benzoylene urea undergoes alkylation to form monoalkyl derivatives. Especially characteristic of 6,8-dibromobenzoylene urea is its insolubility in the ordinary caustic alkalies, and the formation of a sparingly soluble sodium salt which can be precipitated from aqueous solutions at room temperature. This salt offers possibilities to investigators who are interested in the microchemical detection of sodium.

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

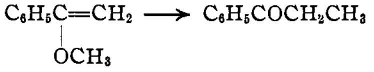
The Molecular Rearrangement of Alpha,Beta-Unsaturated Ethers[1]

BY WALTER M. LAUER AND MARVIN A. SPIELMAN[2]

It has long been known that certain α,β-unsaturated ethers rearrange on heating to form ketones. For the first example we are indebted to Claisen,[3] who found that α-ethoxystyrene readily forms phenyl propyl ketone "on short superheating such as boiling for a few hours under two atmospheres' pressure." Only a few such rearrangements have been recorded,[4] and the reaction is not general, since ethyl β-ethoxycrotonate, α-methoxymesityl oxide and phenyl vinyl ether, substances which might be expected to rearrange, failed to show such behavior.[5]

Previous studies have been confined to the establishment of rearrangement while the present one was undertaken in order to bring into sharper relief certain features dealing with the mechanism of the transformation. The α-alkoxy-styrenes lent themselves admirably to this purpose in view of the ease with which they may be prepared and the simplicity of the products which they form.

A. **The Course of the Reaction.**—When α-methoxystyrene was heated to temperatures in the neighborhood of 250–275° for an hour or more the chief product was always propiophenone formed by the normal rearrangement



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

but it was also evident that the reaction was more complicated than we had anticipated. On unsealing the tube in which the rearrangement was

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(1) The work described in this paper constituted part of the thesis submitted to the graduate faculty of the University of Minnesota by Marvin A. Spielman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in June, 1933.

(2) Du Pont Fellow in Chemistry 1932–1933.

(3) Claisen, *Ber.*, **29**, 2931 (1896).

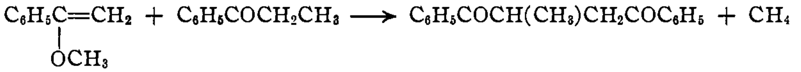
(4) Claisen and Haase, *ibid.*, **33**, 3778 (1900); Claisen, *ibid.*, **45**, 3157 (1912); Haller, *Compt. rend.*, **136**, 788 (1903); Staudinger and Ruzicka, *Helv. Chim. Acta.*, **7**, 386 (1924); Wislicenus and Schroeter, *Ann.*, **424**, 215 (1921).

(5) Wislicenus, *Ber.*, **33**, 1469 (1900); Pauly and Lieck, *ibid.*, **33**, 503 (1900); Powell with Adams, THIS JOURNAL, **42**, 646 (1920); Lauer and Spielman, *ibid.*, **55**, 1572 (1933).

carried out the presence of a combustible gas was noted, and after isolation of the propiophenone there remained a residue from which a colorless crystalline substance melting at 104.5° was isolated.

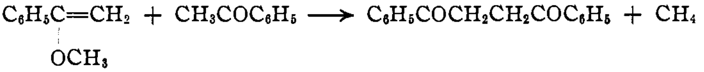
The molecular formula of this solid was established as $C_{17}H_{16}O_2$ and analysis by means of the Grignard machine[6] showed no active hydrogen, but two moles of methylmagnesium iodide were consumed per mole of compound. It formed a dioxime and on boiling with concentrated hydrochloric acid it lost one molecule of water to form a substance $C_{17}H_{14}O$ which upon analysis in the Grignard machine showed neither active hydrogen nor functional groups. The properties are those of a γ-diketone and that the compound $C_{17}H_{16}O_2$ was 1,2-dibenzoylpropane[7] was shown by comparison with a sample synthesized from benzoylacetic ester, α-bromopropiophenone and sodium ethylate, followed by hydrolysis of the resultant ester. This compound $C_{17}H_{14}O$ was therefore 2,5-diphenyl-3-methylfuran.

