of aged paraldehyde have shown in promoting the reaction between olefins and sulfur dioxide can be obtained by use of peracetic acid solutions.

2. Vinyl chloride and vinyl bromide combine with sulfur dioxide in the presence of active paraldehyde or peracetic acid to give a polymer of the composition $[(CH_2{=}CHX)_2SO_2]_n$, rather than the usual one to one type of polymer. A preliminary study of the reaction of the vinyl halide polymer has not indicated its structural unit.

3. Freezing point-composition curves for solutions of styrene, 1-pentene and 10-hendecenoic acid in liquid sulfur dioxide offer no evidence of compound formation. But vinyl chloride and liquid sulfur dioxide form a compound containing approximately 40 mole per cent. of vinyl chloride.

URBANA, ILLINOIS RECEIVED AUGUST 1, 1938

[CONTRIBUTION OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Electronegativities of Highly Branched Aliphatic Groups

BY FRANK C. WHITMORE AND HERBERT BERNSTEIN

Since the well-known Kharasch table of relative electronegativities of univalent organic groups consists chiefly of aromatic groups,[1] we decided to place in the table some of the highly branched aliphatic groups available in this Laboratory. Following the method of Kharasch, the mixed dialkyl mercury compounds were treated with alcoholic hydrogen chloride.

$$R{-}Hg{-}R' + HCl \longrightarrow RHgCl + R'H$$

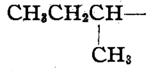
This result would place R′ above R in relative electronegativity. Of the fifteen mixed dialkyl mercury compounds used in the present study, four gave mixtures of R′HgCl and RHgCl. The groups involved in these cases are thus indistinguishable by Kharasch's method. With ten of the other compounds a clear distinction in the relative electronegativity of the groups was obtained.

The results are given in Tables I and II.

TABLE I

ORDER OF DECREASING ELECTRONEGATIVITY

Phenyl
Methyl
Ethyl
n-Propyl
{ *n*-Butyl, $(CH_3)_3CCH_2CH_2$—
{ *n*-Hexyl, $(CH_3)_3CCH_2CH_2CH_2$—



$CH_3CH_2CH(CH_3)$—

$(CH_3)_3CCH(CH_3)$—

……

Benzyl
$(CH_3)_3C$—, $(CH_3)_3CCH_2$—

Groups on the same line or bracketed are not distinguishable by this method. The dotted line above the benzyl group indicates that its relation to the groups immediately above it has not been determined experimentally.

The most interesting feature of this table is the position held by the *t*-butyl and neopentyl groups. Both are less electronegative than the benzyl, which, according to Kharasch, is less electronegative than any alkyl group which he tested. Furthermore, their electronegativities approximate each other. This corresponds to the inertness of *t*-butyl chloride and neopentyl chloride in certain metathetical reactions.[2]

Also of interest is the relationship between the pinacolyl and the secondary butyl groups. The *n*-hexyl and *n*-butyl groups have the same relative electronegativity. However, the pinacolyl, a group very susceptible to rearrangement,[3] is distinctly less electronegative than the secondary butyl group.

Experimental

Neopentyl chloride was prepared by the chlorination of neopentane.[2]

1-Chloro-3,3-dimethylbutane was prepared by slowly adding 29.8 g. (0.25 mole) of thionyl chloride to a solution of 21.7 g. (0.21 mole) of neopentylcarbinol in 19.7 g. (0.25 mole) of pyridine cooled on an ice-bath. A thick white solid formed. When the addition was complete, the ice-bath was removed and the temperature of the flask raised. Decomposition of the solid occurred between 94–133°. The residue was added to a mixture of 45 g. of ice and 30 g. of concentrated hydrochloric acid, the organic layer was separated from the aqueous layer and the latter was extracted with ether. Upon distillation, 15.5 g. of

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[1] Kharasch and Marker, THIS JOURNAL, **48**, 3140 (1926); Kharasch and Flenner, *ibid.*, **54**, 685 (1932).

