218. Sigmatropic Reactions in Carbanions. II[1]) The Rearrangement of Allylic Ammonium Ylides

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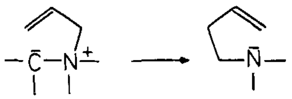
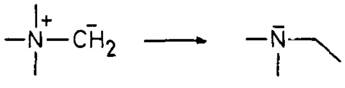
Summary. Two representative cases of the [2, 3] sigmatropic rearrangement



are described, and the mechanism of this reaction is discussed.

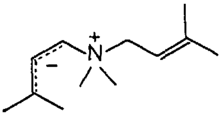
1. Introduction. – Most of the known sigmatropic carbon shifts in carbanions involve migrations from a more electronegative atom to the anionoid center[2]). Among these, all [1, 2] shifts seem to occur by dissociation to a radical pair, followed by recombination [2], while all 'pure'[3]) [2, 3] sigmatropic shifts[4]) clearly have a different mechanism [2] [3] [4], of lower activation energy.

Such anionic shifts have been observed in ammonium ylides, ether anions, sulfide anions, and sulfonium ylides. Since quaternary nitrogen can be taken to be the most electronegative substituent of this series, the rearrangements of ammonium ylides are the most exoenergetic[2]). However, quaternary nitrogen is the simplest substituent, as it is isoelectronic with an sp^3 carbon atom. Accordingly, the *Stevens* rearrangement of the ylide, trimethylammonium methylide **1**, to give dimethylethylamine **2** [6] constitutes the simplest [1, 2] anionic alkyl shift.



1 **2**

No example of the corresponding [2, 3] sigmatropic change was known when we started an investigation of reactions of this type [4] [7] [8]; we therefore studied the rearrangement of allylammonium ylides **3** and **4**, as simple models. *Ollis et al.* have



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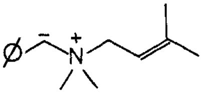

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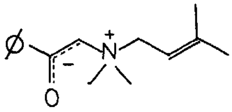

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[1]) For paper I of the series, see [1]; for a review, see [2].

[2]) This is discussed in detail in the introduction of paper I [1] of the series.

[3]) i.e. distinct from [2, 3] shifts resulting from dissociation-recombination.

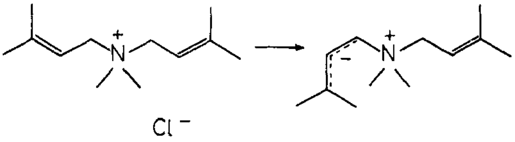
[4]) i.e. [2, 3] shifts involving an allyl group; a benzyl group may react analogously: the *Sommelet* rearrangement of ammonium and sulfonium ylides [2] [5] and related ether rearrangements [2].

subsequently reported the rearrangement of carbonyl-stabilized ylides [9] of type **5** [10]. We now wish to give our results, and to comment on the mechanism of anionic [2, 3] sigmatropic shifts.

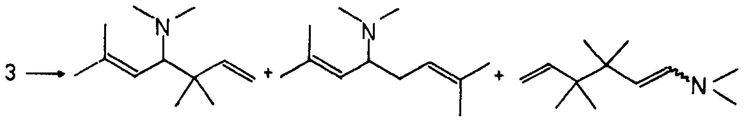
2. Results. – *Formation and rearrangement of ylide* **3**. – Treatment of the bis-allylammonium chloride **6**[5]) with ca. 2 mol-equiv. of sodium amide in boiling ammonia gave a mixture of the amines **7**[5]), **8**[5]) and **9**[5]) in 80% yield. The composition of this mixture was determined by GLPC. (Table 1).

Table 1. *Ratios of products obtained from* **6**

	7	**8**	**9**
–33°	72%	16%	12%
–73°	87%	9%	4%



6 **3**



7 **8** **9**

The analogous reaction at –73° gave the same amines **7**, **8** and **9** in different ratios (Table 1), in 75% yield. These amines were separated by GLPC., and identified by their spectral data (see exp. part). Amines **7** and **8** were stable on GLPC., however, enamine **9** underwent *cis-trans* isomerization. (We isolated *trans*-**9** and assume that *cis*-**9** is formed in the rearrangement [see exp. part].)

