alcohol was added, over a period of twenty-five minutes, to a suspension of 17.0 g. (0.1 mole) of pulverized silver nitrate in 25 cc. of absolute alcohol at a temperature of −70°. A pale yellow suspension was formed which turned black quite rapidly. The mixture was allowed to warm slowly to room temperature, and was then stirred for two hours after which it was refluxed for fifteen minutes. An analysis of the evolved gases gave 0.0208 mole (27.8%) of ethane, 0.0116 mole (15.5%) of ethylene, and 0.0195 mole (52.0%) of butane. The yields are based on the cleavage of one ethyl group.

The residual suspension was filtered and evaporated in a stream of air to a volume of about 50 cc. Then 100 cc. of water was added followed by 30 cc. of 10% hydrochloric acid. During the addition, the mixture was stirred while being cooled in an ice-bath. The large amount of white precipitate was filtered; dissolved in 100 cc. of ether; and the ether solution allowed to evaporate spontaneously almost to dryness. White needles were formed which were washed with 10 cc. of petroleum ether (b. p., 28–38°) and dried. The yield of triethyllead chloride was 18.0 g. (72.7%).

The general results are given in Table I. Gases were analyzed by conventional procedures. All of the organolead products were analyzed, but analytical results are given only for the new organolead compounds. The percentages of *m*-dinitrobenzene are those obtained incidental to the isolation and characterization of the benzene.

Silver Nitrate with Tetraphenylsilicon and Tetraphenylgermanium.—Tetraphenylsilicon was refluxed with an alcoholic suspension of silver nitrate for one hundred and forty-four hours. There was no evidence of reaction, and the RM compound was recovered.

Tetraphenylgermanium was refluxed with silver nitrate, under corresponding conditions, for one hundred and twenty hours. Only a slight darkening of the mixture was apparent and the RM compound was recovered practically quantitatively.

Summary

The fate of the R groups in cleavage reactions of $(C_6H_5)_4Sn$ and $(C_6H_5)_4Pb$ with silver and copper nitrates varies both with the RM compound and the inorganic salt. Tetraphenylsilicon and tetraphenylgermanium are not cleaved, under corresponding conditions, by silver nitrate.

The highly unstable methylcopper has been shown to be an intermediate in the reaction between tetramethyllead and copper nitrate.

AMES, IOWA RECEIVED DECEMBER 28, 1942

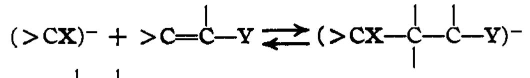
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A Study of Some Michael Reactions

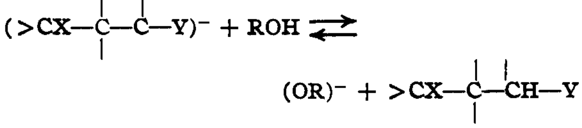
BY C. F. KOELSCH

When a Michael reaction is brought about by treating a mixture of an α,β-unsaturated compound and a substance containing an active methylene group with an alkoxide, it proceeds through the following stages (X and Y are electrophilic groups)

$$>\mathrm{CHX} + (\mathrm{OR})^- \rightleftarrows (>\mathrm{CX})^- + \mathrm{ROH}$$

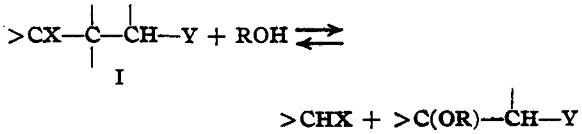


$$(>\mathrm{CX})^- + >\mathrm{C{=}C{-}Y} \rightleftarrows (>\mathrm{CX{-}C{-}C{-}Y})^-$$



$$(>\mathrm{CX{-}C{-}C{-}Y})^- + \mathrm{ROH} \rightleftarrows (\mathrm{OR})^- + >\mathrm{CX{-}C{-}CH{-}Y}$$

But since not only the anion formed from the active methylene compound but also the alkoxide anion can add to the unsaturated substance, the reaction involves effectively the equilibrium



$$>\mathrm{CX{-}C{-}CH{-}Y} + \mathrm{ROH} \rightleftarrows >\mathrm{CHX} + >\mathrm{C(OR){-}CH{-}Y}$$

I II

In most cases the tendency to form an alkoxy compound (II) is relatively small, and the Michael reaction can be carried out successfully in alcoholic solution.[1]

It was found, however, that methyl acrylate and acrylonitrile[2] formed addition products with alcohols with exceptional rapidity. When attempts were made to carry out Michael reactions with these acrylic acid derivatives in alcoholic solutions, only β-alkoxypropionic esters or nitriles were obtained. The following experiments indicate the ease with which alcohol additions took place.

