From the foregoing observations several important conclusions can be drawn. First, copper(II) does promote tridentate behavior in some multidentate amino acids. Second, apical coordination is sufficiently important that it occurs to an appreciable extent even when seven- and eight-membered chelate rings result (see compounds **4**, **6**, and **11**). Finally, ORD spectroscopy is a particularly sensitive tool for detecting apical coordination in these complexes.

Keith M. Wellman, T. G. Mecca,[7] W. Mungall,[7] Curtis R. Hare
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214
Received August 9, 1967

Deuterium Substitution in the 4H-Thiopyran-4-one 1,1-Dioxide System[1]

Sir:

The capability of 4-pyrones and 4-pyridones to undergo deuterium exchange under selected conditions has been recently recognized.[2,3] Interestingly, whereas exposure of 4-pyrone to deuterium oxide at 98° for 26 hr results in exchange exclusively at the 3,5 (α-carbonyl) positions,[2] treatment of N-methyl-4-pyridone with 0.5 N sodium deuterioxide at 100° for 12 hr produces exchange only at the 2,6 positions.[3] The origin of the contrary course of these deuterations has been attributed to the intervention of different mechanisms. Thus, the formation of ring-opened intermediates has been implicated in the pyrone example and reactive ylides produced by vinyl proton abstraction have been proposed for the pyridone series. In this communication we wish to present evidence concerning specific deuterium exchange in 4H-thiopyran-4-one 1,1-dioxides. This system has been studied in an effort to evaluate the effects imparted to such six-membered heterocycles by two powerful, but opposed, electron-withdrawing groups.

When a solution of **1**[4] in neutral dioxane-deuterium oxide (3:1) was maintained at 40° for 16 days,[5] there could be recovered in 60% yield a highly crystalline yellow solid which was shown by spectroscopic criteria and deuterium analysis (falling drop method[6]) to be the

1   **2**

2,6-d_2 counterpart of **1** (**2**). The rather low recovery reflects difficulties encountered in isolation and purification of this substance,[5] since subsequent kinetic runs (see below) indicated only minimal decomposition of **1** under these conditions. The positions of the deuterium atoms in **2** were suggested by comparison of the chemical shifts (δ units, CDCl$_3$) of the protons in **1** and **2** with those observed for **3**,[7] **4**,[8] and **5**.[9] Whereas

3   **4**   **5**
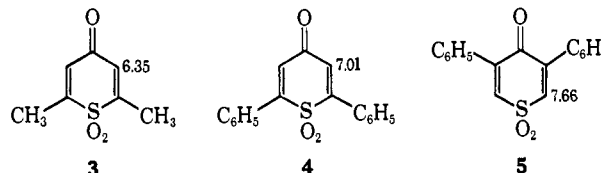
the nmr spectrum of **1** consists of two doublets ($J = 12.0$ Hz) of equal area at 7.92 and 6.74 ppm, that of **2** consists of a broadened singlet at 6.74 ppm and only minor absorption in the 7.92-ppm region.

The rate of deuteration of **1** in dioxane–D$_2$O (3:1) at 40° could be conveniently measured by nmr spectroscopy. The pseudo-first-order rate constant was found to be $(4.06 \pm 0.37) \times 10^{-7}$ sec^{-1} on the basis of four runs, each involving at least eleven points.[12] For the purpose of calibration 1,1,4,4-tetramethylcyclobutanedione was employed as an internal standard.[13]

In subsequent experiments, it was established that **3** and **4** do not undergo isotopic exchange in this medium, even after being heated for 2 weeks at 80°. Although **3** and **4** are considerably more heat stable than **1**, they likewise react immediately with base to give tars. The 3,5-diphenyl isomer **5** was also little affected by these conditions; exposure of **5** to this deuterated medium for 2 weeks at 60° resulted in less than 5% deuterium incorporation.

However, addition of 30% aqueous sodium hydroxide to solutions of **5** in acetone or tetrahydrofuran at 30° gave rise instantaneously to deep red solutions which proved to be stable for considerable time. Acidification of these solutions led to the almost quantitative recovery of the keto sulfone. When the same reaction was performed with 30% NaOD–D$_2$O in acetone-d_6 and the colored solution examined shortly thereafter by nmr, it was seen that the α-sulfonyl protons formerly present in the 7.65-ppm region of the neutral solution were totally absent in the basic medium; rather, the spectrum displayed only the ten-proton phenyl absorption at 7.35 ppm. Acidification of such a solution in

(1) Unsaturated Heterocyclic Systems. XXXV. For the previous paper in this series, see L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, **89**, 6659 (1967).
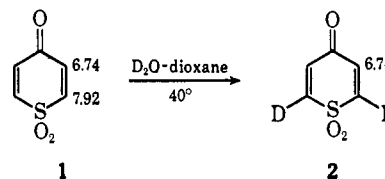
(2) (a) P. Beak and G. A. Carls, *J. Org. Chem.*, **29**, 2678 (1964); (b) D. W. Mayo, P. J. Sapienza, R. C. Lord, and W. D. Phillips, *ibid.*, **29**, 2682 (1964).

