36 g. of acid is collected at 102–104° (0.1 mm.), m.p. 57–62°. The products from four hydrogenations are combined and recrystallized together from petroleum ether. After several recrystallizations the higher melting isomer is isolated: m.p. 76–77°; neutral equivalent 182.2; **amide**, m.p. 123.8–124.2; **anilide**, m.p. 163.8–164.1° (15–20 g. from 149 g. mixture). From the first mother liquor by repeated fractional crystallization is obtained the low melting isomer (about 18 g.), **homoisocamphenilanic acid (VI)**, m.p. 56–57°, neutral equivalent 182; **amide**, m.p. 115.5–115.7°; **anilide**, m.p. 175.8–176.4°, mixed melting points of the acid and its derivatives with those obtained from the acid (VI) derived from the OXO aldehyde show no depression.

Anal. Amide of higher melting isomer (XV). Calcd. for $C_{11}H_{19}ON$: N, 7.71. Found: N, 7.72. Anilide of higher melting isomer (XV). Calcd. for $C_{17}H_{23}ON$: N, 5.44. Found: N, 5.44.

Reduction of the Isomeric Acids (VI), (XV) to the Alcohols.—The reduction is carried out on both acids with lithium aluminum hydride according to the procedure of Nystrom and Brown.[17] From 9.1 g. of acid (VI) and 3.7 g. of lithium aluminum hydride is obtained 7.3 g. of alcohol, homoisocamphenilanol, b.p. 122–123° (9 mm.), $n^{20}D$ 1.4885, d^{20}_{20} 0.9742; ***p*-nitrobenzoate**, m.p. 111.2–111.3°; **3,5-dinitrobenzoate**, m.p. 80.0–80.5°; ***α*-naphthylamine addition compound**[18] of latter, m.p. 129.5–130.5°.

Anal. *p*-Nitrobenzoate. Calcd. for $C_{18}H_{23}NO_4$: C, 68.18; H, 7.25; N, 4.42. Found: C, 68.46; H, 7.22; N, 4.49. 3,5-Dinitrobenzoate. Calcd. for $C_{18}H_{22}N_2O_6$: C, 59.7; H, 6.12; N, 7.74. Found: C, 60.06; H, 6.06; N, 7.76. 3,5-Dinitrobenzoate·*α*-naphthylamine addition compound. Calcd. for $C_{28}H_{31}N_3O_6$: C, 66.5; H, 6.16; N, 8.31. Found: C, 66.6; H, 6.26; N, 8.25.

From 9.1 g. of the higher melting isomeric acid (XV) in the same way are obtained 6.7 g. of alcohol, b.p. 139–140° (22 mm.), $n^{20}D$ 1.4883, d^{20}_{20} 0.9767; ***p*-nitrobenzoate**, m.p. 103.1–103.4°; **3,5-dinitrobenzoate**, m.p. 88.0–88.2°; ***α*-naphthylamine addition compound** of latter, m.p. 140.3–140.8°.

Anal. *p*-Nitrobenzoate. Calcd. for $C_{18}H_{23}NO_4$: C, 68.18; H, 7.25; N, 4.42. Found: C, 68.32; H, 7.37; N, 4.51. 3,5-Dinitrobenzoate. Calcd. for $C_{18}H_{22}N_2O_6$: C, 59.7; H, 6.12; N, 7.74. Found: C, 59.5; H, 6.13; N, 7.95. *α*-Naphthylamine addition compound. Calcd. for $C_{28}H_{31}N_3O_6$: C, 66.5; H, 6.16; N, 8.31. Found: C, 66.6; H, 6.10; N, 8.36.

Reduction of 8-Camphenecarbinol (XIII).—Hydrogenation of 27.6 g. of the carbinol (XIII), 120 g. of ethanol and 8 g. of Raney nickel at 160–170°, 1–1.25 hours with 120–150 atm. gives on distillation a 24-g. mixture of the isomeric alcohols, b.p. 134–135° (18 mm.). The ***p*-nitrobenzoate**, **3,5-dinitrobenzoate** and ***α*-naphthylamine addition compound** melt as follows: 107–108° (after three recrystallizations); 82–83° (after five recrystallizations) and 134–135° (after three recrystallizations), respectively. All these melting points are intermediate between those of the derivatives made above from the pure isomers.

Acknowledgment.—We are indebted to Mr. C. W. Nash and his co-workers for the microanalyses and to Mr. Harold Klenk for the preparation and purification of a few of the derivatives.

PHILADELPHIA, PENNA. RECEIVED OCTOBER 3, 1951

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[17] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

[18] P. Sutter, *Helv. Chim. Acta*, **21**, 1266 (1938).

NOTES

The Dehalogenation Reaction. III. Dechlorination of 1,2-Dichloroethane and 1,1,2-Trichloroethane[1]

BY TURNER ALFREY, JR.,[2] HOWARD C. HAAS AND CHARLES W. LEWIS

RECEIVED JANUARY 22, 1952

In the course of an investigation of the dechlorination by zinc of the copolymers vinyl acetate/*trans*-dichloroethylene and vinyl acetate/trichloroethylene, it became apparent that a better understanding of the reaction could be obtained if a study were made of the prototype molecules 1,2-dichloroethane and 1,1,2-trichloroethane. In this way, the interference of side reactions such as polymer degradation could be avoided. It was found however, that after 44 days at 101.5° a 0.048 *M* solution of dichloroethane in dioxane did not react with zinc dust as evidenced by the absence of measurable amounts of chloride ion.

Experiments were then performed with 0.033, 0.064 and 0.107 *M* solutions of 1,1,2-trichloroethane in dioxane in the presence of 1.000 and 2.000 g. of zinc dust/25 ml. of solution. In every case an induction period was observed. This was followed by a linear rise in the concentration of zinc chloride up to about 40% conversion, and finally an asymptotic approach to 100% conversion, (*i.e.*, one mole of zinc chloride formed per initial mole of trichloroethane). In all cases the reactions were virtually complete (> 98%) after 3.5 days. The induction periods ranged from 4 to 7.5 hours when 2 g. of zinc was used, and from 9 to 10.5 hours when 1 g. of zinc was used. The linear conversion rates varied from 2.4%/hr. to 6.4%/hr. in a rather random fashion, and no reliable correlation could be established between these rates and the amounts of reactants used.

The induction period can be most readily understood if it is assumed that the zinc chloride produced is capable of promoting the reaction in some manner. This assumption is in accord with the observation that a 0.064 *M* solution of trichloroethane containing 1.000 g. Zn/25 ml. underwent complete dechlorination in less than 24 hours without an observable induction period in the presence of 0.025 *M* zinc chloride. However the scatter of the experimental points for an individual run was very great, so that it could not even be established if the initial rate was linear, as was observed in the previous runs. Nevertheless, it was quite evident that the time required to achieve a given conversion had been materially reduced. It is felt that the qualitative aspects of this observation should be of interest in the field of organic synthesis.

When the dechlorination of dichloroethane was

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[1] Taken in part from the Ph.D. thesis of Charles W. Lewis, Polytechnic Institute of Brooklyn, May, 1950.

[2] Dow Chemical Company, Midland, Michigan.

attempted in the presence of zinc chloride, a slow reaction was found to take place. In Table I are tabulated the data for the dechlorination of 0.203 *M* dichloroethane in the presence of different amounts of zinc and zinc chloride.

TABLE I

DECHLORINATION OF 0.203 *M* DICHLOROETHANE, 1.000 G. Zn DUST PER 25 ML. SOLUTION

$ZnCl_2$ (moles/l.)						
0.0035	0.0070	0.0142	0.0283	0.0562	0.1122	
conversion, %						Hr.
0.44	0.34	0.61	0.34	0.10	0.00	66
1.11	1.35	1.22	0.59	0.44	0.24	138
3.19	2.30	1.71	1.93	2.42	2.03	282
4.91	4.92	3.65	4.14	4.85	3.92	426
9.71	8.03	8.69	8.96	8.49	8.20	738

$ZnCl_2$ (moles/l.)		
0.0135	0.0538	
conversion, %		Hr.
0.51	0.19	69
1.29	0.68	141
2.80	2.49	258
4.95	..	402
6.99	7.09	575

DECHLORINATION OF 0.203 *M* DICHLOROETHANE, 0.0269 *M* ZINC CHLORIDE

Zn (g./25 ml. soln.)		
0.500	2.000	
conversion, %		Hr.
0.25	0.57	69
0.52	1.48	141
1.35	..	258
2.61	7.04	402
4.24	11.23	575

The initial rate of reaction appears to have a maximum value in the vicinity of 0.014 *M* zinc chloride. However the effect of the initial zinc chloride concentration on the over-all reaction is surprisingly small.

Experimental

1,2-Dichloroethane (Eastman Kodak Co.) was purified by fractional distillation through a ten-inch glass-bead column; b.p. 83.3–83.6°.

1,1,2-Trichloroethane (Eastman Kodak Co.) was purified by fractional distillation through a ten-inch glass-bead column; b.p. 113.2–113.3°.

Dioxane was purified by the method described by Fieser[3]

C.P. zinc dust was purified by the method of Marvel, Sample and Roy.[4]

Zinc Chloride Solution.—Three or four sticks of C.P. zinc chloride, 5 g. of zinc dust and 400 ml. of dioxane were refluxed for 20 hr. The hot solution was filtered through Pyrex glass wool into a 1-liter erlenmeyer flask which was then stoppered and allowed to cool to room temperature. The supernatant liquid was quickly decanted from the crystalline material that separated. The zinc chloride was recrystallized twice using 400 ml. of dioxane each time and avoiding undue exposure to atmospheric moisture. It was then dissolved in hot dioxane and transferred to a glass-stoppered bottle. The saturated solution that resulted upon cooling was used in all subsequent work by suitable dilution with dioxane.

All dechlorinations were carried out in sealed 25 × 200 mm. Pyrex test-tubes. Details of the method are described in the first paper of this series.[5] In the experiment in which 0.1122 *M* zinc chloride had been used (Table I), it was observed that significant amounts of the salt had been adsorbed on the zinc in the 426- and 738-hr. samples. It was therefore necessary to titrate the entire contents of the tube rather than an aliquot of the supernatant liquid. It was found by a separate experiment that suspended zinc dust does not interfere with the chloride determination. The anticipated fading of the end-point took place so slowly that no difficulty was encountered. In the case of the 738-hr. sample, the concentration of zinc chloride in solution was actually lower than the initial concentration.

Acknowledgment.—This work was carried out as part of a fundamental research project on copolymerization sponsored by the Office of Naval Research at the Polytechnic Institute of Brooklyn.

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The Willgerodt Reaction in the Heterocyclic Series. IV. The Furan Series[1]

BY JOSEPH A. BLANCHETTE AND ELLIS V. BROWN

RECEIVED NOVEMBER 29, 1951

The results of the Willgerodt reaction in the thiophene series, which have been previously reported,[2] made it of considerable interest to investigate the reaction in the furan series. As there have been no reports of successful Willgerodt reactions in the furan series, it was considered advisable to determine whether the furan ring was stable when committed to the conditions of this reaction. When 2-furylacetic acid was treated with ammonium polysulfide at 150°, none of the acid was recovered. When the temperature was lowered to 100° then 65–70% of the acid was recovered. This indicated that the furan ring was less stable than the thiophene ring under the conditions of the Willgerodt reaction and that the temperature must be lowered in the investigation of furan compounds. This conclusion was substantiated by subjecting 2,5-dimethyl-3-furyl methyl ketone, 2-methyl-5-furyl methyl ketone, 2-vinylfuran, furfural, 2-bromo-5-furyl methyl ketone, furfuralacetone and 2-furyl methyl ketone to the conditions of the Willgerodt reaction at 150°. No product was isolated from these reaction mixtures. Direct hydrolysis of the reaction mixtures yielded none of the expected acids. When the reaction temperature was lowered to 100°, the corresponding amides were isolated from the runs on 2,5-dimethyl-3-furyl methyl ketone, 2-methyl-5-furyl methyl ketone and furfural. Alkaline hydrolysis gave the corresponding acids.

Experimental

Furan Compounds.—The furan compounds used in this study were prepared by standard methods given in the literature. Furan and 2-methylfuran were obtained through the courtesy of E. I. du Pont de Nemours and Company. 2,5-Dimethylfuran was obtained from Union Carbide and Carbon Corporation, Chemicals Division.

2,5-Dimethyl-3-furylacetamide. Method A.—2,5-Dimethyl-3-furyl methyl ketone (10 g.), 25 g. of sulfur, 20 ml. of concentrated ammonium hydroxide and 30 ml. of dioxane were sealed in a glass Carius tube and heated for 11 to 12 hours at 100°. The contents of the tube were evaporated to dryness and the residue was extracted with 100 ml. of boiling water. The water extract was treated with Norit and extracted with 50 ml. of ether in three portions. The ether was removed under reduced pressure and the residual oil

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(3) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., p. 368.

(4) C. S. Marvel, J. H. Sample and M. F. Roy, THIS JOURNAL, **61**, 3241 (1939).

(5) T. Alfrey, H. C. Haas and C. W. Lewis, *ibid.*, **73**, 2851 (1951).

(1) In part from the Ph.D. thesis of J. A. Blanchette, Fordham University, 1951.

(2) J. A. Blanchette and E. V. Brown, THIS JOURNAL, **72**, 3414 (1950); *ibid.*, **73**, 2779 (1951).

TABLE I

WILLGERODT REACTION WITH FURAN COMPOUNDS

Furan compound	Yield,[d] % Temp. A[a]	Yield,[d] % 100° B	Yield,[d] % 110° B	Amide m.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Acid m.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2,5-Dimethyl-3-furyl methyl ketone[b,c]	23	18	27	82–83	9.15	9.17	94–95	62.34	62.45	6.49	6.39
2-Methyl-5-furyl methyl ketone	10	10	10	112–114	11.2	11.07	57–58	60.00	60.34	5.71	5.44
Furfural	15	26	20	141–142	12.61	12.77	131–133				

[a] See experimental for details of Methods A and B. [b] Hurd and Wilkinson, THIS JOURNAL, **70**, 739 (1948). [c] At 130° a 29% yield was obtained by Method B. [d] At 150° neither Method A nor Method B gave any product with these three substances.

soon solidified on cooling. Recrystallization of this material from petroleum ether (60–80°) gave 2.5 g. (23%) of 2,5-dimethyl-3-furylacetamide, m.p. 82–83°.

Method B substitutes 50 g. of yellow ammonium polysulfide, 7 g. of sulfur and 60 ml. of dioxane for the above reagents.

2-Methyl-5-furylacetamide.—This compound was obtained from 2-methyl-5-furyl methyl ketone in the same manner by Methods A and B. The product was isolated from the reaction mixture by the procedure described for 2,5-dimethyl-3-furylacetamide.

2-Furoamide.—This compound was obtained from furfural in the same manner by Methods A and B. The crude amide was recrystallized from benzene or water and a mixed melting point with an authentic sample[3] of furoamide showed no depression.

Hydrolysis of the Amides.—These amides were hydrolyzed to the corresponding acids in the usual manner by refluxing with either 12% aqueous potassium hydroxide or 10% aqueous barium hydroxide. The solutions were acidified and extracted with ether. Removal of the ether gave the crude acids which were recrystallized from petroleum ether (60–80°).

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(3) R. Paul, *Bull. soc. chim.*, [5] **4**, 1115 (1937).

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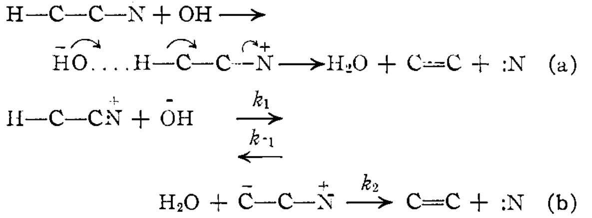
Mechanism of the Hofmann Elimination[1]

BY W. VON E. DOERING AND HERBERT MEISLICH

There are two variations in the current hypothesis of the mechanism of the second order elimination reaction of quaternary ammonium hydroxides. These variations, discussed for example by Dhar, *et al.*,[2] relate to the one- or two-step nature of the reaction; that is, to whether a single operationally significant transition state (a) or an intermediate bounded by two transition states (b) is involved. In the related second order elimination of bromides, Skell and Hauser[3] have shown that 2-phenylethyl bromide, recovered from an incomplete reaction in deuteroethanol, contains no deuterium. It is concluded that path (b) is invalid, this conclusion being justified, at least in terms of the operation of deuterium exchange only when k_{-1} be roughly equal to or greater than k_2, a requirement for which no experimental support was presented. In the face of the actual isolation by Wittig and Wetterling[4] of trimethylammoniummethylide ($(CH_3)_3\overset{+}{N}-\overset{-}{C}H_2$), extension of the Skell–Hauser conclusion to the Hofmann elimination is *a priori* questionable.

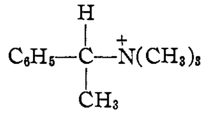


$$H-C-C-\overset{+}{N} + \overset{-}{O}H \longrightarrow$$

$$\overset{-}{H}O\ldots H-C-C-\overset{+}{N} \longrightarrow H_2O + C{=}C + :N \quad (a)$$

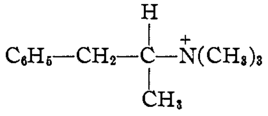
$$H-C-C\overset{+}{N} + \overset{-}{O}H \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_2O + \overset{-}{C}-C-\overset{+}{N} \xrightarrow{k_2} C{=}C + :N \quad (b)$$

The behavior of optically active trimethyl-α-phenylethyl-(I) and trimethyl-β-phenylisopropyl-(II) ammonium ions is pertinent to the one- or two-step nature of the Hofmann elimination. When (+)I and (−)II iodides are heated at 81° for 6720 min. in 0.15 *N* sodium hydroxide, I is recovered quantitatively and unracemized,[5] whereas II has, in part, undergone elimination to 1-phenylpropene, the remainder being recovered unracemized also.



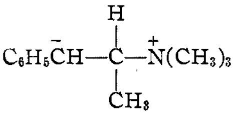
$$C_6H_5-\underset{CH_3}{\overset{H}{C}}-\overset{+}{N}(CH_3)_3$$

I



$$C_6H_5-CH_2-\underset{CH_3}{\overset{H}{C}}-\overset{+}{N}(CH_3)_3$$

II



$$C_6H_5\overset{-}{C}H-\underset{CH_3}{\overset{H}{C}}-\overset{+}{N}(CH_3)_3$$

II″

On the reasonable conditions, first, that the tertiary hydrogen in I, activated by phenyl and adjacent ammonium ions, be more acidic than the tertiary hydrogen in II, activated only by an adjacent ammonium ion, and that the latter, in turn, be more acidic than the methylene hydrogen in II, activated by phenyl and an ammonium ion one carbon removed, and second, that the carbanion or xylides derived from I and II by removal of tertiary hydrogen (I′ and II′, respectively) racemize more rapidly than they react with protons, it is concluded that neither I′ nor II′ are formed, and consequentially, that II″ is not formed either. In terms, therefore, of the conditions for the operation of racemization, the Hofmann elimination of II proceeds by the one-step path (a).

Experimental

Attempted Racemization of Trimethyl-α-phenylethylammonium Iodide (I).—(+)I, prepared according to the procedure of Norcross and Openshaw[6] in 50% of the theoretical yield, was recrystallized from ethanol–ether as colorless prisms, m.p. 156–157.5° (reported[5] m. p. 157–157.5°). A solution of 0.291 g. (10^{-3} mole) of I in 5 cc. of 0.15 *N* sodium hydroxide with $[\alpha]_D + 11.8$ was heated in a sealed am-

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(1) From a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

(2) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

(3) P. S. Skell and C. R. Hauser, THIS JOURNAL, **67**, 1661 (1945).

