# Pyrylium-Mediated Conversion of Primary Alkyl Primary Amines into Olefins via Tetrahydrobenzoacridiniums: A Mild Alternative to the Hofmann Elimination[1]

Alan R. Katritzky* and Azzahra M. El-Mowafy

*Department of Chemistry, University of Florida, Gainesville, Florida 32611, and the School of Chemical Sciences, University of East Anglia, Norwich, England NR4 7TJ*

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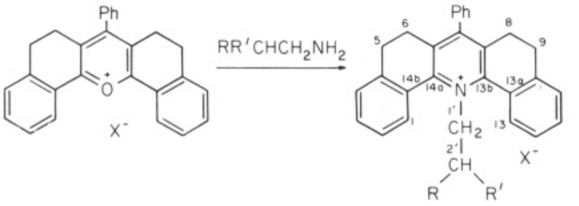
Primary alkyl primary amines react with the pentacylic pyrylium **2** to give the corresponding pyridiniums which thermolyze at 150–180 °C into the olefins in high yield. The terminal olefins are accompanied by *cis*- and *trans*-2-olefinic isomers: proportions are elucidated by GLC and advantageously by $^{13}$C NMR spectroscopy, combining gated decoupling and $(acac)_3Cr^{III}$.

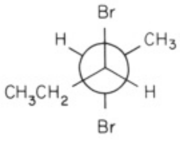
Dehydration, the removal of the elements of a water molecule, is a well-recognized concept in organic chemistry, and many dehydrating agents are known. "Deammoniation", the removal of the elements of ammonia, is much less familiar. We have shown that the conversion by pyryliums of primary amines into pyridiniums followed by nucleophilic[2] or free-radical[3] displacement can give many different functionalities. The use of pyryliums as deammoniating agents has already led to the synthesis of isocyanates from acid hydrazides[4] and of carbodiimides from amidrazones.[5] Although initial experiments directed at the conversion of primary amines into olefins employing pyryliums showed less promise, as high temperatures were required and low yields were obtained,[6] we now find that the use of pentacyclic pyrylium **2** allows this conversion under relatively mild conditions.

**Preparation of Tetrahydrodibenzacridiniums.** Previously reported tetrahydrodibenzoxanthylium tetrafluoroborate **1** and trifluoromethanesulfonate (triflate) **2** reacted with a series of primary alkyl primary amines to give the acridiniums **3** and **4** (Table I). For the preparation of the triflates **4**, sodium-dried ether was an advantageous reaction medium. The acridiniums were characterized by $^1$H NMR and IR spectra (Table II, supplementary material) and showed the expected $^{13}$C NMR signals. In the $^{13}$C NMR spectra (Tables III and IV, supplementary material), the N-substituent signals were assigned by comparison with the spectra of the corresponding alcohols.[7]

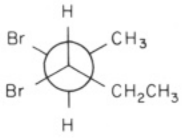


**1** X = $BF_4$
**2** X = $CF_3SO_3$

**3** X = $BF_4$, R = H, R′ = Ph
**4** X = $CF_3SO_3$



**5a** erythro-2,3-dibromopentane



**5b** threo-2,3-dibromopentane

Table I. Preparation of Alkyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium Trifluoromethanesulfonates[a]

| compd | N substituent | yield, % | mp,[b] °C | lit. mp, °C |
|---|---|---|---|---|
| **3** | $CH_2CH_2Ph$ | 65 | 190–200 | |
| **4a** | $CH_2CH_2Ph$ | 62 | 226–228 | 229–231[c] |
| **4b** | $CH_2CH(CH_3)_2$ | 90 | 202–203 | |
| **4c** | $(CH_2)_3CH_3$ | 96 | 192–193 | 150–151[c] |
| **4d** | $(CH_2)_4CH_3$ | 97 | 113–118 | |
| **4e** | $(CH_2)_5CH_3$ | 89 | 158–159 | 101–102[c] |
| **4f** | $(CH_2)_6NH_2$ | 97 | 204–208 | |
| **4g** | $(CH_2)_6CH_3$ | 91 | 183 | |
| **4h** | $(CH_2)_7CH_3$ | 94 | 146–148 | 147–148[c] |
| **4i** | $(CH_2)_{10}CH_3$ | 92 | 157–158 | |
| **4j** | $(CH_2)_{11}CH_3$ | 91 | 156–157 | 155–156[d] |

[a] Analytical data were obtained for all new compounds reported within 0.3% of the calculated except for **3** (0.5% in N). [b] All yellowish prisms. [c] See ref 38.
[d] Katritzky, A. R., and Marzorati, L. *J. Org. Chem.* **1980**, *45*, 2515.

**Thermolysis of Tetrahydrodibenzacridiniums.** Thermolysis of the *N*-(2-phenylethyl) tetrafluoroborate **3** with or without 2,4,6-triphenylpyridine at 160 °C gave styrene (26%) contaminated with ethyl 2-phenylethyl ether, which probably arose from ethanol of crystallization in the starting material. However, better results were obtained with the triflates.

Each triflate **4** was heated with 1.5 equiv of 2,4,6-triphenylpyridine (nonnucleophilic base and flux): the olefin was formed at 140–160 °C, although in some cases the temperature was raised above this where the triflate had a high melting point mp (Table V). The products from the *N*-*n*-butyl, *N*-isobutyl, and *N*-*n*-pentyl derivatives were isolated as the dibromides and the others as such.

