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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INSTITUTE OF POLYMER RESEARCH
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, N. Y.

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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).

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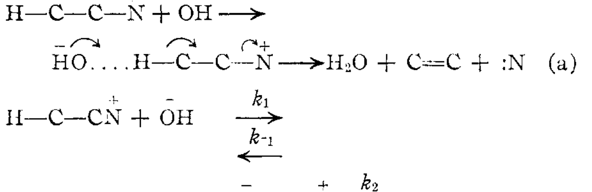
(3) R. Paul, *Bull. soc. chim.*, [5] **4**, 1115 (1937).

DEPARTMENT OF CHEMISTRY
FORDHAM UNIVERSITY
NEW YORK 58, NEW YORK

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



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

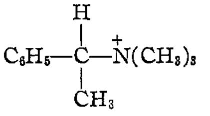
$$\mathrm{\overset{-}{H}O\ldots\ldots H{-}C{-}C{-}\overset{+}{N} \longrightarrow H_2O + C{=}C + {:}N} \quad \text{(a)}$$

$$\mathrm{H{-}C{-}C\overset{+}{N} + \overset{-}{O}H} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}$$

$$\mathrm{H_2O + \overset{-}{C}{-}C{-}\overset{+}{N}} \xrightarrow{k_2} \mathrm{C{=}C + {:}N} \quad \text{(b)}$$

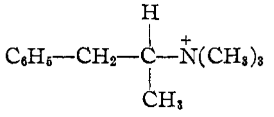
the related second order elimination of bromides, Skell and Hauser[3] have shown that 2-phenylethyl bromide, recovered from an incomplete reaction in deuteroethanol, contains no deuterium. It is concluded that path (b) is invalid, this conclusion being justified, at least in terms of the operation of 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.

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.



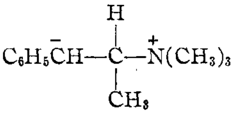
$$C_6H_5{-}\underset{CH_3}{\overset{H}{C}}{-}\overset{+}{N}(CH_3)_3$$

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).