[2] Conant and Hussey, *ibid.*, **47**, 479 (1925); Whitmore and Fleming, *ibid.*, **55**, 4161 (1933).

[3] Whitmore and Rothrock, *ibid.*, **55**, 1106 (1933)

TABLE II

	Melting points, °C.					
RHgR'	RHgCl pure	R'HgCl pure	HCl reaction product, crude	Mixture with RHgCl	Mixture with R'HgCl	Alkyl–HgCl formed by HCl
$(CH_3)_3CCH_2$–Hg methyl	117–118	167–168	117–117.5	117–118		Neopentyl
$(CH_3)_3CCH_2$–Hg butyl	117–118	126.5–127.0	105–112	113.5–116	82–98	Neopentyl
$(CH_3)_3CCH_2$–Hg benzyl	117–118	104–105	110–114	111–114	Below 80	Neopentyl
$(CH_3)_3CCH_2$–Hg –$CH_2CH_2C(CH_3)_3$	117–118	133.0–133.5	112–114	113–116.5	99–110	Neopentyl
$(CH_3)_3CCH_2$–Hg *t*-butyl	117–118	122–123, dec.	95–97[a]	105–115	100–117, dec.	Mixture
$(CH_3)_3CCH_2$–Hg *sec*-butyl	117–118	29–30	94–101			Neopentyl (?)
t-Butyl Hg *n*-butyl	122–123, dec.	126.5–127	119–123,[a] dec.	121–123, dec.	Below 95	*t*-Butyl
t-Butyl Hg benzyl	122–123, dec.	104.5–105	112–117,[a] dec.	117–119, dec.	Below 70	*t*-Butyl
t-Butyl Hg ethyl	122–123, dec.	193–193.5	117–118,[a] dec.	117–118, dec.	108–110, dec. 189–192	*t*-Butyl
s-Butyl Hg –$CH(CH_3)C(CH_3)_3$	29–30	89–91	83.5–88.5	87–91		Pinacolyl
s-Butyl Hg *n*-butyl	29–30	126.5–127	Liquid			*s*-Butyl
$(CH_3)_3CCH_2CH_2$–Hg *n*-butyl	133–133.5	126.5–127	89–109			Mixture
$(CH_3)_3CCH_2CH_2$–Hg —$CH_2CH_2CH_2C(CH_3)_3$	133–133.5	104.5–105	94–97	90–104	93–101	Mixture
$(CH_3)_3CCH_2CH_2$–Hg —$CH(CH_3)C(CH_3)_3$	133–133.5	88.5–90	84–90	85.5–90	75–106	Pinacolyl
$(CH_3)_3CCH_2CH_2CH_2$–Hg *n*-butyl	104.5–105	126.5–127	75–84			Mixture

[a] Dried *in vacuo* with no heat.

material (n^{20}D 1.4161) boiling at 115° resulted. A small portion of the neohexyl chloride was converted to the Grignard reagent, the latter oxidized and the α-naphthylurethan prepared, m. p. and mixed m. p. with the α-naphthylurethan of neopentylcarbinol, 83°.

Pinacolyl chloride (2-chloro-3,3-dimethylbutane) resulted from the chlorination of neohexane.[4] 1-Bromo-4,4-dimethylpentane was made by the addition of hydrogen bromide to neopentylethylene under oxidizing conditions.[5]

Preparation of Alkyl Mercuric Chlorides.—The method used was essentially that of Marvel, Gauerke and Hill,[6] excess mercuric chloride reacting with a Grignard reagent. If the initial halide was a bromide, 70% alcohol and an equimolar quantity of silver chloride were added to the reaction mixture and the whole refluxed for five hours.

t-Butylmercuric chloride could not be recrystallized by the conventional methods, since it decomposed readily. Acetone was added to the reaction mixture at room temperature. After filtration water was added until the solution became cloudy. Enough acetone was added to clarify the solution. The acetone was then evaporated under vacuum at room temperature. The *t*-butylmercuric chloride precipitated out in long needles, m. p. 122–123° (dec.).

