tial, acetate ion the highest potential, and dimethylformamide a potential in between.

For the path by which III is formed in formic acid the choice to be made is between the first two mechanisms. Both mechanisms involve the discharge of a formate ion to give a formyloxy radical, which then abstracts a hydrogen atom from dimethylformamide. For either mechanism, it follows that the electrochemical oxidation of formic acid involves single-electron transfers at the anode rather than a concerted two-electron transfer. The first mechanism involves only radical intermediates, whereas the second mechanism involves the carbonium ion V as well.

It was hoped that this last distinction would provide a basis of choice between the two possibilities. Since only formate ion is discharged when a mixture of acetic and formic acids is electrolyzed, it might be expected that electrolysis of an equimolar mixture of the acids in the presence of dimethylformamide would result only in III if the first mechanism is correct but in a mixture of II and III if the carbonium ion is an intermediate. The experiment, in fact, resulted in a mixture of II and III, but the result is inconclusive, since it was later shown that II added to formic acid gives a mixture of II and III. This experiment led to the previously described conversion of the acetate, II, to the formate, III. The present experiments, thus, do not permit a definite choice between these two possible mechanisms.

The genesis of the ether amide IV is subject to the same uncertainty. This product is probably not a primary one, and it almost certainly results from etherification of N-hydroxymethyl-N-methylformamide. None of our experiments were done under rigorously anhydrous conditions, and all most likely contained sufficient water to account for the amounts of IV isolated. It is pertinent that addition of water prior to the electrolysis of potassium formate in dimethylformamide and formic acid results in a greatly diminished yield of III, indications of formaldehyde formation during distillation and the presence of appreciable quantities of N-methylformamide, a decomposition product of the hydroxymethyl compound, in the distillate. It is also pertinent that IV may be obtained by electrolysis of dimethylformamide with 5–10 vol. % of 1 *M* sulfuric acid[22] and that IV may be prepared by treating N-methylformamide with paraformaldehyde and acid.[9] Furthermore, it can be demonstrated that III is readily hydrolyzed under our experimental conditions.[23] The ester III is a possible precursor of N-hydroxymethyl-N-methylformamide, but the latter compound could also arise from reaction of V with water. This question is not resolved by our experiments.

In the electrolyses in acetic acid, dimethylformamide is discharged at a lower potential than acetate ion, and the third mechanism is the most probable one. This is the strongest statement that is permissible, since the results in Table I indicate that acetate ion is also being discharged under our experimental conditions.[24] Therefore, some of the products I and II could be the result of the first and/or the second mechanism. It is an attractive possibility that in both solvents the carbonium ion V is the critical intermediate but that this intermediate arises *via* different paths in the two solvents.

(22) D. E. Couch, *Electrochim. Acta*, **9**, 327 (1964).

(23) In a solution of III (1 ml.) in dimethylformamide (10 ml.), water (1 ml.), and formic acid (0.5 ml.) approximately 30% of III had reacted within 20 hr. at room temperature. If the solution was then warmed, another 30% reacted within minutes.

(24) The maximum current density involved in the experiments used to investigate the discharge potentials is about one order of magnitude less than that which obtains in the preparative electrolyses.

Reactions of N-Formyloxymethyl-N-methylformamide. A Useful Electrophilic Reagent

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The acid-catalyzed reactions of N-formyloxymethyl-N-methylformamide with carboxylic acids, alcohols, a mercaptan, β-naphthol, anisole, phenol, and thiourea have been studied, and the products have been determined. All of the reactions proceed by the AAL1 mechanism and involve the carbonium ion, III, as an intermediate.

A previous report from this laboratory[1] has described a convenient electrochemical procedure for preparing N-formyloxymethyl-N-methylformamide (I). It was also shown that I can be obtained by treating N-acetoxymethyl-N-methylformamide with formic acid. Such acyl group exchange is indicative of facile carbonium ion formation.[2] In Ingold's classification, the mechanism is of the AAL1 type[3] and may be written as shown in Scheme I in which the rate-determining step is the unimolecular heterolysis of II to give the carbonium ion, III.

This result suggested that N-acyloxymethyl-N-methylformamides would prove to be useful electrophilic reagents, reacting with other nucleophiles under acid catalysis to give a variety of products. This possibility has been explored with N-formyloxymethyl-N-methylformamide (I), and the results are reported in the present communication.