The origin of 1,2-dibenzoylpropane was indeed puzzling and we were finally forced to the conclusion that it resulted from the action of α-methoxystyrene upon its rearrangement product, propiophenone, with the elimination of methane.



$$C_6H_5\underset{\mathrm{OCH_3}}{C}{=}CH_2 + C_6H_5COCH_2CH_3 \longrightarrow C_6H_5COCH(CH_3)CH_2COC_6H_5 + CH_4 \qquad (2)$$

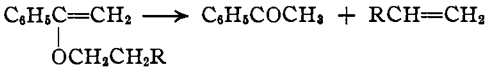
The evidence is as follows: first, propiophenone when heated alone did not yield these products but was recovered unchanged. Second, by heating α-methoxystyrene with a large excess of acetophenone, diphenacyl, a known compound was obtained.



$$C_6H_5\underset{\mathrm{OCH_3}}{C}{=}CH_2 + CH_3COC_6H_5 \longrightarrow C_6H_5COCH_2CH_2COC_6H_5 + CH_4 \qquad (2a)$$

This was found to be identical with a synthetic sample.[8] Third, diphenacyl also resulted when α-ethoxystyrene was heated with acetophenone as did 1,2-dibenzoylpropane when it was heated with propiophenone. Fourth, the gas formed in the reactions involving α-methoxystyrene was analyzed and found to be methane, uncontaminated with other hydrocarbons or hydrogen. When α-ethoxystyrene was heated the gas was ethane containing 6% of ethylene; in the case of α-*n*-propoxystyrene it was propane containing 15.7% of propylene. Similarly, α-isoamyloxystyrene yielded two liquid hydrocarbons, isopentane and isopentene.

The occurrence of unsaturated hydrocarbons indicates another side reaction of a not unexpected type.



$$C_6H_5\underset{\mathrm{OCH_2CH_2R}}{C}{=}CH_2 \longrightarrow C_6H_5COCH_3 + RCH{=}CH_2 \qquad (3)$$

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(6) Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3184 (1927); Kohler and Richtmyer, *ibid.*, **52**, 3737 (1930).

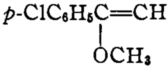
(7) Lutz and Taylor, *ibid.*, **55**, 1175 (1933), have recently obtained this substance by the reduction of dibenzoylmethylethylene. The melting point (105° corr.) is in agreement with ours.

(8) Kapf and Paal, *Ber.*, **21**, 3056 (1888).

The unchanged alkoxystyrene reacting with the acetophenone so produced should yield diphenacyl by reaction 2a. Acetophenone and diphenacyl, along with isoenanthophenone, the normal rearrangement product, were actually isolated from the reaction mixture obtained by heating α-isoamyloxystyrene. The low percentages of unsaturated hydrocarbons show that this side reaction does not play an important role unless the size of the alkyl groups is large.

A number of α-β-unsaturated ethers (see experimental part) were examined. It is noteworthy that no isomerization of radicals took place during rearrangement and that there was γ-diketone formation in all cases wherein rearrangement occurred.

B. The Mechanism of the Reaction.—In developing a mechanism for the rearrangement (Reaction 1) the first possibility considered was that of a purely intramolecular change in which the wandering group at no time becomes free from the sphere of influence of the parent molecule.[9] This was definitely eliminated by means of the following experiment. Two enol ethers I and II were rearranged simultaneously in mutual solution.



