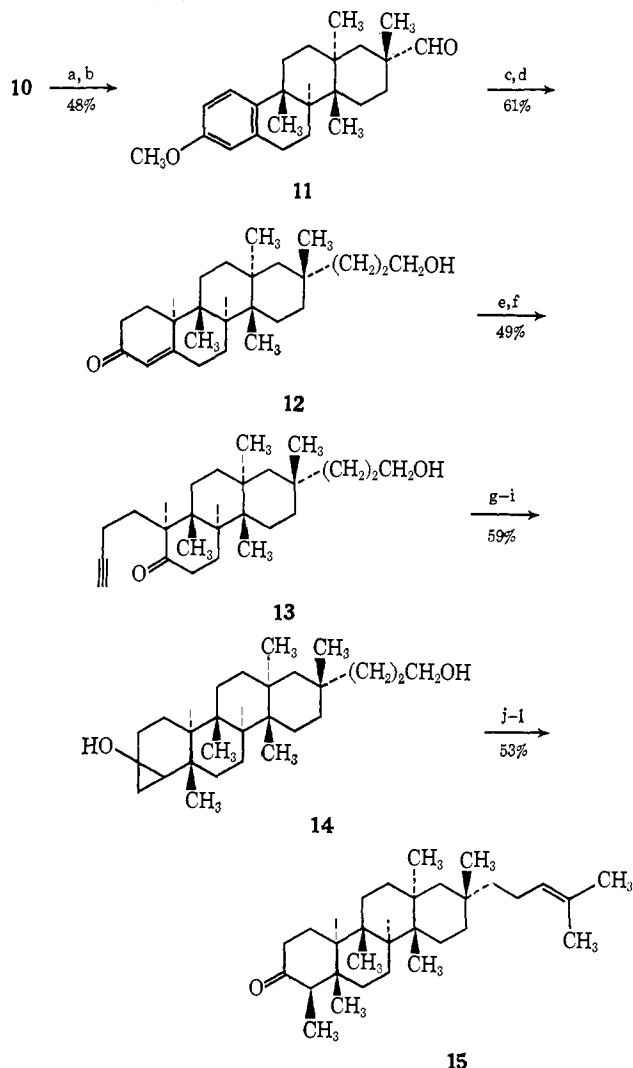


Chart II. Conversion of Tetracyclic Ketone 10 to *dl*-Shionone (15)^{6,a}



^a (a) POCl_3 , DMF, 60° ; (b) Li, NH_3 , THF, CH_3I ; (c) $[(\text{EtO})_2\text{POCHCH}=\text{NC}_6\text{H}_{11}]^-\text{Na}^+$, THF, 60° ; 1% aqueous $(\text{CO}_2\text{H})_2$, C_6H_5 ; (d) Li, NH_3 , EtOH, H_3O^+ , EtOH, reflux; (e) H_2O_2 , aqueous NaOH, $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$; (f) TsNHNH_2 , $\text{HOAc}-\text{CH}_2\text{Cl}_2$; (g) MeLi, THF; (h) $\text{CF}_3\text{CO}_2\text{H}$, $(\text{CF}_3\text{CO})_2\text{O}$, -25° ; (i) $(i\text{-Pr})_2\text{NLi}$, THF, $\text{ICH}_2\text{ZnI}(\text{Ag})$, Et_2O ; (j) H_3O^+ , EtOH, reflux; (k) $\text{CrO}_3 \cdot 2\text{Py}$, CH_2Cl_2 ; (l) $(\text{CH}_3)_2\text{C}=\text{PPh}_3$, THF.

lithium). The final C4 methyl group can conveniently be added through treatment of this enolate with the Simmons-Smith reagent¹⁴ and then acid catalyzed cleavage of the resulting cyclopropanol 14. This sequence, particularly important for future friedelin synthetic work, can be accomplished in 25% overall yield and in our hands is significantly better than a conjugate addition-methylation approach that might seem more apparent.

Completion of the synthesis required only the addition of the terminal isopropylidene grouping with the Wittig reagent, and *dl*-shionone (mp $161.5-163^\circ$ (vac); C, 84.38%; H, 11.90%) was in hand. This synthetic material had identical solution infrared and nmr spectra and R_f value on tlc (silica gel, ether) with those of natural shionone, which was kindly provided by Professor G. Ourisson (University of

(14) H. W. Whitlock, Jr., and L. E. Overman, *J. Org. Chem.*, **34**, 1962 (1969); J. M. Denis, C. Girard, and J. M. Conia, *Synthesis*, 549 (1972).

Strasbourg). Further work on the friedelin synthesis is underway.

