the oily aldehyde layer crystallized and was separated from the water by filtration. The yield of aldehyde after air-drying was 17 g. (81%); m. p. 46–47°. The yield of aniline was 11 g. (79%).

B. From N-Phenyl-*p*-chlorobenzimidyl Chloride.—The imidyl chloride, 37.5 g. (0.15 mole), was dissolved in 100 ml. of ethylene chloride and treated with 125 g. of stannous chloride in 450 ml. of absolute ether saturated with hydrogen chloride. The *p*-chlorobenzaldehyde was isolated by the method employed in the preparation from the oxime: yield 16 g. (78%); m. p. 46–47°. The yield of aniline was 10.8 g. (80%).

Isolation of *p*-Chlorobenzalaniline from Its Double Salt.—The isolation was made by a procedure similar to the isolation of benzalaniline from the corresponding double salt. After recrystallization from 95% alcohol, the compound melted at 57–58°. A mixed melting point with *p*-chlorobenzalaniline prepared from *p*-chlorobenzaldehyde and aniline showed no depression.

Summary

A procedure has been developed for the preparation of aromatic aldehydes directly from ketoximes. This involves a Beckmann rearrangement but not the formation of the substituted amide. Evidence for a suggested mechanism is given.

IOWA CITY, IOWA

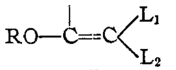
RECEIVED MAY 13, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

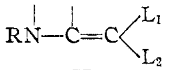
The Reduction of Amide Vinylogs

BY ROBERT H. BAKER AND ARTHUR H. SCHLESINGER[1]

The observation that hydrogen attacks ester vinylogs of the type I

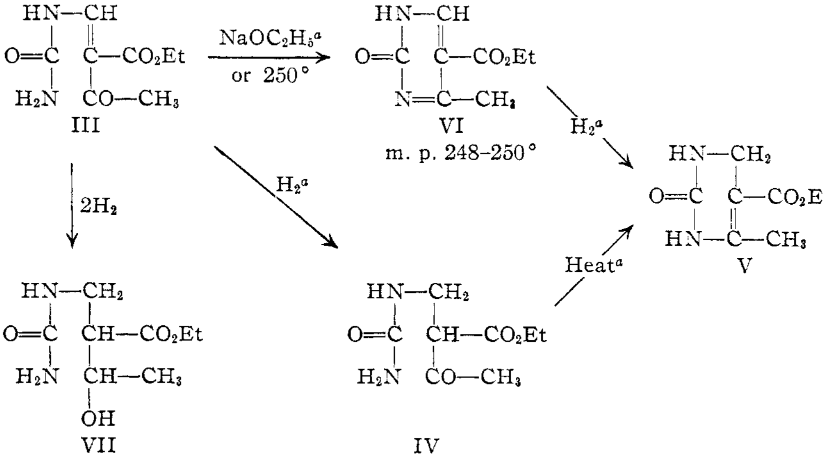


I



II

with preferential cleavage of the alkoxyl group[2] prompted a study of the nitrogen analogs II. In contrast to the behavior of I, which can be hydrogenated at the olefinic linkage without cleavage when only one of the L groups is an acyl, the nitrogen analog of such a compound adds hydrogen exclusively by cleavage. This is clearly demonstrated by the behavior of O-ethylbenzoylacetone from which it is possible to isolate 3-ethoxy-1-phenyl-1-butanol in 57% yield by nickel hydrogenation whereas β-anilinocrotonophenone under similar conditions yields only aniline and butyrophenone.



[a] See Reference 3.