(4) G. Wittig and M. H. Wetterling, *Ann.*, **557**, 193 (1947).

(5) It has already been observed that I is not racemized by sodium ethoxide: E. Biilmann, K. A. Jensen and H. B. Jensen, *Bull. soc. chim.*, [5] **3**, 2925 (1936).

(6) G. Norcross and H. T. Openshaw, *J. Chem. Soc.*, 1174 (1949).

poule at 7° for 6720 min. without change in the specific rotation or production of trimethylamine.

Attempted Racemization of Trimethyl-β-phenylisopropylammonium Iodide (II).—(–)II, prepared by methylation of β-phenylisopropylamine with methyl iodide and aqueous sodium carbonate, was recrystallized from alcohol as colorless needles, m.p. 202–203° (reported[7] m.p. 204–205°). A solution of 0.305 g. (10^{-3} mole) of II in 7 cc. of 0.15 *N* sodium hydroxide with $[\alpha]_D$ –3.9 was heated at 81° for 6720 min. The reaction mixture, smelling strongly ammoniacal, contained an oil which was extracted with ether. The residue from the dried, concentrated ether solution was dissolved in 0.5 cc. of carbon tetrachloride and treated with bromine until permanently colored. Evaporation of the solvent left a solid which was crystallized from ethanol to give 1-phenyl-1,2-dibromopropane, m.p. 65–66.5° (reported[8] m.p. 65–66°), showing no depression of m.p. on admixture with authentic material.

Concentration of the aqueous portion of the reaction mixture gave solid material which was extracted with chloroform. Evaporation of the chloroform left crystalline starting material, $[\alpha]_D$ –3.9 (*c* 4.4, 0.15 *N* sodium hydroxide).

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(7) K. Freudenberg and F. Nikolai, *Ann.*, **510**, 223 (1934).

(8) W. H. Perkin, *J. Chem. Soc.*, **32**, 660 (1877).

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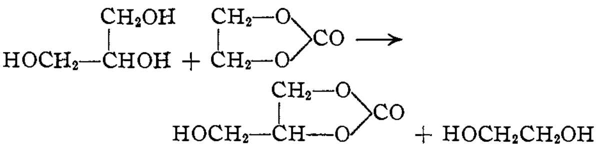
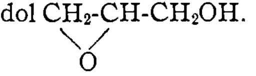
Thermal Decomposition of Glyceryl Carbonates

BY HERMAN A. BRUSON AND THOMAS W. RIENER

RECEIVED OCTOBER 6, 1951

While attempting to prepare glyceryl monocarbonate (I) by heating equimolar proportions of glycerol and ethylene carbonate to effect an ester exchange it was noticed that after the ethylene


I

glycol had been removed by vacuum distillation there remained in the still-pot a thick, balsam-like, resinous material which, upon further distillation *in vacuo*, decomposed almost entirely to yield glycidol  $CH_2\text{-}CH\text{-}CH_2OH$ (epoxide O).

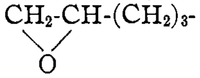
This unexpected reaction affords a convenient method for preparing glycidol in 60–85% yields directly from glycerol.

When an open chain dialkyl carbonate such as for example diethyl carbonate was used in place of the cyclic ethylene carbonate as above (1:1 mole ratio), the alcoholysis did not readily take place without the use of a catalyst because of the immiscibility of diethyl carbonate with glycerol at the boiling point of the mixture. The use of an alkaline catalyst, however, such as sodium or sodium methoxide together with rapid stirring caused a more rapid alcoholysis of the mixture, with formation of a glyceryl carbonate. This product, however, upon further distillation *in vacuo*, gave considerable non-distillable resin and only a very mediocre yield (7%) of glycidol.

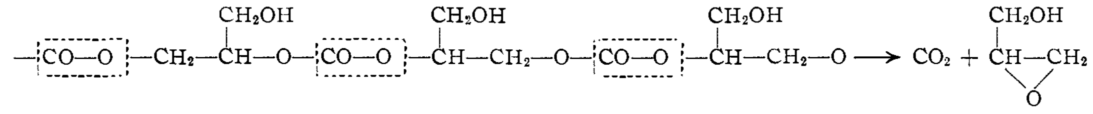
Since it was possible that the alkaline catalyst might exert a deleterious influence upon the yield of glycidol in this decomposition, an attempt was made to prepare glyceryl carbonate by heating glycerol with diphenyl carbonate in the absence of a catalyst, and distilling off under reduced pressure the phenol formed. This reaction is reported[1] to give a crystalline glyceryl tricarbonate $C_9H_{10}O_9$ melting at 148°, when the mole ratio of glycerol to the diphenyl carbonate used is 2:3; and to give liquid or resinous glyceryl carbonates containing free hydroxyl groups when an excess of glycerol is employed. We have confirmed this work and isolated the crystalline glyceryl tricarbonate in pure form. This compound when subjected to vacuum distillation yielded no glycidol but decomposed instead to form a resinous material together with traces of acrolein, and gases which did not condense in a Dry Ice trap at –80°.

Upon heating glycerol with diphenyl carbonate (1:1 mole ratio) and distilling off under reduced pressure the phenol formed, a still-pot residue was obtained which upon further distillation *in vacuo* gave a 60% yield of glycidol.

It is apparent that no glycidol is formed (or can be expected) if all three hydroxyl groups of the glycerol are esterified with carbonate radicals. Obviously, one primary hydroxyl group must be free if glycidol is to be obtained. Ethylene carbonate is superior to diphenyl carbonate because a smaller weight of it is required per mole of glycerol and the reaction is more rapid, giving less opportunity for side reactions and in general a higher yield.

Application of the reaction with ethylene carbonate to glycerol derivatives such as glycerol-mono-α-chlorohydrin and glyceryl-α-ethyl ether did not yield the respective epichlorhydrin or glycidyl ethyl ether. Likewise, an attempt to convert 1,2,6-hexanetriol into the epoxide  $CH_2\text{-}CH\text{-}(CH_2)_3\text{-}CH_2OH$ by heating with ethylene carbonate was unsuccessful.

Since one would expect monomeric glyceryl monocarbonate (I) to be a vacuum-distillable liquid that on prolonged heating might yield a polyester resin, and since the viscous character of the still-pot residue which is obtained in the transesterification of glycerol with ethylene carbonate (1:1 mole ratio) is that of a polymeric resinous material; it is believed that the reaction involves the formation of a poly-(glyceryl-1,2-dicarbonate) which subsequently loses carbon dioxide on further heating with formation of glycidol as



Experimental

Raw Materials.—The glycerol used was anhydrous, vacuum-distilled C.P. grade. The ethylene carbonate was

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(1) German Patent 252,758 (1912), Chem. Fabrik Dr. Rudolf Scheuble and Dr. A. Hochstetter; *Chem. Zentr.*, **83**, II, 1756 (1912).

prepared by heating ethylene chlorohydrin with sodium bicarbonate,[2] and was distilled twice in vacuum before use. It analyzed better than 99% pure.

Preparation of Glycidol.—In a 200-cc. flask attached to an 8″ long packed column arranged for vacuum distillation, a mixture of 92 g. of glycerol (1 mole) and 95 g. of ethylene carbonate (1.08 moles) was heated gradually during the course of 90 minutes to 145° under 75 mm. vacuum; then during 75 minutes at 135–155° under 34–36 mm. vacuum, and finally during 90 minutes at 155–240° under 10–15 mm. vacuum. In the early stages of the heating, ethylene glycol (60 g.) came over in the receiver until the vapor temperature at 11 mm. was 80°. The thick liquid residue during the final heating at 155–240° in vacuum (5–10 mm.) gradually decomposed to give a colorless liquid which distilled over below 60° at 5 mm. Yield of crude glycidol was 64 g. (86%). Upon redistillation, this boiled at 53–55° (10 mm.) and furnished 47 g. (63.5%) of pure product, $n^{25}\text{D}$ 1.4346.

It was identified by means of its phenylurethan[3] derivative, m.p. 60–61° and by treatment with piperidine[3] to give 1-piperidinopropane-diol-2,3 melting at 83°.

In contrast to the above, a stirred mixture of 236 g. of diethyl carbonate (2 moles), 184 g. of glycerol (2 moles) and 1 g. of sodium methoxide when heated at 90–100° under a short column until no more ethyl alcohol distilled over, gave a sirupy residue, which upon distillation *in vacuo* yielded 16 g. of distillate, b. p. 70–80° (13–16 mm), from which 10 g. of glycidol (7% yield) could be recovered upon redistillation (b.p. 62–64° (10–11 mm.)).

Glyceryl Tricarbonate.[1]—A mixture of 100 g. of glycerol (1.087 moles) and 350 g. of diphenyl carbonate (1.63 moles) was heated *in vacuo* (6–8 mm.) at 135–45° under an 8″ column arranged for vacuum distillation. During a heating period of 9.5 hours, 267 g. of phenol (2.84 moles) distilled over into the receiver. The still-pot residue was a sirup which, in part, gradually solidified after standing for several days. It was mixed at room temperature with an equal volume of glacial acetic acid which dissolved most of the impurities, leaving behind 77 g. of crystalline product. After recrystallization from hot glacial acetic acid, it formed colorless crystals, m.p. 146–148°.

A 40-g. sample of this crystalline glyceryl tricarbonate was subjected to vacuum distillation as described above for the preparation of glycidol. After heating at 230–240° at 7 mm. for 1.5 hours, it showed no decomposition. At 300–320° decomposition set in. An acrid smelling liquid (1 g.) containing acrolein collected in the Dry Ice trap, and 7 g. of distillate in the vacuum receiver; neither of which contained glycidol.

Glycidol from Glyceryl Dicarbonate.—A mixture of 149 g. of diphenyl carbonate (0.697 mole) and 64.3 g. of glycerol (0.7 mole) was heated at 135–140° in vacuum at 5–7 mm. for five hours during which time 129 g. of phenol or 98.5% of the theoretical amount, distilled over into the receiver. The viscous still-pot residue was then heated at 185–190° for 3 hours at 5–7 mm. vacuum, yielding 35.5 g. of colorless liquid distillate. Upon redistillation this gave 31 g. (60% yield) of glycidol, b.p. 55–57° (10 mm.), identified by means of its piperidine derivative.[3]

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[2] G. Steimmig and M. Wittwer, U. S. Patent 1,907,891 (1933).

[3] T. H. Rider and A. J. Hill, This Journal, **52**, 1527, 1530 (1930).

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Precision Actinometry at Low Light Intensities with Malachite Green Leucocyanide

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The quantitative measurement of low intensities of ultraviolet light, less than 10^{13} quanta/sec., offers many experimental difficulties. Calibrated thermopile or phototube systems of high sensitivity with which such measurements can be made are not available in many laboratories and recourse to chemical actinometry must be made. Uranyl oxalate solutions are used universally for the measurement of light intensities.[1] However, this actinometer is not ideally suited for the measurement of very low intensities since exposure times necessary to obtain the desired accuracy in these experiments are very great. The use of monochloroacetic acid photolysis[2] as an actinometer is restricted to experiments utilizing 2537 Å. radiation. It is generally unsatisfactory because of the large temperature coefficient of the quantum yield and the dark reaction for which correction must be made in the long experiments necessary at low intensities.

Harris, Kaminsky and Simard have made an important contribution to the problem of measurement of very small light intensities.[3] These authors reported that the photolysis of malachite green leucocyanide, *p,p′*-didimethylaminotriphenylacetonitrile, in ethyl alcohol solution resulted in the formation of an intensely colored dye with a quantum efficiency of 100%. The quantum yield of 1.00 was independent of the initial leucocyanide concentration, the intensity of the absorbed light, the temperature of the solution, and the wave length of absorbed light in the region 2480 to 3300 Å. The colored ion formed in the reaction, presumably $[(CH_3)_2NC_6H_4]_2C(C_6H_5)^+$, was found to be stable in acidified alcohol and identical to the colored ion of malachite green salts in the same solvent. The great sensitivity of this proposed actinometer makes it particularly suited for the measurement of very low light intensities. However, two important factors have prevented its general use. (1) No completely satisfactory method of preparation and purification of the leucocyanide has been available. (2) The reliability of the quantum yield determinations of Harris, *et al.*, has been questioned. These authors reported 1.07 ± 0.06 for the quantum yield of chloride ion formation in monochloroacetic acid photolysis[3]; this value was obtained by a comparison method using malachite green leucocyanide photolysis as a reference standard. A value of 1.05 for the quantum yield of monochloroacetic acid photolysis was reported earlier by Rudberg.[4] Recent redeterminations of this quantum yield indicate that the correct value is 0.32 at 25°.[2] These conflicting results make uncertain the accuracy of the quantum yields of malachite green leucocyanide photolysis reported by Harris, *et al.*[2,5] In the present report these two major limitations to the general use of the leucocyanide actinometer for measurement of low light intensities are eliminated. An improved method of preparation and purification of malachite green leucocyanide has been developed and is presented in this report. The quantum yield results of Harris and coworkers from photolysis of leucocyanide solutions have been confirmed by two independent methods.

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[1] W. G. Leighton and G. S. Forbes, This Journal, **52**, 3139 (1930); G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

[2] R. N. Smith, P. A. Leighton and W. G. Leighton, *ibid.*, **61**, 2299 (1939); L. B. Thomas, *ibid.*, **62**, 1879 (1940).

[3] L. Harris, J. Kaminsky and R. G. Simard, *ibid.*, **57**, 1151, 1154 (1935).

[4] E. Rudberg, *Z. Physik*, **24**, 247 (1924).

[5] W. A. Noyes, Jr., and P. A. Leighton, "Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 83.

In the first method a calibrated thermopile–galvanometer system was used to measure light intensities with an experimental procedure similar to that used by Harris, *et al.* In the second method the quantum yields of the uranyl oxalate actinometer and malachite green leucocyanide solutions were compared in the same beam of 3130 Å. radiation. The results of both methods indicate that at low light intensities the quantum yield of dye formation is 1.00 at all wave lengths employed. At intensities above about 3 × 10^{13} quanta/sec., incident on an area of about 0.3 sq. cm., an apparent quantum yield less than unity is found. (See the data of runs 13 and 14 of Table I and runs 1, 2 and 3 of Table II.) This appears to be due to an appreciable absorption of light by the product dye which is removed inefficiently from the solution near the front of the cell when the rate of dye formation is very great and stirring is inadequate. (In agreement with this interpretation it was found that an increased stirring rate causes an increase in the apparent quantum yield at high intensities. Compare the data of runs 14 and 15 of Table I.) Because of the strong absorption of the product dye in the ultraviolet the leucocyanide actinometer is unsatisfactory for the direct measurement of high intensities of ultraviolet light.

The present work has confirmed the malachite green leucocyanide photolysis results of Harris, Kaminsky and Simard.[3] It appears to the present authors that the only error in the work of Harris, *et al.*, was introduced in the comparison of the yields of leucocyanide and chloroacetic acid photolyses. It is hoped that this confirmation of the accuracy of the original work of Harris together with the method of preparation of the malachite green leucocyanide presented in this report will make possible a much wider use of leucocyanide photolysis as a precision actinometer for the measurement of very low light intensities.

Acknowledgment.—Grateful acknowledgment is made to the U. S. Public Health Service and to the Armed Forces Special Weapons Project, Washington, D. C., under whose joint sponsorship H. J. L. R.'s attendance at the Ohio State University was made possible.

Experimental

Preparation of Malachite Green Leucocyanide.[6]—The leucocyanide is prepared best using pure, anhydrous solvents and reagents. The method given will yield about 4 g. of the pure compound (56% of theoretical yield). (1) To a filtered 1% aqueous solution containing 9.3 g. of malachite green oxalate, add a cold, saturated aqueous solution containing 6 g. of potassium cyanide. Collect the precipitate, and wash with distilled water. (2) Dissolve the precipitate in cold 1% hydrochloric acid. Stir vigorously for one hour. Carefully neutralize the solution with cold 1% aqueous ammonia. Collect the precipitate, wash with distilled water and air dry. (3) Dissolve the crude product in 300 ml. of acetone, and filter the solution. Add 150 ml. of methanol acidified with several drops of glacial acetic acid. Remove rapidly 350 ml. of the mixture by distillation. Cool the remainder and, when crystallization is complete, filter and wash the crystals with 10 ml. of cold methanol. Save the filtrate. (4) Now employ reduced illumination (red safelight); dissolve about 2 g. of the crude product from (3) in 100 ml. of a 50% methanol–ethyl acetate solution. Add 30 ml. of methanol, 1 ml. of acetone, and several drops of glacial acetic acid. Remove about 105 ml. of the mixture rapidly by distillation. Cool the remaining solution and, when crystallization is complete, filter and wash the crystals with a small amount of methanol. Save the filtrates. (5) Repeat step (4) until a product sufficiently free from dye contamination is obtained. (The volume of the accumulated filtrates may be decreased by distillation, and more product may be recovered and reprocessed.) A product containing 0.001% dye and no trace of cyanide ion is obtained after five repetitions of step (4); m.p. 176–177°.

Anal. Calcd. for $C_{24}H_{25}N_3$: C, 81.09; H, 7.09; N, 11.82. Found[7]: C, 80.95, 81.10; H, 7.20, 6.99; N, 11.87, 11.69.

Quantum Yield Determinations. Method I.—The light source was a Hanovia type A burner (500 w.) operated with a current from a Nobitron (model E-200-3.3) d.c. regulated power supply. The desired wave length of the mercury arc spectrum was isolated with a Farrand (model 300 UV) quartz monochromator, and the light intensity was measured with an Eppley thermopile and galvanometer system calibrated with N. B. S. standard lamps. The procedures of photolysis and the calculation of quantum yields were carried out as described by Harris, *et al.*[3] Solutions of the leucocyanide were prepared in absolute ethanol rather than 95% ethanol used in most of the work of Harris. The absorption spectra of the leucocyanide and dye in the absolute ethanol solutions were essentially the same as those reported for the 95% ethanol solutions.[3] Photolyses were carried out in a Beckman quartz spectrophotometer cell (path length, 1.0 cm.). The photolyzed solution consisted of 3.80 ml. of leucocyanide in absolute ethanol to which was added 0.02 ml. of 0.3 *M* hydrochloric acid. This ratio of leucocyanide solution to acid solution was maintained in both Method I and II experiments. The cell containing the exposed solution following photolysis and a matched cell containing an initially identical but unexposed leucocyanide solution were placed in a Beckman (model DU) spectrophotometer; the optical density of the dye at 6200 Å. was determined using the unexposed solution as a blank. The 6200 Å. wave length chosen for concentration determinations was the maximum of a broad absorption band of the dye. The absorption coefficients of the dye formed on complete photolysis of dilute standard solutions of leucocyanide in ethanol (acidified as before) were the same in the visible as those of

TABLE I

QUANTUM YIELDS OF DYE FORMATION IN MALACHITE GREEN LEUCOCYANIDE PHOTOLYSIS IN ACIDIFIED ETHANOL AT ROOM TEMPERATURE

Number of run	Quanta per sec. $\times 10^{-13}$	Concn. of leucocyanide, *M*	Quantum yield of dye
	Wave length 2537 Å.		
1	0.44	3.9×10^{-4}	1.02
2	1.57	1.0×10^{-4}	1.00
3	1.53	1.0×10^{-3}	0.98
	Wave length 2654 Å.		
4	0.98	1.0×10^{-4}	1.03
5	1.20	1.0×10^{-3}	0.99
	Wave length 2804 Å.		
6	1.89	1.2×10^{-4}	0.99
	Wave length 3130 Å.		
7	0.0317	1.0×10^{-3}	0.98
8	.101	1.0×10^{-3}	1.01
9	.83	1.0×10^{-3}	0.95
10	.79	7.5×10^{-4}	1.00
11	.86	3.9×10^{-4}	1.00
12	2.89	1.0×10^{-3}	1.03
13	7.54	1.0×10^{-3}	0.94
14	84.6	1.0×10^{-3}	0.70
15[a]	83.7	1.0×10^{-3}	0.81

[a] Rate of nitrogen bubbling was increased in this experiment.

