Anal. Calcd for $C_{28}H_{46}$: C, 87.88; H, 12.12. Found: C, 87.49; H, 12.45.

3-Deoxy-*A*-homovitamin D_3 (2). The photochemical apparatus consisted of a Hanovia quartz immersion well (Cat. No. 19434) fitted with a 125-ml reaction vessel (equipped with a condenser and nitrogen inlet) and a Hanovia 200-W medium-pressure mercury arc (Cat. No. 654A-36) with a No. 9700 Corex filter sleeve. The lamp was prewarmed for 15 min before exposing the ice cooled reaction solution to irradiation for 3.0 min. The solution was purged thoroughly with nitrogen prior to and during the irradiation. Four irradiation mixtures (125 mg of **3**/100 ml of ether each; 500 mg total) were pooled and concentrated at <30° under vacuum to afford an oily semicrystalline residue. Nmr and uv analysis indicated the residue to contain mainly a mixture of **3** and **2.** Chromatographic separation (140 g, 10% silver nitrate impregnated Woelm neutral alumina prepared with lbpe, 28-mm diameter column) was carried out using lbpe and lbpe–ether combinations.

Early fractions afforded starting material **3** (256 mg, 51%) while later fractions proved to be the homovitamin D **2** (90 mg, 18%; 37% based on recovered **3**). The semicrystalline homovitamin is exceedingly air-sensitive. Prior to measuring any of its physical properties, it was purified by rechromatography (with lbpe on a 15-g Woelm neutral I column) and the single fraction obtained was evacuated to dryness. The nmr spectrum (300 MHz) shown in Figure 1 revealed the following: τ 3.74 and 3.97 ($H_{6,7}$, AB q, $J_{AB} \sim$ 11.0 Hz), 4.93 H_{19Z}, br with a fine structure, $W \sim 6$ Hz), 5.12 (H_{19E}, d, $J \sim 2.2$ Hz; $W \sim 5$ Hz), 7.18 ($H_{9\beta}$, d, $J \sim 12$ Hz), 7.67 ($H_{1\alpha,1\beta,4a\alpha,4a\beta}$, br s, $W \sim 13$ Hz), 9.08 (C_{21}–CH_3, d, $J \sim 6.5$ Hz), 9.14 ($C_{26,27}$–$2CH_3$, d, $J \sim 6.5$ Hz), and 9.46 (C_{18}–CH_3, s); uv (95% ethanol) ϵ_{max} (ϵ) 244 sh (14,000), 252 (16,300), 261 (16,400), 275 br sh (15,100) and λ_{min} 230 (10,700) nm; mass spectrum (80 eV) *m/e* 382 (parent ion).

Registry No.—**2,** 52920-82-8; **3,** 52920-83-9; **5,** 52920-84-0; **6,** 52949-49-2; **7a,** 35569-96-1; **7b,** 35569-95-0; **9,** 24366-12-9; **10,** 52920-85-1; diazomethane, 334-88-3; 1,3-dibromo-5,5-dimethylhydantoin, 77-48-5.

Reference and Notes

(1) (a) For part V in this series, see W. H. Okamura, A. W. Norman, and R. M. Wing, *Proc. Nat. Acad. Sci. U. S.*, **71,** 4194 (1974); (b) for part I, see M. N. Mitra, A. W. Norman, and W. H. Okamura, *J. Org. Chem.*, **39,** 2931 (1974).

