The contents were rinsed from the bomb with chloroform and fractionally distilled under reduced pressure through a 30-cm. Fenske-type column[3] using a trace of trinitrobenzene to inhibit polymerization. Products were 1137 g. of aldehyde-collidine, b. p. 73–75° (20 mm.), $n^{20}\text{D}$ 1.4970, 314 g. of 5-ethyl-2-vinylpyridine, b. p. 64–65° (3 mm.), $n^{20}\text{D}$ 1.5383, and 712 g. of 5-ethyl-2-(2-hydroxyethyl)-pyridine, b. p. 103° (1 mm.), 125° (3 mm.), $n^{20}\text{D}$ 1.5370. Combined yield, accounting for the recovered aldehyde-collidine, was 73%.

The picrate of 5-ethyl-2-(2-hydroxyethyl)-pyridine, crystallized from ethanol, melted at 101–102°.

Anal.[8] Calcd. for $C_{15}H_{16}N_4O_8$: C, 47.37; H, 4.24. Found: C, 47.55; H, 4.18.

The chloroplatinate was prepared by adding aqueous platinum chloride solution to an alcoholic solution of the product. Pink crystals were obtained, m. p. 165–167° (dec.). Prausnitz[7a] reported the chloroplatinate to be a red crystalline compound, m. p. 159° (dec.).

In the preparation paraformaldehyde (1 mole per mole of aldehyde-collidine is optimal) gives better results than formalin. The use of ethanol as a solvent improves the yields, and it is most interesting that the addition of a trace of potassium persulfate (1% of the aldehyde-collidine) does so materially. Ammonium acetate, zinc chloride, sodium hydroxide, silver and potassium ferricyanide showed no such catalytic effect.

5-Ethyl-2-vinylpyridine.—The conversion of 5-ethyl-2-(2-hydroxyethyl)-pyridine to 5-ethyl-2-vinylpyridine was achieved in good yield by catalytic dehydration, either using alumina at 400–420° or, preferably, molten potassium hydroxide at 175°.

A. By Dehydration over Alumina.—A vertical 19-mm. Pyrex tube heated by an electric furnace for a length of twelve inches was packed with 6-mesh activated alumina (Hydralo) and preheated at 450° to drive off moisture. From a separatory funnel attached directly to the top of the tube was passed 170 g. (1.12 moles) of 5-ethyl-2-(2-hydroxyethyl)-pyridine at a rate of one drop per second. The temperature during this time was maintained at 400–420°. An equal volume of chloroform was then added to the product, the water layer separated, and the organic layer dried over potassium carbonate. Fractional distillation, after the addition of a trace of trinitrobenzene as a polymerization inhibitor, gave 88 g. (66%, or 71% accounting for recovery of 12.6 g. of starting material) of 5-ethyl-2-vinylpyridine, b. p. 95–97° (18 mm.); $n^{20}\text{D}$ 1.5380.

B. By Dehydration with Potassium Hydroxide.—The apparatus and procedure was that described previously for the preparation of 3-methoxystyrene.[9] From 160 g. (1.32 moles) of 5-ethyl-2-(2-hydroxyethyl)-pyridine at 175° and 17–18 mm. pressure was obtained 116.3 g. of crude distillate. Redistillation through a 30-cm. Fenske-type column,[3] using a small amount (1:1000) of trinitrobenzene as a polymerization inhibitor, gave 88.8 g. (63%) of 5-ethyl-2-vinylpyridine, b. p. 95–97° (18 mm.); $n^{20}\text{D}$ 1.5383.

The picrate of the product, crystallized from water, melted at 129.5–130.5°.

Anal. Calcd. for $C_{15}H_{14}N_4O_7$: C, 49.72; H, 3.90. Found: C, 49.73; H, 3.90.

Summary

In the condensation of ammonia with paraldehyde the use of a large excess of ammonia leads to 50–70% yields of aldehyde-collidine.

The presence of a trace of potassium persulfate improves the yields of 5-ethyl-2-(2-hydroxyethyl)-pyridine in the condensation of aldehyde-collidine with paraformaldehyde.