Acyl-exchange reactions were also successfully effected on I by benzoic acid and propionic acid. In both reactions small amounts of concentrated hydrochloric acid served as catalyst. The reaction with benzoic acid was run in dimethylformamide as solvent and gave the known N-benzoyloxymethyl-N-methylformamide.[4] In the reaction with propionic acid, the

(1) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **31**, 128 (1966).

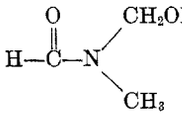
(2) S. G. Cohen, *J. Am. Chem. Soc.*, **66**, 1395 (1944).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 14.

(4) C. H. Bamford and E. F. T. White, *J. Chem. Soc.*, 1860 (1959).

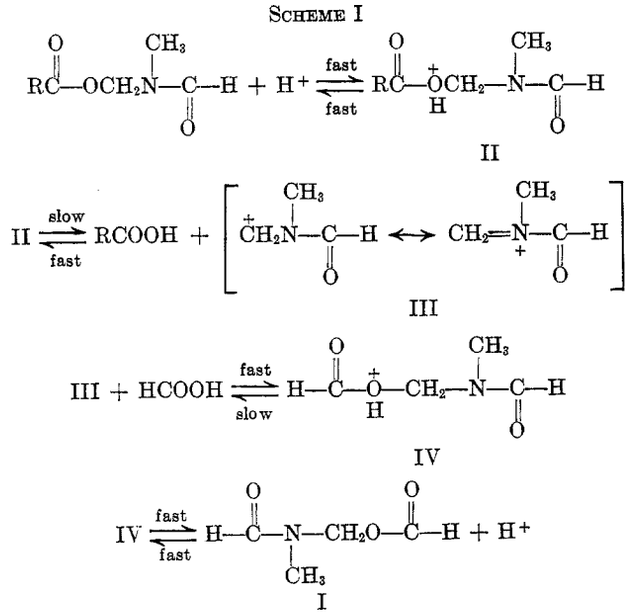
TABLE I

N-ALKOXYMETHYL-N-METHYLFORMAMIDES

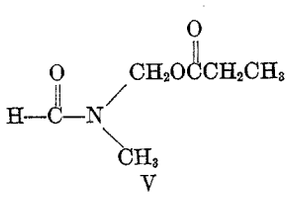


R	B.p., °C. (mm.)	n_D (°C.)	Yield, %	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
CH_3	57–60 (8)	1.4324 (24.5)	83.5	46.59	8.80	13.58	46.71	8.54	13.35
CH_3CH_2	26 (0.012)	1.4317 (24.5)	68	51.26	9.46	11.96	51.70	9.59	11.98
$(CH_3)_2CH$	31 (0.05)	1.4306 (24.5)	77	54.94	9.99	10.68	54.94	9.72	10.69
Cyclohexyl	66–67 (0.01)	1.4720 (24)	87.7	63.13	10.01	8.18	62.85	9.61	7.92
$CH_3OCH_2CH_2$	55–56 (0.01)	1.4440 (24)	79.6	48.97	8.90	9.52	49.12	8.82	9.33

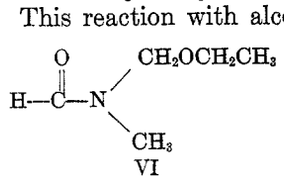
SCHEME I



acid served as the solvent, and V was isolated in good yield.

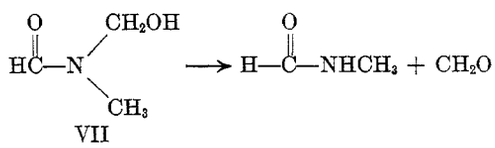


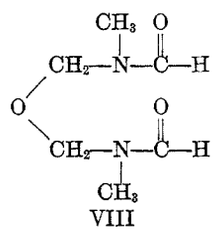
The reactions of I with alcohols constitute additional support for the AAL1 mechanism.[5] A solution of I in ethanol can be shown by v.p.c. to be stable with time at room temperature. If 1 drop of concentrated hydrochloric acid is added, the peak due to I disappears almost immediately, and a new peak, later identified as being due to N-ethoxymethyl-N-methylformamide (VI), appears. This reaction with alcohols is general



and permits the facile synthesis of the N-alkoxymethyl-N-methylformamides shown in Table I.

It might have been expected that N-hydroxymethyl-N-methylformamide (VII)[1,4] would also react with ethanol in the presence of acid to give VI, since the carbonium ion III should be readily generated in this system as well. Some VI is, in fact, formed, but the reaction is not satisfactory, since two side reactions intervene to make it difficult to obtain a good yield or isolate a pure product. In acid solution the reaction by which VII is formed is, in part, reversed to give formaldehyde and N-methylformamide, and the ion III reacts with VII to give 2,6-diformyl-2,6-diaza-4-oxaheptane (VIII), as well as with ethanol to form VI.





