3-Bromomesitylphenylketene.—Thirty grams of 3-bromomesitylphenylacetic acid was covered with 50 ml. of thionyl chloride and the mixture allowed to stand two days. The yield of acid chloride was 27 g. (85.5% of the theory); m. p. 84–87°. The chloride was recrystallized repeatedly from a mixture of low- and high-boiling petroleum ether. It formed light orange crystals; m. p. 85.5–87°.

Anal. Calcd. for $C_{17}H_{16}BrClO$: C, 58.06; H, 4.58. Found: C, 58.42; H, 4.67.

When the acid chloride was heated with a little pyridine, the ketene was obtained as a golden yellow oil boiling at 155–157° (1 mm.).

A more convenient method for preparing the ketene was to treat 3-bromomesitylphenylacetic acid with thionyl chloride and pyridine as illustrated in the synthesis of durylphenylketene. From 31.9 g. of the acid was obtained 12.7 g. of the twice-distilled ketene; b. p. 163° (2 mm.).

Anal. Calcd. for $C_{17}H_{15}BrO$: C, 64.77; H, 4.80. Found: C, 64.65; H, 4.92.

The ketene gave a grayish-black precipitate of silver when treated with silver nitrate.

2-(3-Bromomesityl)-2-phenylvinyl Alcohol.—When 2.8 g. of the ketene was treated with an excess of *t*-butylmagnesium chloride, 2.3 g. of 2-(3-mesityl)-2-phenylvinyl alcohol was obtained. Repeated recrystallization failed to yield a product with a satisfactory melting point; the values varied from 94° to 108° and the range was always wide.

Anal. Calcd. for $C_{17}H_{17}BrO$: C, 64.36; H, 5.40. Found: C, 64.34; H, 6.09.

The acetate, prepared by treating the alcohol with acetic anhydride and pyridine, was recrystallized from ethanol; m. p. 100.5–101.5°.

Anal. Calcd. for $C_{19}H_{19}BrO_2$: C, 63.51; H, 5.33. Found: C, 63.38; H, 5.30.

Summary

Mesitylphenyl-, dimesityl-, durylphenyl- and 3-bromomesitylphenylketene have been reduced by the action of cyclohexyl- or *t*-butylmagnesium chloride to the corresponding 2,2-diarylvinyl alcohols.

The preparation of 2-duryl-2-phenylvinyl alcohol has been described to illustrate the method.

URBANA, ILLINOIS RECEIVED AUGUST 23, 1945

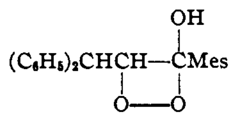
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Vinyl Alcohols. XVII.[1] Cleavage of Enol Peroxides

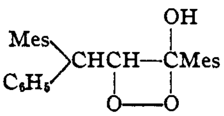
BY REYNOLD C. FUSON, E. W. MAYNERT AND W. J. SHENK, JR.

One of the most important questions to be answered in connection with the chemistry of 2,2-diarylvinyl alcohols concerns the possibility of the existence of the corresponding aldehydes. As yet they have not been obtained either by isomerization of the vinyl alcohols or by methods designed to produce them directly.

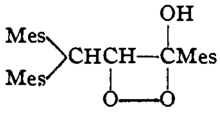
A particularly interesting aldehyde synthesis was discovered by Kohler and Thompson[2] who found that thermal decomposition of the peroxide of the enol form of benzohydrylacetomesitylene (I) yielded diphenylacetaldehyde.



