[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

REDUCTION OF THE *Cis* AND *Trans* 2-ENOL METHYL ETHERS OF 1,4-DIMESITYL-1,2,4-BUTANETRIONE

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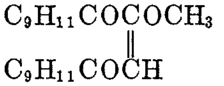
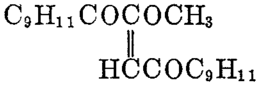
The reduction of 1,4-dimesityl-1,2,4-butanetrione enol (VII) follows a course which is different from that of the reduction of the diphenyl analog (1). It therefore seemed desirable to study the reduction of the enol ethers where fixed structures are involved. This paper deals with the *cis* and *trans* 2-enol methyl ethers (I and II) both of which are known (2).



$$\begin{array}{l} C_9H_{11}COCOCH_3 \\ \qquad\quad \| \\ C_9H_{11}COCH \end{array}$$

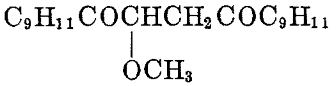
I



$$\begin{array}{l} C_9H_{11}COCOCH_3 \\ \qquad\quad \| \\ \qquad HCCOC_9H_{11} \end{array}$$

II

The reduction of these two ethers by means of sodium hydrosulfite proceeded in similar fashion and in both cases there were produced similar yields of the corresponding saturated methoxy diketone (III) and the fission products, mesitoic acid and acetomesitylene. In both cases the fission reaction was dominant.



$$\begin{array}{l} C_9H_{11}COCHCH_2COC_9H_{11} \\ \qquad\qquad | \\ \qquad\quad OCH_3 \end{array}$$

III

$C_9H_{11}COOH$ $(C_9H_{11}COCHO)$ $CH_3COC_9H_{11}$

Two minor points of difference were noted in these reductions. In the case of the *cis* compound (I) a small amount of mesitylglyoxal hydrate was isolated whereas none was found in the reduction of the *trans* isomer; and in the case of the *trans* compound (II) there was produced a small amount of a new compound which has not been investigated.

The methoxy saturated diketone (III) was not obtained in crystalline form and the samples from the different sources were identified by boiling points, refractive indices and pyrolysis to dimesitoylethylene (IV).[2]

$$\underset{\text{IV}}{C_9H_{11}COCH{=}CHCOC_9H_{11}} \qquad \underset{\text{V}}{C_9H_{11}COCH_2CH_2COC_9H_{11}}$$

It is a striking fact that in neither reduction was there isolated any dimesitylbutanedione (V) which might have been expected from reductive elimination of

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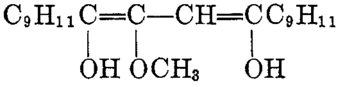
[2] It should be noted in this connection that the diphenyl analog is exceedingly difficult to crystallize and gives dibenzoylethylene and methanol on pyrolysis (3).

the methoxyl group. Except for the extent of cleavage involved, these reductions correspond to the reduction of the diphenyl analog (3), where reductive elimination of the methoxyl group occurs only to a small extent and where the methoxy saturated 1,4-diketone is the chief product.

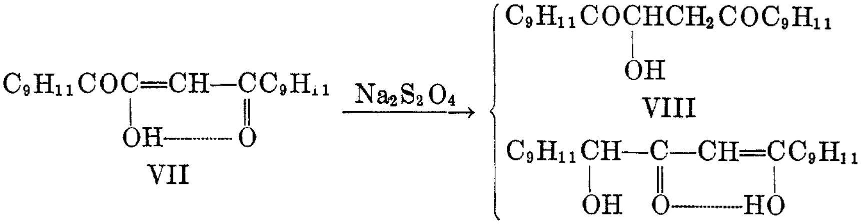
It is probable that the reductions of the two enol ethers (I and II) involve intermediate di-enols such as VI—possibly stereoisomers—which undergo competing rearrangement to the saturated methoxy diketone (III) and hydrolytic fission.



$$C_9H_{11}\underset{OH}{C}=\underset{OCH_3}{C}-CH=\underset{OH}{C}C_9H_{11}$$

VI

For purposes of comparison, the reduction of dimesitylbutanetrione enol (VII) was repeated with sodium hydrosulfite as the reagent. There were isolated from the reaction product a small amount of 2-hydroxydimesitylbutanedione-1,4 (VIII), a large amount of the isomeric 4-hydroxydimesitylbutane-1,3-dione enol (IX), and a trace of mesitylglyoxal hydrate. It is noteworthy that the extent of cleavage in this reduction was very small in comparison with that occurring in the corresponding reductions of the 2-enol ethers (I and II); on the other hand, as in the case of the 2-ethers, no reductive elimination of the 2-oxygen atom was observed.