Under basic conditions (sodium ethoxide as catalyst), the reaction of I with ethanol follows a different course. The attack is on the carbonyl group, and the reaction is one of ester interchange. The products are ethyl formate, obtained in better than 95% yield, and VII, which decomposes during distillation to give N-methylformamide. The failure to react in neutral solution, the ester interchange in basic solution, and the ether formation in acid solution are all consistent with the AAL1 mechanism for the acid-catalyzed reactions of I.

Mercaptans react in a manner similar to alcohols to give thio ether amides. The only mercaptan studied in the present work was *n*-amyl mercaptan, which reacts with I to give a better than 90% yield of N-*n*-amylthiomethyl-N-methylformamide (IX). The structure of IX follows from its analysis and its reaction with β-naphthol to give methyl(2-hydroxynaphthylmethyl)-amine hydrochloride.[6,7]

This last reaction represents an electrophilic attack by III on β-naphthol followed by acid hydrolysis to remove the formyl group. It suggests that I should be capable of reacting with appropriately substituted aromatic structures to give N-arylmethyl-N-methylformamides. Such reactions have been observed with N-hydroxymethyl- and N-chloromethyl-N-alkylamides.[7] With these amides and β-naphthol, hydro-

(5) S. G. Cohen and A. Schneider, *J. Am. Chem. Soc.*, **63**, 3382 (1941).

(6) W. J. Burke, M. J. Kolbezen, and C. W. Stephens, *ibid.*, **74**, 3601 (1952).

(7) H. Böhme, A. Dick, and G. Driesen, *Chem. Ber.*, **94**, 1879 (1961).

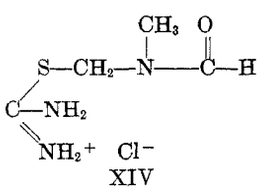
chloric acid was a suitable catalyst, but with less active aromatic compounds (*e.g.*, benzene and toluene), a Lewis acid was required.

The reaction of I and β-naphthol in dimethylformamide, with a small amount of sulfuric acid as catalyst, proceeds at room temperature to give N-methyl-N-(2-hydroxynaphthylmethyl)formamide in 82% yield. Sulfuric acid is also a suitable catalyst for the reaction with anisole, which serves as both reactant and solvent. The product, X, was a high-boiling liquid, giving a correct analysis for $C_{10}H_{13}NO_2$. Hydrolysis of X gave a 56.5% yield of the known N-methyl-*p*-methoxybenzylamine hydrochloride[8] as the only isolable product. Although X may, in fact, be a single pure isomer, the available evidence permits only the conclusion that the major component of X is N-methyl-N-*p*-methoxybenzylformamide, since the possibility that some of the *o*-methoxy isomer was present has not been eliminated.

The reaction of I with phenol, catalyzed by hydrochloric acid, resulted in a 90.3% yield of crude product which was separated by fractional crystallization into two solids, XI having m.p. 135–137° and XII having m.p. 85–88°. Both solids showed the correct analysis for $C_8H_{11}NO_2$. Hydrolysis of XI gave the known N-methyl-*p*-hydroxybenzylamine hydrochloride,[9] and its structure is, therefore, established as N-methyl-N-*p*-hydroxybenzylformamide. XII was shown to be N-methyl-N-*o*-hydroxybenzylformamide, since its hydrolysis resulted in the known N-methyl-*o*-hydroxybenzylamine hydrochloride.[8]

It is of interest that N-phenoxymethyl-N-methylformamide (XIII) was not a product of this reaction. XIII, if formed, would still be capable of reacting with acid to form the carbonium ion, III. In both products, XI and XII, that were obtained a new carbon–carbon bond has been formed. These compounds are less capable of reacting with a proton to form III. It is, therefore, reasonable that only XI and XII should be present and that XIII should be absent when the system reaches equilibrium.

Finally, when I is added to a solution of thiourea hydrochloride in dimethylformamide, the isothiouronium salt XIV precipitates within a few hours. The structure of XIV is established by its analyses and by its reaction with β-naphthol to give methyl(2-hydroxynaphthylmethyl)amine hydrochloride.



