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Condensation of Cyclohexanone with Nitriles

BY HERMAN A. BRUSON, EDWARD RIENER AND THOMAS RIENER

The reaction of phenols with nitriles in the presence of aluminum chloride (Houben–Hoesch method) to yield ketimines and ultimately ketones suggested the possibility that cyclohexanone might react in its enolic form with acetonitrile and aluminum chloride to yield 2-acetylcyclohexanone.

Upon addition of a mixture of acetonitrile and cyclohexanone to a cooled, stirred suspension of anhydrous aluminum chloride in carbon disulfide a semisolid reaction mass forms which soon prevents further stirring. After decomposition of the product with ice water the mixture yields a crystalline solid (I) melting at 140° and having the formula $C_{14}H_{23}O_2N$. This product corresponds to a composition of two moles cyclohexanone and one mole acetonitrile. It may be more readily obtained by using ethylene dichloride instead of carbon disulfide as a solvent, since the reaction mixture then remains fluid and homogeneous, and can be continuously stirred during the reaction period.

The chemical properties of (I) are as follows:

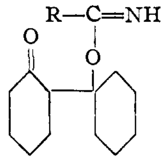
It is a ketone since it yields a crystalline monoxime and a crystalline mono-semicarbazone. It is a base since it dissolves readily in concentrated hydrochloric acid but not in water at room temperature and is reprecipitated unchanged from the acid solution by the addition of excess sodium hydroxide solution.

When the product is steam distilled from an admixture with dilute sulfuric acid the nitrogen is split off as ammonia and an oil steam distills over. The oil was found to be 2-cyclohexenylcyclohexanone. Acetic acid is found in the aqueous steam distillate layer. Since cyclohexanone upon steam distillation from dilute sulfuric acid under the same conditions gave no detectable amount of cyclohexenylcyclohexanone it may safely be concluded that (I) is derived from 2-cyclohexenylcyclohexanone or 2-cyclohexylidenecyclohexanone and not from cyclohexanone itself.

To test this hypothesis, acetonitrile was treated with 2-cyclohexenylcyclohexanone in the presence of an aluminum chloride suspension in ethylene dichloride and the same crystalline product (I) melting at 140° was obtained, although in poorer yield.

That the methyl group of the acetonitrile is not involved in the reaction is shown by the fact that benzonitrile reacts in an analogous manner with cyclohexanone and aluminum chloride to yield a crystalline product (II) melting at 120–121° and having the formula $C_{19}H_{25}O_2N$ corresponding to a molar ratio of cyclohexanone to nitrile of 2:1. Propionitrile likewise reacted with cyclohexanone to yield a crystalline product (III) melting at 92–93° and having the formula $C_{15}H_{25}O_2N$ corresponding to a molar ratio of cyclohexanone to nitrile of 2:1.

A consideration of the above data makes it highly probable that these products are all derived from the aldol of cyclohexanone by the addition of the hydroxyl group thereof to the cyano group to form an iminoether[1] containing a free ketonic group as shown in formula (A).



(I) R = CH_3
(II) R = C_6H_5
(III) R = C_2H_5

(A)

This structure is consistent with all of the above-mentioned facts and reactions except for the possibility that such a formula might *a priori* be suggestive of a rather unstable molecule. The crystalline products obtained by us are however remarkably stable. The product $C_{14}H_{23}O_2N$ (I) obtained from acetonitrile and cyclohexanone or 2-cyclohexenylcyclohexanone is, for example, distillable *in vacuo*. It is also steam distillable from neutral solution and can be boiled for short periods of time with aqueous 10% sodium hydroxide solution without evolution of ammonia or any noticeable change. Only in acid solution does it undergo the complete breakdown upon prolonged standing or upon short boiling which is so characteristic of iminoethers in general.