Saunders & Gold have shown (in one case) that the kinetically controlled deprotonation of an allylammonium salt leads stereospecifically to the *cis*-ylide [11]. We therefore assume that the reaction of **6** with sodium amide gives the *cis*-ylide **3**, which in the temperature range of –33° to –73° undergoes mainly the [2, 3] shift to give amine **7**. At higher temperatures, the competing reactions leading to amines **8** and **9** are favoured.

Formation and rearrangement of ylide **4**. – Similar reaction of the benzylallylammonium chloride **10**[5]) with sodium amide in ammonia at –33° and at –73°, gave amines **11**[5]) and **12**[5]) as major products, along with two minor products to which we tentatively assign structures **13**[5]) and **14**[5]). The yields were 90% for both temperatures. The amines were stable on GLPC. The composition of the mixtures was determined by GLPC. (Table 2).

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[5]) Systematic nomenclature is used in the exp. part.

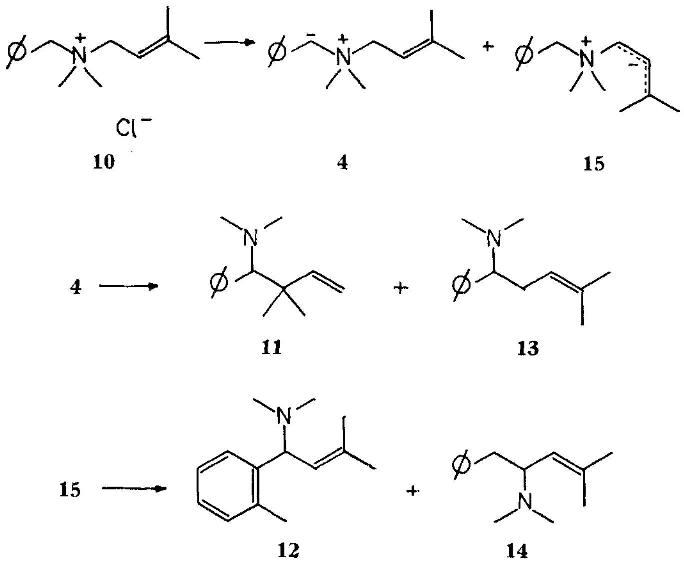

Table 2. *Ratios of products obtained from* **10**

	11	**12**	**13+14**
–73°	38%	46%	16%
–33°	44%	42%	13%

Amines **11**, **12**, **13** and **14** (the latter two as a mixture which we were unable to separate) were isolated by GLPC., and identified on the basis of their spectral data (see exp. part).

We interpret these results as follows. Abstraction of a benzylic or an allylic hydrogen from **10** gives ylides **4** and **15**, respectively. More of **15** is formed at the lower temperature (we again assume that the *cis*-ylide **15** is formed). Ylide **4** then rearranges mainly by a [2, 3] shift, to give **11**, but also undergoes some [1, 2] rearrangement to give **13**. Similarly, the main reaction of **15** is a [2, 3] sigmatropic shift – a *Sommelet* rearrangement [2] [5] – which is accompanied by a [1, 2] shift of the benzyl group to give **14** as a side reaction.

3. Discussion. – Ammonium ylides **3** and **4** thus behave exactly like the corresponding sulfonium ylides [12] and ether anions [3] [7], by reacting in two competing ways, the 'pure'[3]) [2, 3] sigmatropic change and a dissociation/recombination process. Under the conditions presently used, the 'pure'[3]) [2, 3] shift is the more important pathway.

The dissociation/recombination pathway very probably involves the formation of radical pairs [2], which recombine, essentially without escaping from the solvent cage[6]), as formulated.

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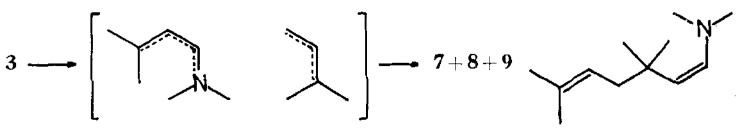
[6]) Some further dissociation has been observed in at least one case [12].