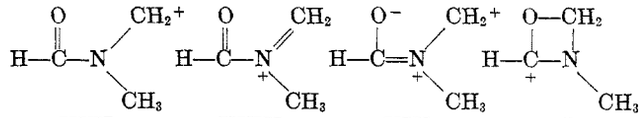
XIV

The transformations which have been described above are related to a large body of reactions for systems having a methylene group bonded to two atoms, both of which have one or more unbonded electron pairs. The most common systems are those containing the grouping, –X–CH_2–Y–, where X is S, O, or N and Y is O or halogen, and the compounds most frequently used are those in which Y is a halogen or the oxygen of a hydroxy group. The compounds which have been studied include the chloromethyl ethers,[10] amines,[11] and sulfides[12] and the N-chloromethyl- and N-hydroxymethylamides,[7,13] lactams,[14] and imides.[13,15]

Of the foregoing classes of compounds the ethers and amines are the most reactive, the sulfides, amides, and lactams are of intermediate reactivity, and the imides appear to be least reactive. A multiplicity of reaction mechanisms is involved in the reactions of these compounds, and, for the most part, these mechanisms have not been elucidated fully. Bimolecular as well as unimolecular reactions are involved, and both acid- and base-catalyzed reactions have been observed.

The diversity of available reaction paths will be illustrated with a single example. N-Ethoxymethylphthalimide (XV) may be prepared by warming N-bromomethylphthalimide with ethanol or by treating the bromomethyl compound with sodium ethoxide at room temperature.[16] However, the mechanism which permits the ready conversion of I to VI is not operable with the phthalimide derivatives. If N-acetoxymethylphthalimide (XVI)[15] is dissolved in ethanol at the boiling point and a catalytic quantity of concentrated hydrochloric acid is added, no reaction takes place, and XVI can be recovered unchanged after the mixture has been left standing overnight at room temperature. If more acid is added and the solution is refluxed 5.5 hr., XVI is transformed almost quantitatively to N-hydroxymethylphthalimide, probably by an acid-catalyzed hydrolysis with the attack on the carbonyl group of XVI.

We have attributed the many transformations of I to an AAL1 mechanism for which the rate-determining step is the formation of the ion III, having the contributing structures XVII and XVIII. Two other possible contributing structures, XIX and XX, were not considered significant, XIX because it has positive



XVII XVIII XIX XX

charges on adjacent atoms and XX because it involves large changes in the bond angles and the spatial arrangement of the atoms. The molecule's geometry does not permit effective overlap of the carbonyl orbitals with the orbitals of the cationic carbon atom. When the carbonyl group is absent, as in the chloromethyl ethers and amines, the reactivity is enhanced.

(8) N. H. Cromwell and H. Hocksema, *J. Am. Chem. Soc.*, **67**, 1658 (1945).

(9) M. Tiffeneau, *Bull. soc. chim. France*, **9**, 825 (1911).

(10) P. Ballinger, P. B. De la Mare, G. Kohnstam, and B. M. Prestit, *J. Chem. Soc.*, 3641 (1955), and references cited therein.

(11) H. Böhme and H. Ellenborg, *Chem. Ber.*, **92**, 2976 (1959), and earlier papers by Böhme, *et al.*

(12) See, for example, F. G. Bordwell, G. D. Cooper, and H. Morita, *J. Am. Chem. Soc.*, **79**, 376 (1957).

(13) H. Hellmann in "Newer Methods of Preparative Organic Chemistry," Vol. II, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1963, p. 277; C. L. Parris, U. S. Patent 3,024,282 (1962).

(14) H. Böhme, G. Driesen, and D. Schünemann, *Arch. Pharm.*, **294**, 344 (1961), and other papers by Böhme, *et al.*; M. F. Shostakovskii, F. P. Sidelkovskaya, E. V. Rogova, F. L. Kolodkin, and F. Ibragimov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1111 (1961), *Chem. Abstr.*, **55**, 27267*h* (1961), and earlier papers by Shostakovskii, *et al.*

(15) See, for example, G. H. L. Nefkens, G. I. Tesser, and R. J. F. Nivard, *Rec. trav. chim.*, **82**, 941 (1963).

(16) G. W. Pucher and T. B. Johnson, *J. Am. Chem. Soc.*, **44**, 817 (1922).

while the lower reactivity of the imides under acidic conditions is attributable to the presence of two carbonyl groups.

Experimental Section[17]

N-Propionoxymethyl-N-methylformamide (V).—Concentrated hydrochloric acid (3 drops) was added to a solution of I (11.7 g., 0.1 mole) in propionic acid (100 ml.), and the solution was left standing overnight at room temperature. Most of the excess propionic acid was removed with the water pump, keeping the bath temperature below 75°. The remainder was dissolved in ether (200 ml.), and the solution was stirred with sodium carbonate (25 g.) and filtered. The ether was removed, and the residue was distilled at 0.02 mm., yielding 11.7 g. (80.7%) of product, b.p. 55–57°, $n^{24}D$ 1.4420. A sample redistilled for analysis had b.p. 50–51° (0.01 mm.), $n^{25}D$ 1.4412.