Experimental

(I) Condensation of Cyclohexanone with Acetonitrile.—To a stirred suspension of 133.5 g. anhydrous, powdered, sublimed aluminum chloride in 300 cc. of carbon disulfide there was added dropwise with cooling to 30–35°, a mixture of 41 g. of acetonitrile and 196 g. of cyclohexanone during the course of forty-five minutes. After about half of this mixture had been added the solid nature of the product prevented further stirring. On standing for about three hours the mixture became a little more fluid and was stirred for eighteen hours at room temperature. It was then poured into 1 liter of chipped ice. After the ice had melted the oil layer was separated and the aqueous layer was extracted with benzene. The combined oil and extract was washed several times with water and the solvent was removed by evaporation in vacuum on a steam-bath. The residue (155 g.) partially solidified on cooling and scratching to a chocolate-colored crystalline magma. For purification it may be recrystallized from diisobutylene or methylcyclohexane with the help of Norite to remove the color; yield 55–75 g. of white crystals, m. p. 140–141°.

Anal. Calcd. for $C_{14}H_{23}O_2N$: C, 70.89; H, 9.70; N, 5.90; mol. wt., 237. Found: C, 71.20; H, 9.72; N, 5.86; mol. wt. (ebullioscopic in acetone), 241.

It is soluble in alcohol, benzene, ether, but insoluble in cold petroleum ether. It is somewhat soluble in boiling water and crystallizes out on cooling.

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[1] A. Pinner, "Die Imidoäther und ihre Derivate," Berlin, 1892; Pinner and Klein, *Ber.*, **10**, 1889 (1877).

The use of 200 cc. of ethylene dichloride instead of the carbon disulfide in the above preparation allows better stirring. The yield of product in this case was 44 g.

Semicarbazone of (I).—This was prepared by heating on a steam-bath under reflux for three hours a mixture of 4.7 g. of (I), 25 cc. of ethanol, 15 cc. of water, 7 g. of sodium acetate and 5.5 g. of semicarbazide hydrochloride. The product was allowed to stand several days at 5° and the white crystalline deposit filtered off. It was recrystallized three times from water to a constant melting point of 194–195° and dried *in vacuo* at 100° for analysis.

Anal. Calcd. for $C_{15}H_{26}O_2N_4$: C, 61.22; H, 8.84; N, 19.04. Found: C, 61.55; H, 9.27; N, 19.00.

A mixed melting point with the semicarbazone of 2-cyclohexenylcyclohexanone of m. p. 195–196° showed a 15° depression.

Oxime of (I).—This was prepared by heating on a steam-bath under reflux for three hours a mixture of 2 g. of (I), 30 cc. of ethanol, 30 cc. of water, 3.3 g. of sodium acetate and 1.7 g. of hydroxylamine sulfate. Since the product did not crystalline on cooling, the solution was evaporated to dryness *in vacuo* and extracted with ether. Upon evaporation of the ether extract a soft mass was obtained which solidified when rubbed with 20 cc. of petroleum ether. The solid material was recrystallized from nitromethane and then from petroleum ether (b. p. 90–100°) to form white crystals, m. p. 163–164°.

Anal. Calcd. for $C_{14}H_{24}O_2N_2$: C, 66.66; H, 9.52; N, 11.11. Found: C, 66.53; H, 9.66; N, 10.85.

(I) **Condensation of Acetonitrile with 2-Cyclohexenylcyclohexanone.**—To a stirred suspension of 89.5 g. of powdered, sublimed, anhydrous aluminum chloride in 150 g. of ethylene dichloride, there was added dropwise a mixture of 27.5 g. of acetonitrile and 118 g. of 2-cyclohexenylcyclohexanone[2] while cooling the reaction mixture to 20–30°. After stirring for twenty-one hours at room temperature the mixture was added to chipped ice and the oil layer separated, washed with water and dried *in vacuo*. The residual oil (109 g.) was distilled under reduced pressure and the fraction boiling at 175–225° (0.5–1 mm.) was collected; yield 17 g. It was recrystallized from petroleum ether (b. p. 90–100°) and formed white crystals, m. p. 140–141°, which gave no depression in melting point with the product (I) obtained from cyclohexanone and acetonitrile.