The olefinic products from the *N*-(2-phenylethyl), *N*-*n*-hexyl, *N*-*n*-heptyl, *N*-*n*-octyl, *N*-*n*-undecyl, and *N*-*n*-dodecyl derivatives showed IR and $^1$H NMR spectra almost identical with those reported for authentic samples.[8]

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(1) For a preliminary communication of part of this work see A. R. Katritzky and A. M. El-Mowafy, *J. Chem. Soc., Chem. Commun.*, 96, 1981.

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(6) B. Leddy, Ph.D. Thesis, University of East Anglia, 1977, p 84.

(7) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Am. Chem. Soc.*, **92**, 1338 (1970).

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Table V. Yields and Reaction Conditions of Thermolysis of *N*-Alkyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium Trifluoromethanesulfonates 4

| | | | | | thermolysis conditions | | |
|---|---|---|---|---|---|---|---|
| reaction | compd | N substituent | procedure | yield, % | temp, °C | pressure, mm | time, h |
| 1 | **4a** | $CH_2CH_2Ph$ | A | 89 | 180-190 | 0.1 | 6 |
| 2 | **4b** | $CH_2CH(CH_3)_2$ | B | 60 | 200-220 | 760 | 7 |
| 3 | **4c** | $(CH_2)_3CH_3$ | B | 62 | 170-180 | 760 | 6 |
| 4 | **4d** | $(CH_2)_4CH_3$ | B | 81 | 180-200 | 760 | 8 |
| 5 | **4e** | $(CH_2)_5CH_3$ | A | 97 | 140-150 | 300 | 6 |
| 6 | **4g** | $(CH_2)_6CH_3$ | A | 84 | 150 | 180 | 2 |
| 7 | **4h** | $(CH_2)_7CH_3$ | A | 72 | 150 | 200 | 3.5 |
| 8 | **4i** | $(CH_2)_{10}CH_3$ | A | 98 | 160 | 20 | 6 |
| 9 | **4j** | $(CH_2)_{11}CH_3$ | A | 81 | 140-160 | 20 | 2 |

Table VI. VPC Product Distribution in the Thermolysis of *N*-Alkyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium Trifluoromethanesulfonates in the Presence of 2,4,6-Triphenylpyridine[a]

| | | | | product distribution of olefins (%)[b] and retention times (s) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| reaction | column | column temp, °C | product | 1-alkene | $t_R$ | *trans*-2-alkene | $t_R$ | *cis*-2-alkene | $t_R$ |
| 1 | OV1 | 60 | styrene | 99 | 390 | | | | |
| 8 | OV1 | 40 | octenes | 72.7 | 546 | 17.7 | 624 | 9.6 | 666 |
| 5 | C20M | 60 | hexenes | 84.2 | 72 | 11.6[c] | 174 | 4.2[c] | 150 |
| 7 | Apiezon L | 80 | heptenes | 72.6 | 300 | 17.1[c] | 330 | 10.3[c] | 345 |
| 9 | C20M | 100 | undecenes | 58.3 | 774 | 26.6[c] | 828 | 15.1[c] | 882 |
| 10 | C20M | 100 | dodecenes | 55.3 | 900 | 27.3[c] | 918 | 17.5 | 1032 |

| | | | | product distribution of dibromo derivatives (%) and retention times (s) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| reaction | column | column temp, °C | product | 1,2-$Br_2$ | $t_R$ | *meso*-2,3-$Br_2$ | $t_R$ | *dl*-2,3-$Br_2$ | $t_R$ |
| 2 | OV1 | 60 | 1,2-dibromo-2-methylpropane | 99 | 444 | | | | |
| 3 | OV1 | 60 | dibromobutanes | 66.3 | 654 | 19.1 | 513 | 12.6 | 582 |
| 4 | OV1 | 60 | dibromopentanes | 74 | 1380 | 16.9[d] | 1074 | 9.1[e] | 1152 |

[a] Chromatographic conditions: stainless-steel columns; carrier gas nitrogen, 20–22 lb/in.$^2$, flow rate ≈ 18 mL/min. [b] Based on the total yield of elimination being 100%. [c] Contains a small amount of either *trans*-3- or *cis*-3-alkene and is difficult to resolve. [d] Erythro stereoisomer. [e] Threo stereoisomer.

However, further study by GLC and $^{13}C$ NMR revealed in all but two cases a mixture of isomers, in an approximate ratio of 70:20:10 of the 1-alkene, *trans*-2-alkene, and *cis*-2-alkene.

Styrene and isobutene (isolated as the dibromide) were >99% pure as shown by gas chromatographic studies (Table VI).

**Gas Chromatographic Investigation of Pyrolysis Products.** Previous workers have studied dibromide mixtures derived from olefins.[9] Using GLC, they were able to separate *meso*- [bp 73–74 °C (50 mm); $t_R$ = 151 s, flow rate 54 mL/min] and *dl*-2,3-dibromobutane [bp 76–77 °C (50 mm); $t_R$ = 212 s, flow rate 54 mL/min]. They also separated *erythro*- [bp 91 °C (50 mm); $t_R$ = 152 s, flow rate 50 mL/min] and *threo*-2,3-dibromopentane [bp 94 °C (50 mm); $t_R$ = 228 s, flow rate 50 mL/min] by GLC. In each case an Apiezon L column modified with Bentone 34 was used (at 120 and 140 °C, respectively).

