

One-pot Conversions of Amines into Olefins *via* Non-isolated Pyridinium Intermediates

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Secondary alkyl primary amines are converted by the pyrylium salt (1) directly at 20 °C into olefins *via* the corresponding secondary carbenium ions. Isomeric olefin mixtures are elucidated and result from carbenium ion rearrangements.

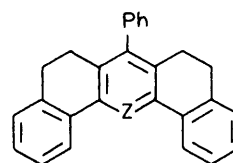
A MAJOR aim in our work¹ on the pyrylium-mediated conversion of primary amines into other functionalities has been the discovery of mild conditions. Following the discovery of amine + pyrylium → pyridinium conversion at 20 °C using Et₃N and HOAc as catalysts,² the emphasis has been on variation of the pyrylium salt.³ Extensive kinetic work⁴ has demonstrated that the mechanism and rate for the transfer of an *N*-substituent from a pyridinium salt depends on both the group transferred and on substitution in the pyridine ring. We now report the first examples of reactions in which the pyridinium intermediate spontaneously reacts further under the conditions of its formation.

Preparation of Olefins from Secondary Alkyl Primary Amines.—The pentacyclic pyrylium salt (1) reacts with primary alkyl primary amines RCH₂NH₂ to give the pyridinium salts (2) which readily react with nucleophiles to give substitution products RCH₂X⁵ and form olefins at 150 °C.⁶ We now find that (1) reacts with secondary alkyl primary amines RCH₂CHR'NH₂ to give, at 20 °C, olefins directly: evidently, pyridinium compounds of type (3) spontaneously form carbenium ions RCH₂CH⁺R' which, in time, give olefins.

Cyclohexene formation from cyclohexylamine and the pyrylium salt (1) in dichloromethane at 20 °C was shown by t.l.c. (CHCl₃) to require 24 h. Using this procedure, alkenes were prepared from a series of secondary alkyl primary amines and isolated as dibromides by distillation with the dichloromethane from the reaction mixture under bromine in chloroform (see Table 1).

The reaction was relatively fast for cyclopentyl-, cyclohexyl-, and cycloheptyl-amine and also for 2-

aminoheptane and 2-amino-6-methylheptane. Formation of the intermediate pyridinium salts is much slower for the more sterically hindered cyclododecylamine, 3-aminopentane, and 2-amino-3-methylbutane. Thus, after being stirred for 5 days, the reaction mixture from



- (1) Z = O⁺
 (2) Z = N⁺CH₂R
 (3) Z = N⁺CHR'CH₂R

cyclododecylamine with (1) gave a mixture of cyclododecenes (yield 33%, conversion 26%) and unchanged amine (see Table 1). 1-Phenylethylamine does not react with the pyrylium salt (1) under the conditions described.

Cyclopentylamine, cyclohexylamine, and cycloheptylamine each gave solely the *trans*-dibromocycloalkane as shown by ¹³C n.m.r. (see Scheme 1 and Table 2) and i.r. spectral comparisons with literature data.⁷ Cyclododecylamine gave both *cis*- and *trans*-cyclododecene as shown by the relative intensities of ¹³C n.m.r. peaks due to the olefinic carbons (33% *cis*- and 67% *trans*-).

Mixtures of dibromides were obtained from the open-chain amines. 3-Aminopentane gave *erythro*- (14) and *threo*-2,3-dibromopentane (15) and also 1,2-dibromopentane (16) (see Table 2) which would be formed from the *trans*- and *cis*- isomers of pent-2-ene (11) and (12)

TABLE 1

Preparation of alkenes from 5,6,8,9-tetrahydro-7-phenyldibenzo[*c,h*]xanthylium tetrafluoroborate and secondary alkyl primary amines