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[6] Based on the work of A. Hantzsch and G. Osswald, *Ber.*, **33**, 307 (1900), and J. Lifschitz and Ch. L. Joffé, *Z. physik. Chem.*, **97**, 426 (1921).

[7] Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

malachite green oxalate in the acidified ethanol. The absorption of the dye solutions at 6200 Å. followed Beer's law within the error of the determinations for solutions in which the dye concentration was in the range of 0.1 to 10 × 10^{-6} *M*. The molecular extinction coefficient, ϵ, at 6200 Å. for the dye in the acidified ethanol solutions (0.02 ml. of 0.3 *M* hydrochloric acid to 3.80 ml. of the leucocyanide in absolute ethanol solution) is 9.49 × 10^4 (an average value), where $\log_{10} (I_0/I) = \epsilon cl$. The time of the exposure was regulated so that the final dye concentration in most experiments was about 1 × 10^{-6} *M*. Exposure times of about 3 and 100 minutes were required for runs at light intensities providing 1 × 10^{13} and 3 × 10^{11} quanta/sec., respectively. Stirring was accomplished during photolysis by bubbling through the solution nitrogen gas saturated with ethanol. All of the experiments were carried out at room temperature (20–25°). The results are summarized in Table I.

Method II.—A ratio of quantum yields of uranyl oxalate and malachite green leucocyanide photolyses at 3130 Å. was determined at room temperature. An optical train providing pure, high intensity 3130 Å. radiation[8] followed the light source described in Method I. A collimated beam of light about 35 mm. in diameter and of constant intensity (±1%) was incident on the cell face. The photolysis of both solutions was effected in a quartz cell with 4.0-cm. path length. The cell contained 55 ml. of solution which was stirred magnetically during exposure. Concentrations of both solutions were such that essentially complete absorption of the light occurred. The uranyl oxalate solution (0.005 *M* in uranyl nitrate and 0.025 *M* in oxalic acid) was photolysed at full intensity. Filters with measured transmissions were placed in the light path to lower the intensity used in the leucocyanide photolyses, since the previous results indicated that absorption of light by product dye may be serious at high light intensities because of inadequate mixing. The concentration of leucocyanide solutions was 6.0 × 10^{-4} *M*. To 55.0 ml. of the alcoholic solution 0.29 ml. of 0.3 *M* hydrochloric acid was added before photolysis. Final dye concentration was about 1 × 10^{-6} *M* in each experiment. The data are presented in Table II.

TABLE II

COMPARISON OF QUANTUM YIELDS OF URANYL OXALATE AND MALACHITE GREEN LEUCOCYANIDE ACTINOMETERS AT 3130 Å. AND ROOM TEMPERATURE

Number of run	(1) Filter % *trans.*	(2) Dye mol. formed/sec. × 10^{-15}	(3) Calcd. dye mol. formed/sec. × 10^{-15} for full intensity	(4) ($H_2C_2O_4$ mol. decompd./sec.[a])/(dye mol. formed/sec.)
1	38.6	1.21	3.14	0.72
2	16.2	0.584	3.60	,63
3	8.81	.338	3.84	.59
4	3.32	.137	4.12	.55
5	1.99	.0820	4.12	.55

[a] Photolysis of uranyl oxalate solution at full intensity gave an average value of 2.27 × 10^{15} molecules of oxalic acid decomposed/sec.

The exposure times necessary in these experiments were about 10 hr. for the uranyl oxalate actinometer (10% oxalate decomposition) and from 19 to 371 sec. for the runs 1 and 5, respectively, in Table II. The data of column (2) of Table II are the measured rates of formation of dye in light decreased from full intensity by the filter of transmission given in column (1). The data of column (3) are calculated rates of dye formation for full intensity, (100) (rate in column (2))/(transmission in column (1)). Data of column (4) are the ratios of molecules of oxalic acid decomposed/sec. at full intensity, 2.27 × 10^{15}, to the calculated number of molecules of dye formed at full intensity, data of column (3). Absorption by dye product in the leucocyanide photolyses at low light intensities is unimportant with the stirring rate used; the data of these experiments, runs 4 and 5 of Table II, indicate a ratio of the quantum yield of the uranyl oxalate actinometer to that of the leucocyanide photolysis to be 0.55. The quantum yield of oxalate decomposition is 0.56 at 3130 Å.[1]; hence the quantum yield of malachite green leucocyanide photolysis at wave length 3130 Å. is estimated to be 1.02.

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(8) R. Hunt and W. J. Davis, THIS JOURNAL, **69**, 1415 (1947).

Some Observations on Neptunium(V) Compounds[1]

BY G. GIBSON,[2] D. M. GRUEN AND J. J. KATZ

RECEIVED JANUARY 10, 1952

Although neptunium has a stable +5 oxidation state in solution,[3] the only Np(V) compounds which have hitherto been reported are Np(V) hydroxide[4] and mixtures of Np(V) oxychlorides of varying composition[5] obtained by rapid evaporation of HCl solutions.

The recent preparation of the oxide Np_3O_8[6] suggested a convenient starting material for the synthesis of Np(V) compounds, and it was of interest to attempt to determine the oxidation state of the neptunium in this compound. In one experiment 1 mg. of Np_3O_8 was dissolved in 5 cm.^{3} of 1 *M* $HClO_4$. Spectrophotometric examination of this solution with a Beckman Model D Spectrophotometer showed that the absorption was due only to Np(V) and Np(VI) ions. Approximately 1% of Np(IV) could have been detected by this means. This experiment does not rule out the existence of Np(IV) in Np_3O_8, however, since under the conditions of the dissolution Np(IV) would rapidly react with Np(VI) to form Np(V).[7] (Dissolution of U_3O_8 results in a mixture of U(IV) and U(VI) but here again the oxidation states in solution give no clue as to the situation in the solid since U(V) disproportionates into U(IV) and U(VI).)

Thermodynamic calculations for $NpCl_5$ give an estimated value of −246 ± 2 kg./mole for the heat of formation and a Cl_2 decomposition pressure of less than 10^{-3} atm. at 500°K.[8] Various attempts were made to prepare $NpCl_5$ from 2- to 4-mg. amounts of Np_3O_8: (a) Refluxing with 0.5 cm.^{3} of redistilled hexachloropropene at atmospheric pressure for 4 hours resulted in no reaction. (b) Bomb tube experiments with either hexachloropropene or carbon tetrachloride between 120–250° and 3–6 atm. also failed to yield a reaction. (c) Vapor phase chlorination with carbon tetrachloride carried out by passing CCl_4 vapors over the sample contained in a platinum boat in a hot tube furnace gave a reaction which resulted only in the formation of $NpCl_4$. A previous attempt to prepare $NpCl_5$ by reaction of $NpCl_4$ with Cl_2 at 500° was unsuccessful.[9] Np_3O_8 is thus quite different from U_3-

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(1) Reported in part at the Spring, 1950, Meeting of the American Chemical Society.

(2) On leave from Illinois Institute of Technology, Chicago, Ill.

(3) L. B. Magnusson, J. C. Hindman and T. J. La Chapelle, National Nuclear Energy Series, Vol. 14B, p. 1059, 1949.

(4) *Ibid.*, p. 1097.

(5) T. J. La Chapelle, UCRL-336, May, 1949.

(6) J. J. Katz and D. M. Gruen, THIS JOURNAL, **71**, 2106 (1949).

(7) R. Sjoblom and J. C. Hindman, *ibid.*, **73**, 1744 (1951).

(8) L. Brewer, L. Bromley, P. W. Gilles and N. L. Lofgren, MDDC-1417 (1947), corrected (1948).

(9) S. Fried and N. R. Davidson, National Nuclear Energy Series, Vol. 14B, p. 1072, 1949.

O_8 which under similar conditions yields mixtures of UCl_4, UCl_5 and UCl_6.[10]

We have, however, succeeded in preparing a well defined oxygenated Np(V) compound. A solution prepared by dissolving 10 mg. of Np(V) hydroxide in 0.1 cc.[8] of 1 *M* HCl was added to 3 cc. of a 10% solution of oxalic acid in anhydrous *t*-butyl alcohol. A pale green precipitate was obtained which after centrifugation was washed 3 times with 3-cc. portions of anhydrous ethyl ether. The final washed and dried precipitate had a distinct but complex X-ray diffraction pattern. The absorption spectrum of 1 mg. of the material in water solution was characteristic of Np(V).[7] A slight shift, from 983 to 990 mμ was observed in the chief absorption peak and may be attributed to complexing of the NpO_2^+ ion by oxalate. The remainder of the product, approximately 10 mg., was analyzed for neptunium spectrophotometrically and by α-count, for oxalate by means of permanganate titration, and for carbon, hydrogen and water by combustion. *Anal.* Calcd. for $NpO_2C_2O_4H \cdot 2H_2O$: Np, 60.15; $C_2O_4^{--}$, 22.33; C, 6.09; H_2O and H, 13.70. Found: 60.80, 60.50 (α-count), 60.11 (spectrophotometric); $C_2O_4^{--}$, 22.82; C, 3.75, 3.37; H_2O and H, 11.29, 11.51.

Studies of the Np(V) oxalate complex in aqueous solution are under way.

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[10] A. Miller and L. B. Dean, Collected Paper, National Nuclear Energy Series, Vol. 6 (to be published).

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Method for Freeing Zirconium of Common Impurities and for Preparing Zirconium Sulfate and Oxide

BY W. STANLEY CLABAUGH AND RALEIGH GILCHRIST

RECEIVED DECEMBER 8, 1951

The complex nature of zirconium salts and the incomplete knowledge of their chemistry have made it a matter of considerable difficulty to purify zirconium compounds.

In the course of a project on the separation of hafnium from zirconium, observations were made which should prove useful in manipulating certain reactions whereby zirconium can be freed of its common impurities.

Many of the salts of zirconium, including methods for their preparation, are described by Meyer and Hauser.[1] The authors give a method for preparing anhydrous $Zr(SO_4)_2$ and its tetrahydrate, by treating the zirconium oxide with sulfuric acid. Included also is a discussion of some of the possible basic sulfates of zirconium.

According to Falinski,[2] who investigated the system ZrO_2–SO_3–H_2O as a function of the concentration of SO_3, when $ZrOCl_2 \cdot 8H_2O$ is added to a sulfuric acid solution containing less than 64% of sulfur trioxide, $Zr(SO_4)_2 \cdot 4H_2O$ is precipitated. With a solution containing from 64 to 72% of SO_3, one obtains well-crystallized $Zr(SO_4)_2 \cdot H_2SO_4 \cdot 2H_2O$, and with an acidity corresponding to 72 to 79% of SO_3, finely crystalline $Zr(SO_4)_2 \cdot H_2SO_4 \cdot H_2O$. With concentrations of SO_3, greater than 79%, it is stated that probably $Zr(SO_4)_2 \cdot H_2SO_4$ crystallizes.

Preparation of Zirconium Sulfate.—It was found in this Laboratory that when concentrated sulfuric acid is poured into a fairly concentrated aqueous solution of zirconium sulfate or chloride, a dense white crystalline precipitate of $Zr(SO_4)_2 \cdot 4H_2O$ is obtained. The optimum proportion appears to be 1 volume of concentrated sulfuric acid to 2 volumes of concentrated zirconium solution. The zirconium sulfate produced in this manner can be readily caught on a sintered glass filter of medium or coarse porosity. Since approximately 1 g. of the salt so produced will dissolve in 1 ml. of water, the zirconium sulfate can be redissolved in water and reprecipitated by adding sulfuric acid

It was further found that the presence of hydrochloric acid was essential for the removal of iron. For instance, zirconium sulfate which was recrystallized 5 times in the absence of hydrochloric acid retained nearly all of its original iron. On the other hand, when recrystallized in the presence of approximately 10% hydrochloric acid, the iron content was reduced by a factor of more than 1000.

The most effective solution tried for washing the precipitate consisted of 75 volumes of water, 40 volumes of concentrated sulfuric acid and 5 volumes of concentrated hydrochloric acid. After several washings with this mixed acid, three washings with acetone are recommended. It should be pointed out that alcohol should *not* be used for this final washing, because, in some way, it causes interference in subsequent recrystallizations, probably through complex-formation.

With a starting material consisting of 1135 g. of a commercial zirconium chloride, corresponding to 1731 g. of $Zr(SO_4)_2 \cdot 4H_2O$, which contained about 0.3% of iron and 2.7% of hafnium, 1212 g. of zirconium sulfate (70% of original) of very high purity was obtained. Spectrochemical analysis of the original zirconium tetrachloride showed that, in addition to the hafnium and iron, it contained calcium, copper and manganese in the range of 1 to 10 p.p.m. of each; silver, aluminum, barium and titanium in the range of 10 to 100 p.p.m. of each; and magnesium and silicon in the range of 100 to 1000 p.p.m. of each. The rapidity of elimination of iron, the volumes of solutions used, as well as the yields of salt in the six crystallizations, may be seen in Table I.

TABLE I

ELIMINATION OF IRON BY REPEATED RECRYSTALLIZATION OF $Zr(SO_4)_2 \cdot 4H_2O$

$Zr(SO_4)_2 \cdot 4H_2O$ taken, g.	Vol. of Zr soln.,[c] ml.	H_2SO_4 added, ml.	$Zr(SO_4)_2 \cdot 4H_2O$ obtained, g.	Yield, %	Fe found in 1 ml. of filtrate, mg.
1731[a]	2100	1000	1640	94	20
...	..	..	..	..	....
1597[b]	2200	1000	1569	98	0.2
1569	2400	1100	1495	95	.02
1495	2200	1000	1451	97	.01
1451	2000	1000	1385	96	.005
1385	1950	950	1212	87	.002

[a] Calculated from 1135 g. of $ZrCl_4$ taken. [b] Amount of soluble $Zr(SO_4)_2 \cdot 4H_2O$ obtained from original precipitate. [c] Includes 250 ml. of concentrated hydrochloric acid.

Chemical analysis of the final product showed that it contained less than 0.1 part per million of iron and also less than 0.1 p.p.m. of copper. Spectrochemical analysis showed that the silver content was less than 1 p.p.m. and that calcium, magnesium, sodium and silicon were each less than 10 p.p.m. No other elements, except hafnium, were detected spectrochemically. The salt did contain approximately 0.01% of chloride ion. This latter impurity can be removed by merely recrystallizing the salt in the absence of hydrochloric acid. It should be emphasized that the refining process above described does not appreciably alter the original hafnium content.

Not every type of zirconium salt is suitable for purification by the foregoing method. The types best suited were found to be the salt formed by dissolving zirconium tetrachloride in water, without resorting to heat, and that formed by dissolving in dilute hydrochloric acid the peroxidized oxide, that is, the product formed by treating a solution or slurry of zirconium salts with sodium hydroxide and hydrogen peroxide.

Composition and Ignition Behavior of the Zirconium Sulfate Obtained.—The theoretical % values in the compound $Zr(SO_4)_2 \cdot 4H_2O$ are: ZrO_2, 34.67; SO_3, 45.05; H_2O, 20.28.

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[1] R. J. Meyer and O. Hauser, "Die Analyse der seltenen Erden und der Erdsäuren," Verlag von Ferdinand Enke, Stuttgart, Germany. 1912.

[2] Marie Falinski. *Ann. chim.*, **16**, 237 (1941).

Spectrochemical analysis of this material showed the hafnium-zirconium ratio to be 0.027 (Hf/Zr = 2.7). The theoretical % values in a compound of this composition are: oxides, 35.09; SO_3, 44.76; H_2O, 20.15.

Determination of the oxides by precipitation with ammonium hydroxide gave 35.0%. Determination of SO_3 by precipitation with barium chloride gave 44.5%. Determination of the water by difference gave 20.5%.

It was observed that samples of the $Zr(SO_4)_2 \cdot 4H_2O$ lost only 0.05% in weight when dried for 18 hours at 105°. The same samples when heated at 400° for 18 hours lost an average of 21.4% which was assumed to be mostly water. Further heating of these same samples at 600° for 18 hours caused them to lose SO_3 to the extent of 41%. The remaining SO_3 was evolved extremely slowly and probably not completely because at the end of 186 hours of heating at 600 to 650° the loss for SO_3 rose to a total of 43.1%. In the last 18 hours of heating at 650° the loss in weight amounted to only 0.15%. If the material remaining after ignition at 650° is oxides, a value of 35.5% oxides in the original salt is indicated.

Examination of the final ignited product, by X-ray diffraction showed it to be ZrO_2, monoclinic form. The zirconium oxide so produced was found to be readily soluble in strong sulfuric acid.

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Effect of Temperature and Aggregation on the Absorption Spectrum of the Amylose-Iodine Complex[1]

BY JOSEPH F. FOSTER AND EUGENE F. PASCHALL

RECEIVED DECEMBER 10, 1951

A relationship between the wave length of maximum absorption of the iodine complex and the molecular weight of the amylose has been indicated by Baldwin, *et al.*[2] Higginbotham[3] has recently shown that the maxima reported by Baldwin are obtained only under conditions of limited iodine binding and that at higher iodine levels there is a shift of approximately 30 mμ in the direction of longer wave lengths. He attributed this shift to the forcing of additional iodine into the amylose helices.

It is the purpose of this note to report some preliminary results which suggest that this shift in absorption spectrum may be related, instead, to the state of aggregation of the complex. The figure summarizes data on the wave length of maximum absorption of two amylose preparations in the presence of excess iodine as a function of temperature. In this experiment the complex was formed at room temperature, then the solution raised to successively higher temperatures. The solution was permitted to equilibrate for approximately 15 minutes at each temperature prior to measuring the absorption spectrum. It will be noted that both amylose preparations give initial absorption maxima which agree approximately with those found by Higginbotham in the presence of excess iodine. At 40° the values agree rather well with those reported by Baldwin, and by Higginbotham in the presence of limited amounts of iodine. Above 40° there is little if any further shift. Furthermore the shift is largely irreversible since the wave length shifts back only partially on re-cooling to room temperature. Solutions held at temperatures of 70° in the presence of excess iodine for many hours showed little if any further shift, which tends to rule out any possibility of explaining the results on the basis of oxidative degradation at temperatures as low as 40°. Solutions of amylose held at 80° for long periods of time and cooled to 25° prior to addition of iodine gave the high values of λ_{max}.

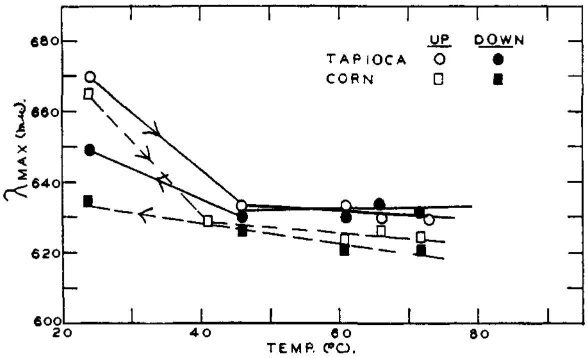

Fig. 1.