[1] Reactions between β-hydroxy- or β-halogenated compounds (II, OH or Br in place of OR) and active methylene compounds in the presence of bases lead to I. These transformations are obviously similar to the Michael reaction and do not involve *direct* interchange of OH or Br for >CX— [*Cf.* Ingold, *J. Chem. Soc.*, **119**, 335 (1921)].

[2] The research described in the present paper was undertaken primarily to discover satisfactory conditions for carrying out condensations of benzyl cyanide with methyl acrylate and with acrylonitrile. It was done during the early months of 1940, but since it forms a part of a larger investigation, it was not published. Publication of the work in its present form is, however, now made desirable by the appearance of a paper by Bruson [THIS JOURNAL, **64**, 2457 (1942)] in which related reactions are described and identical investigations are projected.

TABLE I

REACTIONS WITH BENZYL CYANIDE

Reactant	Product: -B is butyronitrile, -G is glutaronitrile	B. p. °C.	B. p. Mm.	Yield, %	Formula	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
$CH_2{=}CHCOOCH_3$	γ-Carbomethoxy-α-phenyl-B	187–190	18	20–23[a]	$C_{12}H_{13}NO_2$	71.0	6.4	71.2	6.6
$CH_2{=}CHCN$	α-Phenyl-G	198–200	12	20–33[b]	$C_{11}H_{10}N_2$	77.6	5.9	77.6	6.3
$CH_3CH{=}CHCOOEt$	γ-Carbethoxy-β-methyl-α-phenyl-B	170–175	10	63–68	$C_{14}H_{17}NO_2$	72.7	7.4	73.5	7.4
$CH_2{=}CHCH_2CN$[c]	β-Methyl-α-phenyl-G	193–197	14	76	$C_{12}H_{12}N_2$	78.2	6.5	78.1	6.7
$(CH_3)_2C{=}CHCOOEt$	γ-Carbethoxy-β,β-dimethyl-α-phenyl-B	195–200	23	43	$C_{15}H_{19}NO_2$	73.4	7.7	73.3	7.8
Methyl maleate	β,γ-Dicarbomethoxy-α-phenyl-B	198–203	10	50	$C_{14}H_{15}NO_4$	64.4	5.8	64.3	5.9
Ethyl maleate	β,γ-Dicarbethoxy-α-phenyl-B[d]	185–187	1	52–58[e]	$C_{16}H_{19}NO_4$	66.4	6.6	66.2	6.7
$C_6H_5CH{=}CHCOOEt$	γ-Carbethoxy-α,β-diphenyl-B[f]	100–101[g,h]	..	39	$C_{19}H_{19}NO_2$				
		59– 60[g,i]	..	34	$C_{19}H_{19}NO_2$				
$C_6H_5CH{=}CHCN$[j]	γ-Carbethoxy-β,γ-diphenyl-B	118–121[g]	..	50[k]	$C_{19}H_{19}NO_2$	77.8	6.5	77.7	6.5
$C_6H_5CH{=}CHCN$	α,β-Diphenyl-G	101–103[g]	..	81–87	$C_{17}H_{14}N_2$	83.0	5.7	83.0	5.7
$C_6H_5CH{=}CHCN$[l]	α,*p*-Methoxyphenyl-β-phenyl-G	140–142[g]	..	26	$C_{18}H_{16}N_2O$	78.2	5.8	78.4	6.1
$C_6H_5CH{=}CHCN$[m]	α,*m*-Aminophenyl-β-phenyl-G[f]	152–154[g]	..	17	$C_{17}H_{15}N_3$	78.1	5.8	78.4	5.9
		120–122[g]	..	33	$C_{17}H_{15}N_3$	78.1	5.8	78.2	6.0
p-$CH_3OC_6H_4CH{=}CHCN$	β,*p*-Methoxyphenyl-α-phenyl-G	135–136[g]	..	72	$C_{18}H_{16}N_2O$	78.2	5.8	77.8	5.7