Amine	Reaction time (h)	Alkene	Yield of dibromide (%) ^a	B.p. (°C/mmHg)	Lit. b.p. (°C/mmHg)	Ref.
Cyclopentylamine	27	Cyclopentene	63 ^b	35/1.8	72.4—72.6/15	7
Cyclohexylamine	27	Cyclohexene	90 ^b	50/0.8	90.1—92.3/9	7
Cycloheptylamine	27	Cycloheptene	95 ^b	52/0.0075	82—83/1.9	7
Cyclododecylamine	120	Cyclododecenes	33 ^c			
3-Aminopentane	140	Pentenes	45	81/42.5		
2-Amino-3-methylbutane	400 ^d	Methylbutenes	36	94/83		
2-Aminoheptane	24	Heptenes	71	60/2.9		
2-Amino-6-methylheptane	27	Methylheptenes	74	43/0.005		

^a Characterised by i.r., ¹H n.m.r., and ¹³C n.m.r. (see Table 2). ^b Only *trans*-isomer detected. ^c Yield of alkenes calculated from ¹H n.m.r. of a mixture of alkenes (35%) and amine (65%). 33% *cis*- and 67% *trans*-. ^d After 7 days 28%.

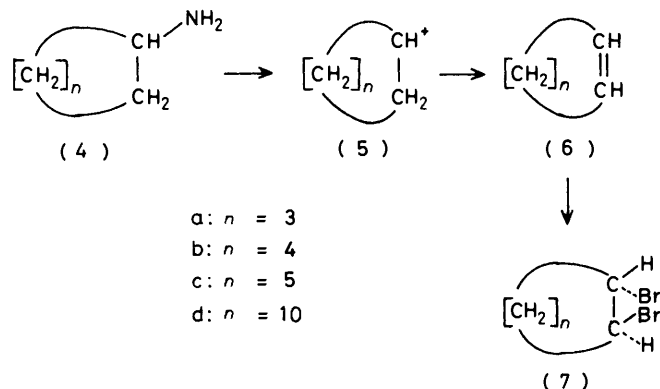
TABLE 2

¹³C N.m.r. chemical shifts of dibromoalkanes ^{a,b}

Compound	Compd. no.	Proportion formed ^c (%)						Me
			C-1	C-2	C-3	C-4	C-5	
<i>trans</i> -1,2-Dibromocyclopentane	(7a)	100	57.2	33.8	21.1	—	—	—
<i>trans</i> -1,2-Dibromocyclohexane (lit. ^d)	(7b)	100	55.0 d	31.8 t	22.3 t	—	—	—
			(54.9)	(31.8)	(22.3)	—	—	—
<i>trans</i> -1,2-Dibromocycloheptane	(7c)	100	59.9	33.0	23.0	26.4 ^e	—	—
<i>erythro</i> -2,3-Dibromopentane (lit. ^f)	(14)	50	25.2 q	51.8 d	63.1 d	30.4 t	11.3 q	—
			(25.3)	(51.8)	(63.2)	(30.5)	(11.4)	—
<i>threo</i> -2,3-Dibromopentane (lit. ^f)	(15)	40	21.6 q	52.1 d	62.1 d	27.5 t	12.6 q	—
			(21.7)	(52.2)	(62.2)	(27.5)	(12.7)	—
1,2-Dibromopentane (lit. ^f)	(16)	10	38.0 t	52.8	36.3	20.1 t	13.3	—
			(38.0)	(52.8)	(36.4)	(20.1)	(13.3)	—
1,2-Dibromo-3-methylbutane (Calc.)	(23)	5–10	34.2	61.6	30.0	15.6 ^g	—	21.7 ^g
			(40.4)	(68.0)	(37.1)	(18.6)	—	(18.6)
2,3-Dibromo-3-methylbutane (Calc.)	(24)	65	23.5 q	59.5 d	68.3 s	28.0 ^g q	—	35.0 ^g q
			(17.4)	(67.0)	(65.1)	(28.6)	—	(28.6)
3,4-Dibromo-3-methylbutane ^h (Calc.)	(25)	25–30	10.0 q	35.2 t	68.8 s	42.0 t	—	30.2 q
			(7.4)	(39.0)	(66.1)	(51.6)	—	(28.6)
1,2-Dibromoheptane (Calc.)	(34)	5	—	51.5 d	—	—	—	—
			—	(58.7)	—	—	—	—
<i>erythro</i> -2,3-Dibromoheptane (Calc.; 2,3-dibromoheptane)	(35)	50	—	52.3 d	61.6 d	—	—	—
			—	(57.7)	(67.4)	—	—	—
<i>threo</i> -2,3-Dibromoheptane	(36)	30	—	53.1 d	60.0 d	—	—	—
3,4-Dibromoheptane ⁱ (Calc.)	(37)	15	—	—	61.5 d	59.1 d	—	—
			—	—	(67.4)	(64.5)	—	—
1,2-Dibromo-6-methylheptane (Calc.)	(43)	—	—	51.4	—	—	—	—
			—	(58.7)	—	—	—	—
<i>erythro</i> -2,3-Dibromo-6-methylheptane (Calc.; 2,3-dibromo-6-methylheptane)	(44)	—	—	52.2 ^j d	61.7 d	—	—	—
			—	(57.7)	(67.7)	—	—	—
<i>threo</i> -2,3-Dibromo-6-methylheptane	(45)	—	—	53.0 d	60.2 d	—	—	—