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[8] Microanalyses were carried out by Mr. Howard Clark.

[9] Frank, Adams, Allen, Gander and Smith, THIS JOURNAL, **68**, 1365 (1946).

URBANA, ILLINOIS RECEIVED MARCH 7, 1946

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

Studies on the Willgerodt Reaction. III. The Use of Simple Aliphatic Compounds

BY JOHN A. KING AND FREEMAN H. McMILLAN

Previous communications from these laboratories have shown that the Willgerodt reaction is by no means restricted to aryl alkyl ketones[1] and have suggested a mechanism[2] for the reaction. Although Willgerodt[3] reported, in 1888, that if oenanthol were heated "a long time" at 300° with yellow ammonium sulfide the product was oenanthylamide, no other successful application of the reaction to an aliphatic compound had been published prior to last October. At that time it was demonstrated by Cavalieri, Pattison and Carmack[4] that the reaction can be carried out successfully on purely aliphatic ketones. Experiments conducted in these laboratories similarly have shown that the reaction is applicable to aliphatic ketones, alcohols, thiols and olefins. The present paper describes some of our results and indicates how all data thus far obtained are in accord with our previously proposed reaction mechanism.

It seemed desirable to select as a typical aliphatic ketone one which contained no tertiary alkyl group, in order that the similarity to an aromatic aliphatic ketone would be lessened. Methyl isobutyl ketone, to which we first applied the reaction, gave an 88% yield of isocaproamide.

In order to determine whether the reaction would proceed satisfactorily when neither of the alkyl groups of the ketone contained a branched chain, the reaction was applied to methyl nonyl ketone. The product was undecanoamide.

Willgerodt,[5] in his initial paper on the treatment of carbonyl compounds with yellow ammonium sulfide, found that at room temperature acetone and ammonium polysulfide formed "duplodithioacetone," of unknown constitution. It was easily verified that when acetone and ammonium polysulfide were sealed in a pressure tube the separation of a heavy red oil occurred;

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[1] King and McMillan, THIS JOURNAL, **68**, 525 (1946).

[2] King and McMillan, *ibid.*, **68**, 632 (1946).

[3] Willgerodt, *Ber.*, **21**, 534 (1888).

[4] Cavalieri, Pattison and Carmack, THIS JOURNAL, **67**, 1783 (1945).

[5] Willgerodt, *Ber.*, **20**, 2467 (1887).

however, when the mixture was heated for four hours at 210° it yielded propionamide. By following Willgerodt's directions, a pure sample of "duplodithioacetone" was prepared and when this was heated with ammonium polysulfide it similarly yielded propionamide.

It was then of interest to extend the reaction to higher homologous ketones in which neither of the alkyl groups was methyl. Accordingly, the reaction was applied to pentanone-3, heptanone-4 and nonanone-5. These three ketones gave, respectively, valeramide, oenanthylamide and pelargonamide when they were heated with ammonium polysulfide at 200°. The yields of the respective amides were 43, 9 and 1%. Such a progressively decreasing yield is what would be predicted by our previously suggested mechanism for the reaction; *i. e.*, the farther a functional group has to travel before it reaches the end of a chain the greater will be the opportunity for side-reactions to consume the intermediates and thereby decrease the yield of ultimate amide.

The course which is followed and the equilibria which are involved in the conversion of these di-*n*-alkyl ketones to amides has been adequately portrayed in our preceding paper.[2]

If mercaptans are intermediates in the reaction, they should form amides just as the ketones do, at the same reaction temperature. The reaction was applied to propanethiol-2, pentanethiol-3, heptanethiol-4 and nonanethiol-5. These four thiols gave, respectively, propionamide, valeramide, oenanthylamide and pelargonamide.

Should these mercaptans be formed by reduction of thioketones the latter also should give amides in the reaction, just as should the olefins if these are mercaptan precursors by virtue of their ability to add hydrogen sulfide. It was decided to first test the olefins. Pentene-3, heptene-4 and nonene-5 gave, respectively, valeramide, oenanthylamide and pelargonamide.

