

1,2,4-TRIAZEPINES FROM THE PHOTOCHEMICAL WALK REARRANGEMENT OF
3,4,7-TRIAZA-2,4-NORCARADIENES¹

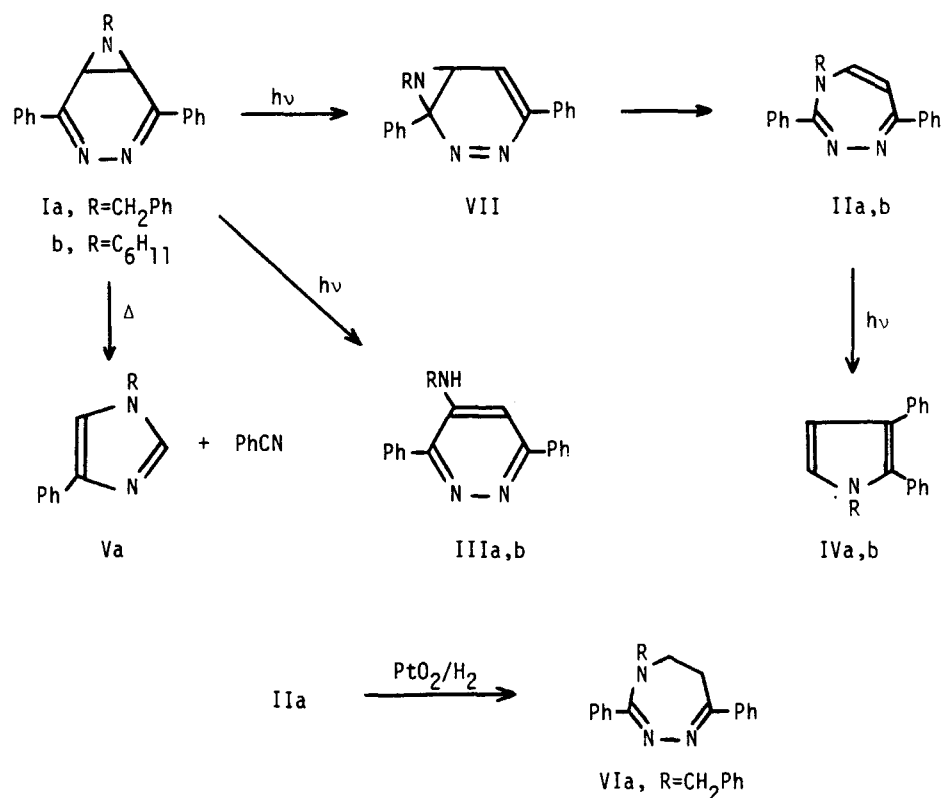
Isao Saito*, Akira Yazaki, and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University
Kyoto 606, Japan

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In recent years much attention has been focussed on the chemistry of seven-membered unsaturated heterocycles such as oxepins,² azepines,² oxazepines,³ and diazepines,⁴ from the question of antiaromaticity and valence bond isomerization in these systems. To date only little is known about the synthesis of triazepines, more highly heterosubstituted relatives.⁵ Some of 2H-1,2,4-triazepine derivatives have been prepared by reacting sym-tetrazines with azirines.⁶ We report here a new type of photorearrangement of triazanorcaradienes leading to 4-alkyl-1,2,4-triazepines by a mechanism in which the aziridine nitrogen undergoes migration along the surface of a heterocyclic π system.⁷ The present reactions provide an efficient and simple synthetic route to some of the unknown 4-substituted 1,2,4-triazepine systems.