^a In p.p.m. downfield from internal Me₃Si with multiplicities obtained by off-resonance decoupling experiments. In CDCl₃. ^b In parentheses, literature shifts or shifts calculated by the 'Lindeman-Adams rule' (refs. 18 and 19). ^c Calculated by the relative intensities of peaks due to the following carbon atoms: C-5 for dibromopentanes, methyl carbons for dibromomethylbutanes, and for dibromoheptanes C-2 for 1,2- and C-3 for 2,3- and 3,4-dibromoheptanes. ^d Ref. 7. ^e Assigned by intensity. ^f Ref. 20. ^g The assignments of these signals may be reversed. ^h 1,2-Dibromo-2-methylbutane. ⁱ Stereochemistry unknown. ^j Tentative assignment.

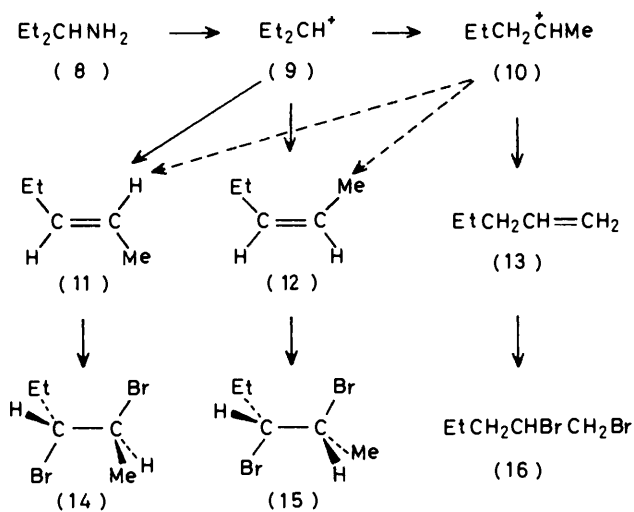
and from pent-1-ene (13), respectively (Scheme 2). 2-Amino-3-methylbutane gave 2,3-dibromo- (24) and 1,2-dibromo-3-methylbutane (23), corresponding to the two expected products of elimination, 2-methylbut-2-ene



SCHEME 1

(21) and 3-methylbut-1-ene (20). However, 1,2-dibromo-2-methylbutane (25) was also formed (see Table 2 and Scheme 3).

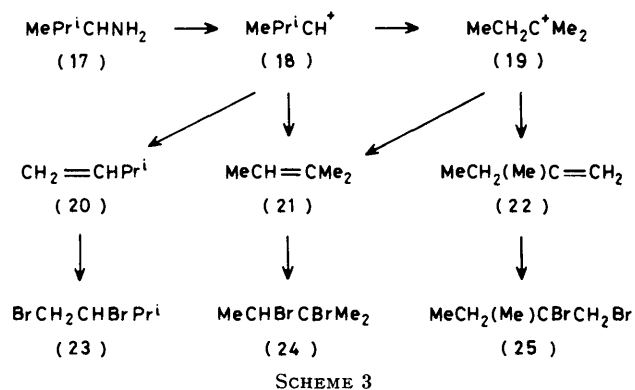
Isomeric dibromides derived from 2-aminoheptane and 2-amino-6-methylheptane were identified by the ¹³C n.m.r. chemical shifts of carbons directly attached to bromine (Table 2). The expected 1,2-, *erythro*-2,3-, and



SCHEME 2

threo-2,3-dibromo-compounds were accompanied by a 3,4-dibromoheptane (from 2-aminoheptane) and by three further dibromomethylheptanes (from 2-amino-6-methylheptane) (see Schemes 4 and 5).