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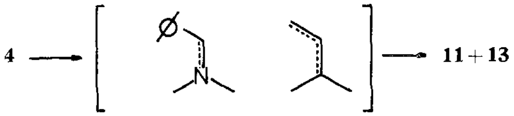
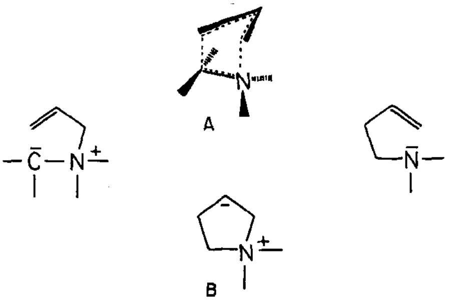


In the rearrangement of **3**, one of the four possible products which result from recombination of the radical pair[7]), enamine **16**, was not found. It is probably also formed [10] in small amounts and has escaped our analysis.

These mechanisms of the side reactions of the ylides **3** and **4** are entirely in accord with the evidence in these and the related systems [3] [7], und furthermore, correspond to the mechanism of the related pure [1, 2] shift.

What is the mechanism of the main reactions of ylides **3** and **4**, the 'pure'[3]) [2, 3] shifts? Both reactions depend on interactions with the solvent, the counterion, and generally on entropy effects. If, as usual, we assume that the enthalpy (of the hypothetical isolated anionic systems) is nevertheless the dominant factor in both reactions, then the lower activation energies of the 'pure'[3]) [2, 3] shifts, as compared to those of the dissociation/recombination processes, can be taken to indicate that some degree of covalent bonding is maintained in these reactions. In other words, they could be concerted ($\mathrm{S_{Ni}}'$) processes, or occur by an addition-elimination sequence.

A frontier orbital analysis [13][2]) indicates that an efficient doubly suprafacial concerted pathway is in fact available (transition state A)[8]). Stereochemical evidence in the case of the [2, 3] *Wittig* rearrangement [3] shows that this particular sigmatropy is in fact doubly suprafacial. Concertedness is usually assumed for the general [2, 3] shift of the type discussed here [3] [7] [10]: this is probably justified, particularly in the present case and in the analogous sulfonium ylide rearrangements.



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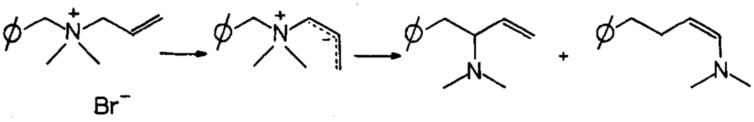
[7]) The corresponding sulfonium ylide [12] and ether anion [7] give all four products.

[8]) The alternative doubly antarafacial process is geometrically unfavourable.

One extreme[9] of an addition-elimination sequence[10] is ring closure to a short-lived five-membered ring carbanion B, followed by ring opening. The resulting separation of charges certainly renders this pathway unfavourable for ylide rearrangements. It may, however, play a role in the related rearrangements of ether and thio-ether anions.

The analogous intramolecular addition of a carbanionoid to a double bond is known: an equilibrium between 5-lithio-pentene-1 and cyclobutylmethyllithium has been demonstrated [14]. The ring-opening step of an addition-elimination sequence resembles the elimination step of an irreversible ElcB process. Related β-elimination reactions are known in the pyrrolidinium system itself [15] and also in the piperidinium [15] and tetrahydropyranyl systems [16].

The deprotonation of the ammonium chloride **10**, as well as the course of the rearrangement of ylide **15** require further comment. Deprotonation of **10** occurred both in the allylic and benzylic positions, to give ylides **4** and **15**, respectively, while *Jenny* & *Druey* have found [18] that benzylallylammonium bromide **17**, on reaction with sodium amide in ammonia or benzene is metallated only in the allylic position, to give ylide **18**. The structurally similar ylides **15** and **18** react quite differently. Under the conditions we used (ammonia at −33°) the main reaction of ylide **18** is rearrangement by a [1, 2] shift of the benzyl group, to give **19** [18]; in a side reaction, the corresponding [1, 4] shift to give **20** also occurs. On the other hand, ylide **15** undergoes mainly a *Sommelet* rearrangement, whereas the [1, 2] shift of the benzyl group to give **14** is only observed as a side reaction, and the corresponding [1, 4] shift is not seen at all.