(3) P. Beak and J. Bonham, *Tetrahedron Letters*, 3083 (1964); *J. Am. Chem. Soc.*, **87**, 3365 (1965).

(4) E. A. Fehnel and M. Carmack, *ibid.*, **70**, 1813 (1948).

(5) It must be pointed out that 1 is extremely unstable to base and to most acids; red-brown or black tars invariably result. Furthermore, when solutions of 1 in a variety of solvents (including dioxane–D₂O) are maintained at elevated temperatures (50–100°) for short periods of time, extensive decomposition is also encountered. The keto sulfone 1 is most conveniently purified by sublimation at 120° (0.1 mm), although some loss in weight due to a residue is inevitably encountered.

(6) This analysis demonstrated that 41% of the available protons (*i.e.*, 82% of the 2,6-hydrogens) had been exchanged. The determination was performed by Josef Nemeth, Urbana, Ill.

(7) F. Arndt, R. Schwarz, C. Martins, and E. Arvon, *Rev. Faculti Sci. Univ. Istanbul*, A13, 57 (1948); *Chem. Abstr.*, **42**, 4178 (1948).

(8) R. Arndt, P. Nachwey, and J. Pusch, *Chem. Ber.*, **58**, 1633 (1925).

(9) Compound 5 represents the first 3,5-disubstituted 4H-thiapyran-4-one 1,1-dioxide to be reported to date; its synthesis was achieved by the sequence 2,6-dimercapto-3,5-diphenyl-4H-thiopyran-4-one[10] → 3,5-diphenyl-4H-thiopyran-4-one[11] → 5.
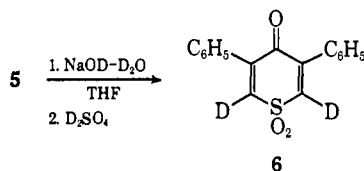
(10) H. Apitzsch, *Chem. Ber.*, **37**, 1599 (1904); **38**, 2888 (1905).

(11) A. Schönberg and R. von Ardenne, *ibid.*, **99**, 3316 (1966).

(12) The limited stability of 1 and 2 in this solvent system at higher temperatures precluded the measurement of activation parameters.

(13) The slight decrease in the relative intensity of the signal at 6.74 (H-3 and H-5) observed at the end of the reaction period was attributed to a small amount of decomposition of 1 and/or 2.

tetrahydrofuran with D_2SO_4 and rapid recovery of product gave a high yield of **6** in 81% isotopic purity (deuterium analysis). Finally, the ultraviolet absorption of **5** [λ_{max}^{EtOH} 240 (ϵ 4500) and 315 mμ (ϵ 2000)] is

$$5 \xrightarrow[\substack{1.\ \text{NaOD-D}_2\text{O} \\ \text{THF} \\ 2.\ \text{D}_2\text{SO}_4}]{} \quad \mathbf{6}$$

seen to be appreciably altered upon addition of 30% sodium hydroxide solution [λ_{max} 253 mμ (ϵ 1500) and considerable tailing into the visible region].
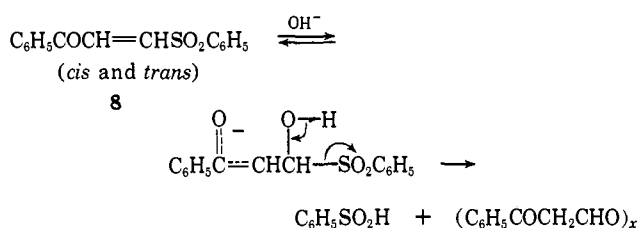
The substitution of deuterium at the 2 and 6 positions in **1** and **5** may proceed by way of intermediate vinyl carbanions (path A) or *via* reversible Michael addition (path B). Precedence for proton abstraction from an sp²-hybridized α-sulfonyl carbon atom was recently

$$\mathbf{7}$$
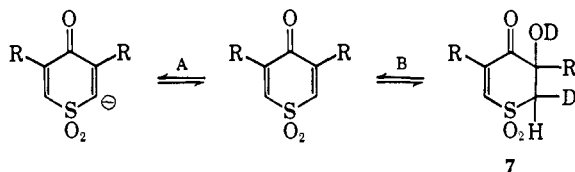
obtained in a study of the base-catalyzed exchange of 2,3-dihydrothiophene 1,1-dioxide.[14] Differences in reactivity of **1** and **5**, however, are not entirely reconcilable with the carbanion mechanism. In agreement with the fact that a phenyl substituent (σ^* 0.6) is slightly more inductively electron withdrawing than hydrogen (σ^* 0.49), no system has yet been found, to our knowledge, wherein exchange rates have shown a decrease due to this effect.[15] The absence of protons at higher magnetic field in the nmr spectrum of **5** in alkaline media could reflect merely very rapid exchange under these conditions.