Anal. Calcd. for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9.65. Found: C, 49.65; H, 7.72; N, 9.55.

N-Benzoyloxymethyl-N-methylformamide.—To a solution of benzoic acid (60 g., 0.49 mole) in distilled dimethylformamide (100 ml.) was added I (11.7 g., 0.1 mole) and concentrated hydrochloric acid (10 drops). The solution was left standing overnight at room temperature and then was dissolved in ether (500 ml.). The ether solution was stirred magnetically with sodium carbonate (53 g.) in water (300 ml.). Additional ether and water were added periodically to facilitate the neutralization of the acid. The organic layer was separated, washed with sodium carbonate solution, and dried over magnesium sulfate. The ether was distilled through a Vigreux column to give 8 g. (41%) of crude product. This crude product was distilled at 0.02 mm., and three arbitrary fractions were taken: (1) 1.8 g., b.p. 111–117°, $n^{24}D$ 1.5326; (2) 2.5 g., b.p. 118–122°, $n^{24}D$ 1.5326; and (3) 2.9 g., b.p. 122–123°, $n^{24}D$ 1.5329. The three fractions were essentially the same, and the infrared spectrum was identical with that for N-benzoyloxymethyl-N-methylformamide, prepared by decomposing benzoyl peroxide in dimethylformamide.[4]

The N-Alkoxymethyl-N-methylformamides.—The same procedure was used to prepare all of the ether amides in Table I. The preparation of VI is typical and follows. Concentrated hydrochloric acid (3 drops) was added to a solution of I (5.85 g., 0.05 mole) in ethanol (50 ml.). After 1.5 hr. v.p.c. showed that I was completely consumed. The solution was dissolved in ether (250 ml.), and the ether solution was stirred with an excess of sodium carbonate for several hours. After filtration the ether was distilled through a Vigreux column, and the residue was distilled at 0.04 mm. to give 4 g. (68%) of VI, b.p. 33–36°, $n^{24.5}D$ 1.4319. Redistillation for analysis gave a middle cut, b.p. 26° (0.012 mm.), $n^{24.5}D$ 1.4317. The analytical results are given in Table I.

Reaction of Ethanol with N-Hydroxymethyl-N-methylformamide.—N-Hydroxymethyl-N-methylformamide was prepared by refluxing a mixture of N-methylformamide (30 g., 0.5 mole), paraformaldehyde (15 g., 0.5 mole), sodium carbonate (0.5 g.), and ethanol (50 ml.) for 2 hr. Neither the sodium carbonate nor the ethanol was removed. The mixture was cooled, and additional ethanol (200 ml.) and concentrated hydrochloric acid (1.5 ml.) were added. The mixture was left standing overnight, stirred with sodium carbonate (2 g.), filtered, and distilled at 8 mm., yielding 22.5 g. of product, b.p. 69–73°, $n^{24}D$ 1.4295. By v.p.c. analysis this product was found to contain 18.4 g. (31.4%) of VI and 4.1 g. (13.6%) of N-methylformamide. The residue from the above distillation was crystallized from ethyl acetate–ether and yielded 8.5 g. (21.2%) of VIII, m.p. 60–62°.

Basic Alcoholysis of I.—A small pellet of sodium was allowed to react with ethanol (50 ml.). I (11.7 g., 0.1 mole) was added, and the solution was left standing at room temperature for 3 days. The reaction mixture was distilled slowly through a Vigreux column, and a fraction of 11.5 g., b.p. 54–79°, was taken. This fraction was found by v.p.c. to contain 7.07 g. (95.5%) of ethyl formate. The residue was distilled at 12 mm. and yielded 3.2 g. (54.2%) of N-methylformamide, b.p. 83–86°, $n^{24}D$ 1.4327.

N-*n*-Amylthiomethyl-N-methylformamide (IX).—A two-phase mixture of I (11.7 g., 0.1 mole) and *n*-amyl mercaptan (50 ml.) was treated with concentrated hydrochloric acid (5 drops). Heat was evolved, and a single phase resulted. V.p.c. analysis indicated that all of the I had reacted within 0.5 hr. The reaction mixture was dissolved in ether, and the solution was stirred several hours with sodium carbonate (43 g.). The solution was filtered, and the ether was removed through a Vigreux column. The excess mercaptan was distilled with the aspirator, and the residue was distilled at 0.05 mm. to give 16.2 g. (92.6%) of crude IX, b.p. 66–71°, $n^{24.5}D$ 1.4886. A sample redistilled for analysis had $n^{25}D$ 1.4883.