17 **18** **19** **20**

Both metallation and the subsequent rearrangement are thus influenced by the presence (or absence) of methyl substituents in the γ-position of the allyl group; these probably change the acidity of the allylic hydrogens (in **10** and **17**, respectively) and the charge distribution in the allylic anions (in **15** and **18**, respectively).

I thank Dr. *G. Ohloff*, research director of *Firmenich* & Cie, for his support and encouragement, Professor *C. W. Jefford* for a helpful discussion and Miss *G. Keller* for technical assistance.

Experimental Part[11]

1. *1-Chloro-3-methylbut-2-ene* (**21**). – To 1 l (680 g, 10 moles) of isoprene were added dropwise 2,5 l of conc. hydrochlorid acid over a period of 90 min, with stirring and cooling with an ice-bath,

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[9] The other extreme would involve an intermediate resembling A (corresponding to a shallow minimum of potential energy).

[10] Such ring-chain rearrangements can be envisaged in both ionic analogues of the [3,3] sigmatropic shift, the [2,3] anionic, and the [3,4] cationic shift; even the corresponding 6-membered ring diradical intermediate (or transition state) in the [3,3] shift has recently been considered energetically acceptable [17].

[11] General remarks as in [1], with the following modifications. NMR. spectra: *Hitachi-Perkin-Elmer* R-20B and *Bruker* HFX90. All amines (except **22**) were measured in d_6-benzene solution, to exclude traces of acid in the solvent; δ-scale relative to benzene (= 7.20 ppm). M.p. were taken on a *Büchi* apparatus (Dr. *Tottoli*), and are not corrected.

and the mixture was then stirred at room temperature for 4 h. The organic phase was taken up in 1,5 l of pentane and the aqueous phase was extracted with 500 ml of pentane. The combined pentane solutions were washed with water and dried over calcium chloride. The pentane was distilled off through a 80 cm glass spiral column, and the residue was fractionally distilled over 1 g of potassium carbonate. The fraction boiling at 110–112°/730 Torr (553 g of **21**, 5.3 moles, 53%) was used and stored in the refrigerator, over a trace of potassium carbonate. It had the reported NMR. spectrum [19].

2. *N,N-Dimethyl-3-methylbut-2-en-1-ylamine* (**22**). – To a stirred and cooled (–15°) solution of 14.5 g (0.32 mole) of dimethylamine in 40 ml of tetrahydrofuran, was added dropwise a solution of 15 g (0.14 mole) of **21** in 5 ml of tetrahydrofuran over a period of 40 min. A white precipitate formed. The mixture was stirred at –15° for 40 min and then at +5° for 2 h. Excess 10% aqueous sulfuric acid was added, the tetrahydrofuran was distilled off on a rotary evaporator, and the remaining aqueous phase was extracted with ether. It was then made alkaline with 20% aqueous sodium hydroxide, saturated with sodium chloride and extracted twice with ether. The combined ether extracts were dried over potassium carbonate. The solvents were distilled off and the residue was distilled through a short *Vigreux* column: b.p. 120°/730 Torr; yield: 11.1 g (98 mmoles, 70%) of **22**. According to GLPC. (5 m, 100°) this product was >95% pure.

Spectral data of **22**:

NMR.: (CCl_4, 60 MHz) 5.17 (1H, *t* (broad), $J = 6.5$ Hz), 2.75 (2H, *d* (broad), $J = 6.5$ Hz), 2.08 (6H, *s*), 1.71 (3H, *s* (broad)), 1.61 ppm (3H, *s* (broad)).

IR.: 3010 (*m*), 2970, 2940, 2850, 2810, 2760 (*s*), 2720 (*m*), 1680 (*w*), 1450, 1370 (*s*), 1360, 1340, 1270, 1260 (*m*), 1200 (*w*), 1170, 1140 (*m*), 1110, 1090 (*w*), 1040, 1010 (*s*), 860, 810 cm^{-1} (*m*).