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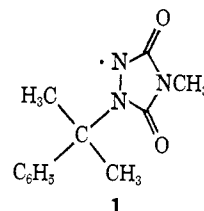
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Non-Aryl Hydrazyls. I. Synthesis, Isolation, and Characterization of 1- α -Cumyl-4-methylurazolyl

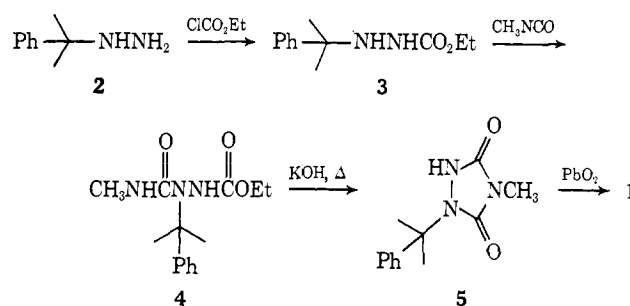
Sir:

We wish to report the synthesis and characterization of 1- α -cumyl-4-methylurazolyl (1), a stable, cyclic non-



aryl hydrazyl, isolatable as its dimer, a tetrazane. Although triarylhydrazyls such as diphenylpicrylhydrazyl (DPPH) are among the most stable and extensively studied free radicals known,¹ only recently have hydrazyls, lacking a directly bonded aromatic group, been examined.²⁻⁹ Heretofore, non-aryl hydrazyls have been

Scheme I



(1) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, Chapter 4.

(2) The first non-arylhydrazyls reported³ were 1,1-dialkylhydrazyls prepared by X-irradiation of the corresponding hydrazine in an adamantane matrix. Subsequent studies of non-arylhydrazyls include 1,1-dialkylhydrazyls,⁴ trialkylhydrazyls,^{5,6} 1,1-dialkyl-2-arenesulfonylhydrazyls,⁷ 1-alkyl-1,2-dicarboxyhydrazyls,⁸ and tris(trialkylsilyl)hydrazyls.⁹

(3) D. E. Wood, C. A. Wood, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 9278 (1972).

(4) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6110 (1973).

(5) S. F. Nelsen and R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 2719 (1973).

(6) S. F. Nelsen and R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 6454 (1973).

(7) A. T. Balaban and R. Istrătoiu, *Tetrahedron Lett.*, 1879 (1973).

(8) V. Malatesta and K. U. Ingold, *Tetrahedron Lett.*, 3311 (1973).

(9) R. West and B. Bichlmeir, *J. Amer. Chem. Soc.*, **95**, 7897 (1973).

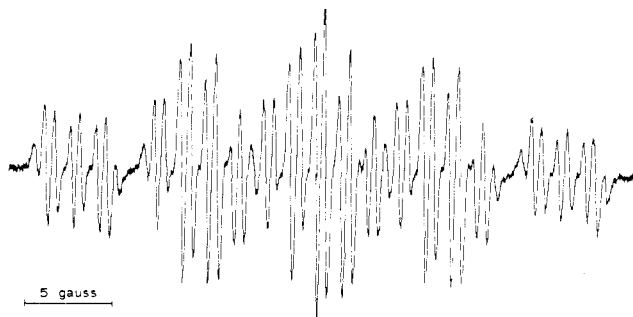


Figure 1. The epr spectrum of urazolyl 1 (ca. 5×10^{-4} M) in benzene at ambient temperature.

characterized only by epr spectroscopy and the nature of the decomposition products formed.¹⁰

In benzene, oxidation of colorless urazole 5, obtained via a modified Ruhkopf procedure,¹¹⁻¹⁵ (Scheme I) with lead dioxide in the presence of anhydrous sodium sulfate affords, after filtration, a deep orange-brown solution. Chromatography (silica gel, chloroform) of the concentrated solution gives rise to a mobile orange-brown band, collection and evaporation of which affords an air-stable tan solid (mp 108–109°, 66%) identified as the tetrazane dimer of urazolyl 1. Although the solid gives rise to an epr signal, magnetic susceptibility studies indicate it to be essentially diamagnetic. The infrared spectra of both urazolyl 1 (CS₂) and its tetrazane dimer (KBr) lack the N–H absorption (3.08 μ) of urazole precursor 5 (KBr). Urazolyl 1 exhibits carbonyl absorptions at 5.74 and 5.86 μ rather than at 5.64 and 5.86 μ (CHCl₃) as does 5; the solid dimer has carbonyl absorptions at 5.54 and 5.78 μ as compared to 5.68 and 5.94 μ (KBr) for 5. The solid dissolves readily in benzene, carbon tetrachloride, or acetonitrile with concomitant dissociation into urazolyl 1. The resultant orange-brown solutions fail to obey Beer's law at higher concentrations. In dilute acetonitrile solution, three ultraviolet absorption bands (206 (ϵ 11,300), 264 (ϵ 2410), and 302 nm (ϵ 2920)) are observed with the latter tailing to ca. 600 nm in the visible region. Owing to paramagnetism, solutions of urazolyl 1 do not afford high resolution nmr spectra but do give rise to very strong epr signals. In carefully degassed benzene solutions, the epr spectrum of 1 (Figure 1) consists of 46 lines from which the hyperfine splitting (hfs) constants have been determined. The hfs constants [$a_{N-1(2)}$ (1 N) = 7.70, $a_{N-2(1)}$ (1 N) = 6.25,

(10) For example, one of the more stable hydrazyls of this type, 3-*tert*-butyl-2,3-diazabicyclo[2.2.2]octyl,⁶ has been characterized by its epr spectrum which can still be observed after the sample (sealed, degassed, in acetonitrile) has stood 3 months at room temperature. However, this hydrazyl reacts readily with oxygen upon exposure to air.