In the present work, the dibromide from the *N*-*n*-butyl compound **4c** gave 1,2-dibromobutane (68.3%) together with the *dl*- (12.6%) and *meso*-2,3-dibromobutanes (19.1%) which were separated satisfactorially on an OV1 column at 60 °C. Similarly, the *N*-*n*-pentyl compound **4d** gave analogous products (see Table VI). The sequence of retention times was assumed to follow a pattern similar to that of ref 9 (vide supra) and also to that of ref 10, where a mixture of *meso*- and *dl*-2,3-dibromobutane was separated on a Chromosorb W with 30% Carbowax column at 130 °C ($t_R$ = 36.6 and 40.4 min, respectively).

The olefinic mixture from the *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-undecyl, and *n*-dodecyl compounds (**4e**–**j**) each gave at least three peaks which were assigned to the 1-alkene, *trans*-2-alkene, and *cis*-2-alkene in the order of increasing boiling points,[11] and although it is now known that there is no invariable correlation between boiling point and retention time,[12] the assignments were confirmed later by the $^{13}C$ NMR method.

**$^{13}C$ NMR Assignments of Dibromides.** $^{13}C$ Chemical shifts have been assigned for 1,2-dibromobutane.[13] We assigned $^{13}C$ shifts for meso and *dl* diastereoisomers of 2,3-dibromobutane by analogy with those for 2,3-dichlorobutane[14] (Table VII); in this way, all the eight peaks displayed by the dibromide mixture from the *N*-*n*-butyl derivative **4c** were satisfactorily accounted for.

Assignment of the 1,2-dibromopentane in the *N*-*n*-pentyl dibromide mixture was made by analogy to that for 1,2-dibromobutane.[13] *erythro*- and *threo*-2,3-dibromopentane (not previously studied by $^{13}C$ NMR) assignments were aided by GLC studies (vide supra) which indicated the

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(10) M. Sanz-Burata, S. Julia, and J. Irurre, *Afinidad*, **No. 238**, 259 (1965); *Chem. Abstr.*, **64**, 12538*b* (1966).

(11) J. G. Grasselli, Ed., "Atlas of Spectral and Physical Constants for Organic Compounds", Chemical Rubber Publishing Co., 1973.

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(13) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, 1972.

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Table VII. $^{13}$C NMR Chemical Shift Assignments and Product Distribution of Dibromide Derivatives[a]

| reaction | product | distrib,[b] % | chemical shift C-1 | C-2 | C-3 | C-4 | C-5 |
|---|---|---|---|---|---|---|---|
| 2 | 1,2-dibromo-2-methylpropane | >99 | 44.9 (44.6)[c] | 62.2 (61.7) | 32.1 (31.8) | | |
| | 1,2-dibromobutane | 61.8 | 35.6 (35.5)[c] | 54.4 (54.3) | 29.0 (29.0) | 11.0 (10.9) | |
| | *meso*-2,3-dibromobutane | 20.9 | 25.3 | 54.0 | 54.0 | 25.3 | |
| 3 | *meso*-2,3-dichlorobutane[d] | | (21.8) | (61.3) | (61.3) | (21.8) | |
| | *dl*-2,3-dibromobutane | 17.3 | 20.5 | 52.3 | 52.3 | 20.5 | |
| | *dl*-2,3-dichlorobutane[d] | | 19.7 | 60.2 | 60.2 | 19.7 | |
| 4 | 1,2-dibromopentane[d] | 70.9 | 38.0 | 52.8 | 36.4 | 20.1 | 13.3 |
| | *threo*-2,3-dibromopentane[d] | 18.6 | 25.3 | 51.8 | 63.2 | 30.5 | 11.4 |
| | *erythro*-2,3-dibromopentane[d] | 10.5 | 21.7 | 52.2 | 62.2 | 27.5 | 12.7 |

[a] Chemical shifts are given in parts per million relative to $Me_4Si$. Typical conditions were as follows: 2 kHz width, 8K data (resolution 0.05 ppm); pulse width 5 ms (28 °C) with a pulse repetition time of 2 s; solutions were ~300-500 mg in 1.5 mL of $CDCl_3$; $Cr(acac)_3$ was added where mixtures were present in a concentration of 0.04 mol $L^{-1}$. In such cases a gated decoupling technique was used in addition with a pulse delay of 20 s, and a signal/noise ratio of 80 was obtained. The values in parentheses are those of the literature. [b] Calculated by taking the total yield as 100%. [c] See ref 13. [d] See ref 14.

threo stereoisomer to be present in an appreciably greater amount (ca. 17%) than the erythro isomer (ca. 10%). Gated decoupling techniques and the presence of a small amount of chromium(III) acetylacetonate also helped in this respect.

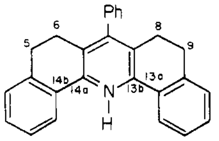
Previous $^{13}$C spectral investigation of *meso*- and *dl*-2,4-dichloropentane showed that each carbon in the *dl* structure appeared at a lower field compared to the analogous carbon of the meso isomer,[15] in contrast to the situation for *meso*- and *dl*-2,3-dibromobutanes.