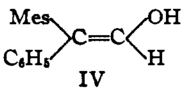
I



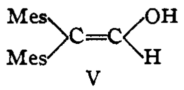
II



III



IV

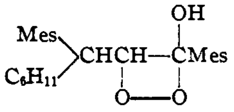


V

If this method could be applied to peroxides such as II or III, the products might be expected to be aldehydes of the desired type. The discovery that phenyl- and mesitylmagnesium bromide condense in the 1,4-manner with mesitalacetomesitylene[3] opened a way to the synthesis of peroxides II and III, for example, and made it possible to test the usefulness of these peroxides for the synthesis of aldehydes. The results are of special interest due to the fact that the products *were not the expected aldehydes but the corresponding vinyl alcohols.*

By the condensation of benzalacetomesitylene and mesitalacetomesitylene with mesitylmagnesium bromide and subsequent treatment of the enol solutions with oxygen, peroxides II and III, respectively, were obtained. Decomposition of the first (II) yielded 2-mesityl-2-phenylvinyl alcohol (IV) and mesitoic acid. The second (III) gave 2,2-dimesitylvinyl alcohol (V) and mesitoic acid. It is difficult to see how the vinyl alcohols could be produced directly from the peroxides. It seems probable that the aldehydes are formed initially and that they enolize spontaneously.

2-*p*-Chlorophenyl-2-mesitylvinyl alcohol, a new compound, was also made by the peroxide method. In an effort to replace the phenyl group by the cyclohexyl group 1,3-dimesityl-3-cyclohexyl-1-propen-1-ol peroxide (VI) was prepared and de-



VI

---

[1] For the preceding communication in this series see Fuson, Kneisley, Rowland, Shenk and Soper, THIS JOURNAL, 67, 1937 (1945).

[2] Kohler and Thompson, *ibid.*, 59, 887 (1937).

[3] Fuson and Meek, *J. Org. Chem.*, in press.

composed. Mesitoic acid was the only product to be identified.

There was still the question as to whether or not the vinyl alcohols in solution are in equilibrium with the aldehydes. An answer was obtained by treating solutions of the vinyl alcohols with semicarbazide. 2-Mesityl-2-phenylvinyl alcohol was converted to a semicarbazone, but 2,2-dimesitylvinyl alcohol was recovered unchanged. The failure of the latter to form a semicarbazone is a manifestation of the greater hindrance at the *beta* carbon atom.

Experimental

p-Chlorobenzalacetomesitylene.—A mixture of 7.0 g. of *p*-chlorobenzaldehyde, 8.1 g. of acetomesitylene, 50 ml. of ethanol and 2 ml. of 10% sodium hydroxide solution was allowed to stand three and one-half hours. The chalcone separated as yellow needles; m. p. 100–101°; yield 91%. After repeated recrystallization from ethanol it melted at 101–102°.

Anal. Calcd. for $C_{16}H_{17}ClO$: C, 75.92; H, 6.02. Found: C, 75.85; H, 6.25.

p-Bromobenzalacetomesitylene.—This compound was made in 91% yield from *p*-bromobenzaldehyde and acetomesitylene by the method just described for the chlorine analog. The crude chalcone melted at 117–119°; after recrystallization from ethanol it melted at 118.5–119.5°.

Anal. Calcd. for $C_{15}H_{17}BrO$: C, 65.54; H, 5.21. Found: C, 65.77; H, 5.44.

1,3-Dimesityl-3-phenyl-1-propen-1-ol Peroxide (II).—The procedure of Kohler and Thompson[2] was followed. To a refluxing solution of a Grignard reagent, prepared from 1.0 g. of magnesium, 9.0 g. of bromomesitylene and 50 ml. of absolute ether, was added over a period of thirty minutes a solution of 4 g. of benzalacetomesitylene in 25 ml. of ether. The heating was continued for an additional thirty minutes and the mixture was poured into an ice-hydrochloric acid mixture. After the layers had been separated the aqueous portion was extracted with portions of cold, low-boiling petroleum ether amounting in all to 200 ml. The organic layer was united with the petroleum ether solution, washed with cold water and introduced through a filter into a 500-ml. graduated cylinder held in an ice-bath. Oxygen was bubbled rapidly through the solution for six hours, and the solvents were then removed by a slow stream of air. The residue was recrystallized by diluting its ether–benzene solution with four or five volumes of low-boiling petroleum ether. The peroxide obtained in this way formed large, colorless prisms; yield 4.5 g.; m. p. 136–137.5°.

