The Conversion of Primary Amines into Olefins: a Mild Alternative to the Hofmann Elimination[1]

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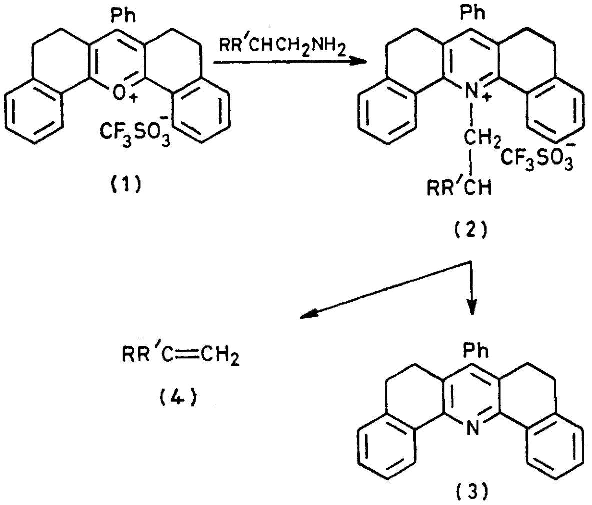
Summary Use of the pentacyclic pyrylium salt (**1**) allows a two-step conversion of the amine $RR'CHCH_2NH_2$ into $RR'C{=}CH_2$ in high yield under mild conditions.

The classical Hofmann exhaustive methylation has remained for over 100 years the preferred method for the conversion of primary amines into olefins, but it requires several stages and vigorous conditions (typically, the pyrolysis temperature ranges from 200 to 300 °C.[2] We therefore attempted to follow our pyrylium salt mediated transformation of primary amines into pyridinium cations[3] by elimination. Experiments with 2,4,6-triphenylpyridinium compounds were not completely satisfactory,[4] but following the kinetic demonstration of the far better leaving-group ability of 7-phenyl-5,6,8,9-tetrahydrodibenzo[*c,h*]acridine (**3**),[5] we now find that primary alkyl primary amines are readily convertible in two high-yield steps into terminal olefins.

In the first step, amines $RR'CHCH_2NH_2$ react with the readily available[6] pentacyclic pyrylium trifluoromethanesulphonate (**1**) to give intermediate acridinium salts (**2**) (average yield for 10 examples 90%). These salts (**2**)¶ were heated to 150 °C with triphenylpyridine (1 equiv.) as non-nucleophilic base: the olefins (**4**) were distilled out at reduced pressure. In this way we prepared butene (62%, isolated as the dibromide), 2-methylpropene (60%, isolated as the dibromide), pentene (81%, isolated as the dibromide), hexene (97%), heptene (84%), octene (72%), undecene (98%), dodecene (81%), and styrene (89%).



The olefins were characterised by i.r. and ^1H and ^{13}C n.m.r. spectroscopy and by v.p.c. The terminal olefins were the principal products formed (*ca.* 75%) but they were accompanied by *ca.* 15% of the *trans*-2-isomer and *ca.* 10% of the *cis*-2-isomer as shown by ^{13}C n.m.r. spectroscopy and v.p.c.

We thank Dr. R. C. Patel for her interest in and help with this work.

(*Received, 20th October* 1980; *Com.* 1126.)

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¶ Satisfactory analytical data were obtained for all new compounds reported.

[1] *Cf.* the series 'Heterocycles in Organic Synthesis.' For Part 42, see *J. Chem. Soc., Perkin Trans.* 1, 1980, 849.

[2] A. C. Cope and E. R. Trumbull, *Org. React.*, 1960, **11**, 381, 383.

[3] For a review see A. R. Katritzky, *Tetrahedron*, 1980, **36**, 679.

[4] B. P. Leddy, Ph.D. Thesis, University of East Anglia, 1977; unpublished work with J. M. Lloyd and R. C. Patel.

[5] A. R. Katritzky, A. M. El-Mowafy, G. Musumarra, K. Sakizadeh, Ch. Sana-Ullah, S. M. M. El-Shafie, and S. S. Thind, in preparation.

[6] A. R. Katritzky, A. M. El-Mowafy, L. Marzorati, R. C. Patel, and S. S. Thind, *J. Chem. Research*, in the press.