heated very cautiously in an atmosphere of nitrogen, the yellow crystals sublime and reform in a cooler portion of the tube. Upon stronger heating, some disproportionation occurs and white crystals of chromium hexacarbonyl are observed further along the tube. Finally, complete decomposition results in the deposition of a metallic mirror of cadmium and chromium.

Acknowledgment.—We are indebted to Dr. Francis J. Norton, of the Research Laboratory of the General Electric Company, for preparing and interpreting mass spectra of our samples of chromium carbonyl, chromium carbonyl hydride, and products produced by spontaneous decomposition of the hydride upon standing at room temperatures.

DEPARTMENT OF CHEMISTRY
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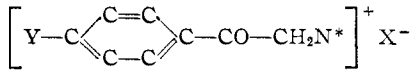
NEW HAVEN, CONNECTICUT RECEIVED JUNE 8, 1951

Preparation of Some Sulfonium Salts as Possible Anticancer Agents

BY HENRY A. RUTTER, JR.[1]

The preparation of sulfonium halides as possible anticancer agents was prompted by the structural similarity between quadrivalent sulfonium compounds and quaternary ammonium derivatives.

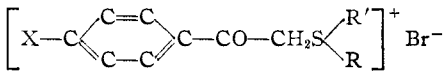
Hartwell and Kornberg[2] prepared several aralkyl quaternary ammonium halides of the type I which had anticancer activity.



I

The nitrogen was contained in a heterocyclic ring such as pyridine or α-picoline.

In the present investigation a series of aralkyl sulfonium bromides of the type II were prepared by reaction of the appropriate phenacyl bromide with dialkyl sulfides according to the method of Bost and Schultze[3] for the preparation of *p*-phenylphenacyl sulfonium bromides.



II

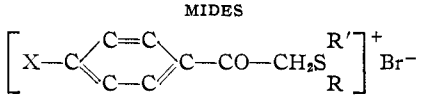
where X is H, CH_3, C_6H_5, Br, Cl and CH_3O and R and R′ are alkyl groups. In addition one meta-nitro derivative has been prepared.

These compounds are listed in Table I.

A preliminary report indicates that six of the phenacyl sulfonium bromides are somewhat effective as tumor necrotizing agents at dosages of 150 to 250 mg. per kilogram of body weight against Sarcoma 37 in mice.[4]

TABLE I

PHENACYL AND SUBSTITUTED PHENACYL SULFONIUM BROMIDES



X	R	R′	Formula	Yield, %	M.p., °C. (uncor.)	Bromide ion, %[a] Calcd.	Found
H	C_3H_7	C_3H_7	$C_{14}H_{21}OSBr$	13	93–94	25.23	25.20
H	C_4H_9	C_4H_9	$C_{16}H_{25}OSBr$	23	88–89	23.18	22.90
H	C_4H_9	C_2H_5	$C_{14}H_{21}OSBr$	63	103–104	25.23	25.05
CH_3	CH_3	CH_3	$C_{11}H_{15}OSBr$	51	112	29.04	28.71
CH_3	C_3H_7	C_3H_7	$C_{15}H_{23}OSBr$	12	98–99	24.12	24.41
CH_3	C_4H_9	C_4H_9	$C_{17}H_{27}OSBr$	28	99–100	22.24	21.99
CH_3	C_4H_9	C_2H_5	$C_{15}H_{23}OSBr$	12	97	24.12	23.74
C_6H_5	C_2H_5	C_2H_5	$C_{18}H_{21}OSBr$	31	123–124	21.9	21.47
C_6H_5	C_3H_7	C_3H_7	$C_{20}H_{25}OSBr$	25	113–114	20.37	20.10
C_6H_5	C_4H_9	C_2H_5	$C_{20}H_{25}OSBr$	14	96–97	20.37	20.21
Br	CH_3	CH_3	$C_{10}H_{12}OSBr_2$	53	127	23.52	23.31
Br	C_2H_5	C_2H_5	$C_{12}H_{16}OSBr_2$	53	119–120	21.73	21.40
Br	C_3H_7	C_3H_7	$C_{14}H_{20}OSBr_2$	49	107–108	20.20	19.9
Cl	CH_3	CH_3	$C_{10}H_{12}OSBrCl$	27	128–129	27.03	27.14
Cl	C_3H_7	C_3H_7	$C_{14}H_{20}OSBrCl$	29	111	22.72	22.85
Cl	C_4H_9	C_4H_9	$C_{16}H_{24}OSBrCl$	21	99	21.04	20.88
Cl	C_4H_9	C_2H_5	$C_{14}H_{20}OSBrCl$	34	102–103	22.72	22.48
CH_3O	C_2H_5	C_2H_5	$C_{13}H_{19}O_2SBr$	13	106–107	25.03	24.71
CH_3O	C_3H_7	C_3H_7	$C_{15}H_{23}O_2SBr$	15	100	23.01	22.62
m-NO_2	C_3H_7	C_3H_7	$C_{14}H_{20}NO_2SBr$	6	97–98	22.06	21.71