The relation of structure to reactivity, however, is explicable on the basis of the Michael addition path. The much slower exchange rate for **5** under neutral conditions would be anticipated from loss of conjugation in proceeding to **7** (R = C_6H_5) or its anion. Despite the fact that the above data suggest that detectable quantities of hydroxide adducts do not appear to be present, it is proposed that their formation in kinetically important quantities is the dominating factor in these isotopic exchanges.

Thus, it is the sulfonyl group which controls the direction of Michael addition in these cyclic keto sulfones. Interestingly, the acyclic keto sulfones **8** react with 5% aqueous potassium hydroxide to afford principally benzenesulfinic acid (>72% yield).[16] However, be-

$$C_6H_5COCH{=}CHSO_2C_6H_5 \xrightleftharpoons{\ OH^-\ }$$

(*cis* and *trans*)

8

$$C_6H_5C{\equiv}CHCH{-}SO_2C_6H_5 \longrightarrow$$

$$C_6H_5SO_2H \ + \ (C_6H_5COCH_2CHO)_x$$

(14) C. D. Broaddus, *J. Am. Chem. Soc.*, **88**, 3863 (1966).
(15) See, for example, A. Streitwieser, Jr., and R. G. Lawler, *ibid.*, **87**, 5388 (1965).
(16) E. P. Kohler and R. G. Larsen, *ibid.*, **57**, 1448 (1935).

cause the products in these examples could well be determined by the elimination step, these observations bear no necessary relation to the direction of Michael addition in the title compounds.

Leo A. Paquette,[17] **Lawrence D. Wise**
Department of Chemistry, The Ohio State University
*Columbus, Ohio 43210*
Received October 26, 1967

Free-Radical Iodination. A Novel Synthetic Method

Sir:

Methods of introducing iodine into unactivated organic substrates have been heretofore unknown. Since free-radical substitution reactions by molecular iodine are energetically unfavorable,[1] the replacement of hydrogen by iodine has been feasible only in electrophilic aromatic substitution and reactions leading to the substitution of hydrogens situated α to an activating carbonyl.

We wish to report here the preliminary results of a novel and synthetically useful free-radical method for the substitution of primary, secondary, and benzylic hydrogens by iodine.

Carbon tetrachloride or Freon 113 solutions of *t*-butyl hypochlorite (2 moles) at 0° react after a short induction period with a suspension of mercuric iodide (1 mole) to yield what can be formally considered to be *t*-butyl hypoiodite. The stochiometric relationship can be determined by observing the change in the nmr absorption of the *t*-butyl protons at various ratios of reactants (*t*-butyl hypochlorite τ 8.69, *t*-butyl hypoiodite τ 8.55) and by the isolation of a nearly quantitative yield (97%) of mercuric chloride which was filtered from the reaction mixture. Iodometric titration of the filtrate showed a nearly theoretical amount of active halogen.

$$2(CH_3)_3COCl + HgI_2 \longrightarrow 2(CH_3)_3COI + HgCl_2$$
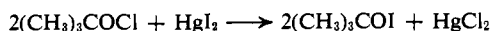
The resulting purple solution shows ultraviolet (λ_{max} 241 mμ ($\epsilon \sim$930)) and infrared absorption very similar to that of *t*-butyl hypochlorite. The ultraviolet spectrum of the reaction mixture also shows absorption for small amounts (2 to 3%) of molecular iodine (λ_{max} 520 mμ (ϵ 840)). Upon standing overnight at 0° or upon immediate irradiation at 0° the solution was found to form a gelatinous precipitate, presumably of dimeric or polymeric trivalent iodine compounds.

$$(CH_3)_3COI \longrightarrow (CH_3)_3CO\overset{\overset{\displaystyle I}{|}}{I}OC(CH_3)_3 \xrightarrow{(CH_3)_3COI} \text{etc.}$$

Both aged and freshly prepared carbon tetrachloride or Freon 113 solutions of the reagent upon irradiation (200-w incandescent light bulb) with hydrocarbon substrates give preparatively useful yields of iodinated hydrocarbons (see Table I).

(1) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 376.