These olefins, in turn, can arise only from dehydration of carbinols or dehydrogensulfidation of mercaptans. If they arise from dehydration of alcohols the latter also should form amides at the same reaction temperature as do the ketones, mercaptans and olefins. When the three alcohols, pentanol-3, heptanol-4 and nonanol-5 were heated with ammonium polysulfide at 200°, no amide was obtained from any of the three. From these results the only conclusion that can be drawn is that the ketone does not proceed via the alcohol to the olefin. Since, as has already been pointed out, the olefin can arise only from the alcohol or the mercaptan, the exclusion of the former as an essential intermediate leaves only the mercaptan, derived from the thioketone, as the source of the olefin. The course of the reaction, then, with these di-*n*-alkyl ketones proceeds via the route: ketone, thioketone, mercaptan, olefin, mercaptan, etc.

However, it has already been shown[1,2] that certain alcohols, for examples phenylmethylcarbinol and phenylisopropylcarbinol, do undergo the Willgerodt reaction to give the same amides, at the same reaction temperatures, as are obtained from the corresponding ketones, olefins and thiols. In order to reconcile these prior findings with the failure of di-*n*-alkyl carbinols to undergo the reaction, one must infer that the ability of an alcohol to undergo the Willgerodt reaction is determined at least in part by the ease with which it undergoes dehydration to an olefin. In the light of this inference one would predict that if conditions were sufficiently drastic to cause dehydration of dialkyl carbinols the latter would then yield amides with ammonium polysulfide, provided the olefins themselves were not destroyed by side-reactions at their high temperature of formation. This prediction was verified experimentally. When pentanol-3 and ammonium polysulfide were heated at 215°, instead of at 200°, valeramide was formed. At 220° heptanol-4 gave butyramide, presumably resulting from cleavage of the intermediately formed heptene-3, and after five hours at 225° nonanol-5 also gave butyramide, presumably resulting from cleavage of the intermediately formed nonene-4.

t-Butyl alcohol, which is well-known to undergo dehydration with relative ease, gave isobutyramide when it was heated at 200° with ammonium polysulfide.

Similarly, the three terminal olefins octene-1, decene-1 and tetradecene-1 all gave the expected corresponding amides when they were heated with ammonium polysulfide at 200°.

One now sees that the behavior of all compounds thus far studied is nicely explained on the basis of the reaction mechanism previously proposed. If reaction conditions, *i. e.*, the reaction temperature or time are sufficient to cause dehydration of the alcohol which can be formed by reduction of the ketone used as a starting material, then the reaction may proceed from the ketone simultaneously by two routes: (1) reduction to the alcohol and dehydration of the alcohol to the olefin; or (2) transposition of the thioketone, then reduction of the latter to the mercaptan which is dehydrogensulfided to the olefin. If the reaction temperature is too low for dehydration of the alcohol only the second route can be followed.

In accordance with this reaction mechanism, one would expect that any primary, secondary or tertiary mercaptan would undergo the Willgerodt reaction normally, provided no quaternary carbon atom blocks the egress of the functional group to an ultimate carbon atom of the chain and provided the thiol group is originally located sufficiently close to the end of the chain for some amide to be formed before side reactions consume all of the mercaptan. This expectation was realized in the successful application of the reaction to a series of monofunctional mercaptans.

The eleven additional mercaptans to which the reaction was applied are listed in Table III (Experimental Part). The yields reported are not particularly indicative of what may be obtained after experimental determination of the optimal conditions for each particular substance. However, from the limited data available, it is offered as a tentative conclusion that whereas the decreasing ease of reactivity of alcohols in the Willgerodt reaction is tertiary, secondary, primary, for the mercaptans the reverse is true; *i. e.*, primary mercaptans give better yields than do secondary ones, which in turn give better yields than tertiary ones.