[a] Mohr analysis, average of two.

Grateful acknowledgment is made to Dr. M. X. Sullivan for his advice and encouragement during this investigation.

CHEMO-MEDICAL RESEARCH INSTITUTE
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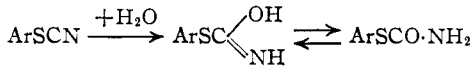
Thiocarbamates. III.[1] Aryl Thiocarbamates from Aryl Thiocyanates

BY R. RIEMSCHNEIDER, F. WOJAHN AND G. ORLICK[2]

As reported elsewhere,[1,3] the action of concentrated sulfuric acid followed by treatment with ice-water serves, in most cases, to transform aryl thiocyanates into the corresponding thiocarbamates



The reaction is of preparative as well as of analytical value. We have found that the reaction is superior to older procedures for the preparation of thiocarbamates[4] with respect to general applicability,

(1) Taken from thesis submitted by Henry A. Rutter, Jr., in partial fulfillment of the requirements for the degree of Ph.D. at The Division of Chemistry, Graduate School, Georgetown University, Washington, D. C.

(2) J. L. Hartwell and S. R. L. Kornberg, THIS JOURNAL, **68**, 868 (1946).

(3) R. W. Bost and H. C. Schultze, *ibid.*, **64**, 1165 (1942).

(4) Acknowledgment is made to Dr. Jonathan L. Hartwell, National Cancer Institute, for the report on the tumor necrotizing activity of the compounds. The final report dealing with the biological activity of these compounds will be made later.

(1) R. Riemschneider, Paper I, *Mitt. physiol. chem. Inst.*, R 30. Feb., 1949; Paper II, *Chimica e industria (Milan)*, **33**, 483 (1951) (presented Sept. 19, 1950, before the VI National Congress of Pure and Applied Chemistry, Milan).

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(3) *Pharmazie*, **4**, 460 (1949); *Chim. et Ind.*, **64**, Sonderheft, Sept., 99 (1950); *Pharm. Zentralhalle*, **89**, 108 (1950); further references may be found in Paper I of this series.[1]

(4) H. L. Wheeler and B. Barnes, *Am. Chem. J.*, **22**, 141 (1899); A. Fleischer, *Ber.*, **9**, 988 (1876); N. A. Langlet, *ibid.*, **24**, 3848 (1891); B. Hohnberg, *ibid.*, **47**, 159 (1914); A. Knorr, *ibid.*, **49**, 1735 (1916); E. Biillmann and J. Bjerrum, *ibid.*, **50**, 503 (1917); M. H. Rivier, *Bull. soc. chim.*, [4] **1**, 733 (1907); R. Conrad and F. Salomon, *J. prakt.*