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Oxidation of 4-Phenylurazole with Activated Isocyanates and Dimethyl Sulfoxide

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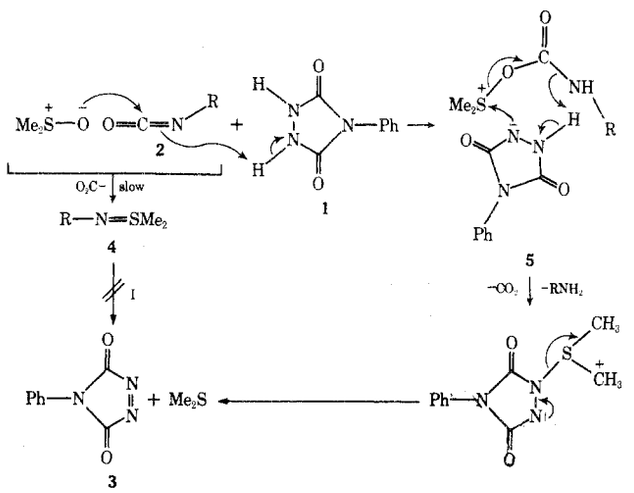
During an investigation of the chemical reactivity of 4-phenyl-1,2,4-triazoline-3,5-dione (**3**), we observed that reaction mixtures in dry (molecular sieves) dimethyl sulfoxide (DMSO) containing 4-phenylurazole (**1**) turned bright red and emitted an unpleasant odor upon addition of trichloroacetyl isocyanate[11] (**2a**). DMSO has been used in a number[1] of oxidizing systems in recent years, *e.g.*, DMSO–dicyclohexyl carbodiimide–H_3PO_4,[2] DMSO–acetic anhydride[3a] (and similar systems **3b**), DMSO–ketenimine,[4] and DMSO–SO_3–pyridine.[5] The rapidity with which the reaction occurred, the intensity of the characteristic red color of **3** which formed, and the increased usage of **3** as a dieneophile and as a chemical reagent in the current literature prompted us to investigate the utility of this pathway as an easy and rapid route to **3**.[6–10]

Purified acetonitrile was found to be the ideal solvent for a spectrophotometric assay for **3** (λ_{max}^{525}, ϵ 157). Under controlled conditions, the products observed when **2a** was reacted with **1** in DMSO were carbon dioxide (as barium carbonate), dimethyl sulfide (trapped at −80° and characterized as trimethyl sulfonium iodide), trichloroacetamide[12] (essentially insoluble in cold $CHCl_3$), and **3** (isolated by sublimation and characterized by spectroscopic comparisons with an authentic sample).[9] The average yield, determined spectrophotometrically, was 98% with **2a.** Difficulty was encountered in isolating pure **3** from this reaction (~20% yield by sublimation) but this is the only respect in which this new reagent suffers in comparison with the other methods. The chemical reactivity of **3** was shown to be unaffected by the system by isolation of its adduct with cyclobutadiene. The major advantage of this approach lies in the rapidity with which **3** may be generated *in situ.* At room temperature, the reaction is over almost instantaneously. Since the isocyanates used and **1** are indefinitely stable, this provides an instantaneous source of **3** in a highly polar solvent (DMSO). N_2O_4 and *t*-BuOCl are relatively unpleasant materials to work with while the isocyanates used herein can be readily transferred in measured amounts with a hypodermic syringe.

Only isocyanates activated by strongly electron-withdrawing substituents were effective. The reaction with *p*-toluenesulfonyl isocyanate (**2b**) was essentially indistinguishable from that with **2a,** benzoyl isocyanate (**2c**) gave 88% of **3,** while phenyl and *n*-butyl isocyanates gave less than 10% conversion in very slow reactions which stopped

within 15 min. Related heterocumulenes, PhNCS and PhNSO, were completely unreactive in this system. For the purpose of comparison, 1 was oxidized using DMSO–DCC–H_3PO_4 (maximum yield, 33% after 30 min), DMSO–Ac_2O (86% yield after 2 hr), and DMSO–P_2O_5 (yield uncertain because of turbid solutions which could not be clarified; no further increase in absorbance was noted after 5–10 min). The reaction appeared to proceed as well in benzene, toluene, chloroform, carbon tetrachloride, 1,2-dichloroethane, ethyl acetate, acetone, neat DMSO, dioxane, tetrahydrofuran, and 1,2-dimethoxyethane but not in diethyl ether or pyridine. The interference of ether in the course of this reaction remains a puzzle. Considering the similarities between this system and the Pfitzner-Moffatt-type systems, we propose the following mechanistic scheme to rationalize our results.