Experimental Part[6]

The ammonium polysulfide used in all of the experiments herein reported was prepared as previously described.[1] Because it permits the facile preparation of a solution that is fairly easily reproducible in strength, one type of apparatus we have used is described. A glass tower, 33¹/₂" by 3³/₄" i. d., was constructed with a gas inlet tube sealed into the center of the base of the tower and ending in a gas-dispersing bulb of 1" diameter. On one side of the base of the tower was a 6 mm.-bore stopcock outlet. The tower was packed with 1" Berle saddles and was supported in a wooden stand. Around the tower was placed a single 5" diameter coil of ³/₈" metal tubing with 1 mm. holes bored at such an angle that a cooling spray from it was directed downward 45° from the horizontal. This cooling spray coil could be raised or lowered to correspond with any desired liquid level within the tower. A measured volume of ammonia (28% NH_3, sp. gr. 0.9015) was charged into the tower and hydrogen sulfide was bubbled in through the base while the cooling spray kept the solution at 20–25°; ten to twelve moles per hour of hydrogen sulfide could be absorbed easily. When the charge of ammonia was saturated the solution was drained out[7] and weighed, then one-tenth its weight of sulfur was added and stirred into solution. The reproducibility of the final solution is indicated by the three following representative and consecutive batches: one contained 5.72 moles per kilo of solution of the complex $(NH_4)_{2.00}S_{1.60}$, the second contained 5.75 moles per kilo of solution of the complex $(NH_4)_{2.00}S_{1.58}$ and the third contained 5.65 moles per kilo of solution of the complex $(NH_4)_{2.00}S_{1.64}$. Approximately one gallon of ammonium sulfide can be prepared in the tower in a period of two to three hours.

TABLE I

PREPARATION OF INTERMEDIATES AND STARTING MATERIALS

Material prepared	Preparative method	Yield, %
Pentanol-3[a]	Ethyl formate and ethylmagnesium bromide	61
Heptanol-4[b]	Butyraldehyde and *n*-propylmagnesium bromide	65
Nonanol-5[c]	Ethyl formate and *n*-butylmagnesium bromide	85
Pentanone-3[d]	Dichromate oxidation of pentanol-3[e]	75
Heptanone-4[f]	Dichromate oxidation of heptanol-4	72
Nonanone-5[g]	Dichromate oxidation of nonanol-5	80
3-Bromopentane[h]	PBr_3 on pentanol-3	69
4-Bromoheptane[i]	PBr_3 on heptanol-4	56
5-Bromononane[j]	PBr_3 on nonanol-5	54[k]
Pentene-2[h]	Hot 60% H_2SO_4 on pentanol-3	67
Heptene-3[l]	Hot 60% H_2SO_4 on heptanol-4	82
Nonene-4[m]	$KHSO_4$ dehydration of nonanol-5	42
Pentanethiol-3[l]	Thiourea on 3-bromopentane[n]	48
Heptanethiol-4[o]	Thiourea on 4-bromoheptane	28
Nonanethiol-5[p]	Thiourea on 5-bromononane	19