Anal. Calcd. for $C_8H_{17}NOS$: C, 54.81; H, 9.78; N, 7.99; S, 18.29. Found: C, 54.83; H, 9.97; N, 7.70; S, 18.47.

Reaction of IX with β-Naphthol.—A solution containing IX (2.75 g., 0.0157 mole), β-naphthol (2.3 g., 0.016 mole), ethanol (10 ml.), concentrated hydrochloric acid (4 ml.), and water (2 ml.) was refluxed 23 hr. The reaction mixture was poured into a large volume of ether. An oil precipitated, but on standing crystals formed. The yield was 1.88 g. (53.4%), obtained in several crops, of methyl(2-hydroxynaphthylmethyl)amine hydrochloride, m.p. 195–200° dec. Two crystallizations from ethanol–ether raised the melting point to 206–207° dec.; no depression on mixture melting with an authentic sample occurred.

Anal. Calcd. for $C_{12}H_{14}ClNO$: Cl, 15.85. Found: Cl, 16.32.

N-Methyl-N-(2-hydroxynaphthylmethyl)formamide.—I (11.7 g., 0.1 mole) and sulfuric acid (10 drops) were added to a solution of β-naphthol (14.4 g., 0.1 mole) in dimethylformamide (75 ml.). After standing 22 hr. the reaction mixture was dissolved in a large volume of ether, and the ether solution was stirred 1 hr. with solid sodium bicarbonate. The solid was filtered, and the filtrate was concentrated from a water bath with the aspirator. The orange residue was dissolved in hot ethyl acetate and allowed to crystallize. After filtration, hexane was added to the mother liquor, and another crop of crystals was obtained to give a total yield of 17.6 g. (82%), m.p. 158–160°. Recrystallization from ethyl acetate raised the melting point to 159–161°.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09, N, 6.51. Found: C, 72.37; H, 5.96; N, 6.35.

N-Methyl-N-*p*-methoxybenzylformamide (X).—Concentrated sulfuric acid (0.75 ml.) was added to a solution of I (11.7 g., 0.1 mole) in anisole (75 ml.). A turbidity appeared on shaking, but this disappeared with time. V.p.c. analysis after 1.5 hr. showed a small amount of unreacted I. Additional sulfuric acid (5 drops) was added, and the solution was left standing overnight. The solution was diluted with ether, washed three times with water, two times with saturated sodium bicarbonate solution, and again with water, and then dried over magnesium sulfate. The solvent and excess reagents were removed with the water pump, and the residue was distilled *in vacuo* to give 12.3 g. (68.7%) of product, b.p. 100–115° (0.01–0.02 mm.), $n^{24}D$ 1.5424. A sample redistilled for analysis had b.p. 103–105° (0.01 mm.), $n^{24.5}D$ 1.5421.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.72; H, 7.85; N, 7.75.

N-Methyl-*p*-methoxybenzylamine Hydrochloride.—A solution of the above product (10.3 g., 0.0575 mole) in ethanol (40 ml.) and concentrated hydrochloric acid (20 ml.) was refluxed 17 hr. The mixture was concentrated with the aspirator, and the residue was crystallized from methanol–ether, yielding 6.1 g. (56.5%) of the amine hydrochloride, m.p. 174–175°. A sample recrystallized for analysis had m.p. 175–176°.[8]

Anal. Calcd. for $C_9H_{14}ClNO$: Cl, 18.89. Found: Cl, 19.06.

N-Methyl-N-*p*-hydroxybenzylformamide (XI) and N-Methyl-N-*o*-hydroxybenzylformamide (XII).—Concentrated hydrochloric acid (3 drops) was added to a solution of I (11.7 g., 0.1 mole) in molten phenol (50 g., 0.53 mole). After standing overnight the mixture was dissolved in ether, and the ether solution was washed with saturated sodium bicarbonate until no further effervescence was observable. The ether was removed with the water pump, and the residue was distilled at 0.08 mm. with the heating bath at 135° until phenol no longer distilled. The thick residue, 14.9 g. (90.3%), was fractionally crystallized from ethyl acetate and eventually from ethyl acetate–hexane. Ultimately 4 g. of XI, m.p. 135–137°, was obtained as the less-soluble material. The more-soluble material, XII, 7.2 g. of crude material, had m.p. 85–88° after crystallization from ethyl acetate–hexane.