Of the nitrogen compounds only those with acyl groups on the nitrogen have resisted cleavage to any extent. Acetamido-, benzamido- and ureidomethyleneacetoacetic ester have been hydrogenated to the corresponding saturated keto esters in limited yields. The latter of these compounds, III, has previously been hydrogenated by Bergmann and Johnson[3] with a limited quantity of hydrogen. Although they made no attempt to isolate the primary product it must have been the ureidomethylacetoacetic ester, IV, because heating with water converted it into 5-acetyldihydrouracil, V, which could also be obtained from the sodium ethoxide condensation product, VI, of III. In the present investigation it was customary to allow hydrogenations to run as long as hydrogen was absorbed at an appreciable rate. Over platinum oxide the ureidomethylene compound, III, took up the equivalent of 1.66 moles of hydrogen to produce mainly the saturated alcohol, VII, along with a small amount of the cleavage product, methylacetoacetic ester, and a trace of an unidentified product, m.p. 250–251°, which depresses the melting point of VI by 15°.

It is of interest to note that the aminomethylene derivatives of the ketones are cleaved with preservation of the keto groups, in spite of the fact that no attempts were made to stop the reduction short of saturation. Since considerable quantities of starting material could usually be isolated it is evident that some product of the reduction, probably the amine, hinders the reduction of the carbonyl group.[4]

It is difficult to correlate the effects of structure

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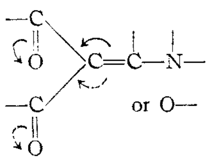
(1) Wade Fetzer Fellow 1945–1946.

(2) Baker and Weiss, THIS JOURNAL, **66**, 343 (1944).

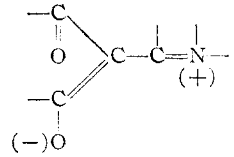
(3) Bergmann and Johnson, *Ber.*, **66**, 1492 (1933).

(4) Weizmann, U. S. Patent 2,367,078; *C. A.*, **39**, 2293 (1945), used amine hydrochlorides and nickel to produce saturated ketones from unsaturated ones.

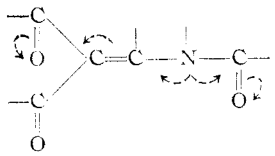
on ease of hydrogenolysis, but some analogies to other reactions may be drawn. Without doubt the ester and amide vinylogs owe their ease of cleavage by hydrogen or other reagents largely to the drain of electrons from the carbon–nitrogen link by the carbonyl groups usually present. Thus in this and the previous work[2] the lability



of the C-hetero-atom bond is qualitatively shown to depend upon the number and electronegativity of the labilizing groups. It might be argued that this effect results in an increase of the double bond character of the hetero atom to such an extent that the bond takes up enough hydrogen to



cause cleavage. In any event the placing of a competing electron sink on another of the nitrogen bonds would diminish or balance these effects. Then, since the compound has been stabilized toward cleavage, saturation of the



olefinic linkage takes place and there is no further cause for cleavage. A similar case has been observed for pyrroles in which carbethoxylation of the nitrogen greatly facilitates hydrogenation to the pyrrolidine.[5]

Generally the products of hydrogenation were separated into fractions on the basis of solubility characteristics prior to identification of the individual compounds. In an early experiment the total product resulting from addition of one mole of hydrogen to anilinomethylenemalonic ester was subjected to low pressure distillation. When the head temperature reached 112° at 36 mm. diphenylurea began to sublime into the receiver along with liquid products. This was easily separated because of its insolubility in petroleum ether or carbon tetrachloride and it was shown to be formed in greater amounts when the liquid product was heated with added aniline. This may have been formed by pyrolysis of a trace of anilinomethylmalonic ester as has been observed for a similar compound.[6]

The easy preparation of methylanilinomethylenemalonic ester and the similarity of its properties to the derivatives of primary amines contributes to our belief that these latter compounds are substituted acrylic esters instead of anils. The ease of their hydrogenolysis at the carbon–nitrogen link is even more convincing evidence for the acrylate structure.

The aminomethylene compounds are easily prepared by warming the amine with the corresponding ethoxymethylene derivative of malonic or acetoacetic ester.[7] Amides react with acetoacetic ester derivatives at elevated temperatures, but not with ethoxymethylenemalonic ester. Claisen[7] reported that benzamidomethylenemalonic ester could be made by acylation of the amino compound, but we have not been able to confirm this.