These mixtures of dibromides indicate that the carbocation ions initially formed from the intermediate pyridinium salts isomerise at least, in part, before elimination to the olefin occurs.



Formation of isomeric dibromides by alkene or dibromide rearrangement was discounted. Alkene rearrangement generally requires the presence of strong base,⁸ acid,⁹ metals or metal complexes,¹⁰ or high temperatures.⁹ Thus, pent-2-ene is stable at 440 °C,¹¹ neither *cis*- nor *trans*-pent-2-ene are isomerised on distillation,¹² and no interconversion of 2-methylbut-2-ene and 3-methylbut-1-ene occurs below 450 °C.¹³ Rearrangement of dibromides also requires high temperatures¹⁴ and equilibrated dibromopentanes^{15,16} and dibromo-methylbutanes¹⁷ give other than vicinal dibromides.

¹³C N.M.R. Assignments of Dibromides.—These assignments (Table 2) were based on (a) literature comparisons,

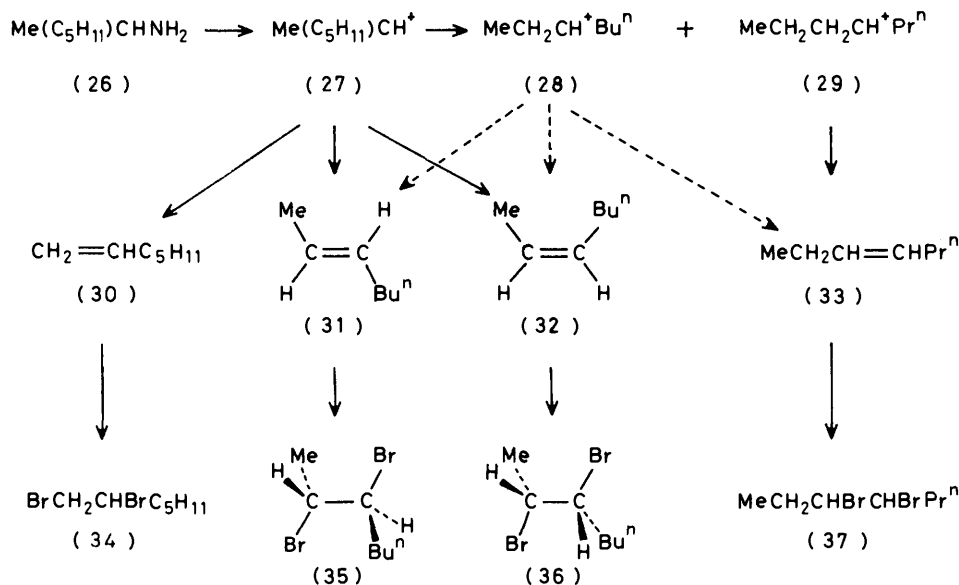
dibromo-3-methylbutane (24), *ca.* 25–30% 1,2-dibromo-2-methylbutane (25), and *ca.* 5–10% 1,2-dibromo-3-methylbutane (23). Such a pattern is expected from the relative stability of carbenium ions. Since the mixture contained three compounds in unequal proportions, peak intensities aided all assignments.

The major isomer, 2,3-dibromo-3-methylbutane (24) was assigned by off-resonance decoupling and analogy with literature chemical-shifts for 1,2-dibromopropane (46) and 1,2-dibromo-2-methylpropane (47).²¹ Of the two bromine-substituted carbons in (24), quaternary C-3 was clearly more deshielded than tertiary C-2. This showed that calculated shifts for branched dibromides could be unreliable, since C-2 of (24) was predicted to appear downfield of C-3 (see Table 2).