Other experiments led us to speculate on the possibility that the long wave lengths were a result of the presence of a special type of aggregate which we have shown to exist in amylose solutions even after dissolving in *N* KOH.[4] Therefore corn amylose was permitted to age in *N* KOH for two weeks, a treatment which has been found to result in an appreciable, though not complete, dissociation of these "native" aggregates.[4]

The λ_{max} shifted from 655 mμ, after 15 minutes and 3 hours standing, to 625 mμ after two weeks. Regeneration of the amylose by ethanol precipitation following this treatment did not affect the spectrum.

Another observation which suggests difference in the state of aggregation as the underlying cause of the spectral shift concerns the stability of the dispersions of the complex. Those showing the high λ_{max}. values invariably settled out of solution within three or four days. On the other hand, the heated complexes did not precipitate even after several weeks.

Within the framework of the theory of the amylose-iodine complex suggested by Rundle, Foster and Baldwin[5] these results suggest the possibility that in the form of the "native" aggregates there is an interaction between adjacent amylose helices which enhances the dipolar field.

We are indebted to Drs. Dexter French and R. E. Rundle for helpful discussions of these observations.

Experimental

The amylose samples were prepared by Dr. T. J. Schoch by pentasol crystallization followed by subfractionation with

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[1] Journal paper Number J-2043 of the Iowa Agricultural Experiment Station, Project 817. Supported in part by a grant from the Corn Industries Research Foundation. Taken from a thesis presented by Eugene F. Paschall in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Iowa State College, 1951.

[2] R. R. Baldwin, R. S. Bear and R. E. Rundle, THIS JOURNAL, **66**, 111 (1944).

[3] R. S. Higginbotham, *J. Textile Inst.*, **40**, T783 (1949).

[4] E. F. Paschall and J. F. Foster, *J. Polymer. Sci.*, in press.

[5] R. E. Rundle, J. F. Foster and R. R. Baldwin, THIS JOURNAL, **66**, 2116 (1944).

n-octyl alcohol.[6] Solutions were prepared by dispersing the required amount of amylose in 1 *N* KOH to yield a concentration of 0.267% following neutralization with 0.5 *N* HCl. Aliquots of the neutralized solutions were diluted to a final concentration of 0.002%. To those solutions which were heated a layer of mineral oil was frequently added to help prevent loss of iodine. Excess iodine was frequently added during the experiments, but with no effect on the wave length of maximum absorption. Spectra were determined in 19 × 105 mm. round cuvettes with the aid of a Model 14 Coleman Universal spectrophotometer.

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(6) S. Lansky, M. Kooi and T. J. Schoch, *ibid.*, **71**, 4066 (1949).

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The Chemotherapy of Tuberculosis. III. Thiosemicarbazide Derivatives

BY THOMAS S. GARDNER, F. A. SMITH, E. WENIS AND J. LEE

RECEIVED DECEMBER 5, 1951

In the course of a program[1,2] on the synthesis of compounds for the chemotherapy of tuberculosis, a number of hitherto unreported thiosemicarbazones, acyl thiosemicarbazides, thiadiazole derivatives, and related classes that have already been reported on by other workers[3-6] have been made.

TABLE I

Thiosemicarbazones	Formula	Crystallized from	Color	Yield, %	M.p., °C.	Analyses, % Calcd. Nitrogen	Calcd. Sulfur	Found Nitrogen	Found Sulfur
Streptomycin trihydrochloride[a]	$C_{22}H_{42}O_{11}N_{10}S \cdot 3HCl$	Aq. HCl + EtOH	Colorless	10	205		4.2		4.4
Anisil mono	$C_{17}H_{17}O_3N_3S$	Acetone	Orange	67	227–228		9.4		9.4
Naphthazarin mono	$C_{11}H_9O_3N_3S$	EtOH	Purple-black	27	160 dec.	16.0		15.7	
Acenaphthenequinone mono	$C_{13}H_9ON_3S \cdot H_2O$	Aq. EtOH	Yellow	50	223–224	15.4[b]		15.5	
Acenaphthenone	$C_{13}H_{11}N_3S$	EtOH	Yellow	88	227–228	17.4		17.1	
2-Methyl-3-hydroxy-5-hydroxymethylisonicotinaldehyde	$C_9H_{12}O_2N_4S \cdot {}^1/_2H_2SO_4$	Water	Yellow	63	194 dec.	9.7[c]	16.6	10.1[c]	16.5
2-Pyrryl methyl ketone	$C_7H_{10}N_4S$	EtOH	Colorless	74	184–185		17.5		16.9
D(+)-Mannose[d]	$C_7H_{15}O_5N_3S \cdot C_2H_5OH$	EtOH	Colorless	>90	175–176 dec.		10.5		10.4[c]
L(−)-Mannose[e]	$C_7H_{15}O_5N_3S$	Water	Colorless	>90	173–174 dec.	[f]			
D(+)-Glucose	$C_7H_{15}O_5N_3S$	80% EtOH	Colorless	>90	190[g] dec.		12.7		12.7
D(−)-Arabinose	$C_6H_{13}O_4N_3S$	[h]	Colorless	>90	151–152		14.4		13.9
L(+)-Arabinose	$C_6H_{13}O_4N_3S$	[h]	Colorless	>90	151–152		14.4		14.3
Nicotinaldehyde S-methyl[i]	$C_8H_{10}N_4S$	Aq. EtOH	Yellow	89	110–111		16.5		16.3
4-Acetamidobenzaldehyde-4′-phenyl-	$C_{16}H_{16}ON_4S$	HOAc	Yellow	94	200–201	[j]			

[a] Reported in solution without being isolated, R. Donovick, G. Rake and J. Fried, *J. Biol. Chem.*, **164**, 173 (1946). [b] Calcd.: C, 57.2; H, 4.0. Found: C, 56.5; H, 3.4. [c] Two nitrogens by Kjeldahl. [d] % volatile calcd. 18.2; Found: 18.5. [e] The L(−)-mannose thiosemicarbazone also formed the alcoholate from ethanol similar to the D(+)-isomer and was not analyzed because it had the same melting point as the D(+)-isomer and did not exhibit a mixed m.p. depression with the D-isomer. [f] Calcd.: C, 33.2; H, 5.9. Found: C, 33.1; H, 5.9. [g] Reported m.p. 204°; Neuberg and W. Neiman, *Ber.*, **35**, 2049 (1902). [h] Triturated with hot methanol instead of being recrystallized. [i] Method of E. Hoggarth *J. Chem. Soc.*, 1579 (1950). [j] Calcd.: C, 61.5, H, 5.1. Found: C, 61.3; H, 5.1.

The compounds in Table I were prepared by the reaction of the parent substance with thiosemicarbazide in aqueous ethanol or aqueous ethanol–acetic acid in cases wherein the parent substance was not soluble in aqueous ethanol.

All of the compounds prepared were inactive in experimental mouse tuberculosis.

Acknowledgment.—We are indebted to Dr. Al Steyermark and his associates for the microanalyses and Drs. R. J. Schnitzer and E. Grunberg for the chemotherapeutic screening.

Experimental

1-(3-Pyridyl)-thiosemicarbazide.—3-Pyridylhydrazine (15 g., 0.137 mole) was refluxed for 6 hours with 12.7 g. of ammonium thiocyanate and 18 ml. of 9 *N* HCl in ethanol in 350 ml. of ethanol. The separated crude product was recovered by filtration and crystallized from aqueous ammonia solution; yield 5 g. (21%), m.p. 223–224°.

Anal. Calcd. for $C_6H_8N_4S$: C, 42.8; H, 4.8. Found: C, 43.0; H, 4.6.

2,3-Dihydro-5-(2′-acetoxy-4′-nitrophenyl)-2-phenylamino-1,3,4-thiadiazole.—Acetyl *p*-nitrosalicylic acid (67.5 g., 0.3 mole) was converted to the acid chloride by 62.4 g. of PCl_5. The acid chloride obtained was treated with 50.1 g. (0.3 mole) of 4-phenyl-3-thiosemicarbazide in nitromethane as a solvent. The reaction solution was heated for 4 hours on the steam-bath. On cooling, 30 g. of the product separated, and further heating and cooling gave 4.3 g. more of the crude product. The combined crude fractions (34.3 g.) were recrystallized from nitrobenzene; yield 23.3 g. (20%), m.p. 316–317°.

Anal. Calcd. for $C_{16}H_{12}O_4N_4S$: C, 53.9; H, 3.4. Found: C, 54.0; H, 3.2.

2,3-Dihydro-5-(2′-hydroxy-4′-aminophenyl)-2-phenylamino-1,3,4-thiadiazole.—2,3-Dihydro-5-(2′-acetoxy-4′-nitrophenyl)-2-phenylamino-1,3,4-thiadiazole (13 g., 0.036 mole) was added in portions to 100 ml. of phenylhydrazine and 150 ml. of anisole. The reduction was heated at reflux for 2 hours and on cooling crystallized a buff-colored product. The recovered product was recrystallized twice from anisole; yield 9.6 g. (92%), m.p. 282–283°.

Anal. Calcd. for $C_{14}H_{12}ON_4S$: C, 59.2; H, 4.2. Found: C, 59.5; H, 4.3.

1-(*p*-Acetamidobenzoyl)-thiosemicarbazide.—*p*-Acetamidobenzoyl chloride (9.5 g., 0.048 mole) was added to 20 ml. of 10% sodium hydroxide solution containing 4.4 g. (0.048 mole) of thiosemicarbazide. The reaction solution became warm and was cooled and stirred for 2 hours. The product was recovered by filtration and washed with water; crude yield 9.1 g. (75%), m.p. 192–194° (dec.). A small sample was recrystallized by solution in ethylene glycol and addition of water to turbidity, m.p. 221° (dec.) of the colorless crystals.

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(2) T. S. Gardner, E. Wenis and F. A. Smith, THIS JOURNAL, **73**, 5455 (1951).

(3) R. Behnisch, F. Mietzsch and H. Schmidt, *Angew. Chem.*, **60**, 113 (1948).

(4) E. Hoggarth, A. R. Martin, N. E. Storey and E. H. P. Young, *Brit. J. Pharmacol.*, **4**, 248 (1949).

(5) B. Croshaw and L. Dickinson, *ibid.*, **5**, 178 (1950).

(6) J. Bernstein, H. L. Yale, K. Losee, M. Holsing, J. Martins and W. A. Lott, THIS JOURNAL, **73**, 906 (1951).

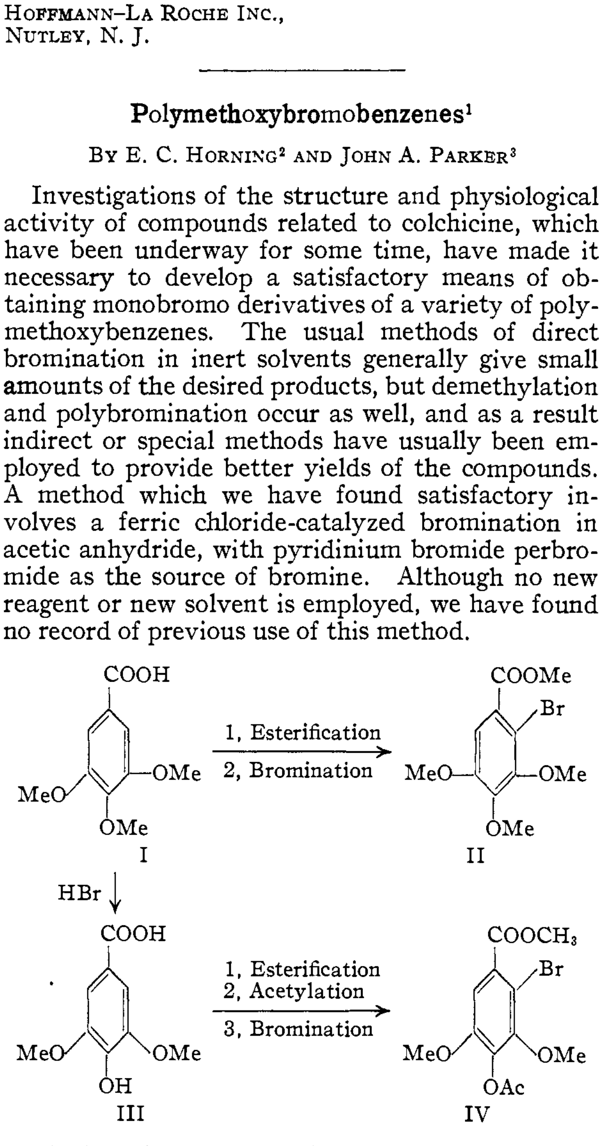
Anal. Calcd. for $C_{10}H_{12}O_2N_4S$: N, 11.1 (2 N by Kjeldahl). Found: N, 10.7.

CONTRIBUTION NO. 285 FROM THE
RESEARCH LABORATORIES OF
HOFFMANN-LA ROCHE INC.,
NUTLEY, N. J.

Polymethoxybromobenzenes[1]

BY E. C. HORNING[2] AND JOHN A. PARKER[3]

Investigations of the structure and physiological activity of compounds related to colchicine, which have been underway for some time, have made it necessary to develop a satisfactory means of obtaining monobromo derivatives of a variety of polymethoxybenzenes. The usual methods of direct bromination in inert solvents generally give small amounts of the desired products, but demethylation and polybromination occur as well, and as a result indirect or special methods have usually been employed to provide better yields of the compounds. A method which we have found satisfactory involves a ferric chloride-catalyzed bromination in acetic anhydride, with pyridinium bromide perbromide as the source of bromine. Although no new reagent or new solvent is employed, we have found no record of previous use of this method.



The bromination of methyl 3,4,5-trimethoxybenzoate by this procedure proceeds smoothly and gives good yields (85%) of product (II). This bromination has been reported several times, but with divergent results. The method reported here leads to a low-melting (34–36°) monobromo ester, correctly described by Feist and Dschu,[4] although if the reaction mixture is heated an unidentified product, m.p. 88–89°, perhaps identical with the material prepared in another way and also described as methyl 2-bromo-3,4,5-trimethoxybenzoate,[5] may also be obtained. A related ester, methyl 2-bromo-3,5-dimethoxy-4-acetoxybenzoate, was prepared by the same bromination method. The generality of the procedure was examined through the bromination of veratrole and 1,2,3-trimethoxybenzene, but has not been extended beyond these examples.

Experimental

Methyl 3,4,5-Trimethoxybenzoate.—A 100-g. quantity of 3,4,5-trimethoxybenzoic acid was suspended in 500 ml. of dry methanol, and hydrogen chloride was bubbled rapidly through the mixture without temperature control until the methanol was saturated and the acid dissolved. The mixture was chilled (24 hours) and the crystalline product was removed by filtration, washed with chilled methanol, and dried to yield 101.5 g. (94%) of the ester, m.p. 83–84° (reported[6] m.p. 83–84°).

Methyl 2-Bromo-3,4,5-trimethoxybenzoate (II).—A few crystals (approximately 200 mg.) of ferric chloride (hydrated) were dissolved in a solution of 22.6 g. (0.10 mole) of methyl 3,4,5-trimethoxybenzoate in 100 ml. of acetic anhydride. A total of 35.5 g. of pyridinium bromide perbromide was added in small portions, with stirring or shaking,[7] and the resulting solution was heated at 50–55° for five minutes to ensure completeness of reaction. The mixture was added slowly with good stirring to 500 ml. of hot (60–70°) water in order to hydrolyze the solvent and, after cooling, the mixture was extracted with 1:1 ether–ethyl acetate. The combined organic extracts were washed with 5% hydrochloric acid, 5% sodium hydroxide solution, water and 2% aqueous acetic acid. The organic material was dried (magnesium sulfate), the solvents were removed, and the crude yield of 32.5 g. of product was distilled under reduced pressure to provide 2.0 g. of fore-run (b.p. to 160° (2 mm.)) and 28.5 g. of product, b.p. 160–161° (2 mm.). The colorless ester was recrystallized from ether–pentane to give 25.8 g. (85%) of methyl 2-bromo-3,4,5-trimethoxybenzoate, m.p. 34–36°. The correct structure was assigned to this compound by Feist and Dschu,[4] who reported m.p. 33°.

When the reaction mixture was heated at 90–100° for periods of 30 minutes or longer, the reaction product was a colorless crystalline material, m.p. 89–90°, of unidentified structure, which was perhaps similar to the products usually obtained by bromination of the ester with bromine in acetic anhydride at room temperature.[5]

3,5-Dimethoxy-4-hydroxybenzoic Acid (Syringic Acid).—A mixture of 50.0 g. of 3,4,5-trimethoxybenzoic acid, 200 ml. of acetic acid and 40 ml. of concentrated hydrobromic acid was heated under reflux for three hours. After dilution with 800 ml. of water, followed by chilling (24 hours), a 38.6 g. (83%) yield of syringic acid, m.p. 202–203° (reported m.p. 204°), was obtained.

Methyl 3,5-Dimethoxy-4-acetoxybenzoate.—A solution of 30.0 g. (0.15 mole) of 3,5-dimethoxy-4-hydroxybenzoic acid in 100 ml. of dry methanol was saturated with hydrogen chloride. After standing for 24 hours, the solvent was evaporated, leaving a residue of 31.2 g. of crude ester. A 30.0 g. quantity of this material was dissolved in 120 ml. of acetic anhydride, and the mixture was heated under reflux for 30 minutes. The solution was added to 500 ml. of warm (50–60°) water, and the crystalline product was separated after chilling. The yield was 24.5 g. (64%) of colorless ester, m.p. 128–129°. This material has been prepared previously.[5]

Anal. Calcd. for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.62; H, 5.46.

Methyl 2-Bromo-3,5-dimethoxy-4-acetoxybenzoate (IV).—The bromination procedure described previously was carried out with 20.0 g. (0.074 mole) of methyl 3,5-dimethoxy-4-acetoxybenzoate and 28.0 g. of pyridinium bromide perbromide in 125 ml. of acetic anhydride. The crude product was crystallized from ether–pentane to yield 16.0 g. (62%) of colorless ester, m.p. 75–76°.

Anal. Calcd. for $C_{12}H_{13}O_6B$: C, 43.26; H, 3.93. Found: C, 43.53; H, 4.19.

1,2,3-Trimethoxy-4-bromobenzene.—To a stirred solution of 67.2 g. (0.40 mole) of 1,2,3-trimethoxybenzene in 400 ml. of acetic anhydride, containing a few crystals of ferric chloride, was added, in small portions, 144 g. of pyridinium bromide perbromide. The solution was heated for

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[1] Aided by a Grant-in-Aid from the American Cancer Society recommended by the Committee on Growth of the National Research Council.

[2] National Heart Institute, Bethesda, Maryland.

[3] National Institutes of Health Predoctoral Fellow, 1950–1951.

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[6] F. W. Semmler, *Ber.*, **41**, 1774 (1908).

[7] It is advisable to follow the precautions mentioned by Bogert,[5] although we have noted no difficulties.

five minutes at 50–55°, and was then poured slowly into 2000 ml. of hot water. The crude product was isolated as described in previous experiments, and amounted to 98.4 g. of oil. Distillation through a Podbielniak column at 50 mm. pressure gave a small fore-run (4.8 g.) and the following fractions: (a) 5.0 g., b.p. 150–153°, of material which solidified and which was identified as starting 1,2,3-trimethoxybenzene; (b) 4.5 g., b.p. 153–179°, of intermediate material; (c) 77.2 g., b.p. 179°, of 1,2,3-trimethoxy-4-bromobenzene (78% yield); (d) 4.5 g. of residue. The product turned dark on standing, and carbon analyses were consistently low. Freshly prepared material was used in Ullmann reactions to yield the expected products.