Experimental[8]

Preparation of Compounds.—Most of the compounds were prepared by Claisen's method. β-Anilinocrotonophenone was prepared by reaction of benzoylacetone with aniline.[9]

Ethyl N-methylanilinomethylenemalonate has not been previously described. It was prepared by heating at 100° for twenty hours one mole each of methylaniline and ethoxymethylenemalonic ester. White crystals, m. p. 54°, were obtained in 90% yield by crystallization from cyclohexane.

Anal. Calcd. for $C_{15}H_{19}O_4N$: N, 5.05. Found: N, 5.09.

Hydrogenations.—The catalysts, apparatus and procedures were similar to those previously described.[10] The platinum oxide was obtained from American Platinum Works, Newark, N. J. Table I summarizes the behavior of the various compounds in ethyl alcohol solution.

Isolation and Identification of Products.—Unchanged starting materials were recovered from the products by taking advantage of their low solubility in ether or petroleum ether. Aniline and methylaniline were usually extracted from ether solutions by means of dilute hydrochloric acid and identified as their benzenesulfonyl derivatives. Diphenylurea was isolated from an experiment similar to Run No. 1 in which the whole product was heated to 170–200°. It was separated by precipitation with petroleum ether and was identified by nitrogen analysis, m. p. and mixed m. p. with an authentic sample, 230–232°. Diethyl methylmalonate was identified by its physical properties, b. p. 59–60° at 3 mm. and n^{20}_D 1.4130; lit.[11] $n^{18.7}_D$ 1.41369. Ethyl methylacetoacetate was converted into its 2,4-dinitrophenylhydrazone, m. p. 58–59°; lit.[12] 56–57°.

Ethyl 2-ureidomethyl-3-hydroxybutanoate was isolated from Run 7. After evaporation of the solvent there remained 11.8 g. of a liquid and a solid. Extraction with ether gave a solution from which methylacetoacetic ester was obtained. The ether insoluble solid was extracted with water leaving an insoluble solid, m. p. 250–251°, which has not been identified. The aqueous solution upon evaporation in a stream of air at 44° yielded an oil crystallizable only with difficulty from absolute ethanol by adding

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(5) Signaigo and Adkins, This Journal, **58**, 709 (1936).

(6) Erickson, *ibid.*, **67**, 1382 (1945).

(7) Claisen, *Ann.*, **297**, 1 (1897).

(8) Microanalyses were performed by Margaret Ledyard.

(9) Turner, *J. Chem. Soc.*, **111**, 1 (1917); Beyer, *Ber.*, **20**, 1767 (1887).

(10) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937; Adams and Voorhees, "Organic Syntheses," 2nd ed., Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 61.

(11) v. Auwers, *Ber.*, **46**, 494 (1913).

(12) Adams and Long, This Journal, **62**, 2289 (1940).

TABLE I

HYDROGENATION OF β-ANILINOCROTONOPHENONE (C) AND THE ETHYL ESTERS OF SUBSTITUTED METHYLENEMALONIC (M) AND ACETOACETIC ACIDS (A)

Run	Compound	Cat.	Moles H_2	P., atm.	*T*, °C.	Time min.	% Products isolated
1	C_6H_5NH-M	PtO_2	1	2	25	50	35 Aniline; 3.6 diphenylurea
2	NH_2-M	PtO_2	0.25	2	25	60	Ammonia
3	$C_6H_5N(CH_3)$-M	PtO_2	2	2	25	394	55 Methylaniline, 55 diethyl methylmalonate
4	Same	Ni(R)	2	60	67	112	67 Methylaniline, 72 diethyl methylmalonate
5	C_6H_5NH-A	PtO_2	2.5	1	25	282	[a]
6	Same	PtO_2	2	2	25	270	32 Aniline, 24 ethyl methylacetoacetate
7	NH_2CONH-A	PtO_2	1.67	2	25	214	43 Ethyl 2-ureidomethyl-3-hydroxybutanoate, 24 ethyl methylacetoacetate
8	C_6H_5CONH-A	Ni(R)	1.75	60	68	145	30 Ethyl benzamidomethylacetoacetate[b]
9	CH_3CONH-A	Ni(R)	1.1	60	67	37	0 Acetamide
10	C	Ni(R)	1.67	60	68	150	79 Aniline, 40 butyrophenone
11	C[c]	PtO_2	2	2	27	30	79 Aniline, 91 butyrophenone

