acids and aldehydes. The dicarboxylic acids were characterized by m.p., and the aldehydes by mixed m.p. of their 2,4-dinitrophenylhydrazones (DNPH) with known preparations. Since all the DNPHs from degradation aldehydes melted in the neighborhood of 106°, reference was made to the present publication in which the individual DNPHs, crystallized from 90–95% ethyl alcohol, are characterized by X-ray diffraction pattern. Diffraction patterns were obtained for rod-shaped pellets with a GE XRD unit, CuKα radiation, and 10-cm. sample-to-(flat)-film distance. The long spacings are shown in Table I for DNPHs from scission products of members of the series 7- through 12-octadecenoic acid, in comparison with values for authentic compounds prepared here and by Malkin and Tranter,[2] who have recently published data for the whole series of DNPHs from C_1- through C_{13}-aldehydes.

TABLE I

LONG SPACINGS (Å.) OF 2,4-DINITROPHENYLHYDRAZONES OF ALIPHATIC ALDEHYDES

Aliphatic chain	Samples from octadecenoic source[a]		Authentic samples	
	From *cis*	From *trans*	This study	M & T[2]
C_6	16.2	[b]	16.3	16.34
C_7	[c]	[c]	17.7	17.78
C_8	19.4	19.2	19.3	19.15
C_9	19.9	19.7	19.8	19.6
C_{10}	21.0	21.1	21.2	21.12
C_{11}	22.3	22.3	22.6	22.38

[a] C_6-aldehyde from 12-, C_7-aldehyde from 11-octadecenoic acid, etc. [b] Not prepared. [c] Original octadecenoic structure established by F. M. Bumpus, W. G. Taylor and F. M. Strong, THIS JOURNAL, **72**, 2116 (1950).

Thus the structures of the synthetic acids are further confirmed, since, for instance, 10-octadecenoic acid (both *cis* and *trans*) gives the expected DNPH with normal C_8-carbon chain. The agreement with Malkin and Tranter[2] is excellent and confirms their reported break in properties between C_8 and C_9. A corresponding crystal habit difference was noted by both macro- and microscopic observation, the C_6, C_7 and C_8 giving in general larger, brighter, more plate-like and less tufted crystals as compared with the more needle-like and highly tufted C_9, C_{10} and C_{11}. No extensive study of possible polymorphism was attempted, but wide variations in alcohol–water proportions and crystallization temperatures effected no change in the form of the C_9-compound.

Some work was done on the DNPHs from C_1- through C_4-aldehydes which were crystallized from ethyl alcohol.

Each compound gave a single polymorphic form:

C_1, m.p. 165.5°, (166°[3]), (166°[2]); l.s. 10.5 Å., (10.3[3]), (7.33, 10.38[2])

C_2, m.p. 167.5°, (166°[3]), (167.5°[2]); l.s. 9.5 A., (9.35, 9.2[3]), (9.40[2])

C_3, m.p. 153°, (150°[3]), (155°[2]); l.s. 9.7 Å., (9.6, 11.03), (10.95, 9.64[2])

C_4, m.p. 121.5°, (123°[3]), (119°[2]); l.s. 14.0 A., (14.0, 11.7,[4] 12.6[3]), (13.5[2])

The single long spacing value here obtained for a given DNPH is readily associated in each case with a value previously twice reported[2,3] except in the case of C_4, for which only one previous observation[3] (14.0 Å.) is checked.

CHEMICAL DIVISION
THE PROCTER & GAMBLE COMPANY
CINCINNATI 17, OHIO

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[2] T. Malkin and T. C. Tranter, *J. Chem. Soc.*, 1178 (1951).

[3] G. L. Clarke, W. I. Kaye and T. D. Parks, *Ind. Eng. Chem., Anal. Ed.*, **18**, 310 (1946).

[4] This form also reported[3] to have a weak spacing of 13.7 Å.