1,2-Dibromo-3-methylbutane (23) was compared with 1,2-dibromopropane (46) and 1,2-dibromobutane (48),²¹ and with (24). The two pairs of geminal methyl groups in (23) and (24) were non-equivalent (*cf.* ref. 22).

1,2-Dibromo-2-methylbutane (25) was assigned by off-resonance decoupling and comparison with 1,2-dibromo-2-methylpropane (47)²¹ and (24). The C-1 of compound (25) was assigned to the peak appearing in the spectrum at very high field as calculated shifts (Table 2) showed this particular carbon to be considerably more shielded than any other carbon of the three isomers.

¹³C N.m.r. spectra of the mixtures of dibromoheptanes



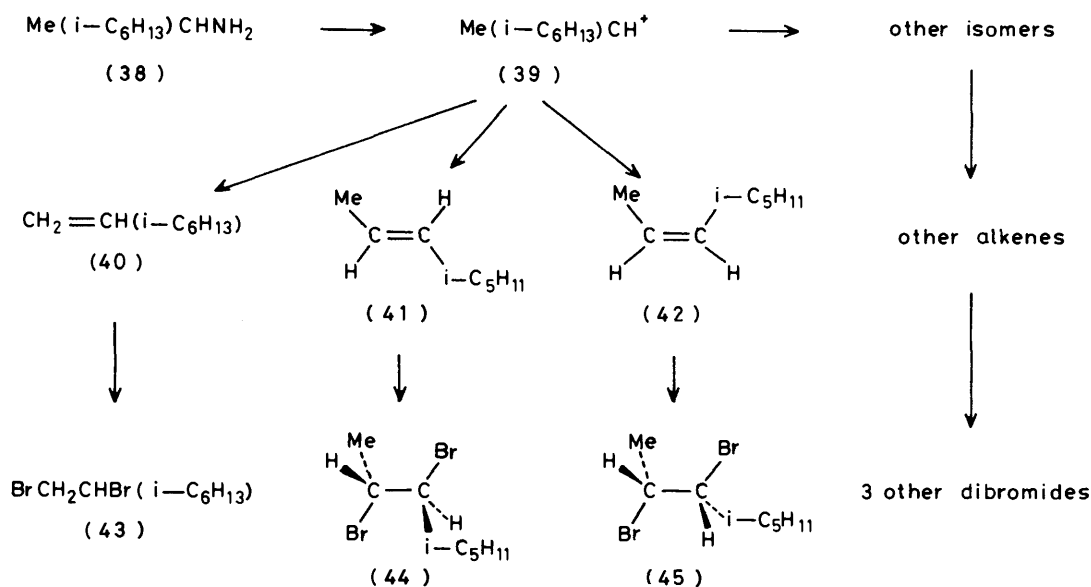
SCHEME 4

(b) off-resonance decoupling, and (c) comparison with chemical shifts calculated by the 'Lindeman-Adams rule'.^{18,19}

The dibromopentanes (14), (15), and (16) were assigned directly by comparison with literature values²⁰ (see Table 2) with which o.r.d. patterns and calculated shifts were consistent.

Off-resonance decoupling indicated *ca.* 65% 2,3-

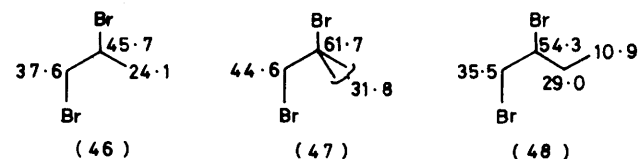
and dibromomethylheptanes could not be fully assigned owing to the larger number of peaks and the absence of literature data for internal dibromides. Assignments of bromine-substituted carbons (Table 2) were based on 1,2-, *erythro*-2,3-, and *threo*-2,3-dibromopentane²⁰ (Table 2), off-resonance decoupling, and calculated shifts (Table 2). In the case of dibromomethylheptanes, partial decoupling and calculated shifts excluded isomers



SCHEME 5

(49) and (50). No peak due to a quaternary carbon was observed in the region of the spectrum containing bromine-substituted carbon atoms.