[a] With excess benzyl cyanide as a solvent and with sodamide as a catalyst, a yield of 24% was obtained. [b] With methanol, ethanol, ether, or excess benzyl cyanide as solvents, yields of 0, 0, 36, and 25%, respectively, were obtained. [c] Allyl cyanide rearranges to crotononitrile in the presence of bases [Bruylants, *Bull. soc. chim. Belg.*, **31**, 225 (1922); v. Auwers, *Ber.*, **56**, 1172 (1923)] and then adds active methylene compounds [Michael and Ross, THIS JOURNAL, **53**, 1168 (1931)]. [d] The formation of a normal product here is noteworthy and is to be ascribed to the use of only a small amount of basic catalyst. Complex products of undetermined structure were obtained by Henze [*Ber.*, **33**, 966 (1900)] from ethyl fumarate and benzyl cyanide in the presence of one equivalent of sodium ethoxide. [e] With ethanol as a solvent, a yield of 46% was obtained. [f] Two diastereoisomeric forms were isolated. [g] M. p., °C, uncorrected. [h] Reported m. p. 99–100° [Erlenmeyer, *Ber.*, **33**, 2006 (1900)]. [i] Reported m. p. 59–60° [Helmkamp, Tanghe, and Plati, THIS JOURNAL, **62**, 3217 (1940)]. [j] The addendum was ethyl phenylacetate. In agreement with the finding of Connor and McClellan [*J. Org. Chem.*, **3**, 570 (1938)] no reaction was caused by sodium ethoxide. In the present experiment, a smooth reaction was brought about by sodamide. [k] Plus 30% of a lower melting substance which was not purified. [l] The addendum was *p*-methoxybenzyl cyanide. [m] The addendum was *m*-amino benzyl cyanide. This substance, heretofore not analyzed, was prepared in yields of 50–55% by reducing *m*-nitrobenzyl cyanide [Heller, *Ann.*, **358**, 357 (1907)] with iron and 5% acetic acid; reduction with stannous chloride or tin and hydrochloric acid [Salkowski, *Ber.*, **17**, 506 (1884)] gave unsatisfactory results. The amino nitrile was a colorless oil that boiled at 183–187° at 13 mm. (Calcd. for $C_8H_8N_2$: C, 72.7; H, 6.1. Found: C, 72.2; H, 6.5); it formed a picrate that melted at 200° with decomposition, and on shaking with acetic anhydride in water it yielded *m-acetylaminobenzyl cyanide*, colorless plates that melted at 100–102° (Calcd. for $C_{10}H_{10}N_2O$: C, 68.9; H, 5.8. Found: C, 68.9; H, 5.9).

A mixture of 65 g. of methyl acrylate and 25 g. of methanol in a 500-ml. distilling flask was treated with two drops of a concentrated sodium methoxide solution. The temperature of the mixture was kept at 30–35° by efficient external cooling until it showed no further tendency to rise (about ten minutes). The mixture was then neutralized with acetic acid and distilled; redistillation gave 68 g. (77%) of methyl β-methoxypropionate that boiled at 137–143° (reported[3] 140–145°).

A mixture of 26.5 g. of acrylonitrile and 30 g. of ethanol treated similarly gave 44 g. (89%) of *β-ethoxypropionitrile*, a colorless pleasant smelling liquid that boiled at 170–173°.

Anal. Calcd. for C_5H_9NO: N, 14.2. Found: N, 14.0.

The alkoxy derivatives showed an unusual reluctance to react with active methylene compounds. For example, methyl β-methoxypropionate was recovered unchanged after it had been boiled for six hours with an equivalent quantity of benzyl cyanide in methanol containing sodium methoxide.

In order to cause Michael condensations to take place with acrylic acid derivatives it was thus necessary to prevent the formation of stable alkoxy compounds by carrying out the reactions in the absence of alcohol. Since some early experiments of Ruhemann and Cunnington[4] had indicated that a solvent was superfluous in certain Michael reactions, no solvent was used

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[3] Purdie and Marshall, *J. Chem. Soc.*, **59**, 474 (1891).

[4] Ruhemann and Cunnington, *ibid.*, **73**, 1006 (1898).

in the present experiments. Quite satisfactory results were obtained, and accordingly the effect of omitting the solvent from some other typical Michael reaction mixtures was studied. Here, too, rather good yields were obtained. The experiments are summarized in Table I, and the experimental procedure is described below.