[a] Lewis, *J. Chem. Ed.*, **7**, 856 (1930). [b] Willcox and Brunel, THIS JOURNAL, **38**, 1838 (1916). [c] Coleman and Craig, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 179. [d] Henderson, Henderson and Heilbron, *Ber.*, **47**, 887 (1914). [e] Yohe, Lauder and Smith, *J. Chem. Ed.*, **10**, 374 (1933). [f] Hamonet, *Bull. soc. chim.*, (2) **50**, 358 (1888). [g] Pickard and Kenyon, *J. Chem. Soc.*, **101**, 629 (1912). These authors reported the b. p. as 181–182°; our material boiled at 84–85.5° (17 mm.). [h] Sherrill, Otto and Pickett, THIS JOURNAL, **51**, 3023 (1929). [i] Dillon and Lucas, *ibid.*, **50**, 1711 (1928). These authors reported the b. p. as 84–85.5° (72 mm.); our material boiled at 99–101° (100 mm.). [j] Grignard and Ono, *Bull. soc. chim.*, (4) **39**, 1592 (1926). [k] An additional 28% of nonene-4, b. p. 55–60° (25 mm.) was obtained. [l] Mailhe, *ibid.*, (4) **15**, 327 (1914). [m] Cox, *ibid.*, (4) **37**, 1551 (1925). [n] Urquhart, Gates and Connor, "Organic Syntheses," **21**, 36 (1941). John Wiley and Sons, Inc., New York, N. Y. [o] The thiourea method was used to convert 4-bromoheptane into heptanethiol-4, b. p. 157–159°, in 42% yield. Mailhe (ref. *l*) reported the b. p. as 136–138°. Because of the discrepancy in the b. p.'s our preparation was repeated. After twenty-six hours of refluxing, the oily heptylthiuronium bromide was converted into dipropylcarbinylthiuronium picrate which melted, after two recrystallizations from aqueous alcohol, at 157°. One-half mole of 4-bromoheptane gave 125 g. (62% yield) of purified picrate. *Anal.* Calcd. for $C_8H_{18}N_2S{\cdot}C_6H_3N_3O_7$: S, 7.94. Found: S, 7.71. (Semimicro Parr bomb analysis by Mr. P. K. Dederick of these Laboratories.) The thiuronium picrate was decomposed by steam distillation from one liter of 10% caustic. Benzene extraction of the distillate gave the pure mercaptan which, after two fractional distillations, boiled at 40° (7 mm.) and weighed 19 g. (46% yield from the thiuronium picrate, 28% over-all yield from the bromide). *Anal.* Calcd. for $C_7H_{16}S$: S, 24.24. Found: S, 24.0. (Semimicro Parr bomb analysis by Mr. P. K. Dederick.) [p] 5-Bromononane (103.5 g., 0.50 mole), thiourea (38 g., 0.50 mole) and 95% alcohol (250 cc.) were refluxed twenty-eight hours. To the cooled reaction mixture there was added an alcoholic solution of 115 g. (0.50 mole) of picric acid. The dibutylcarbinylthiuronium picrate was thrown out of solution with water and, after recrystallization from aqueous alcohol, melted at 135–135.5°. *Anal.* Calcd. for $C_{10}H_{22}N_2S{\cdot}C_6H_3N_3O_7$: S, 7.42. Found: S, 7.54. (Semimicro Parr bomb analysis by Mr. P. K. Dederick.) The picrate was decomposed as described above to give a material which contained only 15–16% sulfur. However, when the picrate was treated with one equivalent of caustic, the nonyl isothiourea extracted with chloroform and, after removal of the solvent, hydrolyzed with 5% aqueous alcoholic (1:1) caustic the pure nonanethiol was obtained, b. p. 72° (7 mm.). *Anal.* Calcd. for $C_9H_{20}S$: S, 20.0. Found: S, 19.4. (Semimicro Parr bomb analysis by Mr. J. H. Hodecker of these Laboratories.)

Willgerodt Reaction with Methyl Isobutyl Ketone.—Methyl isobutyl ketone[8] (3.00 cc., 2.41 g., 0.024 mole) and ammonium polysulfide (15.0 g.) were heated four

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(6) Melting points and boiling points reported in this paper are uncorrected.

(7) In the calculation of the weight of ammonia charged and the molarity of the resultant solution no allowance was made for the slight hold-up in the drainage of the tower.

(8) Purchased from Carbide and Carbon Chemicals Corporation.

hours at 200 ± 5° in the type of tube previously described.[1,9] The cooled reaction mixture was extracted with ether, the extract was washed with sodium carbonate solution, dilute hydrochloric acid and then water. Removal of the ether left 2.45 g. (88% yield) of crystalline solid which, after recrystallization from water, melted at 117–118°, undepressed when mixed with an authentic sample[10] of isocaproamide.