Anal. Calcd. for $C_{27}H_{30}O_3$: C, 80.56; H, 7.51. Found: C, 80.58; H, 7.51.

2-Mesityl-2-phenylvinyl Alcohol (IV).—When 1 g. of the peroxide, contained in a 50-ml. Erlenmeyer flask, was heated gently with a micro-burner it melted and then decomposed suddenly yielding a puff of acrid fumes and a yellow oil. By extraction of an ethereal solution of the oil with 15-ml. portions of 7% potassium carbonate solution and acidification of the carbonate solution mesitoic acid was isolated; m. p. 152–153°. It did not depress the melting point of a known sample of the acid.

The ethereal solution was washed with water and evaporated to dryness. The 2-mesityl-2-phenylvinyl alcohol crystallized from low-boiling petroleum ether in fine needles; m. p. 111–113°. They did not depress the melting point (114–115°) of an authentic specimen of the vinyl alcohol.

The **semicarbazone** of 2-mesityl-2-phenylvinyl alcohol was formed in the usual way. A mixture of 11 ml. of ethanol, 8 ml. of water, 0.21 g. of the vinyl alcohol, 0.15 g. of semicarbazide hydrochloride and 0.25 g. of sodium acetate was heated to boiling and then set aside in a stoppered container. After a few days, 5 mg. of yellow crystals separated; m. p. 256.5–257° (with decomposition). This compound was found to contain 44.01% nitrogen; it was not investigated further. When the experiment was repeated with ethanol which had been distilled from sodium hydroxide none of the yellow solid was formed.

After a longer time 50 mg. of large white needles separated from the filtrate. They were recrystallized from ethanol; m. p. 203–205°.

Anal. Calcd. for $C_{18}H_{21}N_3O$: C, 73.18; H, 7.17; N. 14.23. Found: C, 73.14; H, 7.44; N, 14.26.

The vinyl alcohol gave a positive test after standing several hours with the fuchsin–aldehyde reagent.

1,3,3-Trimesityl-1-propen-1-ol Peroxide (III).—The peroxide was formed and isolated according to the procedure outlined for the peroxide of 1,3-dimesityl-3-phenyl-1-propen-1-ol. Ten grams of the new peroxide was obtained. It crystallized from a mixture of 30 ml. of ether, 10 ml. of benzene and 80 ml. of low-boiling petroleum ether in small colorless prisms; m. p. 153–154°.

Anal. Calcd. for $C_{30}H_{36}O_3$: C, 81.04; H, 8.17. Found: C, 80.93; H, 8.27.

2,2-Dimesitylvinyl Alcohol (V).—Cleavage of 2 g. of the peroxide, carried out by a procedure similar to that described for the peroxide of 1,3-dimesityl-3-phenyl-1-propen-1-ol, yielded 0.45 g. of mesitoic acid (60%) and a neutral product. The latter, when purified by recrystallization from low-boiling petroleum ether, melted at 128–129° and was shown by the mixed melting point method to be 2,2-dimesitylvinyl alcohol.[4]

The vinyl alcohol was recovered unchanged in an attempt to prepare a semicarbazone. It gave a negative test with the fuchsin–aldehyde reagent.

Reduction of 1,3,3-Trimesityl-1-propen-1-ol Peroxide.—A mixture of 0.6 g. of the peroxide, 1.0 g. of potassium iodide and 20 ml. of glacial acetic acid was stirred for four hours at room temperature. The color of iodine appeared almost immediately. When the mixture was added to 100 ml. of water containing 5 g. of sodium bisulfite a bright yellow precipitate formed. It crystallized from absolute ethanol in white cubes melting at 132–133°. However, when treated for a few minutes with boiling aqueous ethanol the compound underwent change, forming fine, shiny needles melting at 186–187°.

Anal. Calcd. for $C_{30}H_{36}O_2$: C, 84.07; H, 8.46. Found: C, 84.16; H, 8.59.