$$C_9H_{11}CO\underset{OH\text{---}}{C}=CH-\underset{\text{---}O}{\overset{\|}{C}}C_9H_{11} \xrightarrow{Na_2S_2O_4} \left\{ \begin{array}{l} C_9H_{11}CO\underset{OH}{C}HCH_2COC_9H_{11} \quad \text{VIII} \\ C_9H_{11}\underset{OH}{C}H-\underset{O\text{---}}{\overset{\|}{C}}-CH=\underset{\text{HO}}{C}C_9H_{11} \end{array} \right.$$

VII

VIII

IX

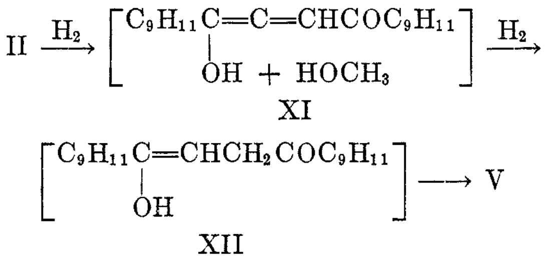
Catalytic reductions of the 2-enol ethers were carried out because it was anticipated that under these conditions the hydrolytic fission would be minimized. This proved to be the case. The *cis* and *trans* isomers reacted in very different ways, however. The *trans* isomer (II) absorbed approximately one molecule of hydrogen and gave a mixture from which a 65% yield of the saturated methoxy 1,4-diketone (III) and a 25% yield of dimesitylbutanedione (V) were obtained. The *cis* isomer (I) absorbed two molecules of hydrogen and gave dimesitylbutanedione (V) in almost quantitative yield. These results are to be contrasted with those of the sodium hydrosulfite reductions, in that elimination of the methoxyl group now appears as a prominent and in one case the dominant reaction, and as predicted, the hydrolytic fission has been almost completely suppressed.

The striking difference in the behavior of the *cis* and *trans* isomers in catalytic reduction led to speculation concerning the mechanism of the reactions. The saturated methoxy diketone (III), once it is formed, is stable under the reducing conditions; therefore the elimination of the methoxyl during reduction must occur directly or in an intermediate step. In one experiment a typical reduction of the *cis* ether was interrupted after addition of one molecule of hydrogen, and the resulting mixture was poured into alcoholic iodine to oxidize any di-enol produced; nevertheless the saturated diketone (V) was obtained in 36% yield. In a second and similar experiment in which the hydrogen absorption had been allowed to proceed to completion, there was produced a 96% yield of the saturated diketone (V). These experiments indicate that no di-enol of the type X was formed in the reduction unless it was an extraordinarily easily ketonized di-enol, stereoisomeric with that obtained in the reduction of dimesitoylethylene (IV) (4).

$$\underset{\displaystyle OH}{C_9H_{11}C}{=}CHCH{=}\underset{\displaystyle OH}{C}C_9H_{11}$$

X

A possible mechanism which would account for the failure to form an oxidizable di-enol is 1,4-reduction of the α-methoxy ketone system followed by reduction of the 2-double bond of the resulting allenic enol (XI) and ketonization to the saturated diketone (V).



$$\text{II} \xrightarrow{H_2} \left[\underset{\displaystyle OH + HOCH_3}{C_9H_{11}C}{=}C{=}CHCOC_9H_{11}\right] \xrightarrow{H_2}$$

XI

$$\left[\underset{\displaystyle OH}{C_9H_{11}C}{=}CHCH_2COC_9H_{11}\right] \longrightarrow \text{V}$$

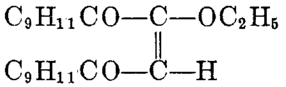
XII

The catalytic reduction of the *trans* ether (II) is best interpreted in terms of competing 1,4-reduction of the α-methoxy ketone system and 1,6-reduction of the unsaturated 1,4-diketone system. That the main course of the reduction did involve the 1,6-reaction mechanism to give the di-enol (VI) as the intermediate was shown by pouring the fresh reaction mixture into alcoholic iodine; in this experiment the starting material was regenerated and recovered in 75% yield, and quantitative determination showed that an approximately equivalent amount of iodine had been used up.

It is interesting to speculate as to why the *cis* ether (I) underwent reductive elimination of the methoxyl group so much more easily than did the *trans* isomer (II). One possible explanation is that, in the *cis* isomer as compared with the *trans*, steric hindrance is greater at the two carbonyls and less at the methoxyl; this would facilitate relatively that mode of reduction which involves the methoxyl oxygen. Another explanation would be in terms of interaction of the *cis* carbonyl groups in such a way as relatively to diminish the reactivity of the 4-carbonyl group in that compound.