[a] This was a micro run for maximum hydrogen uptake. [b] Yield based upon dinitrophenylhydrazone obtained. [c] Absolute ethyl acetate was used as solvent.

ether to the hot solution. The white crystals, m. p. 103°, weighed 5 g. The ferric chloride test is negative and haloform test is positive.

Anal. Calcd. for $C_8H_{16}N_2O_4$: N, 13.61. Found: N, 13.37.

Ethyl Benzamidomethylacetoacetate.—It was not practical to isolate this compound from the reaction mixture (Run No. 8). When the mixture was subjected to distillation at 170–200° at 4 mm. there was obtained by precipitation with ether crude benzamide, m. p. 117° and mixed m. p. 122°, and an ether soluble oil, probably methyleneacetoacetic ester which slowly polymerized to a semi-solid gel. That these products were formed by pyrolytic decomposition of the benzamidomethylacetoacetic ester was proved by preparing from the unheated reaction product its *2,4-dinitrophenylhydrazone*, yellow plates, m. p. 157–157.5°, from alcohol.

Anal. Calcd. for $C_{20}H_{21}N_5O_7$: C, 54.17; H, 4.75; N, 15.80. Found: C, 54.09; H, 4.89; N, 15.69.

Butyrophenone was isolated from the ether-soluble neutral fractions from Runs No. 10 and 11 by distillation *in vacuo*, and was converted into its 2,4-dinitrophenylhydrazone, m. p. 186–187°; lit.[13] 190°.

Summary

1. Open chain vinylogs of the amides are as easily cleaved by hydrogenation as are the ester vinylogs.

2. The vinylogs of N-acylamides are more resistant to cleavage and may be hydrogenated at the olefinic linkage.

3. The formation of a derivative from ethoxymethylenemalonic ester and methylaniline and the similarity of its behavior on hydrogenation to the derivatives of primary amines indicates that these latter compounds are substituted acrylic esters and not anils.

(13) Evans, *J. Chem. Soc.*, 785 (1936).

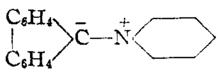
EVANSTON, ILLINOIS RECEIVED JUNE 10, 1946

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, SOILS AND AGRICULTURAL ENGINEERING, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

Behavior of Certain Fluorene Compounds Containing Trivalent Carbon and Tetravalent Nitrogen

BY LOUIS A. PINCK AND GUIDO E. HILBERT[1]

This paper deals with the behavior of three interesting compounds, which have a trivalent carbon and a tetravalent nitrogen, namely, fluorylidenepyridinium I, fluorylidene-α-picolinium II and fluorylidene-9-ammonium fluorene III.



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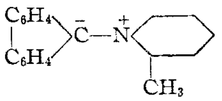

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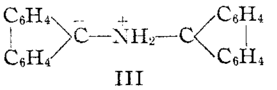

III

Compounds of this type, namely, fluorylidene trimethylammonium and fluorylidene triethylammonium, had been reported by Ingold and Jessop.[2] Their attempts to isolate them met with failure because of the instability of these compounds. In an article by Krollpfeiffer and Schneider,[3] it was briefly mentioned that deep blue colored products (presumably fluorylidene pyridinium) could be prepared from 9-fluorylpyridinium bromide. The preparation of the sulfur analog, namely, fluorylidene dimethyl sulfide had been reported by Ingold and Jessop,[4]

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(1) Present address: Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, Peoria, Illinois.

(2) Ingold and Jessop, *J. Chem. Soc.*, 2357 (1929).

(3) Krollpfeiffer and Schneider, *Ann.*, **530**, 38 (1937).

(4) Ingold and Jessop, *J. Chem. Soc.*, 713 (1930).