$p\text{-ClC}_6\text{H}_5\underset{\displaystyle \text{OCH}_3}{\underset{|}{\text{C}}}{=}\text{CH}_2$

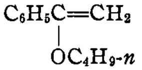
I

$p\text{-ClC}_6\text{H}_4\text{COCH}_2\text{CH}_3$

III

$\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$

V



$\text{C}_6\text{H}_5\underset{\displaystyle \text{OC}_4\text{H}_9\text{-}n}{\underset{|}{\text{C}}}{=}\text{CH}_2$

II

$\text{C}_6\text{H}_5\text{COCH}_2\text{C}_4\text{H}_9\text{-}n$

IV

$p\text{-ClC}_6\text{H}_4\text{COCH}_2\text{C}_4\text{H}_9\text{-}n$

VI

On the basis of a strictly intramolecular change but two products of rearrangement III and IV should result. On the other hand, if the mechanism were such that a radical might wander from one molecule to another at some stage of the process, two additional products V and VI should be engendered. In view of side reactions (2) and (3) the reaction mixture would be expected to possess considerable complexity (there is the possibility of fifteen components, exclusively of gases and starting materials) but the choice of ethers made the isolation of propiophenone V feasible on account of its comparatively low boiling point, granting the practicability of separating it from the acetophenone formed from α-n-butoxystyrene II by reaction (3). The two ethers I and II were accordingly heated in the customary manner and the lowest boiling fraction was converted to a mixture of semicarbazones. After a series of systematic crystallizations the semicarbazone of propiophenone V was isolated in pure form. A strictly intramolecular mechanism therefore becomes untenable.

A common manner of interpreting many molecular rearrangements involves simple dissociation into mobile ions or radicals.[10] Such a process

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[9] This is true in the case of the benzimido phenyl esters. Chapman, *J. Chem. Soc.*, **127**, 1992 (1925).

[10] For leading references on rearrangements see Whitmore, THIS JOURNAL, **54**, 3274 (1932).

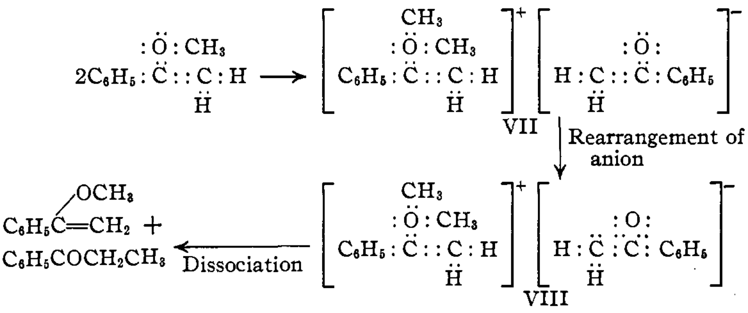
would proceed at a velocity proportional to the concentration of the enol ether and thus exhibit the kinetic behavior of a first order reaction. Kinetic studies[11] have shown that we are dealing with a homogeneous reaction of the second order. The complete absence of certain products formed by the indiscriminate union of free radicals (diphenacyl and ethane in reaction 1) also renders their intermediary existence highly improbable.

Since the rearrangment represents a second order reaction we are forced inevitably to the conclusion that the collision of two activated ether molecules results in the formation of a complex body, thus

$$\text{2 Enol Ether} \rightleftarrows \text{[Complex]} \longrightarrow \text{2 Ketone, or Enol Ether} + \text{Ketone}$$

The experiment demonstrating the intermolecular transfer of radicals imposes, however, an added restriction. In the complex the two potentially migrant groups must be equivalent.

Van Alphen[12] has advanced a theory accounting for phenol ether rearrangements in which oxonium intermediates are involved. This is compatible with our experimental facts if we assume that the molecule adding to the ether is a second molecule of the ether itself.[13] Accordingly, we are inclined to formulate the rearrangement of the α,β-unsaturated ethers in the following manner. The first step represents the formation of an oxonium complex VII. Transfer of a pair of electrons in the anionoid part of the complex shifts the seat of activity from the oxygen to the α-carbon atom as indicated in VIII. Dissociation would then be expected to yield the products propiophenone and α-methoxystyrene.[14]



The transfer of a radical from one molecule to another which seemed so puzzling at first would be predicted on the basis of this mechanism. Thus, the addition of α-*n*-butoxystyrene to *p*-chloro-α-methoxystyrene would yield the complex IX

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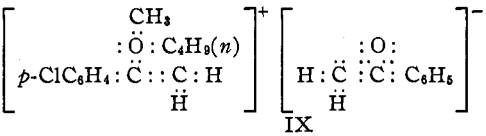
(11) MacDougall, Lauer and Spielman, THIS JOURNAL, **55**, 4089 (1933).