The $^{13}$C NMR assignments of Table VII for *threo*- and *erythro*-2,3-dibromopentanes were achieved as follows.

(a) The off-resonance decoupled spectrum exhibited two sets of two quartets (assigned to $C_1$ and $C_5$), two triplets (assigned to $C_4$), and two sets of two doublets (assigned to $C_2$ and $C_3$).

(b) The proton decoupled spectrum obtained by the gated decoupling procedure and addition of chromium(III) acetylacetonate displayed two distinct five-peak sets.

(c) The shielding of the $\gamma$-carbon by a halogen atom is known.[16,17a] This shielding should apply to $C_1$ in both isomers. However, it is the nonbonded interaction which leads to an upfield shift at the $\gamma$-carbon and this is more effective in the gauche rotamer.[17b] Hence, the signal at 21.7 ppm was assigned to $C_1$ of the erythro isomer **5a** (see diagram), while that at 25.3 ppm was attributed to $C_1$ of the threo isomer **5b**. Similar reasoning was used in assigning $C_4$ in both isomers.



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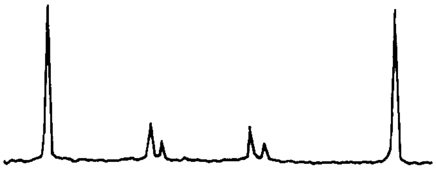

**Figure 1.** Proton noise-decoupled $^{13}$C NMR spectrum of the olefinic region of a mixture of 1-, *cis*-2-, and *trans*-2-octenes: Cr(acac) (0.04 mol $L^{-1}$) and gated decoupling; sample concentration 150 mg/mL; observed width 800 Hz; 2000 pulses; PR = 20 s; 28 °C.

(d) The differences found between the shifts of $C_2$, $C_3$, and $C_5$ in the two isomers are much less and are due to second-order effects.

**$^{13}$C NMR Assignments for Olefins.** Our assignments for styrene *o*-, *m*-, and *p*-carbons (Table VIII) follows that of ref 18, but not that of ref 17c. We rationalized that the *m*-carbon shift, little affected sterically or electronically, should be close to that of benzene (128.7 ppm[17c]). The *p*-carbon is more deshielded by the electronic effect[17d] than the *o*-carbon which is partially affected by a steric effect.[17e]

Carbon shifts for 1-heptene and $C_3$–$C_6$ for 1-hexene (apparently not previously assigned) were correlated with literature values[19] for 1-octene (see Table VIII). Assignments of carbons in *cis*-2- and *trans*-2-undecene were by analogy with the corresponding isomers of dodecene.[20] Assignments of various dodecene isomers (except for *trans*-3-dodecene) were by analogy with the available literature data.[20] Two olefinic signals which remained were assigned to the trans-3 isomer, but the aliphatic carbon signals were not assigned for this isomer. Moreover, the aliphatic carbons of *cis*-3- and *trans*-3-undecene and of *cis*-3- and *trans*-3-dodecene could not be assigned unambiguously due to the lack of literature data.

**$^{13}$C NMR Qualitative Estimation of Product Ratios.** Two common procedures for the use of $^{13}$C NMR for

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(15) Y. Inoue, I. Ando, and A. Nishioka, *Polymer J.* 3 (2), 246 (1972).

(16) Cf. the "rule of six": M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950).

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Table VIII. $^{13}$C NMR Chemical Shift Assignments and Product Distribution of Olefinic Products[a]