By analogy with the behavior of benzohydrylacetomesitylene enol peroxide when reduced, this compound is the corresponding hydroxy ketone, α-hydroxy-β,β-dimesitylpropiomesitylene. It is possible that the original form (m. p. 132–133°) isomerized to the stable modification (m. p. 186–187°).

1,3-Dimesityl-3-cyclohexyl-1-propen-1-ol Peroxide.—This peroxide was prepared from cyclohexylmagnesium chloride and mesitalacetomesitylene. It was isolated and purified in the manner indicated for 1,3-dimesityl-3-phenyl-1-propen-1-ol peroxide. It formed fine, colorless needles melting at 141–142°.

Anal. Calcd. for $C_{27}H_{36}O_3$: C, 79.37; H. 8.88. Found: C, 79.29; H. 9.08.

The yield of the pure peroxide was low. The chief product, amounting to 11 g., was recrystallized repeatedly from a mixture of benzene, ether and low-boiling petroleum ether; m. p. 109–112°. However, a pure product could not be obtained.

Decomposition of the peroxide yielded a relatively large amount of mesitoic acid (m. p. 151–153°) but the neutral compound could not be induced to crystallize.

1,3-Dimesityl-3-(p-chlorophenyl)-1-propen-1-ol Peroxide.—This peroxide was made from *p*-chlorobenzalacetomesitylene and the mesityl Grignard reagent and was isolated and purified in the usual way. The yield of crude peroxide from 14.7 g. of the unsaturated ketone was

---

[4] Fuson and Rowland, This Journal, 65, 992 (1943).

8.6 g.; m. p. 127°. The analytical sample melted at 134–134.5°.

Anal. Calcd. for $C_{27}H_{29}ClO_3$: C, 74.20; H, 6.69. Found: C, 74.07; H, 6.73.

2-(*p*-Chlorophenyl)-2-mesitylvinyl Alcohol.—The decomposition of this peroxide, carried out in the usual way, yielded only a very small amount of the vinyl alcohol. It crystallized from its solution in low-boiling petroleum ether only after standing for several weeks. It was recrystallized from low-boiling petroleum ether. It formed colorless prisms melting at 92–93°. The analytical sample decomposed after standing five months.

Anal. Calcd. for $C_{17}H_{17}ClO$: C, 74.83; H, 6.28. Found: C, 74.65; H, 6.38.

1,3-Dimesityl-3-(*p*-bromophenyl)-1-propen-1-ol Peroxide.—The crude peroxide, prepared from *p*-bromobenzalacetomesitylene and mesitylmagnesium bromide, melted at 109–115°; yield 68% of the theory. It was recrystallized from ether and ligroin; m. p. 126.5–127°.

Anal. Calcd. for $C_{27}H_{29}BrO_3$: C, 67.36; H, 6.07. Found: C, 67.48; H, 6.73.

Attempts to obtain 2-(*p*-bromophenyl)-2-mesitylvinyl alcohol from this peroxide yielded oily materials which failed to crystallize.

Summary

A new method has been developed for the synthesis of 2,2-diarylvinyl alcohols. It consists in the condensation of a chalcone with a Grignard reagent, conversion of the resulting enol to a peroxide and, finally, thermal decomposition of the peroxide.

2-Mesityl-2-phenylvinyl alcohol, 2,2-dimesitylvinyl alcohol and 2-(*p*-chlorophenyl)-2-mesitylvinyl alcohol have been made by the new procedure.

It is concluded that the aldehydes, formed initially, rearrange spontaneously to the vinyl alcohols. Evidence is presented which indicates that this isomerization may be reversible.