(12) Van Alphen, *Rec. trav. chim.*, **46**, 804 (1927).

(13) Niederl and Storch, THIS JOURNAL, **55**, 284 (1933), in discussing certain phenol ether rearrangements perhaps imply this in their reference to "the formation of oxonium compounds between identical ether molecules" and "transitory bimolecular compounds of the quinhydrone type."

(14) Strict analogy with the Van Alphen mechanism requires that the rearrangement take place in the cationoid part of the complex. Between such a view and ours there is at present no means of experimental differentiation.



$$\left[\begin{array}{l} \qquad\quad \mathrm{CH_3} \\ \qquad\ \ :\ddot{\mathrm{O}}:\mathrm{C_4H_9}(n) \\ p\text{-}\mathrm{ClC_6H_4}:\ddot{\mathrm{C}}::\mathrm{C}:\mathrm{H} \\ \qquad\qquad\quad \ddot{\mathrm{H}} \end{array}\right]^{+}\left[\begin{array}{l} \qquad\quad :\mathrm{O}: \\ \mathrm{H}:\ddot{\mathrm{C}}\ :\ddot{\mathrm{C}}:\ \mathrm{C_6H_5} \\ \quad\ \ddot{\mathrm{H}} \end{array}\right]^{-}$$

IX

in which it is seen that the alkyl groups are equivalent. Dissociation would then yield the mixture of products actually encountered.

Experimental Part

Synthesis of Materials.—The ethers used in this work were prepared by a method previously reported.[15] New β-bromo ethers are shown in Table I. All are colorless oily liquids having a fragrant aromatic odor. These on distillation from powdered potassium hydroxide yielded the desired enol ether. Usually two distillations at 100 mm. were necessary, and at a suggestion from Chalmers[16] soda lime has been used with the alkali. It has the virtue of preventing fusion and thus prolongs the life of the flask. Of the enol ethers, two were new.

TABLE I

β-BROMO ETHERS

Compound	Formula	Yield, %	B. p., °C.	Analyses, Br % Calcd.	Analyses, Br % Found
$C_6H_5CH(OCH_3)CH_2Br$	$C_9H_{11}OBr$	65	117–118 (15 mm.)	37.16	37.32
p-$ClC_6H_4CH(OCH_3)CH_2Br$	$C_9H_{10}OBrCl$	51	154–156 (26 mm.)	[a]	
$C_6H_5CH(OC_3H_7\text{-}n)CH_2Br$	$C_{11}H_{15}OBr$	66	146–148 (27 mm.)	32.86	32.79
$C_6H_5CH(OC_4H_9\text{-}n)CH_2Br$	$C_{12}H_{17}OBr$	57	165–166 (32 mm.)	31.13	30.56
$C_6H_5CH(OC_5H_{11}\text{-iso})CH_2Br$	$C_{13}H_{19}OBr$	81	140–143 (12 mm.)	28.47	29.06

[a] Calcd.: C, 43.3; H, 4.04. Found: C, 43.5; H, 4.4.

α-n-Butoxystyrene.—Yield, 70%; b. p. 134.5–135.5° (26 mm.); n^{25}_{D} 1.5193.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.1. Found: C, 81.4, 81.4; H, 9.0, 8.7.

p-Chloro-α-methoxystyrene.—Yield, 59%; b. p. 118–121° (23 mm.); n^{28}_{D} 1.5510.

Anal. Calcd. for C_9H_9OCl: Cl, 21.05. Found: Cl, 20.69, 20.92.

The compound is a very fragrant oil. Treatment with semicarbazide hydrochloride and sodium acetate in dilute alcohol gave p-chloroacetophenone semicarbazone: needles, m. p. 202–204°.

Anal. Calcd. for $C_9H_{10}N_3OCl$: C, 51.0; H, 4.8; Cl, 16.8. Found: C, 50.8; H, 4.7; Cl, 16.8.