Willgerodt Reaction with Methyl Nonyl Ketone.—Methyl nonyl ketone[11] (2 cc.) and ammonium polysulfide (10 g.) were heated four hours at 210 ± 5°. The contents of the cooled tube were washed out with water and benzene and the aqueous solution was extracted three times with benzene. The combined benzene extracts were concentrated to a small volume and the residue was slurried with Skellysolve B to give about 150 mg. of light colored crystals. After several recrystallizations from benzene-Skellysolve B the product melted at 94–95°. Since this is lower than the m. p. reported[12] for undecanoamide, the amide was analyzed.

TABLE II

WILLGERODT REACTION WITH DIVERSE ALIPHATIC COMPOUNDS

Compound used[a]	Acid amide obtained	Time, hr. at 200 ± 5°C.	Yield of amide, %	M. p. °C., of amide
Pentanone-3	Valeric	6	43	100–102
Heptanone-4	Oenanthylic	24	9	93–94[b]
Nonanone-5	Pelargonic	24	1	94–96[c]
Propanethiol-2[d]	Propionic	12	6	76–77
Pentanethiol-3	Valeric	12	5	101–102
Heptanethiol-4	Oenanthylic	12	1	93–95
Nonanethiol-5	Pelargonic	12	1	96–98
Pentene-2	Valeric	5	Small[e]	99–101
Heptene-3	Oenanthylic	14	Small	93–94
Nonene-4	Pelargonic	14	Small	93–95
Pentanol-3	None	14		
Pentanol-3	Valeric	4[f]	Small	99–102
Heptanol-4	None	14		
Heptanol-4	Butyric	5[g]	Small	112–115
Nonanol-5	None	14		
Nonanol-5	Butyric	5[h]	Small	116
2-Methyl-propanol-2	Isobutyric	14	5	125–127
Octene-1[i]	Caprylic	6	4	101–102
Decene-1[i]	Capric	6	6	97–98
Tetradecene-1[i]	Myristic	6	1	102–103

[a] One part of compound and five parts of ammonium polysulfide were used in each experiment; the product was removed either by filtration or by solvent extractions, sometimes after saturation of the reaction solution with potassium carbonate. Each product, after recrystallization from an appropriate solvent, was identified by mixed melting point determination with an authentic sample of the amide. [b] Our authentic sample, m. p. 95–96°. was prepared by the method of Fournier, *Bull. soc. chim.*, (4) 5, 920 (1909); Robertson, *J. Chem. Soc.*, **115**, 1220 (1919). [c] The authentic sample, m. p. 98–99°, was prepared by the procedure of Reid and Ruhoff, "Org. Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 474; Robertson, *loc. cit.* [d] Obtained from Oronite Chemical Company. [e] "Small" refers to one per cent. or less. [f] At 215 ± 5°. [g] At 220 ± 5°. [h] At 225 ± 5°. [i] Purchased from The Connecticut Hard Rubber Company.

Anal. Calcd. for $C_{11}H_{23}NO$: N, 7.56. Found[13]: N, 7.51.

Willgerodt Reaction with Acetone.—Acetone (1 cc.) and ammonium polysulfide (5 g.) were heated four hours at 210 ± 5°. The cooled reaction mixture was washed from the opened tube with water and the aqueous solution was extracted with benzene for four hours in a continuous extractor. The solvent was removed from the extract to leave a residue of about 50 mg. of material which, after recrystallization from benzene, melted at 75–77°, undepressed when mixed with an authentic sample of propionamide.

Willgerodt Reaction with "Duplodithioacetone."—"Duplodithioacetone" was prepared by the procedure of Willgerodt.[5] This material (2 g.) and ammonium polysulfide (10 g.) were heated four hours at 210 ± 5°. The reaction mixture was worked up as described for acetone to give about 50 mg. of propionamide, m. p. 76–77°, alone or when mixed with an authentic sample of the amide.

In order to conserve space, the data on the preparation of a number of intermediates and starting materials are summarized in Table I. With the exceptions noted, the boiling points of the substances prepared agreed with the values given in the literature cited.