3 was not formed when 1 was treated with dimethyl sulfilimine **4b**.[13] Furthermore, the reaction between DMSO and isocyanate alone required 3–5 hr for the formation of the sulfilimine to be complete. Thus the initial adduct between DMSO and 2 is effectively trapped before it can eliminate CO_2. This is in keeping with the observed acidity of 1 (soluble in 50% NH_4OH) and with the inhibitory effect of pyridine on the oxidation.

Experimental Section[14]

General Procedure for *in situ* Generation of 4-Phenyl-1,2,4-triazoline-3,5-dione (3). To 1.77 g (0.01 mol) of 4-phenylurazole[10] dissolved in 5 ml of dry DMSO (molecular sieves), cooled to 0° in an ice–water bath, in a magnetically stirred 25-ml round-bottom flask, sealed with a serum cap, was added 1.33 ml (0.01 mol) of *p*-toluenesulfonyl isocyanate (Upjohn Chemical Co.). Care was taken to avoid freezing of the DMSO solution. The isocyanate addition was made slowly to avoid overheating which leads to formation of the corresponding sulfilimine (4). Gas evolution was allowed to subside between additions of drops of isocyanate. After the addition of isocyanate was completed the cooling bath was removed and the mixture was stirred at room temperature until gas was no longer evolved (~15 min). The chosen diene can be injected into the solution of 3 if it is a liquid, or a DMSO solution of the solid diene can be added. Evidence of the completion of the reaction is the discharge of the characteristic color of 3. The reaction mixture is poured into 100 ml of chloroform and the resulting solution is extracted with 5% aqueous sodium hydroxide solution and then distilled water. The chloroform layer is dried over calcium chloride, filtered, and concentrated to an oil on a rotary evaporator. Ethanol is added to the oil and the solution is warmed to dissolve suspended solid, if any is present. The product is precipitated by addition of water to the ethanol solution and may generally be recrystallized from alcohol.

***N*-Phenyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide.** This compound was obtained from 0.82 g (0.01 mol) of freshly prepared[15] cyclopentadiene, according to the general procedure given above, yield 1.42 g (59%), melting point 138–39° (lit.[8] 131–133°, 142–144°,[16] 142–144°). The nmr spectrum of the product was in accord with that reported in the literature.[16] If a 1 equiv excess of isocyanate was added along with 5 ml more of DMSO, the yield rose to 79%.

***N*,1,4-Triphenyl-1,2,3,4-tetrahydro-1,4-epidioxo-2,3-diazanapthalene-2,3-dicarboximide.** This compound was obtained from 2.70 g (0.01 mol) of diphenylisobenzofuran,[17] according to the general procedure given above, yield 2.4 g (54%), mp 144°.

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Registry No.—1, 15988-11-1; **2a**, 3019-71-4; **2b**, 4083-64-1; **2c**, 4461-33-0; **3**, 4233-33-4; *N*-phenyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide, 15971-63-8; cyclopentadiene, 542-92-7; *N*,1,4-triphenyl-1,2,3,4-tetrahydro-1,4-epidioxo-2,3-diazanaphthalene-2,3-dicarboximide, 52950-79-5; diphenylisobenzofuran, 5471-63-6.

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Medium Effects on the Electron Spin Resonance Hyperfine Splitting Constants of *tert*-Butyl Nitroxide in Mixed Aqueous Solvents

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The substantial variation of the nitrogen hyperfine splitting constants (hfc), A_N, of nitroxide free radicals as a function of substitution pattern or solvent medium has commonly been attributed to a change in spin distribution in the nitroxide π system. In many cases these effects have been rationalized by considering the relative contributions of the two main resonance structures, A and B, to the actual molecular structure.[1,2] In these studies it is assumed that