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SELECTIVE REDUCTION OF C-C DOUBLE BONDS IN CONJUGATED ENONES BY BENZYLAMINE. A VARIANT OF THE SOMMELET REACTION.

Diego Armesto[*a], William M. Horspool[b], Juan Antonio F. Martin[a], and Rafael Perez-Ossorio[a].

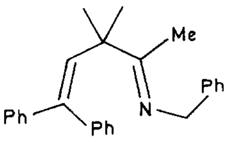
a: Departamento de Química Orgânica, Facultad de Ciencias Químicas,
Universidad Complutense, 28040-Madrid, Spain.

b: Department of Chemistry, The University, Dundee DD1 4HN, Scotland.

Summary: Prolonged reaction of some ketones with benzylamine at reflux converts them into α-benzyl derivatives by a route involving aldol condensation of the related ketimine with benzaldimine followed by exclusive reduction of the resultant C-C double bond by hydride transfer from benzylamine. This efficient procedure is a variant of the Sommelet reaction for the synthesis of aldehydes.

In recent years our research effort has been aimed at the study of the influence of the imine function on the photochemical behaviour of non-conjugated[1] and conjugated azadiene systems[2]. One of the more convenient methods adopted by us for the synthesis of benzylimines of ketones and enones which were more reluctant to react under less vigorous conditions involve heating the ketone or enone in neat benzylamine at reflux temperature[3].

This proved to be a satisfactory method, for example, for the synthesis of the imine (1) from the enone (2) providing that the reaction time was kept short, about 3 hr. If the reaction is allowed to run for much longer (20-40 hr), or if the imine (1) is refluxed in benzylamine for the same time, the imine (1) is no longer present in the reaction mixture. After conventional workup followed by chromatography on silica gel, during which procedure the imines present are hydrolysed, benzaldehyde and a new ketone (47%) were isolated. The spectroscopic details and independent synthesis of this new product identified the compound as the ketone (3)[4]. The new benzyl group incorporated into (2) must come from benzylamine. The most logical manner of bringing about such a benzylation would involve condensation (Aldol type) between the anion (5) produced from imine (1) with benzaldehyde (or an imine such as (4)) to yield the imine (6) followed by reduction. This reduction step is most likely by hydride transfer from benzylamine in a manner analogous to that which occurs in the Sommelet procedure for



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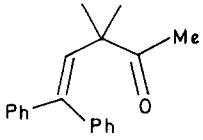

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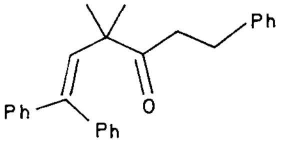
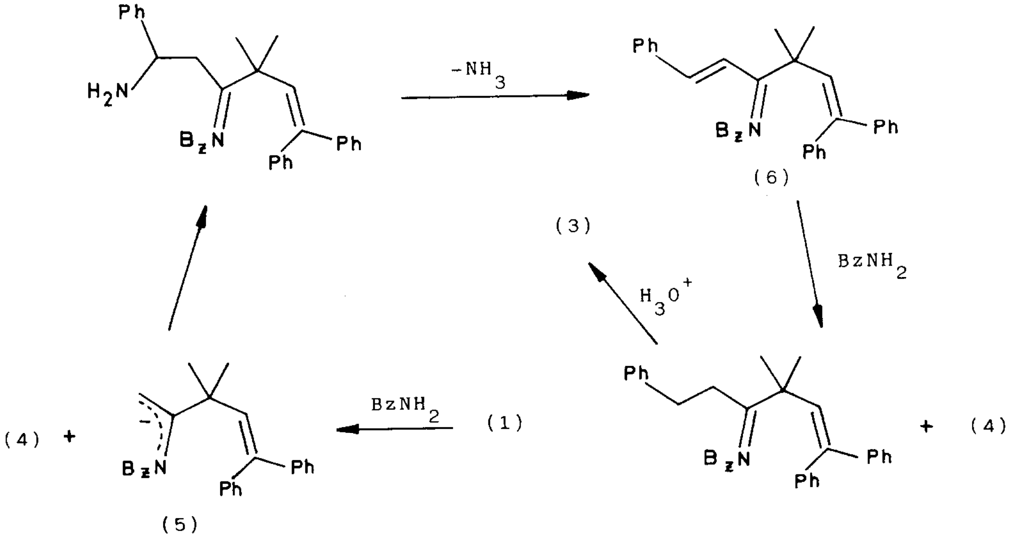