| reaction | product | distrib,[b] % | chemical shift C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 | C-10 | C-11 | C-12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | styrene[c] | 100.0 | 113.7 | 136.9 | 137.6 | 127.7 | 128.5 | 126.2 | | | | | | |
| | | | (112.0)[d] | (135.5) | (136.1) | (126.7) | (126.7) | (125.0) | | | | | | |
| 5 | 1-hexene | 66.7 | 114.1 | 139.1 | 33.6 | 31.3 | 22.3 | 14.0 | | | | | | |
| | | | (113.2)[e] | (137.5) | | | | | | | | | | |
| | *cis*-2-hexene | 10.4 | 12.7 | 123.8 | 130.4 | 29.1 | 22.3 | 13.4 | | | | | | |
| | | | (12.3)[f] | (123.7) | (130.6) | (29.3) | (23.0) | (13.5) | | | | | | |
| | *trans*-2-hexene | 19.0 | 18.0 | 124.8 | 131.5 | 34.9 | 22.8 | 13.4 | | | | | | |
| | | | (17.5)[f] | (124.7) | (131.5) | (35.1) | (23.1) | (13.4) | | | | | | |
| | *cis*-3-hexene | *g* | 14.0 | 21.8 | 130.4 | 130.4 | 21.8 | 14.0 | | | | | | |
| | | | (14.3)[f] | (20.6) | (131.0) | (131.0) | (20.6) | (14.3) | | | | | | |
| | *trans*-3-hexene | 3.9 | 13.4 | 25.7 | 131.0 | 131.0 | 25.7 | 13.4 | | | | | | |
| | | | (13.9)[f] | (25.8) | (131.2) | (131.2) | (25.8) | (13.9) | | | | | | |
| 7 | 1-heptene[h] | *i* | 114.1 | 139.2 | 34.0 | 28.8 | 31.6 | 22.7 | 14.1 | | | | | |
| | *cis*-2-heptene | | 12.7 | 123.6 | 130.9 | 26.7 | 32.0 | 22.4 | 14.1 | | | | | |
| | | | (12.5)[f] | (123.6) | (131.0) | (27.0) | (32.3) | (22.4) | (13.9) | | | | | |
| | *trans*-2-heptene | 18.0 | 18.0 | 124.6 | 131.7 | 32.5 | 32.0 | 22.4 | 14.1 | | | | | |
| | | | (17.7)[f] | (124.6) | (131.8) | (32.8) | (32.4) | (22.7) | (13.9) | | | | | |
| | *cis*-3-heptene | | 14.7 | | 131.7 | 129.2 | 29.4 | 28.3 | 13.7 | | | | | |
| | | | (14.3)[f] | (20.9)[j] | (131.9) | (129.2) | (29.6) | (23.3) | (13.6) | | | | | |
| | *trans*-3-heptene | | 14.4 | 25.7 | 132.2 | 129.2 | 35.4 | 22.7 | 13.4 | | | | | |
| | | | (14.0)[f] | (26.0) | (132.4) | (129.4) | (35.1) | (23.2) | (13.5) | | | | | |
| 8 | 1-octene | 70.5 | 114.1 | 139.1 | 34.0 | 29.1 | 29.0 | 31.9 | 22.8 | 14.1 | | | | |
| | | | (113.2)[k] | (138.2) | (33.2) | (28.4) | (28.3) | (31.2) | (22.0) | (13.0) | | | | |
| | *cis*-2-octene | 10.7 | 12.7 | 123.5 | 130.9 | 26.9 | 29.5 | 31.7 | 22.8 | 14.1 | | | | |
| | | | (11.5)[k] | (122.6) | (130.0) | (26.1) | (28.7) | (30.9) | (21.9) | (13.0) | | | | |
| | *trans*-2-octene | 18.3 | 17.9 | 124.5 | 131.7 | 32.7 | 29.5 | 31.6 | 22.8 | 14.1 | | | | |
| | | | (16.7)[k] | (123.7) | (130.9) | (32.0) | (28.8) | (30.9) | (21.9) | (13.0) | | | | |
| 9 | 1-undecene[f] | 35[l] | 139.1 | 114.1 | 34.0 | 29.8 | 29.8[m] | 29.6* | 29.4* | 29.2* | 32.1 | 22.9 | 14.2 | |
| | *cis*-2-undecene[f] | 15.1 | 12.8 | 123.5 | 130.9 | 27.0 | 32.8* | 29.1–29.8 | 29.1–29.8 | 29.1–29.8 | 32.1* | 22.9 | 14.2 | |
| | *trans*-2-undecene | 26.8 | 18.0 | 124.5 | 131.7 | 34.0 | 32.8* | 29.1–29.8 | 29.1–29.8 | 29.1–29.8 | 32.1* | 22.9 | 14.2 | |
| | *cis*-3-undecene[f] | 9.3 | *n* | | 131.5 | 129.4 | | | | | | | | |
| | *trans*-3-undecene | 10.5 | | | 131.9 | 130.1 | | | | | | | | |
| 10 | 1-dodecene | 44.0 | 139.1 | 114.2 | 34.1 | 29.9 | 29.9 | 29.9 | 29.7 | 29.5 | 29.3 | 32.9 | 23.0 | 14.3 |
| | | | (139.0)[o] | (114.8) | (34.5) | (30.5) | (30.5) | (30.5) | (30.5) | (30.5) | (30.1) | (32.8) | (23.6) | (14.9) |
| | *cis*-2-dodecene | 15.4 | 12.9 | 123.6 | 131.0 | 27.1 | 29.5 | 29.5 | 29.5 | 29.5 | 29.5 | 32.2 | 23.0 | 14.3 |
| | | | (12.3)[o] | (123.3) | (130.6) | (27.2) | (29.9) | (29.9) | (29.9) | (29.9) | (29.9) | (32.3) | (22.9) | (14.2) |
| | *trans*-2-dodecene | 25.9 | 18.1 | 124.6 | 131.6 | 34.1 | 32.2 | 32.2 | 32.2 | 32.2 | 32.2 | 34.1 | 23.0 | 14.3 |
| | | | (18.8)[o] | (125.2) | (132.6) | (33.7) | (31.0) | (31.0) | (31.0) | (31.0) | (31.0) | (33.7) | (23.8) | (15.0) |
| | *cis*-3-dodecene | 6.0 | *b* | | 131.8 | 129.4 | | | | | | | | |
| | | | | | (132.1) | (129.7) | | | | | | | | |
| | *trans*-3-dodecene[f] | 8.7 | | | 131.9 | 129.5 | | | | | | | | |

