ELECTROPHILIC SUBSTITUTION IN THE SERIES OF BICYCLIC CISSOID ENAMINO KETONES

G. V. Grishina, A. I. Vovk,
and V. M. Potapov

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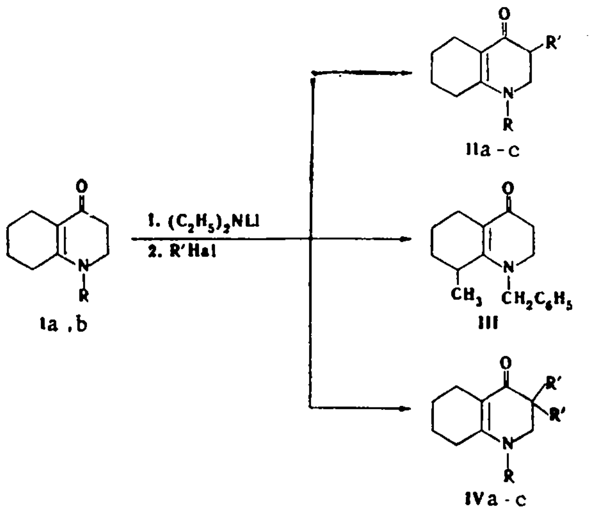
For the synthesis of functionally modified bicyclic cissoid enamino ketones [1], we used the reaction between N-substituted $\Delta^{9,10}$-octahydro-4-quinolones (Ia, b) and halogen alkyls in THF and dimethoxyethane in the presence of lithium amides, and it was established that, depending on the conditions, the reaction of electrophilic substitution takes place with the formation of alkylated enamino ketones II-IV; a variation of the reaction conditions (solvent, lithium amide, ratio of reagents) makes it possible to direct the reaction along the route of monoalkylation with respect to position 3 or 8, and dialkylation with respect to position 3 of the quinolone system:



I a $R=CH_2C_6H_5$; b $R=CH(CH_3)C_6H_5$; II, IV a $R'=CH_3$, $R=CH_2C_6H_5$; b $R'=CH_3$, $R=CH(CH_3)C_6H_5$; c $R'=C_4H_9$, $R=CH(CH_3)C_6H_5$

To a solution of 2.4 mmole of lithium diethylamide, obtained from 2.4 mmole of diethylamine and 1.7 ml of a 1.45 M ether solution of CH_3Li in 5 ml of THF, at 0°C and in an atmosphere of argon, there is added a solution of 0.8 mmole of enamino ketone Ia in 5 ml THF, and, after 30 min, 3 mmole of CH_3I. After 2 h, the reaction mixture is decomposed with water; the substances formed are separated in a column with Al_2O_3, eluting consecutively CCl_4, and a mixture of CCl_4–ethyl acetate, 8:1, 6:1, 4:1, 2:1. There is obtained 60% 3-methyl-N-benzyl-$\Delta^{9,10}$-octahydro-4-quinolone IIa, mp 97-98°C (from heptane), R_f 0.4 (Silufol, benzene–acetone 4:1); mass spectrum: M_{found}^+ 255; M_{cal} 255. IR spectrum (Vaseline oil): 1630 (C=O conjugation), 1570 cm^{-1} (C=C conjugation). UV spectrum (C_2H_5OH): λ_{max} 340 nm (ε_{max} 18,000). PMR spectrum (CCl_4): 1.00 (3H, d, CH_3), 4.47 (2H, d, $CH_2C_6H_5$), 7.27 ppm (5H, s, C_6H_5). The 3-methyl-substituted enamino ketone separated out is identical in spectral properties and melting point with 3-methyl-N-benzyl-$\Delta^{9,10}$-octahydro-4-quinolone, obtained by counter synthesis by the condensation of the methyl ester of 3-(N-benzylamino)-2-methylpropionic acid with cyclohexanone [1]. With further elution, 20% of the starting enamino ketone Ia is evolved.