The Rearrangement and Condensation Reactions

α-Methoxystyrene.—Twenty grams was sealed in a Carius tube and heated for 2 hours in a bomb furnace at approximately 300°. When the tube was unsealed considerable pressure was observed. The contents were transferred to a Claisen flask and distilled. After a forerun of less than 1 g., a single fraction of 13 g. came over at 98–103° (15 mm.). There was a clear brown residue of 5.7 g.

The main fraction was converted to the semicarbazone which after one crystallization melted at 173–173.5°. This is correct for propiophenone semicarbazone. A mixed melting point was not depressed.

The residue remaining after distillation was taken up in 15 cc. of methanol which caused immediate crystallization. After one recrystallization the product weighed 2.0

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(15) Lauer and Spielman, THIS JOURNAL, **53**, 1533 (1931); Swallen and Boord, *ibid.*, **52**, 651 (1930); Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930).

(16) Chalmers, *Canadian J. Res.*, **7**, 464 (1932).

g. and melted at 102–103°. Several crystallizations from petroleum ether gave colorless hexagonal plates; m. p. 104–104.5°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4; mol. wt. 252. Found: C, 80.8, 80.7; H, 6.3, 6.3; mol. wt. 258.

In the Grignard machine the substance reacted with 2.12 moles of methylmagnesium iodide and liberated a negligible amount of methane. The dioxime was prepared by the use of free hydroxylamine in methanol; snow-white needles; m. p. 166–167°.

Anal. Calcd. for $C_{17}H_{18}N_2O_2$: C, 72.3; H, 6.4. Found: C, 72.7; H, 6.3.

Dehydration to 2,5-diphenyl-3-methylfuran proceeded quantitatively on boiling for half an hour in concd. hydrochloric acid; m. p. 57–58°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 87.3, 87.2; H, 6.0, 6.1.

A sample of 1,2-dibenzoylpropane was synthesized by condensing α-bromopropiophenone with ethyl benzoylacetate and hydrolyzing the resultant ester. The directions are those used by Kapf and Paal[8] in the preparation of diphenacyl; m. p. and mixed m. p. 104–104.5°.

Condensation of α-Methoxystyrene and Acetophenone.—Ten grams of the ether and 20 g. of the ketone were heated to 300° for two hours. Unsealing revealed considerable pressure. After distillation a non-volatile fraction of 2.2 g. remained. Washing with ether and crystallization from ethanol yielded pure diphenacyl; m. p. and mixed m. p. 142–144°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found C, 80.7; H, 6.2.

The gas formed in the same condensation reaction was collected and analyzed in the conventional Orsat–Lunge apparatus. Methane was identified by its contraction ratio, which is the ratio of the contraction on burning to the volume of carbon dioxide formed. Calcd.: 2.00. Found: 2.02. No hydrogen or unsaturated hydrocarbons could be detected.

α-Ethoxystyrene (25 g.) was similarly heated to 300° for one hour. The main product weighed 14.4 g. and boiled at 115–121° (20 mm.). The semicarbazone melted at 183–185° and mixture with butyrophenone semicarbazone caused no depression. The residue of 1,2-dibenzoylbutane could not be induced to crystallize. Distillation gave a 1.5 g. fraction; b. p. 234–245° (20 mm.); n^{25}_{D} 1.5795. It was a pale yellow extremely viscous liquid.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.7. Found: C, 81.5, 81.4; H, 7.0, 6.9.

The gaseous products from the condensation proved to be ethane containing 6% of ethylene. After removal of the latter the contraction ratio was found to be 1.23; theory requires 1.25.

α-*n*-Propoxystyrene.—This gave a poor yield (30%) of *n*-valerophenone boiling at 138–143° (28 mm.). The semicarbazone melted at 162.5–163.5° and a mixed m. p. with a sample prepared from the ketone obtained by oxidizing phenyl-*n*-butylcarbinol was not depressed.