TABLE III

WILLGERODT REACTION WITH SIMPLE MERCAPTANS[a]

Mercaptan used	Source of mercaptan	Acid amide obtained	Time, hr. at 200 ± 5°C.	Yield of amide, %	M. p., °C. of amide
Ethyl	*b*	Acetic	14	19	80–81
n-Propyl	*b*	Propionic	12	9	76–77
n-Butyl	*b*	Butyric	12	24	116
iso-Butyl	*b*	Isobutyric	14	15	125–126
s-Butyl	*b*	Butyric	14	0.5	116
t-Butyl	*c*	Isobutyric	14	0.5	125–127
n-Octyl	*d*	Caprylic	5	6	104–105
n-Decyl	*d*	Capric	5	8	97–98
n-Dodecyl	*d*	Lauric	12	62	98–99
Benzyl	*e*	Benzoic	12	53	125–127
α-Phenethyl	*f*	Phenylacetic	4	44[g]	156–157

[a] All of the Willgerodt reactions were carried out in glass tubes, using approximately five parts of ammonium polysulfide to one part of mercaptan. The products were isolated by either extraction or filtration, depending upon the properties of the particular amide. In each case the product was identified by melting point and mixed melting point with an authentic sample of the amide. [b] Obtained from Oronite Chemical Company. [c] Obtained from Phillips Petroleum Company. [d] Purchased from Connecticut Hard Rubber Company. [e] Eastman Kodak White Label material. [f] Phenylmethylcarbinol was treated with concentrated hydrochloric acid to give a 75% yield of α-phenethyl chloride, b. p. 93–95° (30 mm.). Norris, Watt and Thomas, THIS JOURNAL, **38**, 1078 (1916), reported the b. p. as 90–91° (33 mm.). This chloride, by the thiourea method, gave a 58% yield of α-phenethyl mercaptan, b. p. 100–104° (30 mm.). Baumann and Fromm, *Ber.*, **28**, 910 (1895), reported the b. p. as 199–200°. [g] 18% of free acid was also obtained; in no other case was the mixture worked up for the acid.

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(9) The ratio of reactants and the time and temperature of heating in all of the ammonium polysulfide experiments described in the present paper do not necessarily represent the optimal conditions; the experiments described were merely intended to show whether or not the reaction would proceed with the particular compound being tested.

(10) Bentley and Perkin, *J. Chem. Soc.*, **73**, 45 (1898); Marckwald and Nolda, *Ber.*, **42**, 1589 (1909). The latter authors reported the m. p. as 119°; our material melted at 115–117°.

(11) Obtained from Aromatics Division, General Drug Co.

(12) Robertson, *J. Chem. Soc.*, **115**, 1220 (1919), gave 99° as the m. p. of undecanoamide.

(13) Semimicro Kjeldahl analysis by Mr. H. E. Bauer of these Laboratories.

The four Willgerodt reactions described above in detail may be considered as representative and typical of all those carried out. Therefore the remaining experiments are presented in tabular form, Table II consisting of the data on the various and diverse substances discussed in the text of this paper, and Table III consisting of the data on the series of simple mercaptans therein mentioned.

Summary

A series of interrelated experiments has shown that not only aliphatic ketones, but also the corresponding alcohols, thiols and olefins undergo the Willgerodt reaction to produce carboxylic acid amides. The results of these experiments have further elucidated the course of the reaction and offer additional support for the mechanism previously proposed.

RENSSELAER, NEW YORK RECEIVED FEBRUARY 13, 1946

[CONTRIBUTION FROM COLGATE-PALMOLIVE-PEET CO.]

