Novel Features of the 1,3 Rearrangement of *S*-(—)-*N*-(1-Phenylethyl)-diphenylvinylideneamine to *S*-(—)-2,2,3-Triphenylbutyronitrile

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Summary *S*-(—)-*N*-(1-phenylethyl)diphenylvinylideneamine (**1**) rearranges, apparently quantitatively, to *S*-(—)-2,2,3-triphenylbutyronitrile (**2**) in CCl_4, k $(2{\cdot}9 \pm 0{\cdot}3) \times 10^{-4}\,s^{-1}$, and CD_3CN, k $(3{\cdot}9 \pm 0{\cdot}4) \times 10^{-4}\,s^{-1}$, at 60 °C with partial retention of configuration at the migrating centre; *N*-(benzyl)diphenylvinylideneamine (**8**) undergoes a similar rearrangement, but *N*-(t-butyl)diphenylvinylidene amine (**9**) yields only disproportionation type products, at a higher temperature (125 °C).

N-(1-Phenylethyl)vinylideneamine† (**1**) rearranges to 2,2,3-triphenylbutyronitrile (**2**) at 60 °C in CCl_4, k $(2{\cdot}9 \pm 0{\cdot}3) \times 10^{-4}\,s^{-1}$, and in CD_3CN, k $(3{\cdot}9 \pm 0{\cdot}4) \times 10^{-4}\,s^{-1}$, with apparent 100% efficiency.‡

$$\underset{(\mathbf{1})}{Ph_2C{=}C{=}N{-}CHMePh} \xrightarrow{60^\circ} \underset{(\mathbf{2})}{MeCHPhCPh_2CN}$$

Further, this rearrangement proceeds with partial retention of configuration at the migrating centre according to the following experiments. Rearrangement of *S*-(—)-(**1**) ($[\alpha]_D^{25}$ − 35·3°, *c* 6·32, CCl_4) of >98% optical purity§ provided *S*-(—)-(**2**) ($[\alpha]_D^{25}$ − 202°, *c* 5·47, CCl_4) with an optical purity of 52% in CCl_4. In CD_3CN, *S*-(—)-(**2**) ($[\alpha]_D^{25}$

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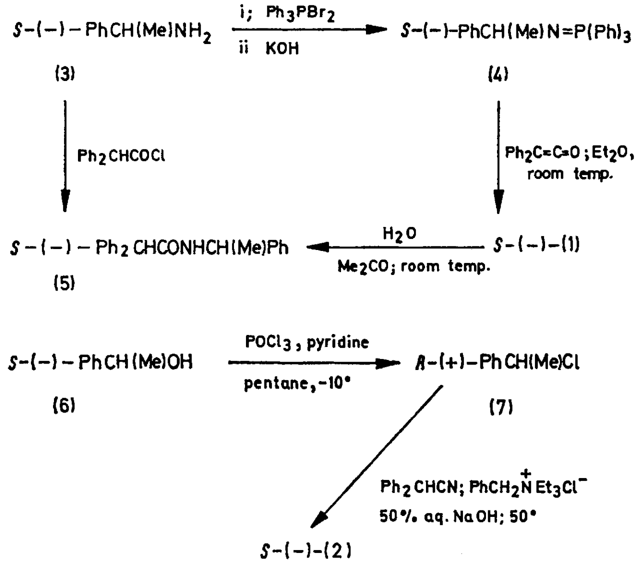
† Satisfactory analytical data were obtained; ν (CCl_4) 2020 cm^{-1}; δ (CCl_4) 1·65 (3H, d), 4·9 (1H, q), and 7·0—7·4 (15H, m).

‡ The rearrangement is conveniently followed by n.m.r. analysis. Within the limits of detection (< 1%), no other products are observed.

§ The assessment of optical purity of *S*-(—)-(**1**) is based on the synthetic sequence and the rotation of starting *S*-(—)-(**3**), α_D^{25} −37·0° (neat, 1 dm) which corresponds to >98% optical purity (W. Theilaker and H-G. Winkler, *Chem. Ber.*, 1954, **87**, 690).