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found for XI: C, 65.60; H, 7.01; N, 8.30. Found for XII: C, 65.37; H, 6.82; N, 8.38.

(17) All microanalyses were by the Clark Microanalytical Laboratory, Urbana, Ill.

N-Methyl-*p*-hydroxybenzylamine Hydrochloride.[9]—A solution of XI (1.35 g., 0.0082 mole) in ethanol (10 ml.) and concentrated hydrochloric acid (3 ml.) was refluxed 17 hr. The reaction mixture was distilled to dryness with the water pump, and the white residue was crystallized from ethanol–ether to give 1.29 g. (91%) of the amine hydrochloride, m.p. 188–189°. A sample for analysis was crystallized first from ethanol–ether and then from methanol–ether; melting point unchanged.

Anal. Calcd. for $C_8H_{12}ClNO$: Cl, 20.42. Found: Cl, 20.73.

N-Methyl-*o*-hydroxybenzylamine Hydrochloride.[8]—A sample of XII (0.884 g., 0.0054 mole) was ground in an agate mortar and refluxed 17 hr. in a solution of ethanol (7.5 ml.) and concentrated hydrochloric acid (3 ml.). The solvent was removed with the aspirator, and the residue was crystallized from methanol–ether to give 0.719 g. (77%) of off-white crystals. Recrystallization from isopropyl alcohol–ether and then ethanol–ether gave the analytical sample, m.p. 141–145°.

Anal. Calcd. for $C_8H_{12}ClNO$: Cl, 20.42. Found: Cl, 20.81.

N-Formyl-N-methylaminomethylisothiouronium Chloride (XIV).—I (5.85 g., 0.05 mole) was added to thiourea hydrochloride (6 g., 0.053 mole) in dimethylformamide (100 ml.). On standing crystals precipitated and within a few hours the reaction was complete. The crude product, 8.0 g. (87%), m.p. 117–121° dec., was crystallized three additional times from methanol–ether for analysis, m.p. 127–128° dec.

Anal. Calcd. for $C_4H_{10}ClN_3OS$: C, 26.16; H, 5.49; N, 22.88; S, 17.46. Found: C, 26.34; H, 5.99; N, 22.57; S, 17.42.

The above product (3.1 g., 0.0169 mole) was refluxed 3 hr. with β-naphthol (2.48 g., 0.0172 mole), ethanol (25 ml.), and concentrated hydrochloric acid (1 ml.). The solution was cooled, and ether was added, precipitating 2.02 g. (53.4%) of methyl-(2-hydroxynaphthylmethyl)amine hydrochloride, m.p. 188–194° dec., m.p. 196–198° dec. after crystallization from ethanol–ether.

Anal. Calcd. for $C_{12}H_{14}ClNO$: Cl, 15.85. Found: Cl, 16.23.

Reaction of N-Acetoxymethylphthalimide (XVI).—XVI (11.5 g., 0.0525 mole), prepared as described by Nefkens, *et al.*,[15] was dissolved by heating in ethanol (100 ml.), and concentrated hydrochloric acid (5 drops) was added. After standing overnight, crystals (7 g.) precipitated. These proved to be unreacted XVI, m.p. 116–118°. The crystals were redissolved in the mother liquor with the aid of more ethanol. Concentrated hydrochloric acid (10 drops) was added, and the solution was refluxed 5.5 hr. The solvents were removed with the water pump, and the crystalline residue was crystallized from acetone. Two crops, 8.5 g. (91.5%), were obtained, m.p. 148–151°. The infrared spectrum was identical with that of N-hydroxymethylphthalimide.

Fragmentation, Rearrangement, and Elimination in Heptamethylpropane Derivatives[1,2]