Analyses for mercury on the new alkylmercuric chlorides prepared were conducted by the method of Sobatzki.[7] The iodine solution was standardized against purified neopentylmercuric chloride.

TABLE III

Alkyl in RHgCl	M. p., °C. RHgCl	% Hg Found	% Hg Calcd.
t-Butyl, $(CH_3)_3C$—	122–123, dec.		
Neopentyl, $(CH_3)_3CCH_2$—	117–118	Ref. 2	
$(CH_3)_3CCH_2CH_2$—	133–133.5	62.5	62.5
Pinacolyl, $(CH_3)_3CC(CH_3)H$—	89–90	Ref. 4	
$(CH_3)_3CCH_2CH_2CH_2$—	104–105	59.5	59.8
n-Octyl, $CH_3(CH_2)_7$—	115–115.5	57.8	57.4

Preparation and Reactions of Dialkyl Mercury.—Neopentyl mercury *n*-butyl will serve as a typical example. *n*-Butylmagnesium bromide was prepared from 2.7 g. (0.02 mole) of *n*-butyl bromide and 0.48 g. (0.02 mole) of magnesium, and 3 g. (0.01 mole) of neopentylmercuric chloride was added to the Grignard reagent in small portions. The reaction was instantaneous and vigorous. The flask was surrounded by an ice-bath and the excess Grignard reagent was decomposed using 8 cc. of 0.5% sulfuric acid solution. The ether layer was decanted, shaken with 7 g. of anhydrous sodium sulfate and separated. The ether was then removed under vacuum at room temperature. The residue was divided into two portions.

To one portion of the dialkyl mercury was added 4 cc. of saturated alcoholic hydrogen chloride. After warming the flask for a minute the reaction proceeded vigorously. A portion of the resulting mixture was dried on a watch glass at 90–100°. No recrystallization was attempted, since this would change the ratio if two alkylmercuric chlorides had formed. Melting points and mixed melting points were taken (Table II).

To the second portion of the dialkyl mercury was added saturated alcoholic mercuric chloride until no more precipitate formed. The reaction was instantaneous. Neopentylmercuric chloride and *n*-butylmercuric chloride were isolated from the reaction products by fractional crystallization in aqueous alcohol, the latter precipitating first.

When the mixed dialkyl mercury compounds were treated with mercuric chloride and the products crystallized from aqueous alcohol, the following observations were made: if one of the alkyls is neopentyl the other alkylmercuric chloride separates first; if only one alkyl is normal its alkylmercuric chloride is least soluble; higher normal alkylmercuric chlorides show decreased solubility; in the case of related groups like the neohexyl and neoheptyl, the alkylmercuric chlorides could not be separated by crystallization.

Summary

1. Fifteen mixed dialkyl mercury compounds containing branched-chain groups have been treated with hydrogen chloride, the resulting alkylmercuric chlorides indicating the relative electronegativities. The *t*-butyl and neopentyl groups are the least electronegative, while the neohexyl

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[4] Whitmore, Bernstein and Mixon, THIS JOURNAL, **60**, 2539 (1938).

[5] Whitmore and Homeyer, *ibid.*, **55**, 4555 (1933).

[6] Marvel, Gauerke and Hill, *ibid.*, **47**, 3009 (1925).

[7] Whitmore and Sobatzki, *ibid.*, **55**, 1171 (1933).

and neoheptyl groups compare with the simpler straight chain groups.

2. Four new alkylmercuric chlorides have been reported. These are of use as derivatives for identifying the alkyl halides.

