octanone was found to contain a precipitate of a white, crystalline compound which was filtered off and washed free of α-chlorocycloöctanone with ether. Two recrystallizations of the substance from 5% hydrochloric acid resulted in a substance, m. p. 140.5–141°, which contained neither chlorine nor nitrogen. A mixed melting point determination with an authentic sample of suberic acid showed no depression of the melting point.

Anal.[9] Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.11. Found: C, 55.28; H, 8.05.

Summary

Two alicyclic α-chloroketones have been found to undergo ring enlargement on treatment with diazomethane. From the yields of ketonic materials obtained, evidence has been adduced for the Stoll and Stoll-Comte[6] hypothesis regarding steric effects in certain alicyclic ring systems.

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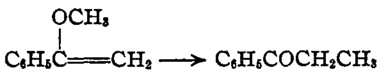
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Condensation of α-Methoxystyrene with Halogen Compounds

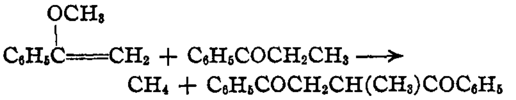
BY C. W. MORTENSON AND M. A. SPIELMAN

In addition to the normal rearrangement (1),[1]



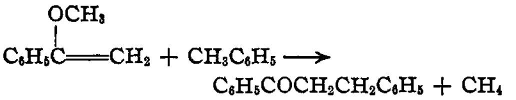
$$C_6H_5\overset{OCH_3}{\overset{|}{C}}{=}CH_2 \longrightarrow C_6H_5COCH_2CH_3 \qquad (1)$$

α-methoxystyrene and a few similar enol ethers undergo a peculiar side reaction (2) in which the unchanged ether condenses with the rearrangement product to eliminate methane and form a γ-diketone. Later[2] it was discovered that at



$$C_6H_5\overset{OCH_3}{\overset{|}{C}}{=}CH_2 + C_6H_5COCH_2CH_3 \longrightarrow CH_4 + C_6H_5COCH_2CH(CH_3)COC_6H_5 \qquad (2)$$

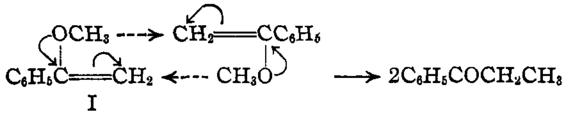
250° α-methoxystyrene also condenses with hydrocarbons such as toluene and cyclohexane (3).



$$C_6H_5\overset{OCH_3}{\overset{|}{C}}{=}CH_2 + CH_3C_6H_5 \longrightarrow C_6H_5COCH_2CH_2C_6H_5 + CH_4 \qquad (3)$$

This reaction, so far as we know, has no analogy except, perhaps, in the recently discovered photolytic condensation of phosgene or oxalyl chloride with cyclohexane.[3] Only ethers capable of undergoing the rearrangement[4] also take part in the condensation, and it is evident that there is some common factor in the two reactions.

The hypothesis here advanced to account for the behavior of α-methoxystyrene is that both the rearrangement and the condensation involve the polarized hetero-enoid system in I. Collision, under the proper circumstances, of two such

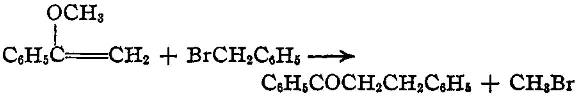


I

molecules leads to the so-called rearrangement which, in the light of such an interpretation, becomes an intermolecular alkylation. The mechanism explains why the reaction is of the second order and why the alkyl group on the oxygen atom of one molecule may, at the end of the reaction, turn up on the carbon atom of another.[1]

Collision of the polarized molecule I with a reactive but different molecular species leads to the condensation reaction. Attack should be at the anionoid center on the methylene carbon atom,[5] and in that event a reaction should take place with alkyl halides which are cationoid in their reactivity and definitely more polarized than hydrocarbons. A few typical halogen compounds of varying degrees of reactivity have been studied.

α-Methoxystyrene when heated with an eightfold excess of benzyl bromide yields β-phenylpropiophenone in 51% of the theoretical yield.



$$C_6H_5\overset{OCH_3}{\overset{|}{C}}{=}CH_2 + BrCH_2C_6H_5 \longrightarrow C_6H_5COCH_2CH_2C_6H_5 + CH_3Br$$

When equimolecular amounts of the halide are used, the yield is 35%, which is well above the 8% yield obtained from toluene under comparable conditions. *n*-Butyl bromide, containing a moderately active halogen atom, condenses in 28% yield, whereas bromobenzene does not react at all.

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(1) Lauer and Spielman, THIS JOURNAL, **55**, 4923 (1933).

(2) Spielman and Mortenson, *ibid.*, **61**, 666 (1939).

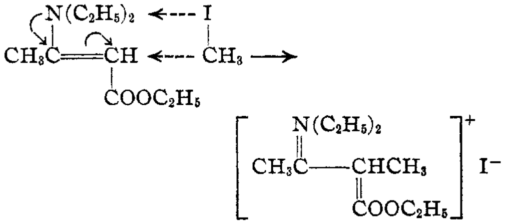
(3) Kharasch and Brown, *ibid.*, **62**, 454 (1940).

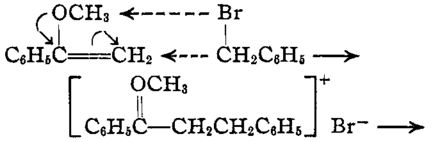
(4) The second order, intermolecular rearrangement of enol ethers (MacDougall, Lauer and Spielman, *ibid.*, **55**, 4089 (1933)) possesses only a formal similarity to the familiar first order, intramolecular rearrangement of allyl ethers (Kincaid and Tarbell, *ibid.*, **61**, 3085 (1939); Hurd and Schmerling, *ibid.*, **59**, 107 (1937)).