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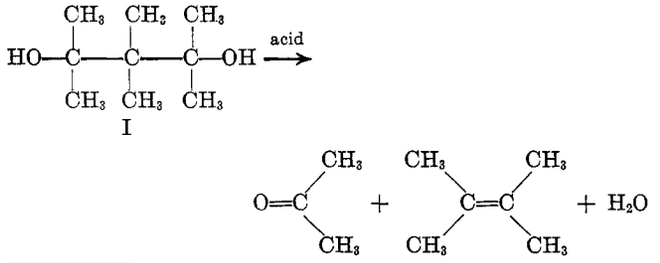
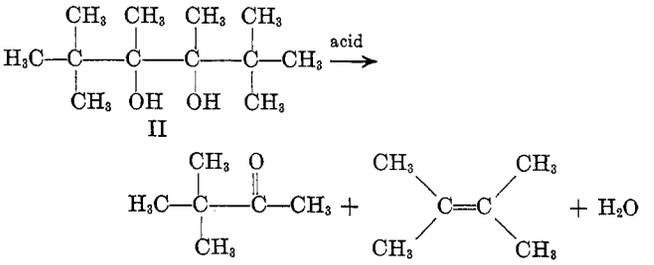
2,3,3,4,4-Pentamethyl-2-chloropentane (XII) was found to solvolyze in 93% aqueous acetone at 25° with the specific first-order rate constant of 2.92×10^{-3} sec.$^{-1}$ to form 2,3,3,4,4-pentamethyl-1-pentene (XI). No fragmentation was observed. 2,2,3,4,4-Pentamethyl-3-chloropentane (V) solvolyzed in 80% aqueous ethanol at 25° with the specific first-order rate constant of 1.725×10^{-4} sec.$^{-1}$. In 70% aqueous dioxane the solvolytic products of the latter compound are 83% 1,1-di-*t*-butylethylene (VIII), 10% methyldi-*t*-butylcarbinol (VI), and 7% 1-methyl-1-triptylethylene (XI). Isotope-exchange studies in dioxane–sulfuric acid-d_2 mixtures show that, for every 200 2,3,3,4,4-pentamethyl-2-pentyl cations (X) formed by protonation of 2,3,3,4,4-pentamethyl-1-pentene (XI), three undergo tertiary butyl migration and one fragments; methyl migration is not observed.

In 1907 Slavjanov[5] reported that treatment of hexamethyl-1,3-propanediol (I) with acids yielded acetone, tetramethylethylene, and water; Couturier[6a] and later Delacre[6b] observed that 1,2-dimethyl-1,2-di-*t*-butylethylene glycol (II) under the influence of acid formed pinacolone, tetramethylethylene, and water. Nasarov[7] examined the reactions with acid of a large number of mono- and di-*t*-alkylcarbinols and of the corresponding unrearranged dehydration products. Earlier, Whitmore and co-workers[8] had started investigations on similar systems. While Nasarov had interpreted his results in terms of a radical mechanism, Whitmore in-





(1) Based upon a thesis submitted by G. F. Meier in July 1964 to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree.

(2) Fragmentations are reactions in which molecules break apart heterolytically or homolytically to form two or more fragments, as indicated in the generalized scheme shown.[3] Where b, c, and d are carbon atoms, this

$$a{-}b{-}c{-}d{-}x \longrightarrow a{-}b^{\oplus} + c{=}d + x^{\ominus}$$

type of reaction has also been referred to as β cleavage and the fragment $a{-}b^{\oplus}$ as "β fragment," in analogy to the well-known related β eliminations where $a{-}b^{\oplus}$ is a hydrogen ion.

(3) C. A. Grob in Theoretical Organic Chemistry, Papers Presented to the Kekule Symposium Organized by the Chemical Society, London, Sept. 1958, Butterworth and Co. (Publications) Ltd., London, 1959, p. 114. See also C. A. Grob, H. R. Kiefer, H. Lutz, and H. Wilkens, *Tetrahedron Letters*, **No. 39**, 2901 (1964), and earlier papers.

(4) Graduate School Fellow, 1962.

(5) A. N. Slavjanov, *J. Russ. Phys. Chem. Soc.*, **39**, 140 (1907); *Chem. Abstr.*, **1**, 2077 (1907).

(6) (a) F. Couturier, *Ann. chim.* (Paris), [6] **26**, 433 (1892); (b) M. Delacre, *Bull. soc. chim. France*, [4] **1**, 539 (1907).

(7) (a) I. N. Nasarov, *Compt. rend. acad. sci. URSS*, **2**, 82 (1934); **3**, 609 (1934); (b) *ibid.*, **10**, 75 (1936); *Ber.*, **69**, 18 (1936); (c) *ibid.*, **70**, 606, 617 (1937).

(8) (a) F. C. Whitmore, *J. Am. Chem. Soc.*, **54**, 3274 (1932); (b) F. C. Whitmore and E. E. Stahly, *ibid.*, **55**, 4153 (1933); (c) *ibid.*, **67**, 2158 (1945); (d) for a complete list of this author's work on the subject, see F. C. Whitmore, L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, and F. J. Evans, *ibid.*, **76**, 1613 (1954), and the preceding papers.