

## Short Communications

## Hydantoin from Chalcone Oxides

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5-Phenyl-5-benzylhydantoin has been obtained in fair yield by boiling chalcone oxide with ethanolic potassium hydroxide in the presence of urea. This reaction involves a rearrangement of the carbon skeleton of the initial molecule. A range of substituted chalcone oxides has been subjected to the same treatment, and the isolated, weakly acidic reaction products are characterized, by analogy, as the corresponding hydantoins.

It is known that chalcone oxides under similar conditions but without urea yield phenylbenzylglycolic acids, a reaction proceeding *via* the isomeric  $\alpha$ -diketone which then undergoes a rearrangement of the benzoic acid type<sup>1</sup>. Recently, Dunnivant and James<sup>2</sup> have presented convincing evidence in favour of a reaction mechanism of the benzoic acid rearrangement type in the well-known formation<sup>3</sup> of 5,5-diphenylhydantoin from benzil with alkali and urea, as well. In conformity with this view *o*-methoxyl groups in the aroyl nucleus of the chalcone oxide should hinder the genesis of a hydantoin about as strongly as they, in the absence of urea, hinder the formation of an  $\alpha$ -hydroxy acid through a rearrangement of the benzoic acid type. This seems to be the case judging from the relevant yields of the present work.

*Experimental.* (All analyses are microanalyses, performed by Dr. A. Bernhardt, Mühlheim, Germany).

*3,4-Dimethoxychalcone oxide.* To 3,4-dimethoxychalcone (2.68 g) in methanol (25 ml) were added hydrogen peroxide (15 %, 4 ml) and 2 N sodium hydroxide (2.5 ml). The mixture was stirred for 3 h and then cooled in a refri-

gerator. The crystals separated by filtration were recrystallised from methanol and from chloroform-light petroleum. Yield 2.3 g (81 %), m.p. 89—90°. (Found: C 72.34; H 5.49; C<sub>17</sub>H<sub>16</sub>O<sub>4</sub> requires C 71.82; H 5.67).

*3,3',4,4'-Tetranethoxychalcone oxide.* Finely powdered 3,3',4,4'-tetramethoxychalcone, (3.28 g, m.p. 111°), was stirred for 6 h together with a solution of hydrogen peroxide (15 %, 5 ml) and 6 N potassium hydroxide (0.83 ml) in methanol (30 ml). Dissolution came about only partly. Filtration of the reacted mixture gave an almost white powder which was recrystallised from methanol and from chloroform-light petroleum to give 2.75 g (80 %) of the epoxide, m.p. 150—151°. (Found: C 66.44; H 5.91; C<sub>19</sub>H<sub>20</sub>O<sub>8</sub> requires C 66.27; H 5.85).

*5-Phenyl-5-benzylhydantoin.* The solution of chalcone oxide (2.24 g, 0.01 mole) in ethanol (20 ml) was kept boiling under reflux. In one operation was added a hot solution of potassium hydroxide (1.23 g, 0.022 mole) and urea (1.32 g, 0.022 mole) in ethanol (20 ml). The refluxing was continued for 2 h and the reaction mixture was then poured into water (400 ml). A tiny precipitate was removed and after that the water solution was saturated with carbon dioxide. The obtained precipitate was collected and recrystallised from dilute ethanol. Yield 2.0 g (75 %), m.p. 210°. Mixing with 5-phenyl-5-benzylhydantoin<sup>4</sup>, m.p. 210°, obtained<sup>5</sup> by treating desoxybenzoin with potassium cyanide and ammonium carbonate in dilute ethanol at 60°, did not depress the m.p.

In the same way were obtained:

*5-Phenyl-5-(4-methoxybenzyl)-hydantoin*, yield 2.55 g (86 %), m.p. 206—208°, (Found: C 68.95; H 5.86; N 9.48; C<sub>17</sub>H<sub>16</sub>O<sub>3</sub>N<sub>2</sub> requires C 68.90; H 5.44; N 9.45) from 4-methoxychalcone oxide (2.54 g), and

*5-Phenyl-5-(3,4-dimethoxybenzyl)-hydantoin*, yield 2.85 g (87 %), m.p. 211—212°, (Found: C 65.61; H 5.44; N 8.66; C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>N<sub>2</sub> requires C 66.24; H 5.56; N 8.66) from 3,4-dimethoxychalcone oxide (2.84 g).