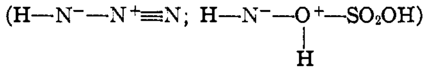
URBANA, ILLINOIS RECEIVED SEPTEMBER 19, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY AT SMITH COLLEGE]

The Reaction of Hydroxylamine-O-sulfonic Acid with Ketones[1]

BY JANET K. SANFORD,[2] FRANCES TATE BLAIR, JUSTA ARROYA AND K. W. SHERK

Keller and Smith[3] have shown recently that the aminating action of both hydroxylamine-O-sulfonic acid[4] and hydrogen azide upon aromatic hydrocarbons proceeds through a common intermediate, NH or NH_2^+. The relationship of these two compounds was also indicated by the preparation of the hydroxylamine derivative from hydrogen azide and fuming sulfuric acid.[5] Since both aminating agents may be considered as the requisite atoms of a neutral molecule coördinated to an HN group



$$(H{-}N^-{-}N^+{\equiv}N;\ H{-}N^-{-}\underset{\displaystyle H}{\underset{|}{O^+}}{-}SO_2OH)$$

it is reasonable to expect both acids to yield the same products under reaction conditions that favor the separation of the neutral molecule (nitrogen or sulfuric acid) and the liberation of the HN fragment.

Keller and Smith offered evidence to show that the direct amination of aromatic hydrocarbons took place by a different mechanism than that of the Schmidt[6] reaction (hydrogen azide with the carbonyl group in the presence of an acidic catalyst, usually concentrated sulfuric acid) which has been the subject of much discussion.[7–13] It seemed to the authors that a series of reactions of hydroxylamine-O-sulfonic acid and hydrogen azide upon ketones might furnish information of interest concerning the mechanisms of these reactions, and carry the similarity of the two compounds a step further.

It has been the practice when utilizing the Schmidt reaction to use a chloroform, benzene or ether solution of hydrogen azide. In this work, the dry gaseous hydrogen azide was led into the ketone, sulfuric acid and solvent. This procedure eliminated the separate preparation of hydrogen azide solutions, was more direct, and was safer since no quantity of hydrogen azide capable of serious damage on explosion ever accumulated.

Experimental

Procedure with Hydroxylamine-O-sulfonic Acid.—This was prepared by the method of Specht, Browne and Sherk.[5] The material was assayed by treatment with acidified potassium iodide and titration of the liberated iodine with standard sodium thiosulfate solution. The product was shown to be 97% hydroxylamine-O-sulfonic acid (iodine equiv., 58.5; calcd., 56.5).

The ketone (0.025 mole) and the reagent were mixed in a large test-tube and, if necessary, slowly warmed in a water-bath until the reaction, noted by the evolution of

---

[1] This paper is based in part upon the theses for the M. A. degree at Smith College by Janet K. Sanford, Frances Tate Blair and Justa Arroya.

[2] Present address, Arthur D. Little, Inc., Cambridge, Mass.

[3] R. N. Keller and Peter A. S. Smith, THIS JOURNAL, **66**, 1122 (1944).

[4] The confusion regarding the naming of the compound, H_2NOSO_3H, has been pointed out by Keller and Smith and, although one of us (K. W. S.) is partially responsible for the name aminomonopersulfuric acid, we are happy to adopt the name suggested by them.

[5] H. E. M. Specht, A. W. Browne and K. W. Sherk, THIS JOURNAL, **61**, 1083 (1939).

[6] K. F. Schmidt, *Ber.*, **57**, 704 (1924); U. S. Patent, 1,564,631.

[7] E. Oliveri-Mandalà, *Gazz. chim. ital.*, **55**, 271 (1925).

[8] K. F. Schmidt, *Ber.*, **58**, 2413 (1925).

[9] A. Bertho, *ibid.*, **59**, 589 (1926).

[10] T. Curtius and A. Bertho, *ibid.*, **59**, 565 (1926).

[11] M. A. Spielman and F. L. Austin, THIS JOURNAL, **59**, 2658 (1937).

[12] C. D. Hurd and Gilman, "Organic Chemistry," 1st ed., Vol. I, John Wiley and Sons, New York, N. Y., 1938, p. 698.

[13] L. H. Briggs and J. W. Littleton, *J. Chem. Soc.*, 421 (1943).