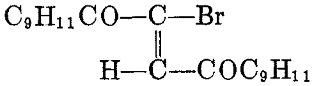
EXPERIMENTAL

cis-*1,4-Dimesityl-2-methoxy-2-butenedione-1,4* (I) (cf. Ref. 5). Three preparations of this ether are given. The first of these (a) involves the transformation of the *cis* ethyl ether (XIII) into the *cis* methyl ether (I). Evidently here, as also in the reaction with the *cis* and *trans* bromo unsaturated diketones (XIV), sodium methoxide adds 1,4 with subsequent elimination of sodium bromide or sodium ethoxide in such a way stereochemically as to produce consistently the *cis* configuration in spite of the greater energy content of this form.



$$\begin{array}{l} C_9H_{11}CO-C-OC_2H_5 \\ \qquad\qquad\quad \| \\ C_9H_{11}CO-C-H \end{array}$$

XIII



$$\begin{array}{l} C_9H_{11}CO-C-Br \\ \qquad\qquad\quad \| \\ \qquad\quad H-C-COC_9H_{11} \end{array}$$

XIV

(a) A methanol solution of 0.68 g. of the *cis* ethyl ether (XIII) and 0.1 g. of sodium hydroxide was refluxed for four hours. Upon cooling and acidification, 0.29 g. of the yellow enol (VII) separated and was identified. Dilution of the filtrate with water gave 0.3 g. (45%) of nearly pure *cis* methyl ether (I).

(b) A methanol solution of 0.75 g. of *trans* bromo unsaturated diketone (XIV) and a slight excess of sodium methoxide was allowed to stand with stirring for thirty minutes at room temperature. Dilution with water gave 0.45 g. (69%) of nearly pure *cis* methyl ether (I).

(c) In an experiment similar to (b) using the *cis* bromo unsaturated diketone (6) the *cis* ether (I) was obtained similarly in 84% yield.

Acid hydrolysis of 2 g. of (I) in 40 cc. of conc'd acetic acid, 10 cc. of conc'd hydrochloric acid, and 5 cc. of water at room temperature for three hours, produced 1.82 g. (94%) of almost pure enol (VII).

Reductions of the cis *2-methyl ether* (I). (a) Catalytic hydrogenation of 1 g. of (I) in ethanol with 0.05 g. of platinum oxide was stopped after absorption of one molecule, and the solution was immediately poured into alcoholic iodine solution. After diluting with water, the resulting oil was washed with sodium bisulfite and then with water, and was then taken up in ligroin from which 0.25 g. (35%) of dimesitylbutanedione (V) crystallized in nearly pure condition. The rest of the material was non-crystalline.

(b) In a similar experiment in which the reduction was allowed to go to completion with absorption of two equivalents of hydrogen, the solution was poured into an excess of alcoholic iodine. The product was isolated as before and proved to be the saturated diketone (V); yield 98%.

(c) In an experiment similar to (b), but bubbling oxygen through the resulting solution instead of using alcoholic iodine, the saturated diketone (V) was isolated in 76% yield.

(d) In another similar experiment in which the reduction mixture was treated with piperidine to hasten ketonization, the saturated diketone (V) was obtained in 94% yield.

(e) Hydrogenation with palladium on barium sulfate as catalyst was without result.

(f) The use of zinc dust and conc'd acetic acid or a mixture of conc'd acetic acid and acetic anhydride, at room temperature or at 60–70°, gave a mixture of products which included some mesitoic acid and the non-crystalline saturated diketone (III) [treated as described under (h)].

(g) Sodium bisulfite in 80% ethanol at refluxing temperature was without action.

(h) A number of reductions with sodium hydrosulfite were carried out. The following experiment is typical.

A mixture of 100 cc. of 80% ethanol, 45 g. of sodium hydrosulfite, and 15 g. of (I) was refluxed for half an hour with mechanical stirring. Upon cooling and diluting with water, an oil separated which was extracted by means of petroleum ether, from which 0.1 g. of colorless crystals was obtained on concentrating (m.p. 100–101°). This was identified by mixture melting point as mesitylglyoxal hydrate. Slow evaporation of the filtrate gave mesitoic acid. Extraction of the filtrate three times with saturated sodium carbonate removed more mesitoic acid which was recovered upon acidification; total yield 2.6 g. (37%).