4-Bromoveratrole.—Veratrole was brominated by this method to provide 4-bromoveratrole, b.p. 164–167° (50 mm.), in 84% yield. This compound has been prepared previously by a variety of methods, including direct bromination,[8] with bromine diluted with air,[9] cyanogen bromide,[10] N-bromosuccinimide,[11] and by methylation[8] of bromoguaiacol.

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(8) R. Y. Moir and C. B. Purves, *Can. J. Research*, **26B**, 694 (1948).

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(10) G. Bargellini and F. Madesani, *ibid.*, **61**, 684 (1931).

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An Unusual Salting-out Effect of Hydrohalogen Acids on Water-Dioxane Mixtures

BY W. T. GRUBB AND ROBERT C. OSTHOFF

RECEIVED JANUARY 5, 1952

In the course of some reaction studies in the solvent system water–dioxane, it was found that the addition of hydrogen chloride or hydrogen bromide caused the formation of two phases over a limited concentration range. This behavior has not been previously reported despite the extensive use of water–dioxane as a medium for reactions under acidic conditions. Infinite miscibility of water with dioxane is ordinarily presumed,[1] although the 1-1-2 ternary compound $H_2O–HClO_4–O(CH_2CH_2)_2O$ has been reported.[2]

The authors therefore undertook a phase study of the ternary system water-dioxane-HX at 25° and atmospheric pressure.

Experimental

1,4-Dioxane.—Fisher Scientific Co. "Purified" 1,4-dioxane was further purified according to the general method which has been described by Kraus and Vingee.[3] However, during the final distillation a stream of dry nitrogen was passed through the condenser and over the collected dioxane to protect the material from atmospheric oxygen.[4] The dioxane was stored in a dark-colored bottle under dry nitrogen. The dioxane prepared in this manner was essentially free of peroxides, as indicated by a test with potassium iodide and acetic acid in the presence of Dry Ice; m.p. 11.78 ± 0.02° (previous value, 11.80[5]), n^{21}_{D} 1.4218 (previous value, n^{21}_{D} 1.4219[4]).

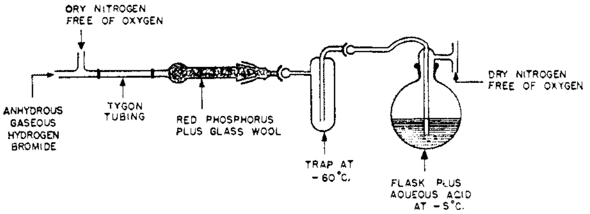

Fig. 1.—Apparatus for production of bromine-free aqueous hydrobromic acid.

Hydrogen Chloride.—du Pont analytical reagent grade hydrochloric acid was used without further purification. In some cases where higher concentrations were required Matheson anhydrous hydrogen chloride was added to the system.

Hydrogen Bromide.—Because reagent grade hydrobromic acid is available in only 42% concentration and may be contaminated by free bromine from atmospheric oxidation, the hydrogen bromide solution for these experiments was prepared by passing gaseous hydrogen bromide into distilled water employing the apparatus indicated in Fig. 1. The red phosphorus was used to remove bromine from the hydrogen bromide and the trap ensured the removal of phosphorus(III) bromide and any other high-boiling substances. At the start of the run dry nitrogen was allowed to pass through the system for 24 hours in order to sweep all oxygen from the lines and from the sample of distilled water. Then the hydrogen bromide was allowed to flow until a saturated solution was obtained (65% by wt.[6] was attained in approximately 5 hours). The colorless solution was stored under nitrogen until used.

Preliminary experiments showed that if a fairly concentrated aqueous acid solution was added with stirring into a sample of pure dioxane, the mixture remained clear up to a certain volume of acid, passed through a region of incom-

TABLE I

COMPOSITIONS OF THE SYSTEM H_2O–HCl–DIOXANE AT THE MISCIBILITY LIMITS

Aqueous acid added Volume,[a] ml.	Normality	Wt. % H_2O	Wt. % HCl	Wt. % Dioxane
0.65	12.00	1.87	1.04	98.08
.42	9.69	1.29	0.57	98.15
.53	7.08	1.73	.52	97.75
.90	4.87	3.06	.60	96.35
.96	2.42	3.44	.32	96.27
.90	3.13	3.18	.39	96.45
.86	4.09	2.98	.48	96.54
3.18	2.57	10.43	1.03	88.54
1.30	1.87	4.61	0.33	95.06
1.53	1.92	5.38	.39	94.30
2.05	2.12	7.05	.56	92.39
4.33	2.97	13.49	1.56	84.95
9.52	4.60	24.05	4.46	71.49
5.58	3.61	16.43	2.34	81.27
0.62	13.35	1.68	1.15	97.18
9.70	12.00	19.49	11.45	69.06
10.86	9.69	22.74	10.08	67.18
11.51	7.08	25.60	7.75	66.64
10.17	4.87	25.08	4.94	70.00
2.72	2.42	9.10	0.84	90.04
4.74	3.13	14.52	1.76	83.70
8.40	4.09	22.30	3.63	74.07
11.03	8.26	23.94	8.74	67.48
11.48	7.17	24.03	4.46	71.51
8.61	13.35	17.09	11.67	71.23
		5.10	7.26[b]	87.63
		7.32	8.81[b]	83.86
		13.22	10.96[b]	75.78
		11.38	10.37[b]	78.21
		14.72	12.98[b]	72.30

[a] Volume of acid added to 25.0 ml. of dioxane in each case.

[b] Gaseous hydrogen chloride added to attain these concentrations (Method I).

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(2) C. Smeets, *Naturw. Tijdschr.*, **19**, 12 (1937).

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(4) K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

(5) P. C. Teague and W. A. Felsing, THIS JOURNAL, **65**, 484 (1943).

(6) H. S. Booth, "Inorganic Synthesis," Vol. I, McGraw–Hill Book Co., Inc., New York, N. Y., 1939, p. 156.

TABLE II

COMPOSITION OF THE SYSTEM H_2O-HBr-DIOXANE AT THE MISCIBILITY LIMITS

Aqueous acid added Volume,[a] ml.	Normality	Wt. % H_2O	Wt. % HBr	Wt. % dioxane
0.71	14.70	1.58	3.15	95.27
3.78	14.70	6.99	13.93	79.09
0.60	13.85	1.41	2.52	96.06
4.49	13.85	8.42	15.04	76.53
0.48	11.97	1.24	1.76	97.00
5.85	11.97	11.34	16.06	72.60
0.43	10.70	1.18	1.41	97.41
6.49	10.70	13.04	15.62	71.35
0.46	8.99	1.35	1.28	97.37
6.95	8.99	14.82	14.07	71.13
0.44	7.59	1.34	1.02	97.63
7.08	7.59	16.00	12.17	71.83
0.48	6.20	1.53	0.91	97.56
6.54	6.20	16.01	9.52	74.46
0.65	4.34	2.19	0.86	96.97
3.57	4.34	10.57	4.15	85.29
1.66	3.69	5.46	1.74	92.78
7.20	7.75	16.05	12.59	71.37
0.84	3.64	2.86	0.93	96.20
7.02	8.37	15.35	13.25	71.40
1.28	3.40	4.31	1.29	94.39
2.72	4.02	8.43	3.07	88.51
5.22	5.00	14.11	6.48	79.41
2.12	3.64	6.82	2.25	90.93
		2.46	5.59[b]	91.98
		3.55	7.91[b]	88.57
		4.56	10.13[b]	85.29
		5.52	11.76[b]	82.70
		6.44	3.19[b]	80.38
		8.22	14.88[b]	76.90

[a] Volume of acid added to 25.0 ml. of dioxane in each case. [b] Gaseous hydrogen bromide added to attain these concentrations (Method I).

plete miscibility indicated by marked visual cloudiness and then suddenly cleared as the acid addition was continued.

The cloud and clear points were determined quantitatively at various acid concentrations in the following manner:

Acids of various known concentrations were added from a buret to a 250-ml. glass-stoppered erlenmeyer flask containing 25 ml. of dioxane and thermostated at 25.0 ± 0.1°. Stirring was accomplished magnetically using a Teflon-covered bit. A cloud point and a clear point were obtained at each acid concentration with a reproducibility of ± 0.05 ml. A blanket of dry nitrogen above the system was provided during these operations. By the addition of acid in this manner, the region of incomplete miscibility is crossed along a line parallel to the volume axis. Two other methods were used to obtain additional points:

I.—The addition of gaseous hydrogen halide to a system containing known amounts of water and dioxane was employed to determine the miscibility limits along a line approximately parallel to the concentration axis. In these cases the entire sample was analyzed by titration with standard sodium hydroxide solution.

II.—The addition of aqueous acid to a system of water and dioxane or the addition of water to a system of aqueous acid plus dioxane was used to obtain points on the curve at intermediate acid concentrations.

The data for hydrogen chloride and hydrogen bromide are summarized in Tables I and II, respectively, on a volume basis. For a constant amount of dioxane (25 ml.) in each of these tables the compositions of the respective system at the miscibility limit is also expressed in terms of wt. per cent. of each component. Conventional phase diagrams for ternary systems are presented in Figs. 2 and 3.

In converting the composition of the systems from a volume basis to a weight per cent. basis, the densities of aqueous hydrochloric acid and hydrobromic acid for the various normalities were obtained by interpolations of the data of the "International Critical Tables."[7]

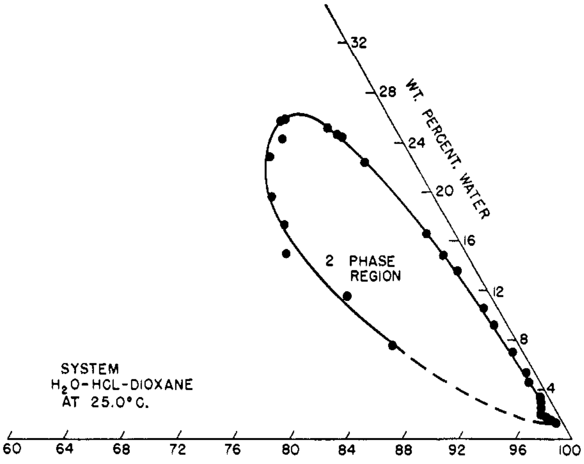

Fig. 2.—The ternary system water–hydrogen chloride–1,4-dioxane at 25.0°.

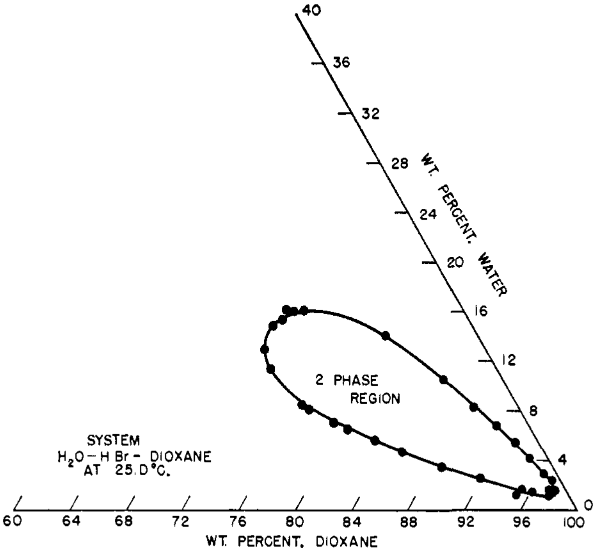

Fig. 3.—The ternary system water–hydrogen bromide–1,4-dioxane at 25.0°.

In Figs. 4 and 5 are presented directly the solubility limits in ml. for various concentrations of aqueous acid in 25 ml. of 1,4-dioxane. The boundary of the two-phase region is actually a closed curve. However, the portions of each curve at higher concentrations of aqueous acid have been omitted from Figs. 4 and 5 because they were obtained by addition of gaseous hydrogen chloride or hydrogen bromide (*cf.* Method I above) to the entire system and represent aqueous acids of concentrations unattainable at atmospheric pressure.

A surprisingly small quantity of aqueous acid is required to produce a two-phase system, *i.e.*, less than 2% of 9.69 *N* hydrochloric acid will cause the formation of two phases (less than 3% of 10.70 *N* hydrobromic acid). However, hydrogen chloride in any concentration will not cause the formation of two phases in the case of a system consisting of at least 34% water in dioxane (at least 29% water in the dioxane in the case of hydrogen bromide).

The data of Figs. 4 and 5 indicate that the maximum range of immiscibility occurs at concentrations corresponding to the approximate composition of the constant boiling acids, as well as the fact that hydrochloric acid solutions

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[7] "International Critical Tables," Vol. III, pp. 54–55.

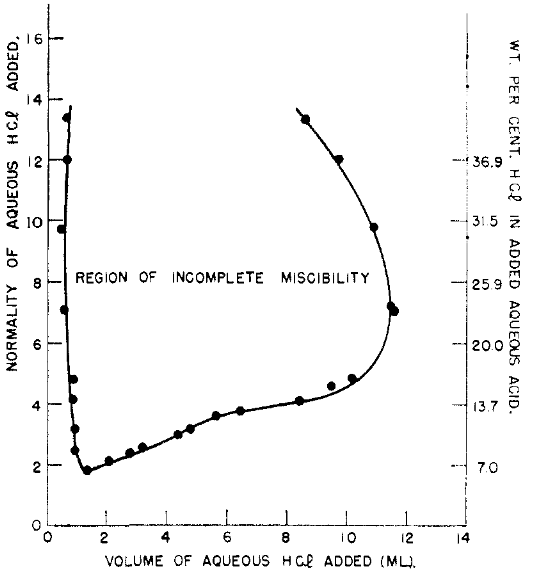

Fig. 4.—Solubility of aqueous hydrochloric acid of various concentrations on 25 ml. of 1,4-dioxane at 25.0°.

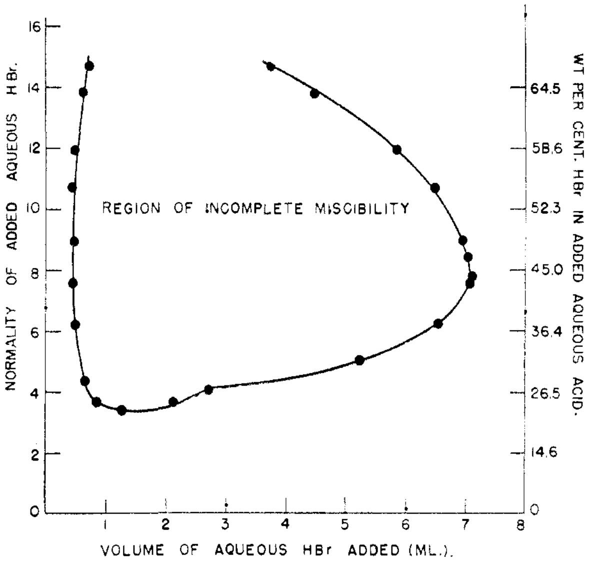

Fig. 5.—Solubility of aqueous hydrobromic acid of various concentrations in 25.0 ml. of 1,4-dioxane at 25.0°.

less than 1.87 *N* and hydrobromic acid solutions less than 3.64 *N* are completely miscible with 1,4-dioxane.

Acknowledgment.—The authors are indebted to Dr. S. W. Kantor, for supplying some of the purified dioxane employed in this study, and to Mr. L. B. Bronk for analysis of some of the aqueous hydrogen chloride samples.

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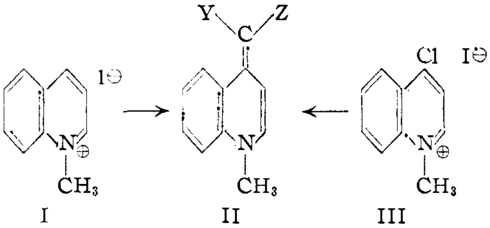
Reactions of Quinolinium Compounds with Malononitrile and Ethyl Cyanoacetate

BY NELSON J. LEONARD AND ROBERT L. FOSTER

Our finding[1] that the product resulting from the condensation of 1-methylquinolinium iodide (I) with nitromethane in the presence of base is 1-methyl-4-nitromethylenequinolane (IIa), a correction of the structure suggested earlier by Kaufmann,[2] prompted the investigation of the reaction of 1-methylquinolinium iodide with other active methylene compounds. Malononitrile and ethyl cyanoacetate, of activity commensurate with that of nitromethane, have now been found to undergo reaction with quinolinium compounds to give similar condensation products (II). The reaction is related to that used for the preparation of dyes of the cyanine and isocyanine type,[3] which possess 4,α-unsaturation.



a, Y = H; Z = NO_2;
b, Y = CN; Z = CN;
c, Y = CN; Z = COOEt

Combination of 1-methylquinolinium iodide (I) with malononitrile in ethanolic sodium ethoxide gave a yellow product, m.p. 291.5–292.5°, in low yield. The analysis was correct for its formulation as 1-methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline (IIb), analogous to the established structure of the product (IIa) from nitromethane. The infrared absorption spectrum was also consistent with structure IIb. This structure was established unequivocally by the synthesis, in quantitative yield, of 1-methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline from 1-methyl-4-chloroquinolinium iodide (III) and malononitrile in alkaline solution. The products from the two reactions were identical. The device of comparing products obtained from 1-alkylquinolinium iodide with those from either the 4-chloro- or 4-iodo-1-alkylquinolinium iodide[4,5] has been useful for proving 4-substitution in the isocyanine dyes.

Malononitrile reacted with 1,2-dimethylquinolinium iodide in the presence of sodium ethoxide to produce 1,2-dimethyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline in 34% yield. The structure of the product as the 2-methyl derivative of IIb was assigned on the basis of homology and effective blocking of the 2-position from attack by the malononitrile anion. The condensation of 1-methylquinolinium iodide with ethyl cyanoacetate gave 1-methyl-4-(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline (IIc), the structure of which was assigned on the basis of elemental analysis, analogy with the preceding examples, and similarity of the infrared spectrum with that of IIb. Similarly, 1,2-dimethylquinolinium iodide and ethyl cyanoacetate yielded 1,2-dimethyl-4-

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[1] N. J. Leonard, H. A. DeWalt, Jr., and G. W. Leubner, THIS JOURNAL, **73**, 3325 (1951).

[2] A. Kaufmann, German Patent 250,154, July 15, 1912; *Frdl.*, **10**, 1317 (1910–1912).

[3] F. M. Hamer, *Quart. Revs.*, **4**, 327 (1950); M. Q. Doja, *Chem. Revs.*, **11**, 273 (1932); E. C. Franklin and F. W. Bergstrom, *ibid.*, **35**, 77 (1944).

[4] A. Kaufmann and E. Vonderwahl, *Ber.*, **45**, 1404 (1912).

[5] F. M. Hamer, *J. Chem. Soc.*, 1008 (1939).

(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline. Diethyl malonate, ethyl acetoacetate,[2] ethyl phenylacetate and acetonitrile failed to yield products analogous to II under similar reaction conditions.

Experimental[6]

Reaction of 1-Methylquinolinium Iodide with Malononitrile.—To a mixture of 13.6 g. (0.05 mole) of 1-methylquinolinium iodide, m.p. 146°, 3.3 g. (0.05 mole) of malononitrile and 100 ml. of absolute ethanol, cooled in an ice-bath, was added with vigorous stirring a solution prepared from 2.3 g. (0.10 gram atom) of sodium in 50 ml. of absolute ethanol. The stirring was continued for 3 hours, and then the mixture was allowed to stand overnight. The product was isolated by filtration. Two recrystallizations from absolute ethanol gave 1.1 g. (10%) of material crystallizing as fine yellow filaments, m.p. 291.5–292.5°.

Anal. Calcd. for $C_{13}H_9N_3$: C, 75.35; H, 4.38; N, 20.28. Found: C, 75.12; H, 4.17; N, 20.30.