$-202°$, $c = 4{\cdot}20$, CD_3CN) was obtained with 31% optical purity (see Scheme).¶



Scheme

Preliminary thermolysis studies have been carried out on the vinylideneamines (**8**) and (**9**) in CCl_4. The results with (**8**) are analogous to those with (**1**) in terms of the predominance and facility, k $(8{\cdot}0 \pm 0{\cdot}6) \times 10^{-5}\,s^{-1}$ at 60 °C, of the rearrangement pathway (**8**) → (**10**). With (**9**), considerably more thermal activation is required for reaction, k $(1{\cdot}5 \pm 0{\cdot}1) \times 10^{-5}\,s^{-1}$ at 125 °C, and the products are quite different.

$$\underset{(\mathbf{8})}{Ph_2C{=}C{=}NCH_2Ph} \xrightarrow[CCl_4]{60^\circ} \underset{(\mathbf{10})\ ca.\ 90\%}{PhCH_2CPh_2CN}$$

$$\underset{(\mathbf{9})}{Ph_2C{=}C{=}NBu^t} \xrightarrow[CCl_4]{125^\circ} \underbrace{Ph_2CHCN + Me_2C{=}CH_2}_{75\text{—}90\%} + \underset{ca.\ 10\%}{Bu^tCl}$$

The diphenylacetonitrile and isobutylene from (**9**) could result from an intramolecular hydrogen transfer–cleavage as suggested by Ciganek for other systems,[1] and/or a homolytic cleavage–disproportionation sequence. t-Butyl chloride most probably arises from homolysis followed by chlorine abstraction from the solvent by t-butyl radicals.

The results with (**1**) are in striking contrast to those with (**9**), and, in particular, any suggested mechanism must explain the absence of disproportionation-type products from (**1**), as well as the absence of chlorine atom incorporation products in CCl_4. The very modest rate increases and similar stereochemical results in going from CCl_4 to CD_3CN argue against heterolysis and rearrangement *via* a proximate ion pair. Further, the less than complete stereospecificity and the restrictions imposed by the linear ketenimine structure would seem to preclude a concerted pathway.[2] Tentatively, and cautiously, we favour rearrangement *via* a proximate radical pair.[3]

CIDNP and other experiments are in progress to clarify the results on the rearrangement of (**1**).

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¶ The phosphinalkylimine synthesis overall proceeds with complete retention of absolute configuration since mild hydrolysis of *S*-(−)-(**1**) gives *S*-(−)-(**5**) of identical optical purity (>98%) ($[\alpha]_D^{25}$ $-30{\cdot}5°$, c 1·12, $CHCl_3$) to that prepared directly from *S*-(−)-(**3**). The stated optical purities for *S*-(−)-(**2**) arising from the rearrangement of *S*-(−)-(**1**) are based on an assumed complete inversion in the phase-transfer alkylation of *R*-(+)-(**7**). (M. Makosa and B. Serafin, *Roca. Chem.*, 1965, **39**, 1799; *Chem. Abs.*, 1966, **64**, 17475g). Consistent calculated values for the corrected specific rotation of *S*-(−)-(**2**) are observed from several syntheses under variable conditions which supports our assumption. The starting *S*-(−)-(**6**) for this sequence showed α_D^{25} $-43{\cdot}5°$ (neat, 1 dm) which corresponds to >99% optical purity (E. Downer and J. Kenyon, *J. Chem. Soc.*, 1939, 1156). The optical purity of *R*-(+)-(**7**) used in our sequence is 80% based on the generally accepted value of α_D^{25} ± 126° for optically pure material. (R. L. Burwell, Jr., A. D. Shields, and H. Hart, *J. Amer. Chem. Soc.*, 1953, **76**, 908.)

[1] E. Ciganek, *Tetrahedron Letters*, 1969, 5179.

[2] J. A. Berson, T. Miyashi, and G. Jones, *J. Amer. Chem. Soc.*, 1974, **96**, 3468, analyse possible mechanisms for a carbon–carbon 1,3 sigmatropic rearrangement having high retention of configuration at the migrating centre.

[3] See P. Caramella, R. Huisgen, and B. Schmolke, *J. Amer. Chem. Soc.*, 1974, **96**, 2997, 2999, for examples of carbon–carbon 1,3 sigmatropic rearrangements proceeding *via* diradical intermediates. For a discussion of the stereochemistry of free radical recombination reactions see J. P. Engstrom and F. D. Greene, *J. Org. Chem.*, 1972, **37**, 968.