1,4-Dimesityl-2-methoxybutanedione-1,4. Final evaporation of the petroleum ether solution obtained in the preceding experiment left an oil (14 g.) which was distilled in a vacuum oven at 60° under 2 mm. pressure, and the distillate was collected dropwise on a cold-finger condenser. The fraction coming over at this temperature (3 g., 44%) was redistilled; it boiled at 126° under 7 mm. pressure and showed n_D^{23} 1.5170–1.5180 which corresponds closely to the value reported in the literature for acetomesitylene. The second fraction which came over at an oven temperature of 140–155° under 2 mm. pressure was 3.9 g. (26%). It was redistilled and showed n_D^{19} 1.5480 which is close to the value found for samples obtained in other reductions, including that of dimesitoylbromomethoxyethylene (7). This compound was not analyzed but its nature was demonstrated as follows. A portion was decomposed in two ways, one by distillation at 190–200° under partially reduced pressure, and the other by heating under an atmosphere of nitrogen at 240–260°. In both cases dimesitoylethylene (IV) was obtained in high yield and was identified.

Trans-*1,4-Dimesityl-2-methoxy-2-butenedione-1,4* (II). Hydrolysis of 0.6 g. of this ether in 20 cc. of conc'd acetic acid, 5 cc. of conc'd hydrochloric acid, and 2.5 cc. of water for three hours at room temperature gave 0.56 g. (97%) of nearly pure enol (VII).

Catalytic reduction of 1 g. of the *trans* ether (II) in 60 cc. of ethanol with 0.05 g. of platinum oxide involved rapid absorption of one molecule of hydrogen. The solution was poured into an alcoholic solution of an excess of iodine, and on working up the product in the usual way 0.75 g. of the methoxy unsaturated diketone (II) was recovered. When a similar reaction mixture from 2 g. of II was treated under hydrogen with two drops of piperidine and allowed to stand for five hours, 0.43 g. of the saturated diketone (V) was obtained. From the filtrates, 1.3 g. of an oil was obtained which was shown to be the methoxy saturated diketone (III) by redistillation at 130–140° under 2 mm. pressure, by refractive index (n_D^{25} 1.5460), and by pyrolysis as described above at 210° under partially reduced pressure, with the formation of dimesitoylethylene in 60% yield. Incidentally, a sample of the oil (III) was subjected to a catalytic reduction and was apparently unaffected; only a small amount of hydrogen was absorbed and a 6% yield of the saturated diketone (V) was isolated (obviously the result of partial reduction).

Sodium hydrosulfite reduction of 5 g. of (II) in 90 cc. of 80% ethanol and 15 g. of the reagent was carried out as described under (I). The oil obtained was dissolved in ligroin and extracted with three portions of sodium carbonate solution from which 0.26 g. of mesitoic acid was recovered upon acidification. The ligroin solution on evaporation left an oil which was distilled at 65° under 2 mm. pressure (yield 1.25 g., 55%); this was identified as acetomesitylene by refractive index; n_D^{25} 1.5205. The residue from the distillation of the acetomesitylene at a higher temperature in the vacuum oven gave a second and crystalline fraction (0.25 g.) which melted at 85° (upon repeated crystallization the melting point was 102°; this compound has not been investigated further). At a still higher temperature (130–140°) a viscous yellow oil distilled, the middle fraction of which showed n_D^{25} 1.5475 and evidently was the methoxy saturated diketone (III). It underwent pyrolysis at 200–220° under partially reduced pressure to give dimesitoylethylene (IV).

Reduction of 1,4-dimesityl-1,2,4-butanetrione enol (VII). A mixture of 5 g. of the enol (VII), 100 cc. of 80% ethanol, and 25 g. of sodium hydrosulfite was heated with stirring at 80–90° for four hours. On dilution with water, an oil was obtained which was dissolved in petroleum ether. Evaporation and digestion with ligroin, and standing, produced 1.15 g. of colorless crystals of m.p. 103–104° which was identified as 4-hydroxydimesitylbutane-1,3-dione enol (IX). Concentration of the filtrate gave 1 g. of the hydroxy saturated diketone (VIII) which was identified. The residue from evaporation of the filtrate was distilled in the vacuum oven at 120° and gave 0.97 g. of dimesitoylethylene (IV), which was identified.

SUMMARY

Sodium hydrosulfite reduction of the *cis* and *trans* 2-enol ethers of 1,4-dimesityl-1,2,4-butanetrione gave the methoxy saturated 1,4-diketone and large amounts of the cleavage products, mesitoic acid and acetomesitylene. Sodium hydrosulfite reduction of the triketone enol itself involved very little cleavage and gave a mixture of the hydroxy saturated diketone and the 4-hydroxy-1,3-diketone enol.

In catalytic hydrogenation the fission was minimized but the *cis* and *trans* ethers gave widely different results: the *trans* ether gave a mixture of the methoxy saturated diketone and the demethoxy compound, 1,4-dimesitylbutanedione; whereas the *cis* ether underwent complete reductive elimination of the methoxyl to give chiefly 1,4-dimesitylbutanedione.

The mechanism of these reactions is discussed and a possible explanation for the difference in behavior of the *cis* and *trans* isomers is offered.

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