MS.: $M^+ = 113$ (55), *m/e*: 112 (59), 98 (71), 82 (12), 70 (12), 69 (36), 58 (100), 45 (87), 43 (12), 42 (55), 41 (74), 39 (17).

3. *Dimethyldi(3-methylbut-2-en-1-yl)ammonium chloride* **6**. – To a stirred solution of 2.00 g (17.7 mmoles) of **22** in 15 ml of methanol were added at +5 (cooling with an ice-bath) 2.19 g (21.0 mmoles) of **21** and the mixture was stirred at +5° for 1 h. The solvent was then removed on a rotary evaporator (25°) and the oily residue was repeatedly decanted with ether; it then crystallised. Solvents and traces of water were removed at 12 Torr and then at 0.01 Torr, at 25°. Yield: 240 g (11.0 mmoles, 63%) of **6**, colorless crystals, m.p. 120–122°. This product was highly hygroscopic; it was used without further purification and only characterised by its NMR. spectrum.

NMR.: (D_2O, chemical shifts relative to HOD = 4.60 ppm, 60 MHz), 5.35 (2H, *t* (broad), $J = 7.5$ Hz), 3.75 (4H, *d* (broad), $J = 7.5$ Hz), 2.85 (6H, *s*), 1.80 (6H, *s* (broad)), 1.70 ppm (6H, *s* (broad)).

4. *Reaction of* **6** *with sodium amide in ammonia.* – a) At –33°: 132 mg (8.7 mmoles) of sodium were dissolved in ca. 10 ml of ammonia, and a crystal of ferric nitrate was added. To the resulting grey suspension of sodium amide were added at reflux 266 mg (1.22 mmoles) of **6**, with stirring. This mixture was stirred at reflux for 2 h. Then 1 ml of methanol, followed by 1 ml of water were added very slowly, ether was added, and the ammonia was allowed to evaporate. More water and ether were then added, the ether layer was separated, and the aqueous layer was extracted once more with ether. The combined ether phases were washed with water and dried over potassium carbonate. The ether was then distilled off. The resulting crude mixture was then analysed by GLPC. (3 m, 110°) and by means of the NMR. spectrum. It was then distilled: b.p. 68–70°/12 Torr; yield 172 mg (≙ 0.95 mmole of **7** and isomers, 78%) of a mixture of amines, and the distillate was again analysed by GLPC. and by means of the NMR. spectrum. In this way, it could be shown that the products were stable on distillation (and also during preparative GLPC.).

b) At –73°: From 276 mg (12.0 mmoles) of sodium, a suspension of sodium amide in ca. 10 ml of ammonia was prepared as described in section 4a. This suspension was then frozen in liquid nitrogen and 1.030 g (47.4 mmoles) of **6** were added to the frozen mixture. Another 10 ml of ammonia were then condensed in (liquid nitrogen bath) and the mixture was warmed to –73°; the ammonia melted and the mixture was stirred at –73° for 5.5 h. It was then worked up as described in section 4a, with the same analytical checks. Yield of distilled product: 761 mg (≙ 35.0 mmoles of **7** and isomers, 75%) of a mixture of amines.

From these runs products **7**, **8** and **9** were isolated by GLPC. (3 m, 110° and 150°, peaks in the order **7**, **8**, **9**). Peak **9** had a shoulder. When peak **9** was collected from the gas-chromatograph, and reanalysed by GLPC., this shoulder now appeared as the main component of the collected material. The collected material was again passed through the gas-chromatograph, and then consisted largely of the product which initially had appeared as a shoulder. Products **7** and **8** were stable on GLPC. The composition of the mixtures obtained at –33° and –73° was determined by GLPC., without correction for detector response, and is given in Table 1.