Chromium Carbonyl Hydride

BY MARY G. RHOMBERG AND BENTON B. OWEN

Investigation in this Laboratory shows that the reactions of chromium hexacarbonyl are more extensive than anticipated, and run parallel to some of the reactions of iron and cobalt carbonyls. Of particular interest is the reaction with alkali which, contrary to previous reports,[1] leads to the formation of a carbonyl hydride. The reaction[2] of alcoholic potassium hydroxide and chromium hexacarbonyl produces a brilliant yellow derivative which, upon acidification, yields a white, volatile, unstable crystalline substance. Mass spectrographic data[3] indicate that this crystalline substance is a chromium carbonyl hydride, and its chemical reactions suggest that the formula is $Cr(CO)_5H_2$ rather than the $Cr(CO)_4H_4$ predicted by Blanchard.[4] The hexacarbonyls of tungsten and molybdenum also react with alkali under similar conditions. When either of these hexacarbonyls is dissolved in alcoholic potassium hydroxide and heated in the absence of oxygen, a yellow solution results which exhibits strong reducing properties.

The yellow product of the reaction of chromium hexacarbonyl with alcoholic potassium hydroxide readily undergoes a series of further reactions. Qualitative tests, color changes and general behavior indicate that the products of these reactions are the chromium counterparts of the derivatives of $Fe(CO)_5H_2$ and $Co(CO)_3H$. For example, an ammoniacal solution of cadmium acetate and an ammoniacal solution of ferroin[5] lead to two derivatives with properties similar to those of $Fe(CO)_5Cd(NH_3)_2$ and $(Fe(CO)_5H)_2Fe(C_{12}H_8N_2)_3$.[6] In the absence of oxygen, the cadmium ammonia derivative of chromium carbonyl hydride slowly changes from brilliant yellow to green with loss in weight: exposure to air produces further loss in weight. The yellow cadmium ammonia derivative is volatile, and passes through an interesting series of steps when decomposed by heat. When first

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[1] W. Hieber and E. Romberg, *Z. anorg. allgem. Chem.*, **221**, 321 (1935).

[2] Temperature is not critical. A good yield is obtainable in one hour at 90°.

[3] F. J. Norton, private communication. Comparison of the mass spectra of a freshly prepared chromium carbonyl hydride sample and of the products of its decomposition, after standing for three days at room temperatures, showed the disappearance of peaks corresponding to possible chromium–hydrogen fragments of masses 51, 55, 56, 57 and 58, and return to the normal pattern of peaks for the chromium isotopes 50, 52, 53 and 54.

[4] A. A. Blanchard, *Chem. Revs.*, **21**, 3 (1939).

[5] 1,10-(ortho)Phenanthroline ferrous sulfate.

[6] For properties of these iron compounds consult J. S. Anderson, *Quart. Rev.*, **1**, 341 (1947), and W. Hieber, *Die Chemie* (*Angew. Chem.*), **55**, 24 (1942).

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.

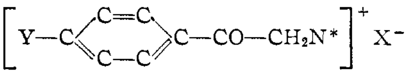
DEPARTMENT OF CHEMISTRY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT
RECEIVED JUNE 8, 1951

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.

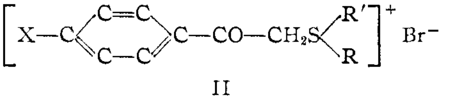
Hartwell and Kornberg[2] prepared several aralkyl quaternary ammonium halides of the type I which had anticancer activity.



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.



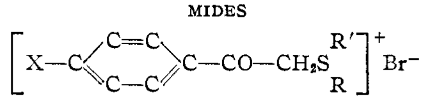
II

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.

TABLE I

PHENACYL AND SUBSTITUTED PHENACYL SULFONIUM BROMIDES



X	R	R′	Formula	Yield, %	M.p., °C. (uncor.)	Bromide ion, %[a] Calcd.	Bromide ion, %[a] 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_2	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	$C_{14}H_{20}NO_3SBr$	6	97–98	22.06	21.71

[a] Mohr analysis, average of two.

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]

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

CHEMO-MEDICAL RESEARCH INSTITUTE
GEORGETOWN UNIVERSITY
WASHINGTON, D. C.
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[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).

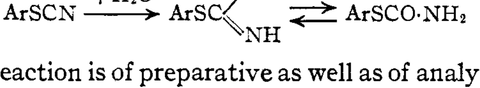
[3] R. W. Bost and H. C. Schultze, *ibid.*, **64**, 1165 (1942).

[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.

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



$$ArSCN \xrightarrow{+H_2O} ArSC\begin{matrix}OH\\NH\end{matrix} \rightleftarrows ArSCO{\cdot}NH_2$$

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,

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[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).

[2] Address of the authors: Hohenzollernplatz 1, Berlin-Nikolassee,

[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.*