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.), $n^{20}\mathrm{D}$ 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.), $n^{20}\mathrm{D}$ 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.

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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

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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.

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

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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).