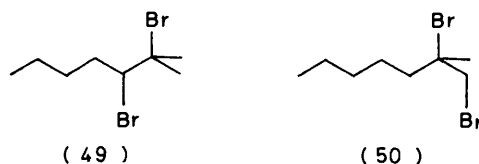
Reaction Mechanism.—Proton loss from secondary carbenium ions may be preceded by alkyl, aryl, or



hydride shifts:²³ the migratory aptitude²⁴ decreases $\text{H} > \text{aryl} > \text{alkyl}$. Endothermic rearrangements of secondary to primary carbenium ions *via* 1,2-hydride shifts do not occur,²⁵ unlike isoenergetic rearrangements of secondary to secondary carbenium ions. The deamination of 2-amino-2-deuteriobutane involves 12% rearrangement.²⁶ Exothermic rearrangements of secondary to tertiary carbenium ions *via* 1,2-hydride shifts are well known. Thus, $\text{Ph}_2\text{CHCD}(\text{OH})\text{Ph}$ in strong acid generates the rearranged cation $\text{Ph}_2\text{C}^+\text{CHDPh}$ quantitatively.²⁷ Although well documented,²⁸ 1,3-hydride shifts of carbenium ions in open-chain systems do not compete.

The alkene mixture obtained²⁹ from the deamination of *s*-butylamine in aqueous nitrous acid differs from that³⁰ from acetolysis of *s*-butyl toluene-*p*-sulphonate (see Scheme 6). The equilibrium mixture, at 25 °C in the gas phase,^{29,31} contains 2% but-1-ene, 23% *cis*-but-2-ene, and 75% *trans*-but-2-ene. In the tosylate

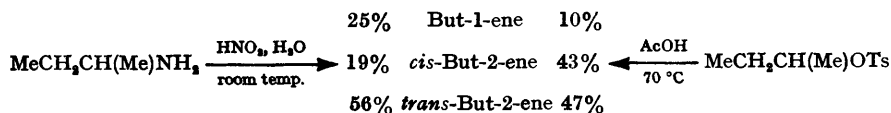
solvolysis the alkenes arise from an intermediate carbenium ion: the alkene composition is independent of the nature of the leaving group.³² In the amine-nitrous acid reaction at least part of the alkenes come from an independent competing reaction, in which product and intermediate-forming steps occur prior to complete C-N scission.²⁹



Comparison of the proportion of the dibromides formed for the 3-methylbutan-2-yl and pentan-2-yl cases (see Table 3) with the literature ratios of alkenes from both solvolysis and deamination reactions show that the present reactions resemble the solvolysis reactions and not the nitrous acid deamination pattern. This is good evidence that the present reactions involve intermediate secondary carbenium ions.

Although no exact comparison is possible, the ratios of dibromides obtained from 2-aminoheptane and 3-aminopentane (see Table 2) are also in general agreement with the ratio of alkenes formed *via* solvolysis of pentan-2-yl toluene-*p*-sulphonate.

Conclusions.—Few methods have been previously available for the conversion of secondary alkyl primary amines into olefins, apart from nitrous acid treatment, and the Hofmann elimination. Alkyldisulphonimides



SCHEME 6

TABLE 3
Preparation of alkenes *via* secondary carbenium ions

Substrate	Reaction	Ref.	Conditions	Methylbut-2-ene			Cyclopropanes	Pent-1-ene (13) (%)	<i>trans</i> -Pent-2-ene (11) (%)	<i>cis</i> -Pent-2-ene (12) (%)
				Methylbut-1-ene (22) (%)	Methylbut-2-ene (21) (%)	Methylbut-3-ene (20) (%)				
3-Methylbutan-2-yl	Solvolysis	<i>a</i>	AcOH, 75 °C	21	77	2	0	—	—	—
			AcOH, 55 °C	13	86	1	0	—	—	—
	Present work		CH ₂ Cl ₂ , 20 °C	25—30	65	5—10	0	—	—	—
			AcOH, 55 °C	19	30	35	17	—	—	—
Pentan-2-yl	Deamination	<i>b</i>	AcOH, H ₂ O, 55 °C	19	34	34	13	—	—	—
			AcOH, 118 °C	—	—	—	0	16	49	35
	Present work		CH ₂ Cl ₂ , 20 °C	—	—	—	0	10	50	40
			Deamination	<i>d</i>	AcOH, H ₂ O, reflux	—	—	—	1.4	31