(11) H. Ruhkopf, *Chem. Ber.*, **73**, 820 (1940).

(12) Addition of an ethereal solution of ethyl chloroformate to a mechanically stirred solution of α -cumylhydrazine¹³ (2) and triethylamine in ether with cooling affords, after vacuum distillation, ethyl 3- α -cumylcarbazate¹⁴ (3, bp 120° (0.05 Torr), 90%). Treatment of carbazate 3 with an excess of methyl isocyanate in refluxing benzene affords 1-carbethoxy-2- α -cumyl-4-methylsemicarbazide¹⁴ (4, mp 144–145.5° (C₆H₆), 82%). Heating semicarbazide 4 in 25% aqueous potassium hydroxide produces 1- α -cumyl-4-methylurazole¹⁴ (5, mp 129–131° [EtOH, lit.¹⁵ mp 126.5–127° (sublimation)], 89%).

(13) C. G. Overberger and A. V. DiGiulio, *J. Amer. Chem. Soc.*, **80**, 6562 (1958).

(14) Satisfactory ir, nmr, and mass spectra and elemental analyses were obtained for this compound.

(15) J. C. Stickler, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1971, p 76.

a_{N-4} (1 N) = 1.47, and a_H (3 H) = 0.56 G] do not vary appreciably with temperature (–80° to +20°, CS₂). That the radical giving rise to the epr spectrum is in fact a true hydrazyl is indicated by the magnitude of the hfs constants for the hydrazyl nitrogens. Ingold has stated¹⁶ that, in all authentic hydrazyls, "the splitting constants of the two nitrogens are of comparable magnitude and are generally in the range of 6–12 G." The elemental composition and molecular weight [Calcd for C₁₂H₁₄N₂O₃: C, 62.06; H, 6.08; N, 18.09; mol wt, 232.1086. Found: C, 62.04; H, 5.98; N, 18.01; mol wt, 232.1080 (mass spec)] are in agreement with the structural assignment and with the observation that the dimer dissociates readily. Finally, reduction of 1 [CH₂Cl₂, H₂O, Na₂SO₃, (*n*-Bu)₄N⁺Br[–]] affords, after sublimation, a white solid (mp 128–129.5°) identical in all respects with authentic urazole 5.

From its failure to obey Beer's law, it is inferred that, in solution, urazolyl 1 is in equilibrium with its tetrazane dimer (eq 1). Association constants for this equilib-



rium have been determined by vapor pressure osmometry at 25.0 \pm 0.2° and are 0.58 \pm 0.30, 4.5 \pm 0.4, and 12 \pm 2 for acetonitrile, benzene, and carbon tetrachloride solutions, respectively. Urazolyl 1 appears to be indefinitely stable either as the solid dimer or when dissolved in inert solvents. It is, however, capable of reacting with compounds having more readily abstractable hydrogens, and hydrazyl reagents of this type may conceivably be of some future synthetic utility.

Analogs of 1 have been prepared, and the chemistry of this type of non-arylhydrazyl is currently being pursued.

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(16) V. Malatesta and K. U. Ingold, *Tetrahedron Lett.*, 3307 (1973).

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A New, General Synthesis of Tropane Alkaloids¹

Sir:

Since the first discovery of the iron carbonyl promoted cyclocoupling reaction between α, α' -dibromo ketones and 1,3-dienes leading to 4-cycloheptenones,² we have been interested in its possible application to the direct synthesis of the tropane alkaloid family.³ Our original plan outlined in eq 1 suffered from two serious limitations: (1) dibromoacetone, unlike other ordinary dibromo ketones, cannot serve as a precursor of the oxyallyl intermediate 1,⁴ and (2) reaction of *N*-methyl-

(1) Carbon–Carbon Bond Formations Promoted by Transition Metal Carbonyls. X. Part IX: R. Noyori, S. Makino, Y. Baba, and Y. Hayakawa, *Tetrahedron Lett.*, 1049 (1974).

(2) R. Noyori, S. Makino, and H. Takaya, *J. Amer. Chem. Soc.*, **93**, 1272 (1971).

(3) Recent reviews: (a) G. Fodor, *Progr. Phytochem.*, **1**, 491 (1968); (b) G. Fodor in "Chemistry of the Alkaloids," S. W. Pelletier, Ed., Van Nostrand Reinhold, New York, N. Y., 1970, p 431; (c) G. Fodor in "The Alkaloids, Chemistry and Physiology," Vol. 13, R. H. Manske, Ed., Academic Press, New York, N. Y., 1971, p 351.

(4) R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi, and S. Tsutsumi, *J. Amer. Chem. Soc.*, **94**, 7202 (1972).