(5) The anionoid reactivity of α-methoxystyrene is shown by the avidity with which it adds water, alcohol, acids, etc. For terminology refer to Robinson, "Outline of an Electrochemical Theory of the Course of Organic Reactions," The Institute of Chemistry of Great Britain and Ireland, London, 1932.

Ethyl chloroacetate yields 36% of ethyl β-benzoylpropionate and a trace of *sym*-triphenylbenzene. Benzoyl chloride heated with equimolecular amounts of α-methoxystyrene produces tribenzoylmethane in 9% yield; in large excess it gives 45% of the theoretical amount of *sym*-triphenylbenzene. The triphenylbenzene is the product of a side reaction and is not related to the condensation. It has its origin in the reaction of hydrogen chloride with α-methoxystyrene. Even at room temperature the ether gives triphenylbenzene in 54% yield simply on saturation with hydrogen chloride.

The condensation of α-methoxystyrene with alkyl halides has the appearance of a novel reaction, but in point of fact it has a close analogy in the addition of methyl iodide to ethyl β-diethylaminocrotonate (4).[6] The reaction between α-methoxystyrene and benzyl bromide may be similarly formulated (5); the only real difference is that in the former addition the nitrogen atom is sufficiently basic to form a stable salt, whereas the onium compound formed from α-methoxystyrene decomposes instantaneously.


(4)



$CH_3Br + C_6H_5COCH_2CH_2C_6H_5$ (5)

Experimental Part

All condensations were carried out in Pyrex tubes heated in an electrical bomb furnace.

Condensation with Benzyl Bromide.—Ten grams of α-methoxystyrene and 76 g. of benzyl bromide were heated for seventeen hours at 220°. When the cooled bomb was opened, a slight pressure was evident. The unreacted benzyl bromide and the propiophenone formed by normal rearrangement were removed by vacuum distillation. An 8.3-g. fraction was collected at 150° (1 mm.). It soon solidified, and after one crystallization from alcohol yielded 8.0 g. of β-phenylpropiophenone; m. p. and mixed m. p. 72–73°.[7] No dibenzyl could be detected in the residues.

In order to identify methyl bromide as a reaction product a mixture of α-methoxystyrene and benzyl bromide was heated under a reflux while the effluent gas was passed into a boiling solution of sodium saccharin in butyl carbitol and water. N-Methylsaccharin separated on dilution; m. p. 132°.[8]

Condensation with *n*-Butyl Bromide.—A mixture of 4.6 g. of α-methoxystyrene and 105 g. of *n*-butyl bromide heated to 245° for thirty-six hours gave 1.7 g. of *n*-caprophenone boiling at 108–110° at 7 mm. It was characterized as the semicarbazone; m. p. and mixed m. p. 131–132°.[9]

Condensation with Ethyl Chloroacetate.—Ninety-seven grams of ethyl chloroacetate and 7.7 g. of α-methoxystyrene were heated to 200° for twenty-five hours. Fractionation yielded 90 g. of ethyl chloroacetate, 1.7 g. of acetophenone and 4.3 g. of ethyl β-benzoylpropionate; b. p. 143–145° at 6 mm. The semicarbazone melted at 138–139° and a mixed melting point was not depressed.

Anal. Calcd. for $C_{13}H_{17}O_3N_3$: N, 16.0. Found: N, 16.1.

The non-volatile residue upon treatment with ether gave 0.3 g. of *sym*-triphenylbenzene; m. p. and mixed m. p. 173–174°.[10]

Condensation with Benzoyl Chloride.—Equimolecular amounts of α-methoxystryene and benzoyl chloride (4.5 g. and 4.7 g., respectively) heated to 180° for seven hours gave 0.5 g. of a white solid, sparingly soluble in organic solvents. It melted at 210° and gave a ferric chloride color test. The melting point was not depressed by a synthetic sample of tribenzoylmethane.[11]

Similar heating of 5.2 g. of the ether with 134 g. of the acid chloride gave as the only identifiable substance 1.8 g. of *sym*-triphenylbenzene; m. p. and mixed m. p. 173–174°.[10]

Reaction between Hydrogen Chloride and α-Methoxystyrene.—Dry hydrogen chloride was passed into 2 g. of α-methoxystyrene for two hours. The reaction mixture solidified to a brown mass. Crystallization from alcohol–acetone gave 0.8 g. of triphenylbenzene; m. p. and mixed m. p. 173–174°.

Summary

α-Methoxystyrene condenses with benzyl bromide, *n*-butyl bromide, ethyl chloroacetate and benzoyl chloride, but not with bromobenzene. A methyl halide is eliminated and a phenacyl derivative is formed. An interpretation of the course of the reaction is presented.

MADISON, WISCONSIN RECEIVED MARCH 23, 1940

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[6] Robinson, *J. Chem. Soc.*, **109**, 1038 (1916); Lauer and Lones, THIS JOURNAL, **59**, 232 (1937).

[7] Kohler, *Am. Chem. J.*, **42**, 391 (1909).

[8] Merritt, Levey and Cutter, THIS JOURNAL, **61**, 15 (1939).

[9] Schroeter, *Ber.*, **40**, 1603 (1907).

[10] Engler and Berthold, *ibid.*, **7**, 1123 (1874).

[11] Abell, *J. Chem. Soc.*, **101**, 998 (1912).