Preparative photolysis of 7-benzyl-2,5-diphenyl-3,4,7-triaza-2,4-norcaradiene⁸ (Ia) (5 mmol) in benzene solution with a high pressure mercury lamp (Pyrex filter) at room temperature produced one major photoproduct IIa⁹ (53%), a yellow solid, mp 152-153°, together with minor amounts of IIIa^{8b} (6%), IVa^{9,10} (1%) and Va^{8b,11} (17%).¹² The NMR spectrum of the major photoproduct showed the presence of two adjacent vinyl hydrogens [AB quartet ($J = 7.2$ Hz, δ 5.67 and 6.40)], in addition to the methylene protons (2 H, s, δ 4.26) and aromatic protons (15 H, m, δ 7.15-7.76). The ultraviolet spectrum showed absorptions at 207 ($\log \epsilon$ 4.36), 257 ($\log \epsilon$ 4.27), and 365 nm ($\log \epsilon$ 2.92); cf. the 225, 252 and 388 nm absorptions of 2H-1,2,4-triazepines.^{6a} The mass spectrum showed a prominent ion peak at m/e 309 ($M^+ - N_2$) along with the molecular ion peak at m/e 337. These spectral data and following chemical reaction led us to assign structure IIa to the photoproduct. Catalytic hydrogenation (PtO_2) of IIa in ethanol gave the dihydrophotoproduct VIa (50%), mp 144-146°; uv (EtOH) 241 ($\log \epsilon$ 4.00), 324 nm ($\log \epsilon$ 3.68); NMR ($CDCl_3$) δ 3.08 (2 H, t, $J = 5.9$ Hz), 3.93 (2 H, t, $J = 5.9$ Hz), 4.06 (2 H, s),



7.01-7.97 (15 H, m); mass spectrum (m/e) 339 (M^+), 311 ($M^+ - N_2$).

Under similar conditions irradiation of Ib in benzene at room temperature yielded the corresponding 1,2,4-triazepine IIb (59%) [mp 131-133°; uv (EtOH) 205 ($\log \epsilon$ 4.41), 259 ($\log \epsilon$ 4.41), 259 ($\log \epsilon$ 4.30), 362 nm ($\log \epsilon$ 2.94); NMR (CDCl_3) δ 1.00-2.25 (10 H, m), 3.17 (1 H, m), 5.54 (1 H, d, $J = 7.1$ Hz), 6.49 (1 H, d, $J = 7.1$ Hz), 7.13-7.45 (6 H, m), 7.53-7.7 (4 H, m); mass spectrum (m/e) 329 (M^+), 301 ($M^+ - N_2$)], along with IIIb^{8b} (8%) and IVb (4%).

Prolonged irradiation of Ia and Ib increases the yields of IVa and IVb, respectively, suggesting that the pyrrole IV is a secondary product. Actually, irradiation of IIb resulted in the quantitative formation of IVb under the conditions. Thus, at low conversion photolysis of I with careful temperature control led to the clean formation of a mixture of II and III. Quantum yields for the formation of IIa and IIb measured at ca. 6% conversion were 0.0034 and 0.0031, respectively.¹³

The formation of IIIa was efficiently quenched by added piperylene ($k_{q\tau} \sim 14 \text{ mol}^{-1} \text{ s}$),

whereas that of IIa could not be quenched by the quencher. The result suggests that the photochemical rearrangement leading to II involves a singlet state and that the triplet state gives the pyridazine III. The formation of the triazepine II may be rationalized by a mechanism involving an intermediate such as VII formed by the walk rearrangement from I.¹⁵ While the photochemical walk rearrangement in which methylene group^{7a-d} or oxygen atom^{7e,7f} moves around the π system have been detected in several systems, the present results provide the first example of such a photochemical walk rearrangement in which the aziridine nitrogen undergoes migration.

It is interesting to note that the triazanorcaradiene I undergoes the walk rearrangement via the singlet state with almost same efficiency as those observed in the case of 7,7-dimethyl-2,5-diphenyl-3,4-diazanorcaradiene.^{7a}

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- (9) Satisfactory elemental analyses were obtained for all new compounds.
- (10) Mp. 110-112°; uv (EtOH) 247 (log ϵ 4.17), 281 nm (log ϵ 3.86); NMR (CDCl₃) δ 4.95 (2 H, s), 6.48 (1 H, d, J = 3.0 Hz), 6.66 (1 H, d, J = 3.0 Hz), 7.10-7.37 (15 H, m); mass spectrum (m/e) 309 (M⁺).
- (11) Control experiments have shown that the product Va results from the spontaneous thermal decomposition of Ia under the irradiation conditions.^{8a}
- (12) The products were isolated by thick-layer chromatography (neutral alumina).
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- (15) An alternative dissociation-recombination mechanism involving nitrenes seems to be highly unlikely, since benzylnitrene generated by pyrolysis of benzyl azide has been shown to give only complex mixture of products.¹⁶
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