The condensation product, presumably 1,2-dibenzoylpentane, could not be isolated analytically pure. Propane was formed. Calcd. contraction ratio: 1.00. Found: 1.07. It contained 15.7% propylene.

α-*n*-Butoxystyrene.—From 5 g. heated to 300° for one hour, 3.7 g. of *n*-caprophenone of m. p. 24–26° was obtained. The semicarbazone melted at 131–132°. Other products were not characterized.

***p*-Chloro-α-methoxystyrene.**—Fifteen grams heated in the usual way gave 10.2 g. of *p*-chloropropiophenone which boiled at 134–137° (31 mm.). The semicarbazone formed well-developed needles; m. p. 175–176°.

Anal. Calcd. for $C_{10}H_{12}N_3OCl$: C, 53.2; H, 5.3; Cl, 15.7. Found: C, 53.0; H, 5.4; Cl, 15.8.

From the residue about 1.8 g. of a gummy solid was obtained. This was reduced to 0.6 g. before analytically pure 1,2-di-(*p*-chlorbenzoyl)-propane was isolated as snow-white needles melting at 116.5–117.0°.

Anal. Calcd. for $C_{17}H_{14}O_2Cl_2$: C, 63.6; H, 4.4; Cl, 22.1. Found: C, 63.3; H, 4.6; Cl, 22.2.

α-Isoamyloxystyrene.—Twenty grams was heated to 300° for seventy-five minutes. The tube was cooled in ice and on unsealing little pressure was observed. The product had the odor of crude gasoline. Distillation gave the following fractions: A, 29–40°, 1.2 g.; B, 90–115° (17 mm.), 1.9 g.; C, 122–143° (17 mm.) 1.8 g.; D, 143–147° (17 mm.), 11.0 g.; E, to 223° (5 mm.), 2.9 g.

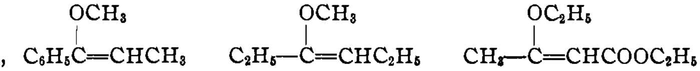
Fraction A was shaken with 70% sulfuric acid to remove isopentene, dried over calcium chloride and distilled, b. p. 28.5–30.0°, n^{20}_{D} 1.3570. The values for isopentane taken from Beilstein are b. p. 27.97 to 30.0°, n^{20}_{D} 1.35485. Fractions B and C were redistilled and 1.7 g. of acetophenone was obtained; b. p. 93–105° (17 mm.), m. p. and mixed m. p. of the semicarbazone 198–202°. Fraction D and the higher boiling parts of B and C were combined and redistilled. Practically all came over as pure isoenanthophenone (phenyl isohexyl ketone); b. p. 145–148° (18 mm.); n^{26}_{D} 1.5067.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 81.8, 81.6; H, 9.4, 9.4.

The semicarbazone formed colorless leaflets; m. p. 144–145°.

Anal. Calcd. for $C_{14}H_{21}N_3O$: C, 68.0; H, 8.6. Found: C, 68.0; H, 8.7.

Fraction E was seeded with a single crystal of diphenacyl and placed in the ice box. About 5 mg. was obtained; m. p. and mixed m. p. 143–145°.

The ethers,  $C_6H_5\overset{\overset{\displaystyle OCH_3}{|}}{C}{=}CHCH_3$ $C_2H_5{-}\overset{\overset{\displaystyle OCH_3}{|}}{C}{=}CHC_2H_5$ $CH_3{-}\overset{\overset{\displaystyle OC_2H_5}{|}}{C}{=}CHCOOC_2H_5$ failed to rearrange under the conditions studied. They were recovered unchanged except α-methoxy-β-methylstyrene which was shown, on the basis of a Zeisel determination, to be approximately half decomposed after four and one-half hours. No ketone could be found in the tar-like mixture.