Spectral data of N, N-dimethyl-3, 3, 6-trimethylhepta-1, 5-dien-4-ylamine **7**:

NMR.: (d_6-benzene, 60 MHz), 7.16 (1H, *q*, $J_1 = 10$, $J_2 = 18$ Hz), 4.85–5.50 (3H, *m*), 2.96 (1H, *d*, 11 Hz), 2.27 (6H, *s*), 1.65 (3H, *d*, J = ca. 1 Hz), 1.58 (3H, *d*, J = ca. 1 Hz), 1.27 (3H, *s*), 1.06 ppm (3H, *s*).

IR. 3080 (*m*), 2960, 2940, 2860, 2820, 2780 (*s*), 1670, 1630 (*m*), 1470, 1450, 1440 (*s*), 1410 (*m*), 1380 (*s*), 1360, 1250 (*m*), 1170 (*w*), 1150 (*m*), 1090 (*w*), 1050 (*m*), 1020, 910 (*s*), 850 (*w*), 830, 820 (*m*), 760 (*w*), 690 cm^{-1} (*m*).

MS.: $M^+ = 181$ (weak), *m/e*: 112 (100).

Spectral data of N, N-dimethyl-2, 7-dimethylocta-2, 6-dien-4-ylamine **8**:

NMR.: (d_6-benzene, 60 MHz), 5,05–5,60 (2H, *m*), 2.9–3.4 (1H, *m*), 2,25 (6H, *s*), *m* centered at 2.2 (2H), 1.70 (6H, apparent *s*), 1.60 ppm (6H, apparent *s*).

IR.: 2960, 2920, 2860, 2820, 2770 (*s*), 1670 (*w*), 1450, 1370 (*s*), 1270, 1250, 1210, 1170, 1140 (*w*), 1040, 1010 (*m*), 980 cm^{-1} (*w*).

MS.: $M^+ = 181$ (weak), *m/e*: 112 (100).

Spectra data of *E*-N, N-dimethyl-3, 3, 4, 4-tetramethylhexa-1, 5-dien-1-ylamine **9**:

Despite repeated purification by GLPC., we did not succeed in obtaining a pure sample: it contains an aldehyde as a (minor) impurity, which manifests itself in the NMR. (signal at 9.6 ppm) and in the IR. (1720 cm^{-1} (?)) spectrum.

NMR.: (d_6-benzene, 90 MHz), 6.1 (1H, *m*), 5,86 (1H, *d*, $J_1 = 14$ Hz), 4.85–5.20 (2H, *m*), 4.37 (1H, *d*, $J_1 = 14$ Hz), 2.36 (6H, *s*), 1.09 (6H, *s*), 1.08 ppm (6H, *s*). The coupling constant (J_1) clearly shows that **9** has *trans*-geometry [20].

IR.: 3080, 3060 (*m*), 2970, 2860 (*s*), 2830, 2780, 1720 (?) *m*, 1645 (*s*), 1470, 1440 (*m*), 1410 (*w*), 1370, 1360, 1340, 1330 (*m*), 1220, 1200 (*w*), 1140 (*m*), 1070 (*s*), 1050 (*m*), 1040, 1010 (*w*), 940, 910 (*m*), 860, 800, 690 cm^{-1} (*w*).

MS.: $M^+ = 181$ (weak), *m/e*: 112 (100), 69 (10) ?, 41 (18).

5. *Benzyldimethyl(3-methylbut-2-en-1-yl)ammonium chloride* **10**. – To a stirred solution of 2.00 g (17.7 mmoles) of **22** in 15 ml of methanol, at +5° (cooling with an ice bath) were added 2.40 ml (2.66 g, 21.0 mmoles) of benzyl chloride, and the mixture was then stirred at +5° for 2 h. The solvent was removed on a rotary evaporator (25°) and the oily residue was repeatedly decanted with ether; it then crystallised. Solvent and traces of water were removed at 12 Torr and then at 0.01 Torr, at 25°. Yield 2.60 g (11.0 mmoles, 62%) of **10**, colorless crystals, m.p. 167–169°. This product was somewhat hygroscopic; it was used without further purification.