Carrying out an analogous reaction at −70°C and using a tenfold excess of lithium diethylamide and an equimolar ratio of CH_3I (0.8 mmole of the enamino ketone Ia, 8.0 mmole lithium diethylamide, 0.8 mmole CH_3I), there is evolved 8-methyl-N-benzyl-$\Delta^{9,10}$-octahydro-

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4-quinolone (III) in a yield of 50%; this is an isomer of the enamino ketone IIa with respect to the position of the methyl group, which is confirmed by the data of mass-spectral resolution and ^{13}C NMR; mp 142-143°C (from heptane); R_f 0.3 (Silufol, benzene—acetone, 4:1); mass spectrum: M_{found}^+ 255; M_{cal} 255. IR spectrum (Vaseline oil): 1630 (C=O conjugation), 1560 cm^{-1} (C=C conjugation). PMR spectrum (CCl_4): 0.97 (3H, d, CH_3), 4.46 (2H, d, $CH_2C_6H_5$), 7.20 ppm (3H, m, C_6H_5). Of the starting enamino ketone Ia, 40% is also separated out.

Under analogous conditions, there are obtained the following enamino ketones: IVa, yield 48%, mp 120-121°C (from heptane), M_{found}^+ 269, M_{cal} 269; IVb, yield 51%, mp 98-99°C (from heptane), M_{found}^+ 283, M_{cal} 283; IVc, yield 40%, M_{found}^+ 367, M_{cal} 367; IIb, yield 80%, M_{found}^+ 269, M_{cal} 269; IIc, yield 20%, M_{found}^+ 311, M_{cal} 311.

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NAME REACTIONS IN THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

Ya. P. Stradyn'

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After the publication of K. V. Vatsuro and G. L. Mishchenko's basic reference book (Moscow, Khimiya, 1976), a review of which by the most prominent specialist in the history of chemistry, G. V. Bykov, appeared in our journal (Khim. Geterotsikl. Soedin., No. 10, 1427-1430 (1977)), our attention was turned to the circumstance that the book contains relatively few name reactions bearing the names of Soviet organic chemists. Inasmuch as a second edition of this reference book and a French translation of it are being prepared, we carried out a poll of well-known heterocyclic chemists in order to clarify what reactions should bear the names of the scientists who discovered them (or made fruitful use of them).

Participants in the poll noted that in recent times new name reactions have, indeed, begun to appear less frequently than in the thirties, for which, at least in part, the low activity of colleagues and of the chemical community as a whole is to blame. There are no clear criteria for a name reaction, but an evaluation should take into consideration the novelty of the reaction (or method), the frequency with which it is mentioned in the literature and used by colleagues at other scientific centers, the breadth of application (generality), etc. Strict control of the creation of name reactions from the names of the scientists who discovered them would hardly be appropriate. Basically, the process is spontaneous and should hardly be referred to the competence of a Committee on Discovery and Invention. However, this process is not always free of subjectivity.

For more objective evaluation, the novelty and importance could be usefully shown by: publication of reviews of the annual progress in the field of heterocyclic chemistry, in which new, major results could be set out; publication of science history articles with an indication of the progress of the work of scientific schools and their influence on developments in the field; public discussions at all-union conferences and authoritative scientific colloquia of sections of the D. I. Mendeleev All-Union Chemical Society; information about new reactions in the pages of popular science journals (Priroda, Khimiya i Zhizn', Nauka i Zhizn'), participation of groups of competent scientists in specific discussions of the priority and importance of specific reactions; etc. New name reactions could be discussed also at sessions of editorial boards of specialized journals in organic chemistry. Here, one must keep in mind the time factor, but this does not preclude great effectiveness in specific cases when striking, unusual transformations are discovered.

Publishing the results of this preliminary poll, we hope that readers of the journal will contribute new suggestions as well as turn their attention to original and significant reactions or methods discovered or developed by our chemists, especially in the past decade.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
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