lated effects are of correct order of magnitude, as regards both the rates of substitution and the values of the resonance moments. It is of particular interest that orientation in 5-hydroxyhydrindene and 2-naphthol is accounted for without the assumption of appreciable fixation of bonds in the unreacting molecules.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 24, 1941

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

Some Esters of Thiodiglycol

BY WEAVER R. CLAYTON[1] AND E. EMMET REID

Though thiodiglycol has been known for a long time[1a] and has been manufactured on a large scale for making "mustard gas," it has not been extensively studied. It seemed worth while to prepare it and some of its esters in high purity so as to determine their properties. The formate, acetate, benzoate and phthalate are mentioned in a patent[2] but not fully characterized. The *p*-nitro and *p*-aminobenzoates have been made.[3]

Experimental

Thiodiglycol.—The crude thiodiglycol which had been made from chlorhydrin contained a considerable amount of dithiane and its polymers. Distillation at 153° (8 mm.) removed much of the impurities. The polymeric material is said to break down at 160°.[4] The distillate was diluted with sufficient water to bring its boiling point down to 165° and superheated steam passed through it. After evaporating off the water the thiodiglycol was distilled at 147.5° (6 mm.).

Purified thiodiglycol melts at −10°, distills at 147.5° (6 mm.), 165° at 20 mm., 181.5° at 40 and has d^{0}_{4} 1.1973, d^{25} 1.1793 and n^{26}_{D} 1.5146. It is miscible with water, the lower alcohols, chloroform and ethyl acetate. At 25° 100 g. of benzene dissolves 1.07 g., 100 g. of absolute ether 7.09 g. and 100 g. of ligroin 0.06 g. Alone, or with an organic acid, it is stable at 180° for many hours. Heated at 100° for thirty minutes with 2.5 parts of 0.1 *N* sodium hydroxide an appreciable amount of sulfide ion is formed and much more with 1 *N*, though it is only half decomposed by solid sodium hydroxide at 140° in ten hours. Lead acetate and cupric nitrate decompose it at 100°, but barium hydroxide, calcium oxide and alumina have little effect even at 180° for ten hours. It was hoped that calcium oxide or alumina would dehydrate it to vinyl sulfide but they did not.

Esters.—The esters of Table I were made by heating thiodiglycol to 150–160° with the acid anhydrides for five hours or with the acids (caproic and *i*-valeric) for ten. At the end of the heating, suction was applied and the excess reagent, together with acid or water that had been formed, distilled out. To the residue of ester and unreacted glycol 1 volume of water and 1.5 of benzene were added. The benzene layer was twice washed with 0.5 volume of water and the benzene removed under vacuum. The esters were distilled twice at 8 mm. In making the formate, the glycol was refluxed with two parts of 85% formic acid, the acid and water distilled off and the refluxing repeated with one part of the acid. The yields of the esters were high, up to 95%. The saponification numbers were determined in the usual way.

TABLE I

ESTERS OF THIODIGLYCOL

Ester	M. p., °C.	B. p., °C.	Press., mm.	d^{0}_{4}	d^{25}_{4}	n^{25}_{D}	Saponification no. Calcd.	Saponification no. Found
Formate	−15.5	134.5[b]	8	1.2525	1.2275	1.4804	533.8	531.7
Acetate	..	139.5[b]	8	1.1626	1.1382	1.4679	470.9	470.9
Propionate	−23	158	8	1.1112	1.0874	1.4648	421.2	419.9
Butyrate	−28	172	8	1.0716	1.0491	1.4627	375.6	374.1
Butyrate[a]	..	172–3	8	1.0721	1.0496	1.4630	..	..
i-Valerate	..	181–2	8	1.0384	1.0171	1.4598	348.1	247.4
i-Valerate[a]	..	182	8	1.0372	1.0158	1.4593	..	..
Caproate	7	207	7	1.0198	1.0024	1.4627	320.3	320.3

[a] From the potassium salt and mustard gas. [b] Kränzlein and Corell[2] give 130–7° (7 mm.) for the formate and 142–50° (12 mm.) for the acetate.

Two of the esters were also made by refluxing mustard gas in 6 to 8 parts of absolute alcohol with the potassium salt of the acid for five hours. The most of the alcohol was taken off at reduced pressure and the salt filtered off and washed with alcohol. The crude ester was distilled at 8 mm., purified with the water–benzene treatment and again distilled. Acetyl chloride converts about two-thirds of thiodiglycol into the acetate and the rest to mustard gas.

---

(1) From Dissertation, June, 1928. Original manuscript received July 28, 1941.

(1a) Carius, *Ann.*, **124**, 263 (1862).

(2) Kränzlein and Corell, U. S. Patent 1,422,869 (1922).

(3) Major, *Bull. soc. chim.*, **41**, 634 (1927).

(4) Masson, *J. Chem. Soc.*, **49**, 236 (1886).