$C_{14}H_{22}NCl$ (239.5) Calc. C 70.14 H 9.18 N 5.84% Found C 69,83 H 9.08 N 6.22%

Spectral data of **10**:

NMR.: (D_2O, chemical shifts relative to HOD = 4.60 ppm, 60 MHz), 7.48 (5H, *s*), 5.38 (1H, *t* (broad), J = 7.5 Hz), 4.35 (2H, *s* (broad)), 3.80 (2H, *d* (broad), J = 7.5 Hz), 2.85 (6H, *s*), 180 (3H, *s* (broad)), 1.70 ppm (3H, *s* (broad)).

IR.: (KBr) 3090, 3060 (*w*), 3010 (*m*), 2990, 2980, 2940, 2860 (*s*), 1670 (*m*), 1490, 1470, 1450, 1410, 1380 (*s*), 1360, 1320 (*m*), 1270, 1230 (*w*), 1210 (*m*), 1200, 1150 (*w*), 1080, 1050, 1030 (*m*), 1000, 930, 920, 880 (*s*), 820, 790 (*w*), 780, 720, 700 cm^{-1} (*s*).

6. *Reaction of* **10** *with sodium amide in ammonia*. – a) At –33°: From 310 mg (13.5 mmoles) of sodium, a suspension of sodium amide in ca. 10 ml of ammonia was prepared. To the refluxing suspension were added 741 mg (3.11 mmoles) of **10**, and the mixture was then stirred at reflux for 1 h. After work-up as described in section 4a, and distillation (b.p. 110–113°/12 Torr) 556 mg (2.76 mmoles of **11** and isomers, 89%) of a mixture of amines were obtained. Analytical checks by NMR. and GLPC. (1.6 m and 3 m, 155°) were carried out as described in section 4a.

b) At –73°: From 328 mg (14.3 mmoles) of sodium, a suspension of sodium amide in ca. 10 ml of ammonia was made, and then treated with 786 mg of **10** (3.31 mmoles) as described in section

4b, stirred at $-73°$ for 3.5 h and then worked up as described in section 4a. B.p. 110–112°/12 Torr, yield 594 mg (2.96 mmoles of **11** and isomers, 89%) of a mixture of amines.

From these runs, amines **11**, **12**, **13** and **14** were isolated by GLPC. (3 m, 155°), peaks in the order **11**, **12**, **13**+**14**. We were unable to separate **13** and **14**. All four compounds were stable on GLPC. The composition of the distillates in the two runs, as determined by GLPC., is given in Table 2.

Spectral data of N,N-dimethyl-1-phenyl-2,2-dimethylbut-3-en-1-ylamine **11**:

NMR.: (d_6-benzene, 60 MHz), 7.20 (5H, *s*), 6.35 (1H, *q*, $J_1 = 10.5$, $J_2 = 18$ Hz), 4.85–5.30 (2H, *m*), 3.17 (1H, *s*), 2.19 (6H, *s*), 1.23 (3H, *s*), 1.03 ppm (3H, *s*).

IR.: 3080, 3060, 3020 (*m*), 2980, 2930, 2900, 2860, 2820, 2780 (*s*), 1630 (*m*), 1600 (*w*), 1490, 1470 (*m*), 1450 (*s*) 1440, 1410, 1370, 1360, 1250, 1180, 1150 (*m*), 1090, 1080 (*w*), 1050 (*m*), 1020 (*s*), 930 (*w*), 910 (*s*), 860 (*m*), 780 (*w*), 750, 700 (*s*), 640 (*m*), 550 cm^{-1} (*w*).

MS.: $M^+ = 203$ (weak), *m/e*: 134 (100).

Spectral data of N,N-dimethyl-1-(*o*-tolyl)-3-methylbut-2-en-1-ylamine **12**:

NMR.: (d_6-benzene, 90 MHz), 7.69 (1H, *m*), 6.95–7.30 (3H, *m*), 5.47 (1H, *d* (broad), $J = 10$ Hz), 4.00 (1H, *d*, $J = 10$ Hz), 2.36 (3H, *s*), 2.21 (6H, *s*), 1.60 (3H, *d*, $J = 2$ Hz), 1.54 ppm (3H, *d*, $J = 2$ Hz).

