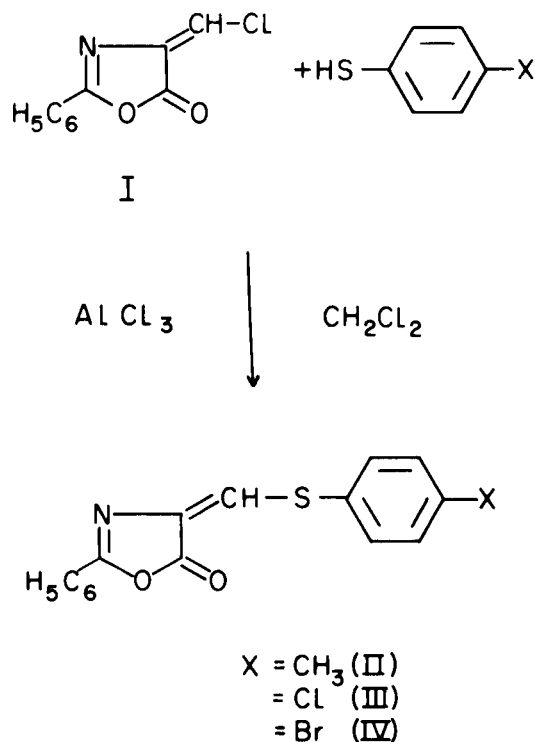


Brookhaven National Laboratory
and
Mount Sinai Medical and Graduate Schools

Friedel-Crafts Reaction of a Vinyl Chloride with Thiophenol and Benzylmercaptan (1)

Roderich Walter, Hans Zimmer (2) and Irving L. Schwartz

The reaction of the vinyl chloride, 2-phenyl-4-chloromethylene-5(4*H*)-oxazolone (I), with *p*-cresol, catalyzed by aluminum chloride, yielded the nuclear alkylated phenol, 2-phenyl-4-(2-hydroxy-5-methylbenzylidene)-5(4*H*)-oxazolone (3). However, when thiophenols were employed in this reaction instead of *p*-cresol, in all instances we isolated the thioether derivatives, *viz.*, the substituted 2-phenyl-4-(phenylthiomethylene)-5(4*H*)-oxazolones rather than nuclear alkylated thiophenols.



The decreased effectiveness of the sulfur moiety in promoting electrophilic substitution in the aromatic nucleus of thiophenols, as compared with the oxygen moiety in the case of phenols, has been

attributed by some (4) to the electron-withdrawing effect resulting from resonance structures in which sulfur expands its valence shell and by others (5) to the decreased ability of sulfur to form resonance structures via interaction of a sulfur 3*p* electron with the π -system.

The structures proposed for compounds II-IV (Table I) are based on infrared spectra as well as analytical data. Compounds II-IV exhibited the lactone carbonyl stretching vibration at 1780 cm^{-1} accompanied by a less intense absorption at 1797 cm^{-1} , while the C=N stretching absorption appeared at 1629 cm^{-1} . The absence of an S-H stretching vibration in the region of 2600-2550 cm^{-1} coincided with the negative color test for a thiol group using *N*-ethyl maleimide (6). The possibility of dimer formation through a disulfide linkage was eliminated by molecular weight determination.

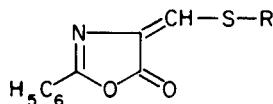
When *p*-chlorobenzylmercaptan was employed instead of thiophenol in the reaction with I we again isolated a thioether, *viz.*, 2-phenyl-4-(4-chlorobenzylthiomethylene)-5(4*H*)-oxazolone (V), as indicated by its molecular weight and infrared spectrum (ν C=O 1770 cm^{-1} , ν C=N 1624 cm^{-1}). On treatment of V with isoamyl nitrite (7) and sodium nitrite (8) the green color characteristic for thioethers resulted.

EXPERIMENTAL

Melting points are uncorrected. Molecular weight determinations, obtained by the osmometer method with benzene as solvent, and elementary analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The infrared spectra were recorded by a double-beam grating Perkin-Elmer Model 337 spectrophotometer. The samples were measured at a concentration of 0.3% in potassium bromide discs.

Alkylation Reaction.

To a clear solution of 4.8 *mM* of I and 4.8 *mM* of thiophenol (or benzylmercaptan) in 30 ml. of dichloromethane 9.8 *mM* of anhydrous aluminum chloride was added. After 16 hours the reaction mixture was decomposed with water and acidified with dilute hydrochloric acid. The organic layer was separated, washed with water and dried over anhydrous sodium sulfate. The drying agent was filtered off and the solvent concentrated to 10 ml. The addition of a few ml. of



No.	R	Formula	Carbon % Calcd. Found	Hydrogen % Calcd. Found	Nitrogen % Calcd. Found	M. P. °C	Yield %
II		C ₁₇ H ₁₃ NO ₂ S	69.1 69.2	4.44 4.47	4.74 4.91	161 - 162	75
III		C ₁₆ H ₁₀ ClNO ₂ S	60.9 61.2	3.19 3.45	4.44 4.64	157 - 159	68
IV		C ₁₆ H ₁₀ BrNO ₂ S	53.4 53.3	2.80 2.91	3.89 3.97	153 - 155	78
V		C ₁₇ H ₁₂ ClNO ₂ S	61.9 61.9	3.67 3.63	4.25 4.28	173 - 174	83

methanol induced the immediate crystallization of the product in yellow needles, which were recrystallized from dichloromethane-methanol. The final recrystallization was performed with ethyl acetate.

Acknowledgment.

The infrared spectra were carried out by Mr. Louis Trauth. The authors wish to thank the Evans Chemical Company, New York, N. Y. for supplying the sulfur compounds employed in this study and Dr. Fred Kaplan for interpretation of NMR spectra.

REFERENCES

(1) This work was supported by the U. S. Atomic Energy Commission and U. S. Public Health Service Grant No. AM 10080-02 of

the National Institute of Arthritis and Metabolic Diseases.

- (2) Chemistry Department, University of Cincinnati, Ohio.
- (3) H. Behringer and K. Falkenberg, *Chem. Ber.*, **96**, 1428 (1963).
- (4) D. S. Tarbell and J. C. Petropoulos, *J. Am. Chem. Soc.*, **74**, 244 (1952).
- (5) W. E. Parham, I. Gordon and J. D. Swalen, *ibid.*, **74**, 1824 (1952).
- (6) R. Benesch, R. E. Benesch, M. Gutcho and I. Laufer, *Science*, **123**, 981 (1956).
- (7) G. Hesse and I. Jorder, *Chem. Ber.*, **85**, 924 (1952).
- (8) H. Rheinboldt, *ibid.*, **60**, 184 (1927).

Received March 9, 1966

Upton, New York 11973
New York, New York 10029