The infrared spectrum showed strong absorption in the nitrile region, at 2197 and 2176 cm.$^{-1}$, and indicative of conjugation with the nitrile groups, also a band at 1625 cm.$^{-1}$ and a double band at 1619–1620 cm.$^{-1}$.

1-Methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline (IIb).—1-Methyl-4-chloroquinolinium iodide, prepared by heating 4-chloroquinoline[7] under reflux with excess methyl iodide,[5] was recrystallized from ethanol as yellow needles, m.p. 204–206°. A mixture of 1.3 g. (0.004 mole) of 1-methyl-4-chloroquinolinium iodide, 0.3 g. (0.004 mole) of malononitrile and 75 ml. of absolute ethanol was cooled in an ice-bath. A solution of sodium ethoxide prepared from 0.1 g. (0.004 gram atom) of sodium and 50 ml. of absolute ethanol was added with vigorous stirring. The reaction appeared to take place immediately but stirring was continued for 8 hours to ensure completeness of reaction. The product was collected by filtration, and the yield was quantitative. Two recrystallizations from ethanol gave yellow filaments, m.p. 291.5–292°, which did not depress the melting point of the $C_{13}H_9N_3$ product obtained from 1-methylquinolinium iodide and malononitrile. The infrared spectra were also identical.

Reaction of 1,2-Dimethylquinolinium Iodide with Malononitrile. 1,2-Dimethyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline.—To a mixture of 14.2 g. (0.05 mole) of 1,2-dimethylquinolinium iodide, m.p. 195–196°, 3.3 g. (0.05 mole) of malononitrile, and 100 ml. of absolute ethanol, cooled in an ice-bath, was added with vigorous stirring a solution prepared from 1.2 g. (0.05 gram atom) of sodium in 50 ml. of absolute ethanol. Stirring was continued for 4 hours and the reaction mixture was allowed to stand at 25° for an additional 4 hours. The product was isolated by filtration and was recrystallized from absolute ethanol as yellow needles, m.p. 267.5–268°; yield 3.8 g. (34%).

Anal. Calcd. for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 18.99. Found: C, 76.16; H, 5.26; N, 19.14.

1-Methyl-4-(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline (IIc).—This compound was obtained from equimolar quantities of 1-methylquinolinium iodide, ethyl cyanoacetate and sodium ethoxide, following the same directions as those given in the preceding paragraph. The product was isolated as yellow needles from ethanol, m.p. 181.5–182.5°; yield 2.9 g. (23%).

Anal. Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.84; H, 5.55; N, 11.02. Found: C, 70.86; H, 5.66; N, 11.10.

The infrared spectrum showed strong absorption at 2189 cm.$^{-1}$, indicative of nitrile, and 1671 cm.$^{-1}$, indicative of carbonyl, as well as bands at 1624 and 1617 cm.$^{-1}$, similar to those exhibited by IIb.

1,2-Dimethyl-4-(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline.—This compound was prepared by the same method, using equimolar quantities of 1,2-dimethylquinolinium iodide, ethyl cyanoacetate and sodium ethoxide. The product was recrystallized from acetone as yellow needles, m.p. 172.5–173.5°.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.32; H, 6.20; N, 10.25.

Reactions of 1-Methylquinolinium Iodide with Other Active Methylene Compounds.—The reactions of 1-methylquinolinium iodide with diethyl malonate, acetonitrile and ethyl phenylacetate in ethanol with sodium ethoxide failed to produce any isolable condensation product. The reaction of 1-methylquinolinium iodide with ethyl acetoacetate in aqueous sodium hydroxide solution failed to produce the condensation product described by Kaufmann.[2] When sodium ethoxide in ethanol was used, the same result was obtained.

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(6) Melting points are corrected. The authors are indebted to Miss Elizabeth M. Petersen for determination of the infrared absorption spectra and to Miss Emily Davis, Mrs. Jean Fortney and Mrs. Katherine Pih for the microanalyses.

(7) B. Riegel, G. R. Lappin, B. H. Adelson, R. I. Jackson, C. J. Albisetti, Jr., R. M. Dodson and R. H. Baker, THIS JOURNAL, **68**, 1264 (1946).

Spectrophotometric Studies of Complex Formation with Sulfosalicylic Acid. V. With Chromium(III)

BY ALFRED M. LIEBMAN AND ROBBIN C. ANDERSON

RECEIVED NOVEMBER 23, 1951

The reaction of chromium(III) with sulfosalicylic acid has been studied as part of a series of investigations on complex formation in solution between sulfosalicylic acid and ions of various elements.[1]

Figure 1 shows, for comparison, the absorption spectrum of an equimolar mixture of chromium(III) nitrate and sulfosalicylic acid and those for corresponding solutions of each separately. Curve B shows the net difference in transmittance when the absorption curve for the mixture was determined using the chromium(III) as a blank. It is evident that some colored product is formed, with a maximum in absorption at 550 mμ. It was also found that the presence of sulfosalicylic acid increased materially the pH at which precipitation of chromium(III) hydroxide could occur.

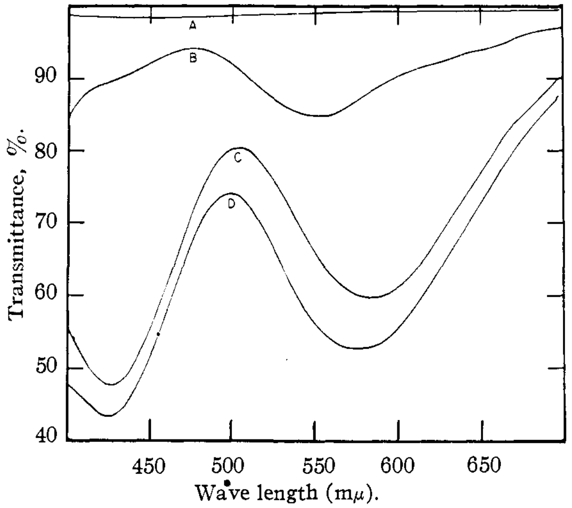

Fig. 1.—Absorption spectra: A, 0.0025 SSA *vs.* H_2O blank: B, 1:1 Cr(III)/SSA total molarity = 0.005 *vs.* Cr(III) blank (0.0025 *M*); C, Cr(III) (0.0025 *M*) *vs.* H_2O blank; D, 1:1 Cr(III)/SSA total molarity = 0.005 *vs.* H_2O blank.

Measurements in solutions of different pH values showed maximum color intensities in the range of

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(1) R. T. Foley and R. C. Anderson, THIS JOURNAL, **70**, 1195 (1948); **71**, 909 (1949); **72**, 5609 (1950); S. E. Turner and R. C. Anderson, *ibid.*, **71**, 912 (1949).

*p*H 3.5. The *p*H at which the color change to green first appeared decreased as the concentration of sulfosalicylic acid was increased. These *p*H effects indicate that complex formation probably involves the $^{-}OOCC_6H_3OHSO_3^{-}$ ion. The second dissociation constant[2] for the acid is in the range $1.5\text{–}3.2 \times 10^{-3}$. Thus in the *p*H range 3–5, the second dissociation is from 60 to virtually 100% complete.

The extent of complex formation decreased somewhat with increased temperature. Heating from 23 to 32°, for example, decreased the intensity of color.

Addition of excess sulfosalicylic acid increased the color intensity, with the maximum absorption shifting slightly toward longer wave lengths. With a 1:3 ratio of chromium(III) to sulfosalicylic acid, the peak occurred at 570 mμ. Small increases in absorption were also observable in the region of 430 and 630 mμ.

The Job method of continuous variations[3] was employed to determine the composition of the complex at a *p*H 5.0. The four wave lengths indicated by the previous discussion were used: 430, 630, 550 and 570 mμ. Typical data are shown graphically in Fig. 2, at 550, 570 and 630 mμ. The data at 430 mμ were inconclusive because of the relatively large corrections which had to be made for absorption by the chromium(III).

The optical density data recorded on Fig. 2 are values of $\bar{D}$, which is the observed optical density of the particular mixture minus the absorption which the chromium(III) and sulfosalicylic acid would show had no reaction occurred. A plot of $\bar{D}$ against mole fraction of chromium(III) should exhibit a maximum value of $\bar{D}$ corresponding to the mole ratio in which the reagents combine to form the complex.

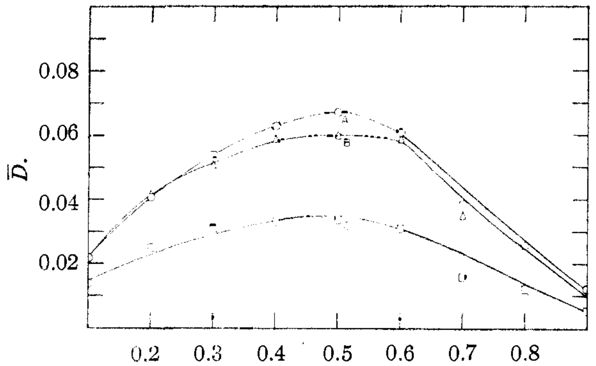

Fig. 2.—Method of continuous variations: A, 550 mμ; B, 570 mμ; C, 630 mμ.

The peaks which occur at a mole fraction of 0.5 correspond to a 1:1 mole ratio of the two components in the complex. Since the data at 570 mμ still indicate a 1:1 complex with only a small shift toward higher ratios, it may be concluded that, although other complexes may be present in the system, they occur in low enough relative concentrations to make their detection by the present methods uncertain.

The experimental errors, arising particularly from the relatively large corrections necessary for absorption by the chromium(III) nitrate, make it impractical to use the spectrophotometric technique for studies of the structure of the complex. It is notable, however, that the color effects, etc., with the sulfosalicylic acid resemble closely those reported with sulfate.[4]

The experimental difficulties also make infeasible calculations of the extinction coefficient of the complex and the equilibrium constant for its formation. Approximate evaluation of these by the methods already outlined[1] indicates that the extinction coefficient for the complex is approximately 40 at 550 mμ and that the equilibrium constant for formation of the complex from chromium(III) and sulfosalicylate ions is of the order of magnitude of 10^{-3}.

Experimental

Materials.—Chromium(III) nitrate stock solutions were prepared by dissolving accurately weighed quantities of the monohydrate in water at 25°. The concentration was checked by gravimetric analysis as chromium(III) oxide.

Sulfosalicylic acid and sodium hydroxide were prepared as described earlier.[1] Sodium nitrate solution was prepared by dissolving a weighed quantity of the salt in water.

Absorption measurements were made with a Beckman DU type spectrophotometer and a General Electric Hardy Recording Spectrophotometer.

In the preparation of all solutions at constant *p*H, the chromium(III) nitrate and sulfosalicylic acid were added in such amounts as to give the desired final concentration. A relatively large excess of sodium nitrate was then introduced to maintain a constant final ionic strength of 0.30. Water was added to the mixture to a point only several cubic centimeters short of the required volume. Acid or base was then added to adjust the solution to the desired *p*H before diluting to the final volume with water.

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[2] C. V. Banks and James H. Patterson, *ibid.*, **73**, 3062 (1951). See also footnote 1.

[3] P. Job, *Ann. Chim.*, **11**, 97 (1936); *cf.* Vosburgh and Cooper, THIS JOURNAL, **63**, 436 (1941).

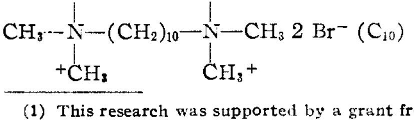
[4] *Cf.* for example: Graham, *Am. Chem. J.*, **48**, 187 (1912); Colson, *Ann. chim. phys.*, [8] **12**, 433 (1907).

A Curarimimetic Analog of Decamethylene Ditrimethylammonium (C_{10})[1]

BY F. W. SCHUELER AND CALVIN HANNA

RECEIVED SEPTEMBER 10, 1951

In a previous communication,[2] the synthesis and pharmacological properties of several hydrazonium analogs related to acetylcholine and tetraethylammonium have been reported. The present communication extends these previous studies to the synthesis of a new curarimimetric analog of C_{10} obtained through the quaternarization of unsymmetrical dimethylhydrazine with decamethylene dibromide.



$$CH_3\text{—}\overset{CH_3}{\underset{+CH_3}{N}}\text{—}(CH_2)_{10}\text{—}\overset{CH_3}{\underset{CH_3{+}}{N}}\text{—}CH_3\ 2\,Br^{-}\ (C_{10})$$

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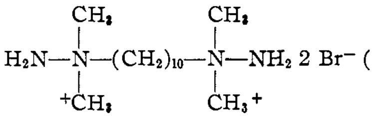
[1] This research was supported by a grant from the United States Public Health Service.

[2] F. W. Schueler and Calvin Hanna, *Arch. intern. pharmacodynamie*, **88**, 351 (1951).



$H_2N-N^{+}(CH_3)_2-(CH_2)_{10}-N^{+}(CH_3)_2-NH_2\ 2\,Br^-$ (hydrazonium analog of C_{10})

The replacement of a single nitrogen methyl group in the trimethylammonium series by an amino group of similar dimensions makes this type of analog of theoretical as well as practical interest in the field of pharmacological activity and chemical constitution.

A synthesis of unsymmetrical dimethylhydrazine through the reduction of nitrosodimethylamine using lithium aluminum hydride has already been reported.[3] During the present research it was found expedient to prepare decamethylene dibromide starting with ethyl sebacate using lithium aluminum hydride. The preparation of decamethylene dibromide from the glycol makes use of a method essentially similar to that outlined by McEwen.[4] Preparation of the hydrazonium analog of C_{10} is given in the experimental section and requires no special comment. A preliminary report upon the pharmacological properties of this material have been detailed elsewhere.[5]

The LD_{50} for mice of the hydrazonium C_{10}-analog is 26 mg. per kg. and the head drop dose (HDD) for rabbits 2.9 mg. per kg. The ratio of the LD_{50} for mice to the HDD for rabbits is, therefore, of the same order as C_{10}.

Experimental

Decamethylene Glycol.—To a slurry of 4 g. of lithium aluminum hydride in 350 ml. of dry tetrahydrofuran contained in a 1-liter 3-necked flask under reflux and vigorous stirring was added 26 g. (0.1 mole) of dry diethyl sebacate in 200 ml. of tetrahydrofuran. The addition requires 45 to 60 minutes but the time of addition may be shorter than that given above but care should be exercised in order to avoid excessive refluxing of the solvent. At the completion of the addition of the diethyl sebacate the flask contents are allowed to stand until cool (about 30 minutes). Anhydrous ethyl acetate is used to destroy any excess reagent, lumps are broken up with a stirring rod and the mixture decomposed with about 500 ml. of dilute hydrochloric acid after which the mixture is cooled. The oily layer is separated, washed twice with 100-ml. portions of cool water and finally chilled to a white solid. If the washings are likewise chilled together with the hydrochloric acid layer a further small quantity of white solid is obtained. The collected solid is washed twice with 100-ml. portions of cold water by filtration. The product represents an 80% yield of decamethylene glycol which is white if the initial reagents are pure. It melts at 71.5° (cor.) and corresponds without further purification in quality to the purified material obtained through sodium alcohol reduction.

Decamethylene Di-(dimethylhydrazonium) Dibromide.—In 10 ml. of dry ether are mixed 3.0 g. (0.01 mole) of pure decamethylene dibromide[4] and 1.2 g. (0.02 mole) of dry unsymmetrical dimethylhydrazine. The mixture is allowed to stand at room temperature in a stoppered bottle for one week. At the end of this time, 3.2 g. (98% of the theory) of a non-hygroscopic white solid is obtained after filtration and washing with small portions of dry ether; m.p. 114–115.5° (cor.). *Anal.* Calcd. for $C_{14}H_{36}N_4Br_2$: N, 16.22. Found: N, 15.88.

Unsymmetrical dialkylhydrazines react with alkyl bromides and iodides to form "onium" ion on the alkyl substituted nitrogen.[6] In the case of the hydrazonium C_{10}-analog a marked change in the curarimimetic activity would result depending on whether the compound was an "onium" bromide or an amino hydrobromide.

To 0.5 g. of the above product was added 50 ml. of cold 30% sodium hydroxide. No oil separated out and no ammoniacal odor could be detected. This solution (A) was extracted with six 50-ml. portions of ether. The combined ether extracts were evaporated to dryness and the residue (B) was extracted with 100 ml. of absolute ether. The ether was treated with dry hydrobromic acid and no crystals formed even on slow evaporation to 5 ml. The residue (B) gave a positive test for sodium ions and the aqueous solutions were alkaline. The alkaline solution (A) was allowed to remain in an uncovered beaker for 26 days during which time crystals formed over the top of the solution. In this solid, oily drops formed which were mechanically separated giving 0.12 g. of an oily semi-solid. This oil was soluble in a drop of water and on treatment with 20 ml. of a satd. sodium bromide solution no organic compound could be separated by fractional crystallization. These results would indicate that the compound prepared above is decamethylene di-(dimethylhydrazonium) dibromide since no tertiary amine could be isolated from solution (A).

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[3] F. W. Schueler and Calvin Hanna, This Journal, **73**, 4996 (1951).

[4] W. L. McEwen, *Org. Syntheses*, **20**, 24 (1940).

[5] Calvin Hanna and F. W. Schueler, Abstracted in the Proceedings of the Society for Pharmacology and Experimental Therapeutics, Omaha Meeting, 1951.

[6] Renauf, *Ber.*, **13**, 2172 (1880); Wieland and Schamberg, *ibid.*, **53**, 1333 (1920); Westphal, *ibid.*, **74B**, 759, 1365 (1941).

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On the Question of Mercury(I) Intermediates in Reactions between Hg_2Cl_2 and Ammonia

BY LIES NIJSSEN AND WILLIAM N. LIPSCOMB

RECEIVED JANUARY 14, 1952

The formation of the mercury(II) compounds $Hg_2NCl{\cdot}H_2O$ (chloride of Millon's base), $HgNH_2Cl$ (infusible precipitate) and $Hg(NH_3)_2Cl_2$ (fusible precipitate) has been demonstrated[1-4] in reactions among ammonia, ammonium chloride and mercury(I) chloride. The claim[4] of an intermediate Hg_2O has now been disproved.[1] Extensive evidence for the existence of the mercury(I) analogs of these three mercury(II) compounds has been presented by Gleditsch and Egidius.[2,3] In the present study we have repeated these chemical preparations[3] and have taken X-ray diffraction patterns with a standard General Electric XRD-3 unit. While our diffraction patterns agree favorably with those of the earlier papers[2,3] our conclusions are completely different.

The diffraction pattern attributed by Gleditsch and Egidius[2] to Hg_2NH_2Cl corresponds with our pattern of $Hg_2NCl{\cdot}H_2O$. The diffraction pattern given by Egidius[3] for $Hg_2(NH_3)_2Cl_2$ is that of a mixture of $Hg(NH_3)_2Cl_2$ and Hg_2Cl_2. The pattern[3] of Hg_2NH_2Cl is actually that of $HgNH_2Cl$ and is different from that given in an earlier paper[2] for Hg_2NH_2Cl. The pattern given[3] for $Hg_4NCl{\cdot}(H_2O)_x$ is actually that of $Hg_2NCl{\cdot}H_2O$, and we have been unable to identify the pattern given[3] by Egidius for $Hg_2NCl{\cdot}H_2O$, but unfortunately the method of preparation is not given. The struc-

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[1] S. D. Arora, W. N. Lipscomb and M. C. Sneed, This Journal, **73**, 1015 (1951).

