HETEROCYCLES, Vol. 11, 1978

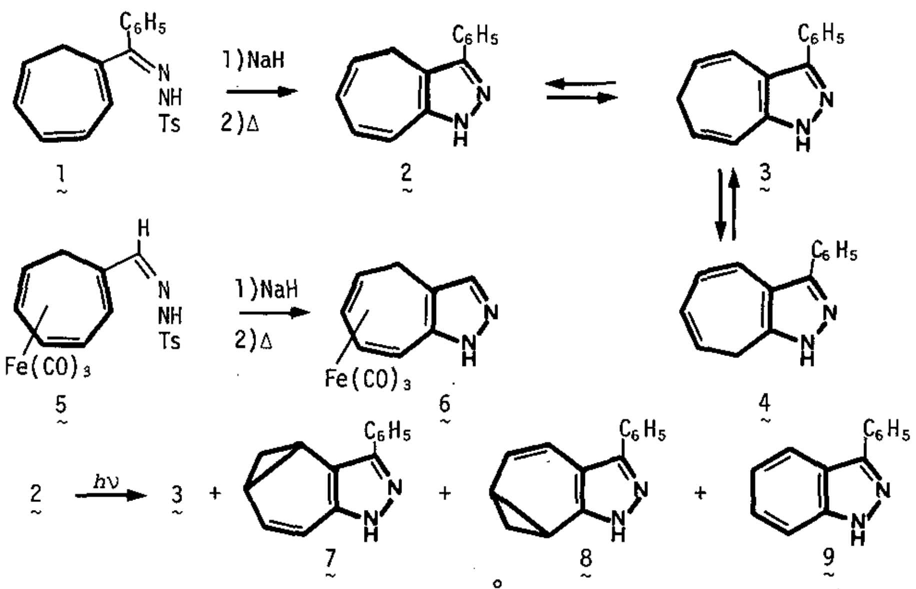
SYNTHESES, PHOTOCHEMICAL AND THERMAL ISOMERIZATIONS OF PYRAZOLOTROPILIDENES AND PYRAZOLONORCARADIENES[1]

Tsutomu Miyashi, Yoshinori Nishizawa, and Toshio Mukai*
Department of Chemistry, Faculty of Science, Tohoku University,
Sendai 980, Japan

Syntheses of several pyrazolotropilidene derivatives (2, 3, 4 and 6) and irradiation of the phenyl derivative (2) were studied to know the effect of the fused pyrazole ring on photochemical and thermal valence isomerizations of pyrazolonorcaradienes (7 and 8).

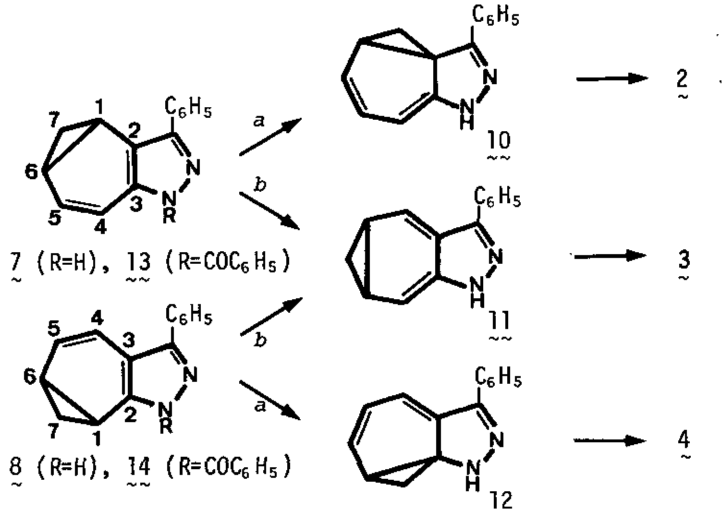
For the past ten years, photochemical[2] and thermal[3] isomerizations of benzonorcaradienes have been extensively studied. Whereas, those of norcaradienes fused with hetero-aromatic rings are little known. In order to investigate the effect of the hetero ring on photochemical and thermal isomerizations of norcaradienes, syntheses and photochemistry of pyrazolotropilidenes have been studied.