(3)

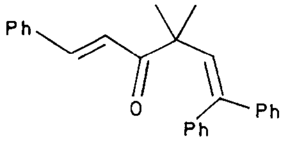
the synthesis of aldehydes[5]. In this case, however, we are interested in the reduction and not the oxidation product. These proposals are outlined in the scheme. The reduction step provides a further source of the benzaldehyde unit (4) which can subsequently react in the condensation. Thus only a minimal oxidation of the original benzylamine is required to initiate the reaction. Workup and hydrolysis affords the isolated ketone (3).

$$BzNH_2 \xrightarrow[\text{reflux}]{\text{air}} \underset{(4)}{PhCH{=}NH \text{ (or } PhCH{=}NBz)} \qquad Bz{=}PhCH_2$$



Scheme

Proof for the intermediacy of the unsaturated imine (6) in the reaction sequence was readily demonstrated by subjecting ketone (7), synthesized independently, to the same reaction conditions as the enone (2). After workup in the usual manner the ketone (3) was obtained, again in good yield[6].



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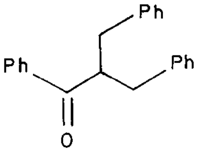

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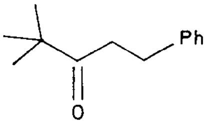

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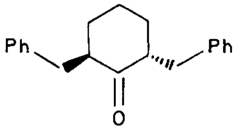

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In an effort to establish the scope of this benzylation procedure we have studied the reactions of three simpler ketones, acetophenone, 3,3-dimethylbutan-2-one, and cyclohexanone. All of these were converted into their corresponding benzylimine and then subjected to 25 hr reflux in benzylamine. Alternatively the ketones could be simply dissolved in benzylamine and then refluxed for the same time. The results obtained from this set of reactions indicate that the reaction is, to some extent,dependent upon steric factors and substitution patterns. Thus acetophenone affords the bis benzylated product (8, 70%) the identity of which was proved by independent synthesis[7]. When a bulky group is present as in 3,3-dimethylbutan-2-one only mono benzylation takes place to afford the ketone (9, 63%)[9]. Lastly cyclohexanone was converted into the bis benzylated product (10, 58%)[11].

The benzylation described above might have good applicability to most types of ketones which have at least a methyl or a methylene attached to the carbonyl group. In the examples studied so far the reduction is totally specific and occurs at the new C-C double bond produced by the aldol condensation of the ketimine with benzaldimine. There is no evidence for reduction at the carbonyl (or imine) functional groups.

We are at present carrying out detailed studies on the procedure to establish the scope and generality as regards stereochemistry and substrate type.

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3. D. Armesto, W. M. Horspool, J. A. F. Martin, and R. Perez-Ossorio, Unpublished results.
4. Aldol condensation of ketone (2) with benzaldehyde followed by catalytic reduction afforded ketone (3); b.p. 158-160°C/0.1mmHg; νmax(KBr), 1695 cm^{-1}; δ_H 1.15 (3H, s, Me), 2.65 (4H, s, CH_2CH_2), 6.0 (1H, s, vinyl), 7.00-7.35 (15H, m, aryl); δ_C 127.67, 127.92, 128.07, 129.97, 133.91, 139.35, 142.94, 143.30, 209.77 (C=O).
5. S. J. Angyal, *Organic Reactions*, **8**, 197 (1954).
6. All the yields quoted are for the isolated purified compounds.
7. Reaction of acetophenone with KOH and benzyl chloride affords ketone (8), m.p. 75-76°C (lit.[8] m.p. 76°C).
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9. Ketone (9) b.p. 65°C/0.04 mm Hg (lit.[10] b.p. 261°C/746 mm Hg); νmax(liq. film) 1655 cm^{-1}; δ_H 1.15 (9H, s, 3Me), 1.80 (3H, s, Me), 4.40 (2H, s, Me), 7.10-7.30 (5H, m, aryl).
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11. Ketone (10) m.p. 113-114°C (lit.[12] m.p. 116-118°C for the trans-isomer).
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