Esters could not be made with chloro- or bromoacetic acids. With phthalic anhydride at 130–140° for one hour the bis-monophthalate, the sodium salt of which gave precipitates with salts of the heavy metals, was formed along with a heavy neutral oil which could not be purified, apparently the neutral ester. This predominates when the reaction temperature is higher, 150–160°, regardless of the proportion of the anhydride.

Other Reactions.—Condensation took place when thiodiglycol was heated with dimethylaniline, raising the temperature gradually from 120 to 160° in eighteen hours with the addition of zinc chloride in portions. The product was a heavy oil boiling at 204–210° (8 mm.), containing sulfur and dissolving in dilute acids.

Mustard gas sulfoxide, $(ClCH_2CH_2)_2SO$, was refluxed with potassium acetate in absolute alcohol and also in acetic acid but no reaction could be detected in either case.

The sulfone, $(ClCH_2CH_2)_2SO_2$, was refluxed with potassium acetate in acetic acid solution; a reaction took place. After filtering off the salt and volatilizing the acetic acid, a reddish viscous liquid remained for which no method of purification could be found. Potassium *i*-valerate gave a similar product. From the sulfone and sodium benzoate in absolute alcohol the calculated amount of sodium chloride was obtained along with benzoic acid. The benzoate of thiodiglycol has been oxidized to the corresponding sulfoxide and sulfone.[5]

Summary

Thiodiglycol has been purified and its properties determined. Several esters have been made from it and their properties determined.

(5) Fromm and Kohn, *Ber.*, **54**, 321 (1921).

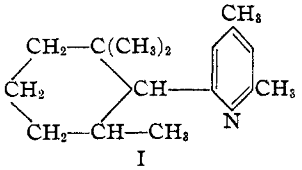
Baltimore, Md. Received January 3, 1942

[Contribution of the Chemical Laboratory of the University of Texas]

The Nitrogen Compounds in Petroleum Distillates. XXIII. The Structure of a $C_{16}H_{25}N$ Base from California Petroleum[1]

By Billie Shive,[2,3] Stiles M. Roberts,[4] R. I. Mahan[5] and J. R. Bailey[6]

In Edeleanu kerosene extract from California petroleum[7] there occurs in relatively large amounts a $C_{16}H_{25}N$ base which was first isolated by Thompson and Bailey[8] and for which several provisional structures have been proposed.[8,9,10] It has now been shown that the base is 2-(2,2,6-trimethylcyclohexyl)-4,6-dimethylpyridine (I).



I

Earlier positive contributions to the structure indicated that the compound contained a pyridine nucleus with two methyl groups and a C_9H_{17}-alicyclic radical as substituents in positions 2, 4 and 6, the exact location of the individual groups being indefinite.

The present investigations deal both with the chemical behavior of the hydrogenated product of the $C_{16}H_{25}N$ base and with the ozonization of the original base. Approximately 48% of the hydrogenation product solidified and melted at 60.5° after purification, while 52% of the product is a liquid, the two compounds evidently being geometrical isomers. Ring cleavage and removal of the nitrogen atom was achieved by the method of von Braun,[11] by which benzoylpiperidine may be converted to pentamethylene dibromide. The steps involved in this degradation are

$$C_{16}H_{25}N \xrightarrow[\text{Raney nickel}]{H_2} C_{16}H_{31}N \xrightarrow[\text{anhydrous pyridine}]{\text{Benzoylation in}}$$

$$C_{16}H_{30}NCO(C_6H_5) \xrightarrow{PBr_5} C_{16}H_{30}NCBr_2(C_6H_5) \xrightarrow[\text{in vacuum}]{\text{Distillation}}$$

$$C_{16}H_{30}Br_2 \text{ (II) and } C_6H_5CN$$

The dibromide (II), obtained by this method, was converted into an olefin, $C_{16}H_{28}$ (III), by treatment with methyl alcoholic potassium hydroxide. In conformity with formula (I) for the $C_{16}H_{25}N$ base, the structure of (III) should be $C_9H_{17}CH{=}CH{-}CH(CH_3){-}CH{=}CH{-}CH_3$. Complete analysis established the existence of two double bonds and a cyclic structure within

---

(1) From Ph.D. theses of R. I. Mahan (1938), Stiles M. Roberts (1939), and Billie Shive (1941).

(2) University of Texas Research Institute Research Assistant (1941).

(3) Present address: Chemistry Department, University of Illinois, Urbana, Illinois.

(4) Present address: Research Laboratory, Texas Company, Beacon, N. Y.

(5) Present address: Union Oil Company, Wilmington, California.

(6) The experimental work on which this paper is based was completed before the death of Professor Bailey.

(7) The authors are indebted to the Union Oil Company for donation of large supplies of petroleum bases.

(8) Thompson and Bailey, This Journal, **53**, 1002 (1931).

(9) Armendt and Bailey, *ibid.*, **55**, 4145 (1933).

(10) Lackey and Bailey, *ibid.*, **56**, 2741 (1934).

(11) von Braun, *Ber.*, **37**, 3210 (1904); **38**, 2339 (1905).