[a] See footnote a in Table VII. The spectral width was 4 kHz for qualitative analysis and 800 Hz for quantitative analysis. [b] Calculated by taking the total yield of each reaction as 100%. [c] C$_1$–C$_6$ refers to C$_\beta$, C$_\alpha$, C$_i$, C$_o$, C$_m$, and C$_p$, respectively. [d] See ref 18. [e] C$_1$ and C$_2$ only have been assigned before: J. K. Becconsal and P. Hampson, *J. Mol. Phys.*, 10, *21* (1965). [f] Literature values are those of J. W. Haan and A. van der Ven, *Org. Magn. Reson.*, 5 (3), 147–153 (1973). [g] Difficult to determine due to overlap with C-3 of the cis-2 isomer. [h] No literature data available; assigned by analogy with 1-octene. [i] Ratio was not determined by this procedure. [j] Could not be assigned due to overlap. [k] See ref 19. [l] The 4-undecenes were also present (3.2%). Chemical shift assignments (in parts per million) of olefinic carbons were as follows: C-4, cis-4 at 130.3; C-5, cis-4 at 129.6; C-4, trans-4 at 130.6; C-5, trans-4-undecene at 130.3. [m] The asterisk indicates ambiguity. [n] Could not be assigned unambigously. [o] See ref 20.

quantitative analysis are pulse-modulated decoupling[21] and the use of a paramagnetic species.[22,23] We tested each technique on authentic samples of 1-hexene and 1-octene. With the first, varying the pulse delay between 5 and 30 s still showed differences in signal intensity of $C_1$ and $C_2$ of the alkenes.[24]

The use (0.04 mol $L^{-1}$) of copper(II) acetylacetonate or chromium(III) acetylacetonate gave an improvement, but only when we combined the two procedures, gated decoupling and addition of 0.04 mol $L^{-1}$ of chromium(III) acetylacetonate, did we obtain satisfactory results at spectral widths of 800 (for olefinic products) and 2000 Hz (for dibromides). Thus, for example, Figure 1 illustrates the almost total elimination of the NOE among the olefinic carbons, leading to almost equal intensities. The isomer ratios were calculated from the peak intensities of nonoverlapping olefinic carbons (see Table VIII for details of product distribution). Thus, the ratio of 1-, *cis*-2-, *trans*-2-, and *trans*-3-hexenes was calculated from the intensities of the corresponding $C_2$, $C_2$, $C_2$, and $C_3$ peaks, respectively. The amount of cis-3 isomer was difficult to determine due to overlap.

The ratios obtained from the quantitative $^{13}C$ NMR measurements we consider more reliable than those from the GLC results: e.g., poor resolution gave only three partially overlapping peaks in the GLC of the undecenes mixture, shown by $^{13}C$ NMR to contain seven isomers. The quantitative $^{13}C$ NMR spectral analysis error is estimated as (i) 5% from the remaining NOE and (ii) 5% from the difference in the spin relaxation times of the olefinic carbons.

**Base-Induced Isomerization of Alkenes.** Alkenes undergo isomerization under drastic conditions: thus, 1-heptene with *t*-BuOK in *t*-BuOH at 142 °C gives,[25] after 44 h, 15% of *cis*-2-heptene and 52% of *trans*-2-heptene.

We heated 1-octene with 2,4,6-triphenylpyridine at 150 °C for 48 h or with sodium hydride in THF at 80 °C for 4 h without change, indicating that our results did not involve base-catalyzed isomerization under the thermolysis conditions. 1-Decene with 5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium triflate (**6**) and 2,4,6-triphenylpyridine (as a flux) at 160 °C for 5 h gave a mixture of 1-, *trans*-2-, *cis*-2-, *trans*-3-, and *cis*-3-decenes in the ratio of 59.7:13.3:8.9:18.11 (in addition, two peaks at $\delta$ 115.6 and 120.6 were observed in the $^{13}C$ NMR of the mixture and could not be identified). That only 35% of the 1-undecene was obtained in the thermolysis of **4i**, indicates that isomerization by another process in addition to the acid-catalyzed one was involved: under the thermolysis conditions the olefin is being distilled over and removed from the reaction mixture subsequent to its formation, while in the above acid-induced isomerization the olefin remains in the reaction mixture for a period of 5 h before it is allowed to distill at diminished pressure.

## Conclusions

For the hexene, heptene, and octene cases, the proportion of terminal olefin was ca. 70% (Tables VII and VIII) together with the *trans*-2-, *cis*-2, and 3-olefins in decreasing amounts. This product distribution could indicate an E1 elimination mechanism, with the formation of primary carbonium ions which partially rearrange before elimination of a proton. Solvolysis experiments[26] support this interpretation.

Previous methods for the conversion of a primary amine into an olefin include the Hofmann elimination which requires methylation to $RCH_2CH_2N^+Me_3I^-$, conversion to the quaternary hydroxide, and pyrolysis.[27] Hunig et al. recently reported a simple variant[28] involving heating alkyltrimethylammonium iodides at 140–170 °C; however, dimethylamines are formed in considerable amounts. The Cope reaction[29] converts tertiary amines into amine oxides which pyrolyze to olefins at 80–160 °C.[27] Distillation of an amine with phosphoric acid to yield an olefin[30] (≤50%) has also been reported. Acylamines with phosphorus pentoxide give olefins.[31] Quaternary ammonium salts with phenyllithium in ether or with potassium amide in liquid ammonia form olefins via ylides.[27b,32]

Baumgarten and DeCristopher[33] carried out deamination via *N*-alkylsaccharin derivatives most succesfully for styrene (65%), and with other *N*-alkyl derivatives, substitution products were also obtained. A similar procedure utilizing the disulfonylamines leads to mixtures.[34] The nitrous acid reaction of amines[35] and the nitrosamide pyrolysis reaction[36] give olefinic byproducts but are not practical from a synthetic standpoint. The present reaction is superior to most of the previous methods for the conversion of primary amines into olefins.