Intermolecular Transfer of Radicals.—Ten grams each of *p*-chloro-α-methoxystyrene and α-*n*-butoxystyrene were heated together to 265° for three hours. The material was placed in a modified Claisen flask with a 15-cm. indented column and distilled. The first fraction came over at 94–101–105° (16 mm.). The temperature then rose rapidly and further fractions were not examined. The distillate (1.7 g.) gave a negative Beilstein test for chlorine. It was converted to a mixture of semicarbazones which was subjected to a systematic series of twenty-six crystallizations from dilute alcohol to which was added from time to time a little semicarbazide hydrochloride and sodium acetate to suppress hydrolysis. At the conclusion of the separation 0.1 g. of acetophenone semicarbazone was isolated: m. p. and mixed m. p. 199–201°. A mixed fraction of 0.1 g. remained: m. p. 144–158°. The important part (0.11 g.) was pure propiophenone semicarbazone which melted at 172–174° alone and when mixed with an authentic sample. It was mixed with the semicarbazones derived from each of the lower phenyl ketones and marked depressions were observed in every case. A blank experiment was run on the unheated components and the first drop distilled at 110° (14 mm.). Experience gained in numerous practice separations leads to the opinion that the reaction mixture contained at least 1 gram of propiophenone.

Summary

1. Certain alkoxystyrenes rearrange upon heating to form ketones.

2. The unchanged ether condenses with its rearrangement product: a hydrocarbon is eliminated and a γ-diketone results.

3. Not all enol ethers undergo these reactions.
4. A mechanism for the transformation is advanced. It involves complex formation between two ether molecules followed by rearrangement in either of the two parts of the complex body.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Syntheses in the Olefin Series. V. Completing the Survey of the Hexenes and Including Certain Heptenes and Octenes[1]

BY IMAN SCHURMAN[2] AND CECIL E. BOORD

In the third paper of this series Schmitt[3] and one of us in a survey of the hexenes, described eleven of the thirteen isomers as prepared by the bromo ether method. This method is not applicable to the tetra-alkylethylenes, type V, or to the *tert*-alkylethylenes of type I. It has seemed desirable, therefore, to seek other methods for the preparation of tetramethylethylene, the highest boiling hexene, and *tert*-butylethylene, the lowest boiling member of this family, and to measure their physical constants under conditions wholly comparable with those used for the other isomers.

Tetramethylethylene has been described by numerous investigators, its physical constants having been measured under widely varying conditions. It is most conveniently prepared by the dehydration of isopropyldimethylcarbinol, this method yielding also *as*-isopropylmethylethylene in smaller amounts.[4]

$$(CH_3)_2COH{-}CH(CH_3)_2 \longrightarrow \left\{ \begin{array}{l} (CH_3)_2C{=}C(CH_3)_2 \\ (CH_3)_2CH{-}(CH_3)C{=}CH_2 \end{array} \right.$$

For the present purpose the above carbinol was dehydrated over anhydrous oxalic acid, the two heptenes being obtained in yields of 80 and 20%, respectively. Their physical constants were measured under the conditions previously used in this series.

It is well known that *tert*-butylmethylcarbinol (pinacolin alcohol) does not yield the normally expected *tert*-butylethylene as the principal dehydration product. Alcohols of this type upon dehydration undergo a skeletal rearrangement. Such rearrangements have been frequently studied, and most recently by Whitmore and his co-workers,[5] who found only 3% of

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[1] (a) For the earlier papers of this series see Soday and Boord, THIS JOURNAL, **55**, 3293 (1933). (b) Presented before the Organic Division of the American Chemical Society in Washington, March, 1933, and before the Chemical Section of the Ohio Academy of Science, May, 1933.

[2] Research Associate under a Grant-in-Aid from the National Research Council, to whom our best thanks are due for making this work possible.

[3] Schmitt and Boord, THIS JOURNAL, **54**, 751 (1932).

[4] (a) Henry, *Bull. soc. chim. Belg.*, **22**, 140 (1907); (b) Couturier, *Bull. soc. chim.*, [4] **9**, 898 (1911).

[5] Whitmore, THIS JOURNAL, **54**, 3274 (1932); Whitmore and Rothrock, *ibid.*, **55**, 1106 (1933); Whitmore and Meunier, *ibid.*, **55**, 3721 (1933).