IR.: 3060, 3050, 3020 (*m*), 2980, 2940, 2930, 2910, 2860, 2820, 2760 (*s*), 1670, 1600 (*w*), 1480 (*m*), 1450, 1440 (*s*), 1370, 1330 (*m*), 1290, 1280 (*w*), 1270, 1250, 1220, 1200, 1170, 1150, 1110 (*m*), 1040, 1000 (*s*), 990 (*m*), 940 (*w*), 890, 860, 830 (*m*), 750, 730 (*s*), 700 (*m*), 630, 570 cm^{-1} (*w*).

MS.: $M^+ = 203$ (6), *m/e*: 160 (12), 159 (100), 158 (40), 144 (16), 143 (29), 131 (10), 129 (10), 128 (15), 117 (10), 112 (63), 105 (17).

Spectral data of N,N-dimethyl-1-phenyl-4-methylpent-3-en-1-ylamine **13** and of N,N-dimethyl-1-phenyl-4-methylpent-3-en-2-ylamine **14** (assignment of these structures is tentative and the spectra given below are of a ca. 1:1 mixture of **13** and **14**):

NMR.: (d_6-benzene, 90 MHz), 6.8–7.5 (10H, *m* (two broad *s*)), 4.95–5.30 (2H, *m* (broad *d*)), 3.85 (1H, *m*), 2.70–3.40 (5H, *m*), 2.20 (6H, *s*), 2.10 (6H, *s*), 1.55 (6H, *s* (broad)), 1.39 (3H, *s*), 1.19 ppm (3H, *s*).

IR.: 3080, 3060, 3020 (*m*), 2960, 2920, 2860, 2820, 2760 (*s*), 1660, 1600 (*w*), 1590 (*m*), 1550 (*s*), 1370 (*m*), 1350, 1320, 1300, 1240, 1210, 1170 (*w*), 1140 (*m*), 1100, 1090, 1070 (*w*), 1040, 1030, 1000 (*m*), 940, 910, 870, 860, 830, 800 (*w*), 770 (*m*), 740, 700 cm^{-1} (*s*).

MS.: $M^+ = 203$ (weak), *m/e*: 135 (10), 134 (100), 112 (84), 91 (10).

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219. Studies in the Helicene Series

NMR. Evidence of 'Helicene-like' Conformations in the *cis* 1,2-Diarylethylenes

Part XVII[1]

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(26. VI. 72)

Summary. The *cis* and *trans* isomers of eight 1,2-diarylethylenes, precursors of helicenes, have been studied by NMR. spectroscopy. The observed differences in chemical shifts, specific solvent effects and steric effects (bromo derivatives) can be explained by the contribution of 'helicene-like' conformers in the *cis* isomers.

In the course of our work on the photosynthesis of helicenes, we have frequently observed that the NMR. spectra of the *cis*-1,2-diarylethylenes and of the corresponding helicenes show striking similarities[3].

Independent and similar observations made by *Laarhoven et al.*[4] prompt us to describe briefly some of our findings[5].

1. The 1-aryl-2-(benzo [c] phenanthryl) ethylene series. – When the NMR. spectra of the *cis* isomers are compared to the NMR. spectra of the corresponding *trans* isomers (Table 1A), the following upfield shifts are observed, by first order analyses:

Ethylenic protons and H_1 ($H_{\alpha 4}$ *ortho* to the side chain). Similar shifts were observed, long ago, in the NMR. spectra of *cis* versus *trans* stilbene [2].

A particularly large upfield shift in the case of H_{11} and H_{12} (except for H_{11} in **I**). This shielding increases according to the sequence: phenyl $<$ 3-phenanthryl $\simeq$ 2-benzo[*c*]phenanthryl $<$ 2-naphthyl.

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[3] The main conclusion of this work is included in the PhD thesis of one of us (*J.J.S.*) presented 10 March 1972.
[4] Private communication from Dr. *W. H. Laarhoven*, University of Nijmegen.
[5] An X-ray diffraction study of *cis* 1-(2-benzo[*c*]phenanthryl)-2-(3-phenanthryl) ethylene is presently under way. Preliminary results show that the crystals belong to the $P2_1$ space group; personal communication from *G. Germain, H. Kagan, A. Moradpour, G. de Rango & M. Tsoucaris.*