## Experimental Section

Melting points (uncorrected) were determined with a Kofler or a Reichart hot-stage apparatus. IR spectra were measured for $CHBr_3$ mulls with a Perkin-Elmer 257 instrument. $^1H$ NMR and $^{13}C$ NMR spectra were recorded with Perkin-Elmer R12 (60 MHz) and JEOL FX100 spectrometers, respectively ($Me_4Si$ as an internal standard). Gas–liquid chromatograms utilized a Perkin-Elmer Model F11 flame-ionization chromatograph.

**14-(2-Phenylethyl)-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium Tetrafluoroborate (3).** 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]xanthylium tetrafluoroborate[37] (4 g, 0.0098 mol) in magnesium-dried ethanol (15 mL) and 2-phenylethylamine (2.5 mL, 0.019 64 mol) were stirred for 72 h at 20 °C: **3** precipitated (see Table I).

***N*-Alkyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium Trifluoromethanesulfonates (4). General Procedure.** 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]xanthylium trifluoromethane sulfonate[38] (2 g, 0.0039 mol) was suspended in

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sodium-dried ether (20 mL). The amine (0.0047 mol) was added dropwise, and the mixture was stirred for 6 h at 20 °C. The yellowish product was filtered off and washed with ether to give the product (see Table I).

**Thermolysis of Tetrahydrodibenz[*c*,*h*]acridinium Tetrafluoroborate 3.** The dried salt **3** (2.5 g, 0.0045 mol) and 2,4,6-triphenylpyridine (1.4 g, 0.0045 mol); dried for 2 h, 1.0 mm, 20 °C) were finely ground and dried at 60 °C (2.5 mm, 30 min). The temperature was then raised to 150–160 °C (2.5 mm, 40 min) and the sample finally heated with a direct flame for 5 min. The distillate collected to give styrene (120 mg, 26%), contaminated with 15% ethyl 2-phenylethyl ether.

**General Procedure for the Thermolysis of *N*-Alkyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium Trifluoromethanesulfonates (4). Procedure A.** The dried derivative **4** (4 g, 0.0064 mol) and 2,4,6-triphenylpyridine (3 g, 0.0098 mol; dried at 40 °C, 0.5–1.0 mm, 2–3 h) were finely ground. The mixture was dried for a further 30 min (60 °C, 500 mm) in the thermolysis apparatus. The trap was then cooled with liquid nitrogen. The temperature was raised until the mixture melted and continuous bubbling was observed (temperature, pressure, and time are recorded in Table V). When the thermolysis appeared to be complete (30 min after bubbling ceased), the temperature was raised to 200 °C (200 mm) for an additional 20 min.

**Procedure B.** In a typical experiment **4d** (4 g, 0.0069 mol) and 2,4,6-triphenylpyridine (3 g, 0.0098 mol) were dried and ground together finely. The thermolysis flask was heated at 180-200 °C (760 mm) for 8 h, while the trap, containing bromine (1.2 g, 0.0075 mol) dissolved in chloroform (7 mL), was cooled with a salt-ice bath. The chloroform solution was washed with saturated aqueous sodium thiosulphate (3 × 5 mL) and then with $H_2O$ (3 × 5 mL) and dried over anhydrous magnesium sulphate for 2 h. Chloroform was removed in vacuo and the residue distilled at 5 mm to give the product (see Table 5, 6).

**Thermolysis of 14-*n*-Dodecyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium Triflate (4j) in the Absence of 2,4,6-Triphenylpyridine.** Salt **4j** (3 g, 0.0044 mol) was thermolyzed at 160 °C (20 mm) for 4 h. The temperature was then raised to 180 °C, (20 mm) 2 h to complete distillation. The product (0.73, 99%) was shown by $^{13}$C NMR quantiative and qualitative analysis to be a mixture of 1-, *trans*-2-, *cis*-2-, *trans*-3-, *cis*-3-, *trans*-4-, and *cis*-4-dodecenes in the ratio of 36.9:23.8:20.5:12.3:5.4:2.9 (the percentage of the last isomer being difficult to determine). The thermolysis residue was recrystallized from acetic acid to give **5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium trifluoromethanesulfonate (6)**: 99%; yellow prisms; mp 280–285 °C; IR ($CHBr_3$) 1620 cm$^{-1}$; $^1$H NMR (TFA) $\delta$ 3.0 (8 H, m), 7.28–7.90 (11 H, m), 8.02–8.38 (2 H, m); $^{13}$C NMR ($Me_2SO$-$d_6$/$CDCl_3$) $\delta$ 25.1 (t, $C_5$, $C_9$), 27.0 (t, $C_6$, $C_8$), 126.2 (d, $C_4$, $C_{10}$), 126.9 (d, $C_3$, $C_{11}$), 127.4 (d, $C_2$, $C_{12}$), 127.6 (s, $C_{6a}$, $C_{7a}$), 128.0 (d, $C_o$), 128.7 (d, $C_p$), 128.9 (d, $C_m$), 131.6 (d, $C_1$, $C_{13}$), 132.7 (s, $C_i$), 134.9 (s, $C_{13a}$, $C_{14b}$), 139.1 (s, $C_{4a}$, $C_{9a}$), 146.0 (s, $C_{13b}$, $C_{14a}$), 154.4 (s, $C_7$). Anal. Calcd for $C_{28}H_{17}F_3NO_3S$: C, 66.0; H, 4.4; N, 2.8; S, 6.3. Found: C, 65.7; H, 4.3: N, 2.8; S, 6.3.