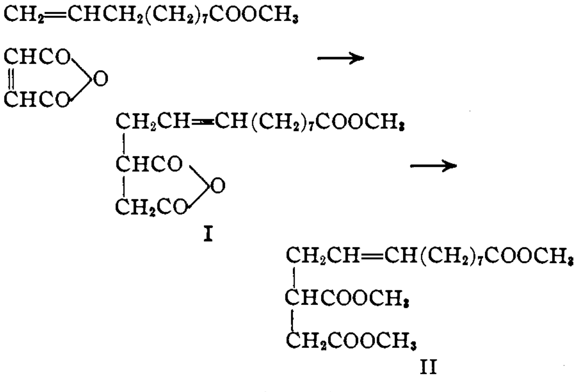
The Addition of Olefinic Esters to Maleic Anhydride

BY JOHN ROSS, ARTHUR I. GEBHART AND J. FRED GERECHT

There have been several reports in the patent and technical literature[1] where it is claimed that maleic anhydride reacts with mono-olefinic and non-conjugated poly-olefinic acids or esters at temperatures of 200–250° to give addition compounds. The structure of the products obtained and the nature of addition reaction involved have not been established. We have examined the conditions under which maleic anhydride will unite with long chain mono-olefinic acids and esters and have determined the constitution of the major addition products of undecylenic and oleic esters.

Mono-olefinic esters and maleic anhydride react at temperatures of about 200–250° to give good yields of the simple addition compound of one molecule of ester with one molecule of maleic anhydride and under these conditions only negligible amounts of higher molecular weight or polymeric material is formed.

With undecylenic ester, maleic anhydride gives a product which consists mainly of stereomeric forms of structure I. The crude condensation product was converted to the trimethyl ester II which was distilled. The acids corresponding to this ester were separated into two fractions by crystallization of the potassium salts, from which were obtained a solid acid m. p. 98.5° and a liquid acid fraction. Di-hydroxylation of the solid acid from the less soluble potassium salt gave a mixture of isomeric lactones of 4,5-dihydroxydodecane 1,2,12-tricarboxylic acid III. The lactone form of III could not be oxidized with periodic acid in acid media.



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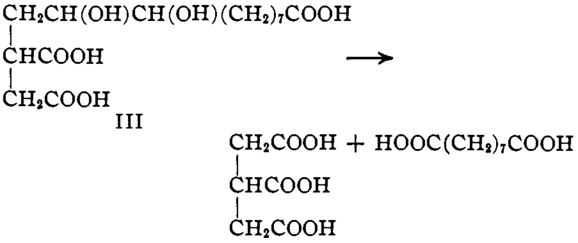
II



$$\begin{matrix} CH_2CH(OH)CH(OH)(CH_2)_7COOH \\ | \\ CHCOOH \\ | \\ CH_2COOH \end{matrix} \longrightarrow \begin{matrix} CH_2COOH \\ | \\ CHCOOH \\ | \\ CH_2COOH \end{matrix} + HOOC(CH_2)_7COOH$$

III

However, periodate oxidation of an alkaline solution of this lactone *i. e.*, a solution of the trisodium salt of the dihydroxy tricarboxylic acid III, proceeded quantitatively and by oxidation of the resulting aldehydes there was obtained azelaic and tricarballylic acids which demonstrated the structure of the addition product. The solid acid m. p. 98.5° which was thus shown to correspond to the ester II, upon hydrogenation took up two atoms of hydrogen to give dodecane 1,2,12-tricarboxylic acid.

The liquid tricarboxylic acid fraction remaining after removal of the less soluble potassium salt gave no dodecane 1,2,12-tricarboxylic acid after reduction and consequently could not have this skeletal structure. This material therefore could not be the geometrical stereomer of the solid acid m. p. 98.5° although it had the same approximate analysis. It is therefore concluded that this fraction is probably an impure mixture of position isomers of the solid acid and was not further examined.

With methyl oleate at a temperature of 200° maleic anhydride gives rise to an isomeric mixture of addition products formed by attachment of the maleic residue to C_9 or C_{10} and the remaining double bond shifting to the C_{10}–C_{11} or C_9–C_8 positions, respectively, of the octadecenoic acid chain.

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(1) E. A. Bevan, *Oil and Colour Chem. Assoc.*, **34**, 1939 (1940); *C. A.*, **34**, 5960 (1940); E. T. Clocker, U. S. Patent 218,882–90 (1940); *C. A.*, **34**, 3845 (1940); W. G. Bickford, P. Krauczunas and D. H. Wheeler, *Oil and Soap*, **19**, 23 (1942).