A mixture of one-half mole of each of the reactants was stirred by hand and treated with two or three drops of a solution of 1 g. of sodium in 20 ml. of ethanol (or methanol if a methyl ester was involved). In most cases the ensuing reaction was exothermic, and external cooling was used to keep the temperature of the mixture below 50°. Completion of reaction was recognized when the temperature of the mixture began to fall, and when a further rise was not caused by the addition of one drop more of the catalyst solution. The mixture was then neutralized with acetic acid. Solid products were crystallized from alcohol; liquid products were washed with water, if necessary after dilution with carbon tetrachloride, and then distilled under reduced pressure. Distillation was usually preceded by decomposition; acrid pyrolysis products condensable in a liquid air trap were formed. This decomposition involved by-products, however, whose presence was also indicated by non-volatile residues from the first distillations, for redistillation of the products was accompanied by no decomposition and no distillation residues.

The assistance of Mr. E. E. Renfrew in carrying out the micro analyses reported in this paper and that of the Dow Chemical Company of Midland, Michigan, in furnishing the acrylonitrile are gratefully acknowledged.

Summary

When attempts are made to condense benzyl cyanide with methyl acrylate (or acrylonitrile) in alcoholic solutions, alcohol addition takes place rather than a Michael reaction, and methyl β-methoxypropionate (or β-ethoxypropionitrile) is formed. γ-Carbethoxy-α-phenylbutyronitrile (or α-phenylglutaronitrile) can be obtained, however, if the reaction is carried out without a solvent. Other Michael additions of benzyl cyanide to various α,β-unsaturated compounds also proceed well in the absence of a solvent.

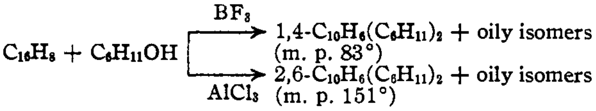
Minneapolis, Minnesota Received October 21, 1942

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Dialkylation of Naphthalene. II. The Synthesis of 2,6-Diphenylnaphthalene

By Charles C. Price and Arthur J. Tomisek

Two crystalline dicyclohexylnaphthalenes have been reported from the alkylation of naphthalene. The lower melting isomer (m. p. 83°), obtained by alkylation with cyclohexanol using boron fluoride as a catalyst,[1] was shown to be the 1,4-isomer by dehydrogenation to 1,4-diphenylnaphthalene (m. p. 133°). The higher melting isomer (m. p. 151°) obtained by Bodroux[2] by alkylation with cyclohexanol and by Pokrovskaya and Stepentseva[3] with cyclohexene, in each instance using aluminum chloride as a catalyst, was dehydrogenated by Pokrovskaya and Stepentseva to a high-melting diphenylnaphthalene[3] (m. p. 230°) of unknown structure. This material has now been shown to be identical with a sample of synthetic 2,6-diphenylnaphthalene. Thus, as in the dialkylation of benzene,[4] orientation in the dialkylation of naphthalene using boron fluoride differs from that using aluminum chloride.



$$C_{16}H_8 + C_6H_{11}OH \begin{cases} \xrightarrow{BF_3} 1,4\text{-}C_{10}H_6(C_6H_{11})_2 + \text{oily isomers (m. p. 83°)} \\ \xrightarrow[AlCl_3]{} 2,6\text{-}C_{10}H_6(C_6H_{11})_2 + \text{oily isomers (m. p. 151°)} \end{cases}$$

The synthesis of 2,6-diphenylnaphthalene was accomplished by the series of reactions shown.

The Friedel–Crafts condensation of biphenyl with phenylsuccinic anhydride gave a mixture from which the acid (I) was isolated as the principal product by repeated fractional crystallization. This product (I) was shown to have been formed by condensation of phenylsuccinic anhydride in the 4-position of biphenyl by oxidation to *p*-phenylbenzoic acid. The other phenyl group was assigned the position β to the carboxyl group. Had it been in the alternative α position, the diphenylnaphthalene obtained as the final product would have been the known 2,7-isomer, m. p. 143°.[5] The orientation of the condensation thus corresponds to that observed for the con-

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[1] Price, Shafer, Huber and Bernstein, *J. Org. Chem.*, **7**, 517 (1942).

[2] Bodroux, *Ann. chim.*, [10] **11**, 511 (1929).

[3] Pokrovskaya and Stepentseva, *J. Gen. Chem.*, (U. S. S. R.), **9**, 1953 (1939).

[4] McKenna and Sowa, This Journal, **59**, 470 (1937).

[5] Hey and Lawton, *J. Chem. Soc.*, 375 (1940.)