**Acid-Induced Isomerization of 1-Decene.** 1-Decene (1 g, 0.006 mol), salt **6** (3.1 g, 0.006 mol), and 2,4,6-triphenylpyridine (1.8 g, 0.006 mol) were refluxed at 160 °C for 5 h. The product was distilled at diminished pressure to give a mixture of 1-, *trans*-2-, *cis*-2-, *trans*-3-, and *cis*-3-decene in the ratio of 59.7:13.3:8.9:18.1 as shown by $^{13}$C NMR qualitative[20] and quantitative[20] analyses.

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**Registry No. 1**, 53217-56-4; **2**, 73377-38-5; **3**, 82135-18-0; **4a**, 76017-85-1; **4b**, 82135-20-4; **4c**, 76017-66-8; **4d**, 82135-22-6; **4e**, 76017-70-4; **4f**, 82135-24-8; **4g**, 82135-26-0; **4h**, 73377-30-7; **4i**, 73377-32-9; **4j**, 73377-34-1; **5a**, 22415-74-3; **5b**, 22415-73-2; **6**, 82135-27-1; $PhCH_2CH_2NH_2$, 64-04-0; $Me_2CHCH_2NH_2$, 78-81-9; $BuNH_2$, 109-73-9; $Me(CH_2)_5NH_2$, 111-26-2; $H_2N(CH_2)_6NH_2$, 124-09-4; $Me(CH_2)_6NH_2$, 111-68-2; $Me(CH_2)_7NH_2$, 111-86-4; $Me(CH_2)_{10}NH_2$, 7307-55-3; $Me(CH_2)_{11}NH_2$, 124-22-1; 2,4,6-triphenylpyridine, 580-35-8; 1,2-dibromo-2-methylpropane, 594-34-3; 1,2-dibromobutane, 533-98-2; *meso*-2,3-dibromobutane, 5780-13-2; *dl*-2,3-dibromobutane, 598-71-0; 1,2-dibromopentane, 3234-49-9; styrene, 100-42-5; 1-hexene, 592-41-6; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8; 1-heptene, 592-76-7; *cis*-2-heptene, 6443-92-1; *trans*-2-heptene, 14686-13-6; *cis*-3-heptene, 7642-10-6; *trans*-3-heptene, 14686-14-7; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9; 1-undecene, 821-95-4; *cis*-2-undecene, 821-96-5; *trans*-2-undecene, 693-61-8; *cis*-3-undecene, 821-97-6; *trans*-3-undecene, 1002-68-2; 1-dodecene, 112-41-4; *cis*-2-dodecene, 7206-26-0; *trans*-2-dodecene, 7206-13-5; *cis*-3-dodecene, 7239-23-8; *trans*-3-dodecene, 7206-14-6.

**Supplementary Material Available:** Tables II-IV containing $^1$H and $^{13}$C NMR and IR spectral data for various acridinium trifluoromethanesulfonates (3 pages). Ordering information is given on any current masthead page.

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# Solvolysis of *N*-*n*-Alkylacridiniums in Phenol and Carboxylic Acids. Primary Carbonium Ions as Possible Intermediates

Alan R. Katritzky* and Azzahra M. El-Mowafy

*Department of Chemistry, University of Florida, Gainesville, Florida 32611, and the School of Chemical Sciences, University of East Anglia, Norwich, England NR4 7TJ*

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*N*-*n*-Octyl (**1a**) and *N*-*n*-dodecylacridinium (**1b**) ions solvolyze in phenol to give mixtures of the *n*-alkyl phenyl ethers and all the isomeric secondary straight-chain *o*- and *p*-alkylphenols. Solvolyses of **1a** in carboxylic acids give a mixture of 1-, 2-, 3-, and 4-octyl carboxylic esters. Structures are deduced by GC/MS. Mechanisms are discussed.

Pyrolyses of the *N*-*n*-alkylacridiniums **1** (Chart I) give olefins in high yield: the isomer distribution led us to conclude that an E1 mechanism involving a primary carbonium ion was probably operative.[1] We have now studied the solvolysis in phenol solution of two representative examples of **1**, i.e., the *n*-octyl (**1a**) and *n*-dodecyl (**1b**) derivatives, and present further evidence in support of our former conclusions.

Initially we carried out a typical bimolecular substitution reaction. The *N*-*n*-octyl derivative **1a** with 1.2 equiv of sodium phenoxide in ethanol gave the $S_N2$ nucleophilic substitution product **2** (81%) in >99% purity as shown

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