[2] E. Gleditsch and T. F. Egidius, *Compt. rend.*, **202**, 574 (1936); *Z. anorg. Chem.*, **226**, 265 (1936); *ibid.*, **228**, 249 (1936).

[3] T. F. Egidius, *ibid.*, **240**, 97 (1938).

[4] H. Freche and M. C. Sneed, This Journal, **60**, 518 (1938).

ture determinations of $Hg_2NCl \cdot H_2O$,[5] $HgNH_2Cl$[6] and $Hg(NH_3)_2Cl_2$[7] provide conclusive evidence that these are really mercury(II) compounds. Thus the investigations of Gleditsch and Egidius do not prove the existence of mercury(I) intermediates in these reactions.

In addition, we have found no mercury(I) intermediates in investigations over the full ranges of concentrations of aqueous solutions, whether diffraction patterns are taken of wet or dry precipitates.

An interesting change occurs in the precipitates at the early stages of the reaction. When wet or immediately after drying, Hg_2Cl_2 may not be observed, but gradually appears on standing, sometimes rapidly, and sometimes after a day or so. We believe that this phenomenon is due to the presence of Hg and other reaction products formed at the surface of Hg_2Cl_2 crystals, which are therefore obscured from the relatively non-penetrating $CuK\alpha$ radiation. Subsequent agglomeration and evaporation of the Hg thus makes these crystals of Hg_2Cl_2 available for diffraction.

The chloride of Millon's base appears to show also a crystalline modification which is a very slight distortion of the cubic form previously reported.[6] The (222) reflection shows splitting into two nearly equal components 0.6° apart on the diffraction pattern. This split reflection becomes single on conversion to the base by treatment with 20% aqueous KOH, and becomes split again when the base is reconverted to the chloride in 20% aqueous KCl. The nature of this distortion has not been ascertained, partly because the particle size broadening of the reflections makes the details of the pattern obscure, especially at higher scattering angles. The variations of this small distortion may be related to the degree of hydration of this compound, or to the degree of substitution of OH^- for Cl^-.

Aid of part of this research by a Grant from the Graduate School of the University of Minnesota is gratefully acknowledged.

(5) W. N. Lipscomb, *Acta Cryst.*, **4**, 156 (1951).

(6) W. N. Lipscomb, *ibid.*, **4**, 266 (1951).

(7) C. H. MacGillavry and J. M. Bijvoet, *Z. Kristall.*, **94**, 231 (1936).

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The Reaction of Sodium Tungsten Bronze with Molybdenum(VI) Oxide. The Sodium Molybdenum Bronze[1]

BY M. E. STRAUMANIS AND K. K. IRANI

RECEIVED JANUARY 7, 1952

Sodium tungsten bronze easily dissolves tungsten(VI) oxide at elevated temperatures, forming solid solutions.[2] It was expected that molybdenum (VI) oxide, which is very similar in its properties to tungsten(VI) oxide, would also form solid solutions with the sodium tungsten bronze. The purpose of this paper is to describe the reactions that occurred during the heating of a mixture of the two compounds just mentioned.

Closely related to the reactivity of molybdenum (VI) oxide with sodium tungsten bronze is the preparation and existence of alkali molybdenum bronzes. Sodium molybdenum bronze was first mentioned by Stavenhagen and Engels,[3] who obtained the bronze, by the electrolytic decomposition of fused sodium molybdate in the form of a dark bluish-grayish, or reddish-violet powder, having the properties of the bronzes. Later the lithium, sodium and potassium molybdenum bronzes were prepared by Canneri,[4] using the same method and with a small yield. However, the next year Burgers and van Liempt[5] showed that the bronzes mentioned by Canneri were mixtures consisting of molybdenum(IV) oxide and molybdenum blue. Finally, according to Magnéli, only molybdenum oxides were obtained by Hägg in similar experiments.[6]

An attempt was made to prepare sodium molybdenum bronze by a method described previously.[2]

Experimental

The materials for the experiments were sodium tungsten bronzes containing 10 and 22% by weight tungsten(VI) oxide,[2] dry molybdenum(VI) oxide and sodium molybdate. The molybdenum metal used was an electrolytically produced powder.

Calculated amounts of these reagents were weighed, intimately mixed, and ground. Then the mixtures were put in porcelain crucibles with a copper lid and heated in a furnace which could be evacuated. Or else the mixtures were put into quartz glass bulbs, evacuated, sealed off, and heated at different temperatures between 450 and 1000°.

The reaction products were well washed with water.[2] The composition of all water soluble and insoluble compounds were identified by their X-ray diffraction patterns. The corresponding compounds for the identification were synthesized (*e.g.*, $Na_2WO_4(MoO_3)_x$, $x < 1$). All reagents used were of the highest purity obtainable.

Results and Discussion

Sodium Tungsten Bronze and Molybdenum(VI) Oxide.—Qualitative tests showed that a reaction proceeds between these two substances, because the mixture turns deep blue when heated. Samples of sodium bronze (with 10% tungsten(VI) oxide) containing 5, 10, 15, 20 and 30% by weight of molybdenum(VI) oxide were prepared and heated for two hours at 800°. This resulted in there still being a bronze in the first four cases, but with a lattice parameter which rapidly decreased from 3.8436 kX. to 3.8310 kX. as the molybdenum(VI) oxide content was increased. However, the appearance of strange lines in the patterns of samples even with 5% molybdenum(VI) oxide testified that no equilibrium was reached during the heating and that a chemical reaction occurred. The strange lines belonged to the powder pattern of molybdenum(IV) oxide. Hence, the following reactions occur during heating in a vacuum, assuming that reaction (1) represents the equilibrium of the sodium bronze at elevated temperatures as shown previously[2]

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(1) Excerpt from a thesis submitted by K. K. Irani to the Graduate School of the University of Missouri, School of Mines and Metallurgy, in partial fulfillment of the requirements for a Master's Degree.

(2) M. E. Straumanis, THIS JOURNAL, **71**, 679 (1949).

(3) A. Stavenhagen and E. Engels, *Ber.*, **28**, 2281 (1895).

(4) C. Canneri, *Gazz. chim. ital.*, **60**, 113 (1930).

(5) W. G. Burgers and J. A. M. van Liempt, *Z. anorg. Chem.*, **202**, 325 (1931).

(6) A. Magnéli, *N. Acta Reg. Sc. Upsaliensis*, **14**, No. 8, 16 (1949).

$$2NaWO_3 \rightleftarrows 2Na + 2WO_3 \qquad (1)$$

$$2Na + MoO_3 \longrightarrow Na_2O + MoO_2 \qquad (2)$$

$$Na_2O + xWO_3 \longrightarrow Na_2WO_4(WO_3)_{x-1}\ x > 1 \qquad (3)$$

The excess ($2 - x$) of WO_3 dissolved in the unreacted bronze, forming bronzes with a deeper (red or blue) color showing a smaller lattice constant

$$NaWO_3 + yWO_3 \longrightarrow NaW^{V}O_3(W^{VI}O_3)_y,\ y = 2 - x \qquad (4)$$

If the molybdenum(VI) oxide content was increased $Na_2W_2O_7$ as an added product, according to reaction (3), was formed.

Thus, as a final product, a mixture of a deeper colored bronze and molybdenum(IV) oxide resulted, while the sodium bitungstate was removed by the washing operation. Qualitative tests showed that there was only a trace of molybdenum in the sodium bronze. Therefore, molybdenum (VI) oxide was not dissolved by the bronze and acted only as an oxidizer, making solid solutions of the type $NaW^{V}O_3(Mo^{VI}O_3)_x$ impossible. Even the copper lid of the crucible (with larger amounts of molybdenum(VI) oxide present) was attacked: $Cu + MoO_3 \rightarrow MoO_2 + CuO$. This strong oxidizing property of molybdenum(VI) oxide at elevated temperatures was also observed by others.[7]

In the case of 30% molybdenum(VI) oxide, the reactions (2) and (4) proceeded far enough to leave very little of the original bronze which, in addition, was transferred into the tetragonal bronze because of the large amount of tungsten(VI) oxide dissolved according to (4). The formation of $Na_2Mo_2O_7$, and of a water-soluble compound $Na_2WO_4(MoO_3)_x$ ($x < 1$) instead of (3) is also possible. The powder patterns of these three substances including $Na_2W_2O_7$ are identical except that the sodium tungstate containing molybdenum(VI) oxide has a contracted lattice.

The experiments performed with a sodium bronze containing 22% tungsten(VI) oxide at 1000° for two hours led to the same final products.

No molybdenum(VI) oxide containing sodium bronze was obtained when molybdenum was chosen instead of tungsten as a reducer

$$2Na_2WO_4 + 2WO_3 + Mo \longrightarrow 4NaWO_3 + MoO_2 \qquad (5)$$

Of course, the bronze $NaWO_3$ always contained a dissolved excess of tungsten(VI) oxide.

All other combinations of the 3 substances, as shown on the left side of equation (5), being partly replaced by the corresponding molybdenum (or tungsten) compounds after the reaction at 800–900° in a vacuum gave only molybdenum(IV) oxide. The products such as Na_2WO_4, $Na_2W_2O_7$, $Na_2WO_4(MoO_3)$ and $Na_2Mo_2O_7$ were washed away in the subsequent treatment with water.

The Alkali Molybdenum Bronzes.—Completely replaced the initial products of reaction (5) by the corresponding molybdenum compounds, in no case gave any molybdenum bronzes. The chemical reason of the failure to prepare these bronzes might be as follows: For the formation of the bronzes it is necessary that the heavy metal should have the property to coexist in two valency stages at the elevated temperatures of formation. In the alkali tungsten bronzes tungsten is hexa- and pentavalent.[8] This, evidently, is impossible in the case of molybdenum bronzes because of the high oxidizing power of molybdenum(VI) oxide. Glemser and Lutz[9] showed that all lower molybdenum oxides above 700° were decomposed into molybdenum-(VI) and -(IV) oxides.[9] But four-valent molybdenum, similar to four-valent tungsten, does not enter the lattice of the bronzes.

The only possibility of obtaining molybdenum bronzes seemed to be by synthesis below 700°. Dry sodium molybdate, molybdenum(VI) oxide and molybdenum powder were heated in a vacuum in two separate experiments at 510 and 450° for 24 and 50 hours, respectively. After the soluble compounds were washed away, only molybdenum (IV) oxide remained.

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[7] G. W. Rathenau and J. L. Meijerding, *Metallurgia*, **42**, 167 (1950).

[8] G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1935); A. Magnéli, *Nova Acta Soc. Sc. Ups.*, [IV] **14**, No. 8, 14 (1949).

[9] O. Glemser and G. Lutz, *Z. anorg. allgem. Chem.*, **263**, 2 (1950).

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Adsorption and Reaction of Carbon Monoxide on Promoted Iron Catalysts

BY R. E. PROBST, SEYMOUR MEYERSON AND HERMAN S. SEELIG

RECEIVED DECEMBER 10, 1951

Adsorption of carbon monoxide on iron catalysts has been the subject of many investigations,[1] and it has been inferred[1e,f,h] that it is possible to make such studies up to 150° without interfering chemical reactions. However, during the course of studies at 0–108° on the adsorption of carbon monoxide on potassium carbonate promoted iron catalysts, it has been found that chemical reactions occur that produce iron pentacarbonyl and carbon dioxide.

The experiments were carried out in an adsorption apparatus of conventional design[2] and operating at constant pressure.[3] The iron catalyst was of a type used for the synthesis of hydrocarbons from carbon monoxide and hydrogen. It consisted of mill scale in the form of a powder finer than 100 mesh, promoted with 0.5 wt. % K_2O.[4] After reduction with hydrogen at 340° under 250 p.s.i., the promoted catalyst was degassed at 450° until a pressure of 1.5×10^{-6} mm.

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[1] (a) R. A. Beebe and N. P. Stevens, THIS JOURNAL, **62**, 2134 (1940); (b) O. Beeck, "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., 1950, p. 164; (c) S. Brunauer and P. H. Emmett, THIS JOURNAL, **62**, 1732 (1940); (d) J. C. Ghosh, N. V. C. Sastri and K. A. Kini, *Current Sci. (India)*, **15**, 283 (1946); *C. A.*, **41**, 1907^c (1947); (e) S. Kodama, S. Matsumura, K. Tarama, T. Ando and K. Yoshimori, *J. Soc. Chem. Ind. (Japan)*, **47**, 1 (1944); *C. A.*, **43**, 2413^d (1949); (f) S. Kodama, S. Matsumura, K. Yoshimori, Y. Nishibayashi, N. Kadota and Z. Iwamura, *J. Chem. Soc. (Japan)*, *Ind. Chem.*, **51**, 98 (1948); *C. A.*, **44**, 9136^b (1950); (g) S. Matsumura, K. Tarama and S. Kodama, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **37**, 302 (1940); (h) H. H. Podgurski, J. T. Kummer, T. W. Dewitt and P. H. Emmett, THIS JOURNAL, **72**, 5382 (1950).

[2] A. Weissberger, "Physical Methods of Organic Chemistry," Second Edition, Part I, Interscience Publishers, Inc., New York, N. Y., 1949, pp. 466–472.

[3] H. S. Taylor and C. D. Strother, THIS JOURNAL, **56**, 586 (1934).

[4] S. W. Walker, U. S. Patent 2,485,945 (October 25, 1949).

was obtained. Hydrogen adsorption experiments in this Laboratory indicated that temperatures from 350 to 400° remove most of the hydrogen, but it has been reported[5] that even under these conditions the surface will still contain some hydrogen. In each experiment the dead volume of the adsorption cell was determined with helium, and then the helium was pumped off at 350° until a vacuum of 10^{-6} mm. was obtained. The gas used in the adsorption experiments contained (in volume per cent.) 98.4 carbon monoxide, 0.1 carbon dioxide, 0.7 hydrogen and 0.8 nitrogen.

Four apparent adsorption isotherms were measured at 0, 25, 65 and 108° and 280 mm. pressure. The results, plotted in Fig. 1, cover only the first 11 hours of each experiment, although in each case the adsorption was followed much longer. Even after 144 hours, the catalyst was still "adsorbing" gas at a slow but finite rate. An experiment with an unpromoted mill-scale catalyst showed essentially the same "adsorption" isotherm at 25°.

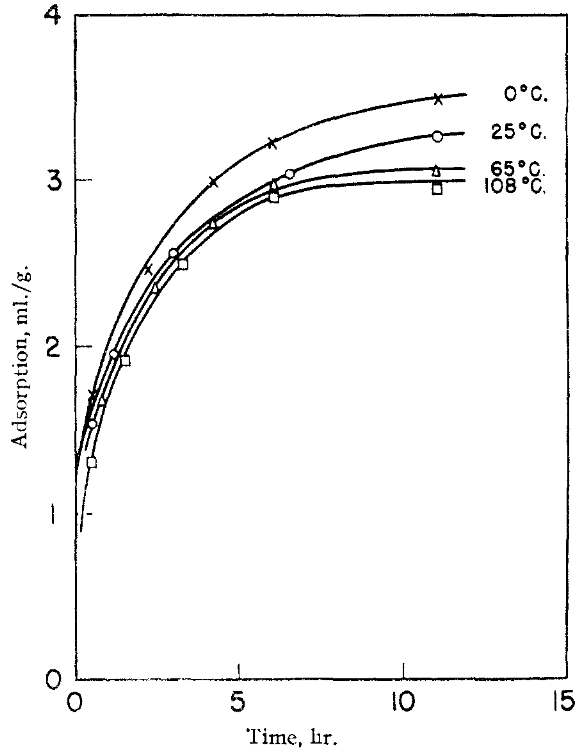

Fig. 1.—Apparent adsorption isotherms of carbon monoxide on a promoted iron catalyst.

After the measurement of each isotherm had been completed, a sample of the gas in the adsorption cell was transferred directly to the mass spectrometer for analysis. During this operation, the temperature and pressure of the cell were held constant to prevent readsorption. The gas analyses, given in Table I, unexpectedly revealed iron pentacarbonyl and large amounts of carbon dioxide. The absolute values of the iron pentacarbonyl concentrations are subject to some question, but comparisons of the concentrations at the different temperatures are believed to be valid.

TABLE I

COMPOSITION OF GAS IN ADSORPTION CELL AFTER 144 HOURS

Temp., °C.	Composition, volume per cent. $Fe(CO)_5$	CO_2	H_2	N_2	CO
0	0.05	0.1	0.3	0.6	98.9
25	.6	8.9	.7	.8	89.0
25[a]	.6	9.1	.8	.9	88.6
65	.3	12.3	.3	1.0	86.1
65[a]	.3	12.0	.1	0.9	86.7
108	<0.05	16.7	.09	1.0	82.2

[a] Duplicate adsorption experiment.

The results indicate that, at temperatures as low as 25°, carbon monoxide will react with reduced iron to form iron pentacarbonyl. The concentrations of iron pentacarbonyl in the adsorption cell after 144 hours at 0 and 25° are lower than would have been predicted from equilibrium considerations[6]; it is assumed that this is the result of a low reaction velocity. The observed pentacarbonyl concentration at 65° is ten times the calculated value for some unexplained reason. At 108° the calculated concentration is 0.0038%, which is well below the sensitivity of the mass spectrometer.

The carbon dioxide in the adsorption cell could have been produced by the iron-catalyzed conversion of carbon monoxide to carbon and carbon dioxide. However, extrapolation of the kinetic data for this reaction[7] eliminates it as the source of the carbon dioxide. It is possible that the carbon dioxide, and presumably iron carbide, were produced by the decomposition of iron pentacarbonyl[8]; kinetic or equilibrium data on this reaction are not available.

In any event, the interpretation of carbon monoxide adsorption experiments at temperatures above 25° is subject to question unless gas analyses are made to confirm the absence of chemical reactions.

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Reversal of 2-Ethylhex-2-enal to Butyraldehyde

BY Y. SPRINZAK

Self-condensation of butyraldehyde leads *via* the aldol[1] to 2-ethylhex-2-enal[2] (I)

$$C_2H_5CH_2CHO \longrightarrow C_2H_5CH_2CHOHCH(C_2H_5)CHO \longrightarrow$$
$$C_2H_5CH_2CH{=}C(C_2H_5)CHO \quad (I)$$

In an attempt to condense (I) with fluorene by azeotropic distillation in presence of freshly fused potassium hydroxide,[3] a hydrocarbon of m.p. 55°

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[5] J. T. Kummer and P. H. Emmett, *J. Phys. Colloid Chem.*, **55**, 337 (1951).

[6] H. Pichler and H. Walenda, *Brennstoff-Chem.*, **21**, 133 (1940).

[7] C. I. Chufarov and M. F. Antonova, *Bull. acad. sci., U. R. S. S., Classe sci. tech.*, 381 (1947).

[8] A. Mittasch, *Z. angew. Chem.*, **41**, 827 (1928).

[1] V. Grignard and co-workers, *Bull. soc. chim. France*, [4] **37**, 425 (1925); *Compt. rend.*, **177**, 300 (1923); *Ann. chim.*, [10] **2**, 282 (1924); [10] **9**, 5 (1928); Ch. Weizmann and S. F. Garrard, *J. Chem. Soc.*, **117**, 324 (1920).

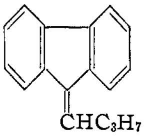
[2] V. Grignard and A. Vesterman, *Bull. soc. chim. France*, [4] **37**, 425 (1925).

[3] D. Lavie and E. Bergmann, *ibid.*, 250 (1951).

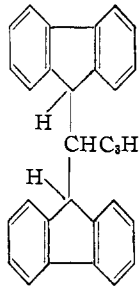
was obtained which had an unexpectedly low boiling point. It was identified as 9-butylidenefluorene[3a] by comparing with a sample prepared from 9-butylfluorenol by dehydrating with a mixture of concentrated hydrochloric and glacial acetic acids.