3. A method of recrystallizing tertiary alkylmercuric halides is given.

4. Neohexyl chloride (1-chloro-3,3-dimethylbutane) has been prepared.

STATE COLLEGE, PENNA. RECEIVED AUGUST 22, 1938

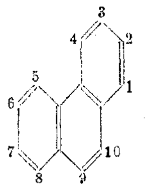
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

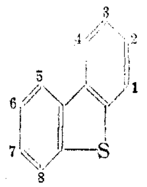
Isosteric Compounds. I. Acyl Derivatives of Dibenzothiophene

BY ALFRED BURGER, WILLIAM B. WARTMAN, JR., AND ROBERT E. LUTZ

The similarity between the physical characteristics of benzene and thiophene and their corresponding derivatives, and the agreement in the physiological behavior of certain of these compounds[1] have been subject to frequent speculation. In 1933 Erlenmeyer[2] advanced the theory that divalent sulfur contains a shell of orbit electrons similar to that of the group or "pseudoatom,"—CH=CH—, and that this similarity in electronic structure known as isosterism,[3] accounted for the formation of mixed crystals and the many like physical properties of the two series. In a few cases, isosteric compounds are interchangeable in serological reactions and cannot be differentiated by the precipitin reaction.[2a]

The present paper is the first in a series of studies on the physical and pharmacological changes effected by introducing a thiophene nucleus into condensed ring systems in place of an aromatic nucleus. The first case under investigation is dibenzothiophene (I) which may be regarded as a pseudophenanthrene. Amino alcohols derived from dibenzothiophene, characterized by the groups $-CHOHCH_2NR_2$ and $CHOHCH_2CH_2NR_2$, may be expected to resemble the corresponding alkamines of the phenanthrene series in analgesic action.[4] Their similarity to the corresponding alkamines derived from dibenzofuran[5] and carbazole[6] should be less marked, since oxygen and the imino group are not isosteric with the —CH=CH— group.





I

The preparation of acetyldibenzothiophenes as starting materials for the proposed dibenzothienyl alkamines is described in this communication. The direct introduction of the acetyl group by the Friedel–Crafts reaction was chosen as a suitable approach. The only ketone derived from dibenzothiophene known heretofore is stearoyl dibenzothiophene, prepared by the Friedel–Crafts reaction in boiling carbon disulfide.[7] No proof for the position of the stearoyl group has been offered, but the group is presumed to have entered position 3 which is known to be preferred in nitration, sulfonation, and halogenation.[8]

Friedel–Crafts reaction on dibenzothiophene with acetyl chloride at low temperature yielded a difficultly separable mixture of methyl ketones, from which one (II), melting at 111–112°, was separated by laborious fractional crystallization and was the major product. An isomeric monoketone, melting at 128–129°, was isolated in small amounts during this procedure. The structure of the major constituent of this mixture, 3-acetyldibenzothiophene (II), was proved by Beckmann rearrangement of its oxime. The resulting acetaminodibenzothiophene and the amine obtained from it by hydrolysis were

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[1] Steinkopf and Ohse, *Ann.*, **437**, 14 (1924); **448**, 205 (1926); Gilman and Pickens, THIS JOURNAL, **47**, 245 (1925); Hartmann and Wybert, *Helv. Chim. Acta*, **2**, 60 (1919); Jaffé and Levy, *Ber.*, **21**, 3458 (1888).

[2] (a) Erlenmeyer, Berger and Leo, *Helv. Chim. Acta*, **16**, 733 (1933); (b) Erlenmeyer and Leo, *ibid.*, **16**, 1381 (1933).

[3] Grimm, *Naturwissenschaften*, **17**, 536, 557 (1929).

[4] Mosettig, Shaver and Burger, THIS JOURNAL, **60**, 2464 (1938), footnote 2.

[5] Mosettig and Robinson, *ibid.*, **57**, 2186 (1935).

[6] Ruberg and Small, *ibid.*, **60**, 1591 (1938).

[7] Ralston and Christensen, *Ind. Eng. Chem.*, **29**, 194 (1937).

[8] (a) Courtot and Pomonis, *Compt. rend.*, **182**, 893, 931 (1926); (b) Courtot and co-workers, *ibid.*, **186**, 1624 (1928); **192**, 1667 (1931); **198**, 2003, 2260 (1934); (c) Cullinane, Davies and Davies, *J. Chem. Soc.*, 1435 (1936).