*5-(3,4-Dimethoxyphenyl)-5-(3,4-dimethoxybenzyl)-hydantoin*, yield 2.8 g (72 %), m.p. 212—213°, (Found: C 62.05; H 5.84; N 7.48;

$C_{20}H_{22}O_6N_2$  requires C 62.16; H 5.74; N 7.25) was obtained from 3,3',4,4'-tetramethoxychalcone oxide (3.44 g) in the same way with the exception that the main part of the epoxide remained undissolved in the initial boiling ethanolic mixture.

*5-Phenyl-5-(1-phenylethyl)-hydantoin.* The boiling solution of 2.38 g of dypnone oxide<sup>6</sup>, (the crude epoxide containing both of the isomers may be used), in ethanol (20 ml) was treated with ethanolic potassium hydroxide and urea as above. The precipitation of a voluminous potassium salt followed close on the addition of the reagents. After refluxing the mixture for 2 h the precipitate was separated by filtration and washed with a small amount of ethanol. It was then dissolved in water (200 ml) by heating and adding a little sodium hydroxide. The solution thus obtained was saturated with carbon dioxide and the precipitated mass collected and recrystallised from ethanol. Yield 1.0 g (36%), m.p. 305—307°. (Found: C 72.82; H 5.82; N 10.07;  $C_{17}H_{16}O_2N_2$  requires C 72.84; H 5.75; N 9.99). The filtrate from the insoluble potassium salt was poured into water (400 ml). The solution was clarified by filtration and was then saturated with carbon dioxide. The obtained precipitate was collected and recrystallised from ethanol. Yield 1.1 g (39%) of m.p. 265—266°, (Found: C 72.69; H 5.80; N 10.05;  $C_{17}H_{16}O_2N_2$  requires C 72.84; H 5.75; N 9.99). The two products of this preparation are presumably the diastereoisomers of 5-phenyl-5-(1-phenylethyl)-hydantoin.

*5-(2-Methoxyphenyl)-5-benzylhydantoin.* 2'-Methoxychalcone oxide<sup>7</sup> (2.54 g) was treated with ethanolic potassium hydroxide and urea analogously with the model preparation above. After pouring the reaction mixture in water, the solution, however, was extracted with ether instead of being filtered, by reason of the stickiness of the cloudy precipitate. Saturation of the water phase, from which all the ether had been removed, with carbon dioxide, and repeated recrystallisation of the obtained precipitate from dilute ethanol gave 0.3 g (10%) of m.p. 224°, (Found: C 69.11; H 5.87; N 9.44;  $C_{17}H_{16}O_2N_2$  requires C 68.90; H 5.44; N 9.45).

*Benzyl-(2-methoxyphenyl)-glycolic acid.* The above procedure was repeated but without urea. The filtrate after precipitating  $\alpha$ -hydroxy-2'-methoxychalcone with carbon dioxide was acidified with dilute sulphuric acid and the obtained precipitate recrystallised from dilute ethanol, yielding 0.35 g (13%) of m.p. 183—184°, (Found: C 70.44; H 5.84;  $C_{16}H_{16}O_4$  requires C 70.57; H 5.92).

$\alpha$ -Hydroxy-2',4',6'-trimethoxychalcone<sup>7</sup> but no hydantoin or hydroxy acid was obtained when 2',4',6'-trimethoxychalcone oxide was subjected to the described treatment with or without urea.

Work is in progress to find out suitable conditions for hydrolysis of the present hydantoin.

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## A Contribution to the Principles of Electrodiffusion

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Electrodiffusion was suggested by E. Mysels<sup>1</sup> and Lamm<sup>2</sup> as a method for studying the equilibrium kinetics of certain reactions involving ions. The term refers to the increased diffusion which occurs on the superposition of an electric field in the diffusion direction. The magnitude of this effect is related to the field characteristics and to the kinetics of the system studied. More recently, Giddings<sup>3-5</sup> and Bak and Kauman<sup>6</sup> have contributed to the theory of electrodiffusion.

The theory of Mysels and that of Bak and Kauman refer (although this is not explicitly stated) to the case of selfdiffusion or to the case where a large excess of an electrolyte, which does not partake in the kinetic equilibrium, is added in order to maintain a constant field throughout the diffusion column. In this case the