A second product of the reaction was a hydrocarbon $C_{30}H_{26}$ of m.p. 186–187°, which exhibited the spectrum of fluorene[4] (Fig. 1). It is assumed that this compound is 1,1-di-(9'-fluorenyl)-butane (III) and that it had been formed by a Michael reaction between 9-butylidenefluorene and excess fluorene. Such a reaction has been observed in the case of dibiphenylene ethylene and benzylidenefluorene[5]; it is made possible by the polar character of the semicyclic double bond in fulvenes and their benzologs.[3,6] As the central carbon atom of the fluorene system constitutes the negative end of these dipoles, it is likely that II adds fluorene to form III.

Whilst it was known that aldols[7] and ketols[8] revert to the constituent carbonyl compounds from which they are formed, no such reversion appears to be known generally for the α,β-unsaturated aldehydes and ketones which result from the dehydration of these aldols and ketols.[9] It must, therefore, be assumed, that either 2-ethylhex-2-enal (I) or its condensation product with fluorene, primarily formed, undergo hydration at the original α,β-double bond, followed by formation of two moles of butyraldehyde or one mole each of 9-butylidenefluorene (II) and butyraldehyde, respectively.



II



III

Experimental

9-Butylidenefluorene (II) (a) From 2-Ethylhex-2-enal (I).—A mixture of fluorene (33.2 g., 0.20 mole) and 2-ethylhex-2-enal (27 g., 0.21 mole) was refluxed azeotropically and with stirring for 6 hours with toluene (100 cc.) in the presence of freshly fused and powdered potassium hydroxide (14 g., 0.25 mole). A small amount (0.7 cc.) of water was liberated. The dark mixture was treated with water and the toluene layer separated, washed with dilute sulfuric acid and water and dried. High-vacuum distillation yielded fluorene (in the fraction b.p. 105–110° (0.08 mm., 11 g.) and a main fraction, b.p. 135–150° (0.08 mm.) (22 g.), which soon started to crystallize. By crystallization from hexane at low temperature, the crystalline part was isolated; yield 5 g. The m.p. (52°) was raised to 55° by recrystallization from alcohol. A second crop of 5 g. was obtained by evaporating the hexane mother liquor, dissolving the residue in alcohol and cooling the solution to −20°; the crystals formed were freed from adherent oil by washing with ice-cold alcohol.

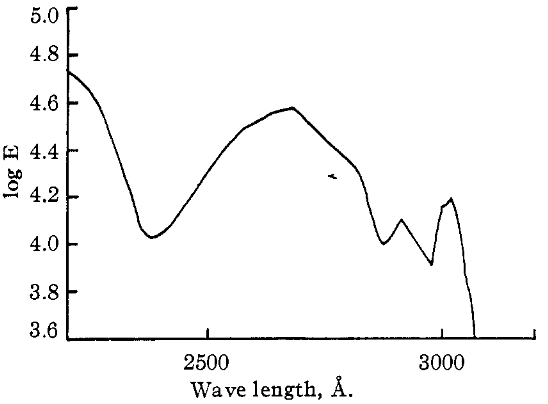


Fig. 1.—Absorption spectrum of the presumed 1,1-di-(9-fluorenyl)-butane in dioxane.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3; mol. wt., 220. Found: C, 92.8; H, 7.4; mol. wt., 213 (Rast), 220 (benzene).

(b) A solution of fluorenone (8 g.) in ether (100 cc.) was added to the Grignard solution prepared from butyl bromide (6.4 g.) and magnesium (1.3 g.) in ether (75 cc.). The reaction product was refluxed for 30 minutes and decomposed by means of ice and ammonium chloride. The residue of the ether solution crystallized spontaneously (7 g., 66%). Recrystallization from alcohol gave **9-butylfluorenol**, m.p. 129–131°.[10]

Concentrated hydrochloric acid (2.5 cc.) was added to a boiling solution of 9-butylfluorenol (1 g.) in glacial acetic acid (12.5 cc.). The crystals formed on cooling were filtered, washed with water and alcohol and recrystallized from heptane; m.p. 55°. The products of the two syntheses (a) and (b) did not depress the melting points of each other.

9-Butylidenefluorene (III) is autoxidized easily, turning gradually yellow and soft and developing the odor of butyraldehyde.[11] No deterioration was observed in a sample kept under nitrogen for four months.

9-Butylidenefluorene dibromide was prepared in carbon tetrachloride and recrystallized from alcohol; m.p. 93–94°.

Anal. Calcd. for $C_{17}H_{16}Br_2$: Br, 42.1. Found: Br, 42.5.

1,1-Di-(9'-fluorenyl)-butane (III).—The residue of the distillation of the reaction product from fluorene and (I) (10 g.) was triturated with warm petroleum ether, which left a white powder (2.3 g.) undissolved, m.p. 183–186°. After recrystallization from heptane, it had m.p. 186–187°.

Anal. Calcd. for $C_{30}H_{26}$: C, 93.3; H, 6.7; mol. wt., 386. Found: C, 93.2; H, 6.3; mol. wt., 378 (benzene).

[3a] Schultz and Smullin, This Journal, **62**, 2904 (1940).

[4] W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.* (*London*), **A158**, 634 (1937).

[5] L. A. Pinck and G. E. Hilbert, This Journal, **68**, 2014, 2739 (1946): the structure of the condensation product with benzylidenefluorene has been determined by E. Bergmann and D. Lavie, *ibid.*, **74**, in press (1952).

[6] A. Pullman, G. Berthier and B. Pullman, *Bull. soc. chim. France*, 1097 (1950) (also for previous literature); E. Bergmann and E. Fischer, *ibid.*, 1084 (1950).

[7] See, *e.g.*, for acetaldol: Beilstein, 2nd Suppl., Vol. I, p. 868.

[8] See, *e.g.*, H. Hammarsten, *Ann.*, **421**, 293 (1920).

[9] L. Claisen (*Ber.*, **7**, 1168 (1879)) and C. Harries (*ibid.*, **32**, 1326 (1899)) have described the reversion of mesityl oxide to acetone by boiling dilute sulfuric acid and alkali, respectively.

[10] W. Schlenk, Jr., *Ber.*, **64**, 742 (1931).

[11] Compare, for 9-ethylidenefluorene: M. Daufresne, *Bull. soc. chim. France*, [4] **1**, 1233 (1907).

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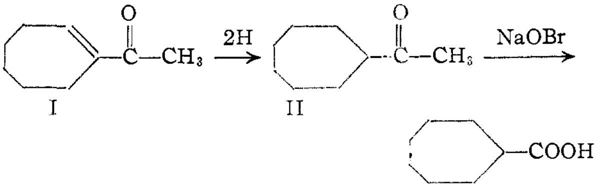
Received August 3, 1951

Synthesis of Acetylcycloheptene

By William Taub and Jacob Szmuszkovicz

Received December 10, 1951

In connection with experiments directed toward the synthesis of tricyclic compounds containing seven-membered rings, acetylcycloheptene (I) has been prepared by the condensation of cycloheptene and acetyl chloride in carbon disulfide in the presence of aluminum chloride; it is the only defined product of the reaction and is obtained in 22% yield, isolated as the semicarbazone. (I) had been



previously prepared[1] by treatment of 1-ethinylcycloheptanol with formic acid; the reported ultraviolet spectrum of the product and the melting point of its semicarbazone are in good agreement with our observations. Friess and Pinson[2] have found that under the condition of Nenitzescu and Cioranescu[3] for the condensation between cycloheptene and acetyl chloride rearrangement and hydrogen transfer took place, and a mixture of acetylmethylcyclohexanes is obtained. The structure of (I) was, therefore, rigidly demonstrated. Hydrogenation led to acetylcycloheptane (II); the melting point of its semicarbazone agreed with that reported[2] for the product obtained through the reaction between cycloheptylmagnesium bromide and acetic anhydride.

Furthermore, hypobromite oxidation of (II) afforded cycloheptanecarboxylic acid which was characterized as its amide.

Experimental[4,5]

Cycloheptene was prepared by reduction of technical cycloheptanone[6] with aluminum isopropoxide,[7] and distillation at atmospheric pressure of the crude cycloheptanol over β-naphthalenesulfonic acid, b.p. 113–115° (756 mm.); yield 74%.

Acetylcycloheptene (I).—Aluminum chloride (166 g., 1.25 moles) was added in small portions over a period of 2.5 hours to a stirred solution of cycloheptene (120 g., 1.25 moles) and acetyl chloride (100 g., 1.27 moles) in 650 ml. of dry carbon disulfide. The temperature of the reaction mixture was maintained between −5 to 0°. Practically no hydrogen chloride was evolved. Stirring was continued for an additional hour at the same temperature; then the reaction mixture was poured into a vigorously stirred mixture of concentrated hydrochloric acid and crushed ice. The organic layer was washed with water and sodium bicarbonate solution and dried over calcium chloride. The solvent was evaporated and the residue distilled from 150 g. of anhydrous sodium carbonate at atmospheric pressure. The oil (75 g.) which came over at 208–215°, was distilled again from 50 g. of anhydrous sodium carbonate and yielded then 60 g. of a colorless liquid, b.p. 208–211° (756 mm.).

This product (57 g.) was treated with semicarbazide acetate and afforded 34 g. of a semicarbazone, melting at 194–195° (dec.) after two recrystallizations from ethanol; ultraviolet λ_{max} 264 mμ (log ε 4.39).

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.5; H, 8.8. Found: C, 61.5; H, 8.7.

A second crop of 17 g. (m.p. 188–190°) was isolated from the mother liquor.

Decomposition of the semicarbazone was carried out by refluxing with an aqueous solution of oxalic acid, b.p. 103.5° (20 mm.); ultraviolet λ_{max} 236 mμ (log ε 4.01); 308 mμ (log ε 1.66).

Anal. Calcd. for $C_9H_{14}O$: C, 78.3; H, 10.2. Found: C, 78.4; H, 9.9.

Acetylcycloheptane (II).—(I) (6.9 g.) was dissolved in 50 ml. of 95% ethanol and hydrogenated in the presence of 0.2 g. of 5% Pd-charcoal in an Adams hydrogenation apparatus. The theoretical amount of hydrogen was absorbed during 16 minutes. The mixture was filtered and concentrated to 10 ml. The semicarbazone was prepared as before; m.p. 177–178°; unchanged on recrystallization, yield 9.0 g. (97%).

Anal. Calcd. for $C_{10}H_{19}ON_3$: C, 60.9; H, 9.6. Found: C, 60.6; H, 9.3.

The semicarbazone (6.7 g.), oxalic acid (30 g.) and 150 ml. of water were refluxed for three hours, and the product worked up as usual. (II) (3.8 g., 80%) boiled at 101–102° (29 mm.).

Anal. Calcd. for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 77.3; H, 11.7.

Cycloheptanecarboxylic Acid.—The hypobromite oxidation of (II) was carried out according to the known procedure.[8] The alkaline reaction mixture was steam distilled, acidified and extracted with ether. The ethereal solution was washed with water, dried on sodium sulfate and evaporated. The resulting oily acid was converted into the acid chloride with thionyl chloride and the latter treated, without further purification, with a concentrated aqueous ammonia solution. The crude amide, m.p. 150–165°, was recrystallized from boiling water, which left some brown, oily impurity undissolved. The amide crystallized in large colorless plates, m.p. 191–193.5°. After one further recrystallization from water it melted at 193.5–194.5°.[9]

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[1] I. Heilbron, E. R. H. Jones, J. B. Toogood and B. C. L. Weedon, *J. Chem. Soc.*, 1827 (1949).

[2] S. L. Friess and R. Pinson, Jr., THIS JOURNAL, **73**, 3512 (1951).

[3] C. D. Nenitzescu and E. Cioranescu, *Ber.*, **69**, 1820 (1936).

[4] All melting points are uncorrected.

[5] The ultraviolet absorption spectra were determined by Dr. Y. Hirshberg, with a Beckman quartz spectrophotometer; 95% ethanol was employed as solvent.

[6] Courtesy of Messrs. J. R. Geigy, Ltd., Basle.

[7] H. Lund, *Ber.*, **70**, 1520 (1937).

[8] L. T. Sandborn and E. W. Bousquet in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 526.

[9] E. Buchner and A. Jacobi, *Ber.*, **31**, 2008 (1898); W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948); R. Willstaetter, *Ber.*, **31**, 2498 (1898).

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REHOVOTH, ISRAEL
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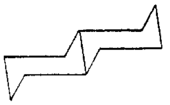
Energy Differences in the *cis*- and *trans*-Decalins

BY RICHARD B. TURNER

Barton's[1] semi-theoretical treatment of the non-bonded repulsive interactions in *trans*-decalin (I) and in the two constellations, II and III,[2] of *cis*-decalin gives I > II > III as the stability order of these forms. Uncertainties in van der Waals radius for hydrogen and in the magnitude of the repulsion term appearing in Barton's calculations, however, vitiate any quantitative estimate of the energy differences in this system, at least within an order of magnitude of ten. Thus, depending upon the choice of the above parameters, a series of values ranging from 0.52 to 8.23 kcal. was obtained for the energy difference between I and II. Estimation of the rotational barrier in ethane by the same procedure gave energy values, 0.09 to 0.39 kcal., appreciably lower than the gener-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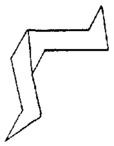
II


III

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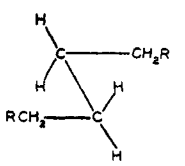
[1] D. H. R. Barton, *J. Chem. Soc.*, 340 (1948).

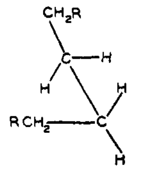
[2] Electron diffraction data of O. Bastiansen and O. Hassel, *Nature*, **157**, 765 (1946), verify II as the stable structure of *cis*-decalin. Structure III is therefore to be regarded as hypothetical.

ally accepted value of approximately 2.8 kcal., for which there is considerable support.[3,4]

In calculating statistical entropies (gas phase, 25°) for *n*-butane and for a number of other hydrocarbons including cyclohexane and the alkylcyclohexanes, Pitzer[4,5] achieved a remarkable degree of correspondence with observed entropies by employing 0.8 kcal. for the steric energy of the skew form (V) of the *n*-butane structure as compared with the stable staggered constellation IV, and 3.6 kcal. for the barrier to rotation through the eclipsed form VI. Application of these values to the "boat" and "chair" constellations of cyclohexane (VII and VIII, respectively) led to an estimated energy difference (gas phase, 25°) of 5.6 kcal. in favor of the "chair" form (VIII), since this structure possesses 6 skew interactions of the *n*-butane type, whereas the "boat" form involves 4 skew and 2 eclipsed interactions.



IV



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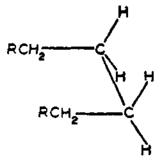
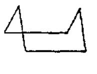


VI



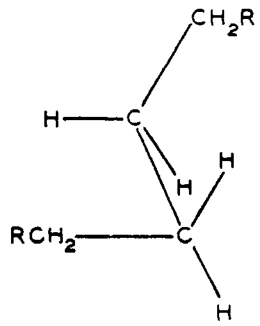
VII

VIII

Extension of these ideas to the *cis*- and *trans*-decalins gives a stability order, I > II > III, with an energy difference of 2.4 kcal. between I (6 staggered, 12 skew) and II (3 staggered, 15 skew). The heat of isomerization, I → II, determined by careful measurement of the heats of combustion (liquid phase, 25°) of pure samples of *cis*- and of *trans*-decalin is 2.12 kcal.[6]

For the purpose of direct comparison the calculated value (2.4 kcal.) must be corrected by a small factor for the difference in heats of vaporization of the two isomers at 25°. Such a correction could be derived from a knowledge of vapor pressure–temperature relationships by use of the Clausius–Clapeyron equation. Unfortunately, although the requisite data have been reported,[7] their validity, particularly at temperatures below 50° is doubtful.[8] The correction factor has therefore been approximated from an empirical equation, $\lambda_{25} = 5.4 + 0.036t_{\text{normal b.p.}}$, employed for a similar purpose by Klages.[9] Using the boiling points of *cis*- and of *trans*-decalin, 194.6 and 185.5°, respectively, the energy difference between I and II, corrected to the liquid phase at 25°, is estimated to be 2.07 kcal. Correspondence between the calculated and observed values is considerably better than could reasonably be expected of such a method of approximation.

The energy difference between II and III is more difficult to estimate. The "2-boat" form III possesses, in addition to 4 staggered, 8 skew, and 4 eclipsed *n*-butane interactions, 2 interactions of type IX, produced by a rotation of 60° from the stable staggered configuration (IV). The magnitude of this interaction cannot be evaluated in a simple way, owing to discontinuities in the rotational potential barrier curve of the Pitzer treatment. Neglecting these interactions, however, it is possible to arrive at a minimum value for the energy difference between II and III of 8.8 kcal.



Introduction of an angular methyl group (*cf.* the steroids) into *cis*- and *trans*-decalin (II and I, respectively) has the interesting consequence of lowering the energy difference between these structures from 2.4 to 0.8 kcal. In *trans*-decalin (I) the angular methyl group, being polar with respect to both rings, gives rise to 4 additional skew interactions, whereas in *cis*-decalin (II), in which the angular methyl group is polar with respect to one ring and equatorial with respect to the other, only 2 additional skew interactions result.

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[3] G. B. Kistiakowsky, J. R. Lacher and F. Stitt, *J. Chem. Phys.*, **7**, 289 (1939).

[4] K. S. Pitzer, *Chem. Revs.*, **27**, 39 (1940).

[5] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

[6] G. F. Davies and E. C. Gilbert, *ibid.*, **63**, 1585 (1941).

[7] W. F. Seyer and C. W. Mann, *ibid.*, **67**, 328 (1945).

[8] W. F. Seyer, *ibid.*, **67**, 2281 (1945) (correction). In this connection it should be noted that in reference 7 the constants A, B and C (Table II) of the equation $\ln P = AT^{-1} + B \ln T + C$ do not correspond to the data of Table I, nor to the heats of vaporization, *cis*, 10210 cal.; *trans*, 9960 cal., calculated for these substances at their respective boiling points.

[9] F. Klages, *Ber.*, **82**, 358 (1949). Application of the above expression to the analogous case of the *cis*- and *trans*-1,2-dimethylcyclohexanes gives an estimated difference between the heats of vaporization of these substances at 25° of 227 cal. The experimentally determined value (A.P.I. Reports) is 325 cal.

DEPARTMENT OF CHEMISTRY
THE RICE INSTITUTE
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NEW COMPOUNDS

N-Methyl-di-β-propionyloxyethylamine[1]

To 59.6 g. (0.5 mole) of N-methyldiethanolamine was added dropwise with rapid stirring 65.1 g. (0.5 mole) of propionic anhydride. After 2 hours, when the mixture had cooled, 65.1 g. of additional propionic anhydride was added. Saturated K_2CO_3 solution was then added to the cooled reaction mixture until evolution of CO_2 had ceased. The mixture was extracted twice with ether and the ethereal solution was dried over sodium sulfate. After removal of the ether, the yellowish fluid was distilled twice under reduced pressure; distilling range, 114.8 to 115.2° (1 mm.); yield 91.5 g. (79%). The product was water-clear; $d^{29.3}_4$ 1.0072; $n^{29.1}_D$ 1.4367; R_D calcd. 60.25 cc., R_D exptl. 60.12; pK'_a 6.62 (37°).

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[1] This compound was prepared in the course of work under a contract, recommended by the National Defense Research Committee between the Office of Scientific Research and Development and the Johns Hopkins University.