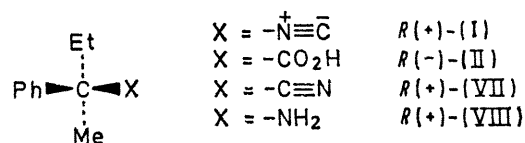


Novel Olefin Formation in the Thermal Rearrangement of Isocyanide to Cyanide

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Summary Thermal rearrangement of the optically active (ethylmethylphenyl)methyl isocyanide $R(+)$ -(I) gave three elimination products (IV)—(VI) together with almost racemic cyanide (III) *via* a novel radical mechanism.



PREVIOUSLY¹ we reported a novel radical mechanism for the thermal rearrangement of isocyanide to cyanide. We now report results for the thermal rearrangement of the optically active isocyanide $R(+)$ -(I) which afforded an almost

racemic cyanide (III) together with the olefins (IV)—(VI) by loss of hydrogen cyanide.

Optically active isocyanide $R(+)$ -(I), $\alpha_D^{20} +0.090^\circ$ ($l = 0.1$ dm, neat), optically purity 80.9%, prepared from

TABLE

Conditions	(III)			Yield (%) ^c		
	Yield (%) ^c	Optical rotation ^d (C ₆ H ₆)	Retention of configuration (%) ^e	(IV)	(V)	(VI)
a	61	$[\alpha]_{300}^{17} 0^{\circ}$ (C ₆ H ₆)	0	10	1	11
b	21	$[\alpha]_{300}^{16} + 6.0^{\circ}$ (C ₆ H ₆)	19	35	4	28

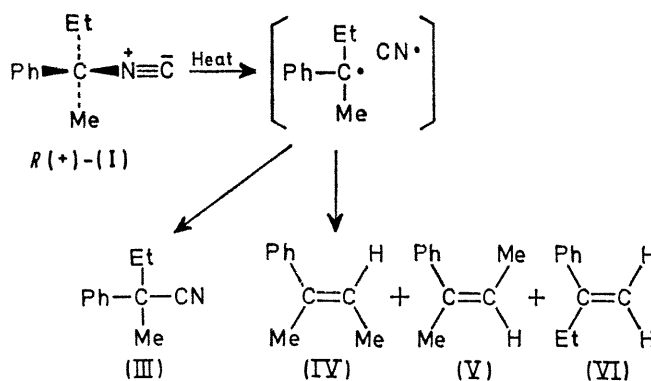
^a Heating for 5 h at 260 °C without solvent under N₂. ^b Heating for 3 h at 280 °C in diphenyl ether under N₂. ^c Yields were determined by gas chromatography. ^d Optical rotation of (III) was measured by o.r.d. after purification by column chromatography. ^e The degree of configuration retention was calculated by comparison with the optical rotation of *R*(+)-(VII), $[\alpha]_{300}^{17} + 30.0^{\circ}$ (C₆H₆) optical purity 75.3%, prepared from *R*(-)-acid (II).

R(-)-acid (II), $\alpha_D^{15} -24.9^{\circ}$ (C₆H₆) optical purity 80.9%, was heated either without solvent or in diphenyl ether, under nitrogen (see Table). Compounds (III)–(VI) were identified by comparison with authentic samples.²

The following experiments showed that the racemization of (III) occurred in the transition state of the rearrangement. When the thermal rearrangement of *R*(+)-(I) without solvent was interrupted at about 50% conversion, *R*(+)-(I) was hydrolysed to *R*(+)-amine (VIII), in which no racemization had taken place. Optically active *R*(+)-cyanide (VII) was not racemized under the same condition as in the thermal rearrangement.

This olefin formation by the elimination of HCN is the first such example in the thermal rearrangement of isocyanide. When we added Bu₃SnH as a radical scavenger to the reaction medium, no olefins were formed and only *s*-butylbenzene was obtained (61%). This suggests that the diradical after homolytic C–N bond fission afforded almost racemic cyanide by a coupling reaction and gave olefins by disproportionation.

Studies on the relation of the structure of isocyanide to the mechanism of thermal rearrangement are in progress in our laboratory.



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¹ S. Yamada, K. Takashima, T. Sato, and S. Terashima, *Chem. Comm.*, 1969, 812.

² D. J. Cram, *J. Amer. Chem. Soc.*, 1949, **71**, 3883.