Hydrolysis of (I).—A mixture of 1000 g. of 10% sulfuric acid and 179 g. (I), prepared from cyclohexanone and acetonitrile was blown with steam for five hours and the distillate (3500 cc.) collected. The oil layer was separated from the distillate and the aqueous layer extracted with ether. The combined oil and ether extract upon distillation *in vacuo* at 10 mm. yielded 52 g. of 2-cyclohexenylcyclohexanone, b. p. 133–136° (10 mm.), identified by its semicarbazone, m. p. 194–195°, and by its mixed melting point with an authentic sample of the semicarbazone of 2-cyclohexenylcyclohexanone of m. p. 195–196° with which it gave no significant depression.

(II) **Condensation of Cyclohexanone with Benzonitrile.**—The procedure given for (I) above was followed, using 133.5 g. of anhydrous aluminum chloride, 300 cc. of ethylene dichloride, 103 g. of benzonitrile and 196 g. of cyclohexanone. The crude product was a brown oil weighing 264 g. Upon extraction with hot petroleum ether (b. p. 90–100°) a light brown powder (82 g.) was left behind as a residue. This was recrystallized several times with considerable loss from petroleum ether and finally from ethylcyclohexane to a constant m. p. 120–121°.

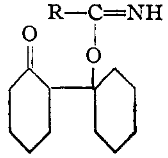
Anal. Calcd. for $C_{19}H_{25}O_2N$: C, 76.25; H, 8.36; N, 4.68. Found: C, 76.74; H, 8.58; N, 4.66.

(III) **Condensation of Propionitrile with Cyclohexanone.**—The procedure given for (I) above was applied to a mixture of 133.5 g. of anhydrous aluminum chloride, 200 cc. of ethylene dichloride, 55 g. of propionitrile and 196 g. of cyclohexanone. The crude product was a brown oil (154 g.) which gradually crystallized in part after several days standing. The sticky crystalline product was spread out on porous tile which absorbed the oily impurity leaving about 80 g. of pinkish crystals. This material was recrystallized from petroleum ether (b. p. 90–100°) to a constant m. p. 92–93°; yield 60 g.

Anal. Calcd. for $C_{15}H_{25}O_2N$: C, 71.71; H, 9.96; N, 5.68. Found: C, 71.88; H, 10.18; N, 5.55.

Summary

Cyclohexanone condenses in the presence of aluminum chloride with nitriles R–CN to yield crystalline compounds which appear to be iminoethers of the aldol of cyclohexanone having the general formula



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[2] Hückel, Neunhoffer, Gerche and Frank, *Ann.*, **477**, 119 (1930).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

A New Synthesis of Organosilicon Compounds[1]

BY F. W. PIETRUSZA,[2] L. H. SOMMER AND F. C. WHITMORE

In a previous communication[3] we reported the preparation of *n*-octyltrichlorosilane in almost quantitative yield from the reaction of 1-octene with trichlorosilane in the presence of a small amount (7 mole %) of diacetyl peroxide. The use of a weak ultraviolet source as the catalyst gave a 24% yield.

$$RCH{=}CH_2 + SiHCl \xrightarrow[\text{or U. V. L.}]{(CH_3COO)_2} RCH_2CH_2SiCl_3 \quad (1)$$

In extension of these results, the present paper reports that this new synthesis[4] is generally applicable to the addition of $SiHCl_3$ to olefins of varied structure, *i. e.*, $RCH{=}CH_2$, $RCH{=}CHR$, $R_2C{=}$

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[1] Paper XV in a series on organosilicon compounds. See THIS JOURNAL, **70**, 445 (1948), for XIV.

[2] This paper comprises part of the subject matter of a thesis submitted by E. W. Pietrusza in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of The Pennsylvania State College. Allied Chemical and Dye Corporation Fellow 1945–1947.

[3] Sommer, Pietrusza and Whitmore, THIS JOURNAL, **69**, 188 (1947).

[4] An excellent treatment of other syntheses of organosilicon compounds is given in Rochow, "Introduction to the Chemistry of the Silicones," John Wiley and Sons, New York, N. Y., 1946, pp. 18–30.