^a S. Winstein and J. Takahashi, *Tetrahedron*, 1958, **2**, 316. ^b M. S. Silver, *J. Org. Chem.*, 1963, **28**, 1686. ^c H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, 1955, **77**, 3607. ^d A. T. Jurewicz, Ph.D. Dissertation, Case Western Reserve University, 1967.

with nucleophiles give mixed substitution and elimination products,³³ secondary alkyl disulphonimides give predominantly elimination, cyclododecene was thus prepared.³⁴ Recently,³⁵ alkenes have been prepared from s-alkyl disulphonimides by thermal decomposition at $\geq 90^\circ\text{C}$.

We believe that the present method offers the best procedure for olefin formation from secondary alkyl primary amines, with a minimum of skeletal rearrangement.

EXPERIMENTAL

Melting points were determined with a Reichert apparatus and are uncorrected. I.r. spectra were recorded with a Perkin-Elmer Model either 137 or 283B grating spectrophotometer, and ^1H n.m.r. spectra with either a Varian Model A-60A, a Varian Model EM360L or a JEOL Model JNM-PMX60 60 MHz spectrometer (Me_4Si as internal standard). ^{13}C N.m.r. spectra were recorded with a JEOL Model FX-100 spectrometer operating in the Fourier Transform Mode at 25.05 MHz and locked to the deuterium resonance of the solvent (CDCl_3). Typical spectrometer conditions were: 3 kHz width, 8 K data; pulse width 9 μs (45°); repetition time 2.25 s.

5,6,8,9-Tetrahydro-7-phenyldibenzo[*c,h*]xanthenylium tetrafluoroborate was prepared by a literature method,³ m.p. 254–256 $^\circ\text{C}$ (lit.,³ m.p. 265 $^\circ\text{C}$).

General Procedure for Preparation of Alkenes as Dibromides (Table 1).—The amine (4.4 mmol) and 5,6,8,9-tetrahydro-7-phenyldibenzo[*c,h*]xanthenylium tetrafluoroborate (1) (1.00 g, 2.2 mmol) in dichloromethane (7 ml) were stirred, at 20 $^\circ\text{C}$. The alkenes and dichloromethane were distilled at 760 mmHg into a trap containing bromine (0.36 g, 2.2 mmol) in chloroform (4 ml), cooled at -12°C . The distillate was washed with aqueous 0.18 M-sodium thiosulphate (2 \times 25 ml) followed by water (25 ml), and then dried (MgSO_4), and distilled (Table 1).

Cyclododecene (Table 1).—Cyclododecylamine (0.60 g, 3.2 mmol) and 5,6,8,9-tetrahydro-7-phenyldibenzo[*c,h*]xanthenylium tetrafluoroborate (1) (0.73 g, 1.6 mmol) in dichloromethane (7 ml) were stirred, at 20 $^\circ\text{C}$, for 5 days. Fractional distillation gave a mixture of cyclododecenes and cyclododecylamine (0.202 g) containing the alkenes (0.071 g, 26%) as shown by i.r. and ^1H n.m.r. spectral comparisons with those of pure cyclododecene and cyclododecylamine;⁷ ^{13}C n.m.r., $\delta(\text{CDCl}_3)$ 21.3, 22.0, 23.4, 23.7, 23.8, 24.3, 24.6, 25.0, 25.6, 26.2, 26.9, 32.2, 33.1, 47.7 (d, C-1 cyclododecylamine), 130.3 (d, C-1 *cis*-cyclododecene, lit.³⁶ 130.3), and 131.4 (d, C-1 *trans*-cyclododecene).

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