When the sodium salt of the tosylhydrazone (1) (mp 112°C)[4] prepared from the readily accessible corresponding ketone[5] was decomposed in diglyme at 135°C, (2) (mp 104°C) was isolated in 92% yield [ν_{max}^{KBr}, 2900 cm^{-1}; λ_{max}^{EtOH}, 246 nm (log ε, 4.08); m/e, 208 (M^+, 100%), 207, 131, 104, 77]. On the other hand, thermolysis of the sodium salt of the iron carbonyl complex (5) (mp 148°C, dec)[6] in diglyme at 100°C resulted in the formation of (6) (mp 122°C, dec)[7] in rather poor yield (28%) [ν_{max}^{KBr}, 3300, 2050, 1985, 1950 cm^{-1}; λ_{max}^{EtOH}, 220 (sh, log ε, 4.34) and 298 nm (sh, log ε, 3.68); m/e, 272 (M$^+$, not observed), 244, 216, 188 (100%), 132, 131, 105, 104, 77]. The silica gel - catalyzed equilibrium among (2), (3) and (4) was also found. Thus, upon treatment of (2) with silica gel (WAKO Q-22) in benzene for 12 hr at room temperature, red coloration developed on the surface of silica gel and (2), (3) and (4) were isolated in 23, 15 and 23% yields, respectively.[8] The structures of these pyrazolotropilidenes were straightforwardly determined by their nmr spectra.[9]



Irradiation of (2) (Rayonet RUL 3000 Å lamps) in dioxane for 11 hr afforded (3), (7), (8) and (9) in 6, 1, 62 and 6% yields, respectively. In order to know the sequence of these transformations, the ratios of products were monitored by the nmr spectroscopy. It was found that the starting (2) disappeared completely at the early stage of irradiation where the rapid formation of (7) was at its maximum. Furthermore, the slow formation of (3) and the delayed but rapid formation of (8) in proportion to the decrease of (7) were also observed. The formation of (4), however, could not be detected at all.

From these results, the formation of (3), (7), (8) and (9) from (2) can be explained by the sequence, (2) → (7) ⇄ (3) ⇄ (8) → (9), which is easily figured by the results observed in benzonorcaradienes.[2] Intriguing features, however, appeared in the directional selectivity of the photochemical carbon 1,5-shift termed a Berson-Willcott Bones rearrangement[10] of (7) and (8).

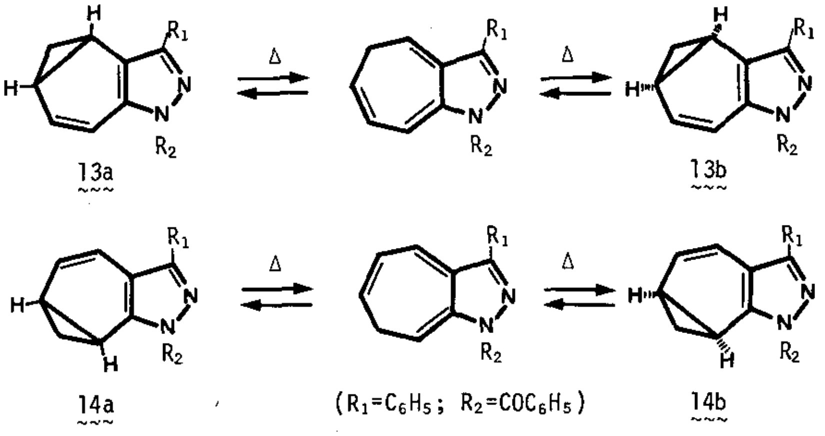


There are two possible pathways, *a* and *b*, for 1,5-shifts in this system. In pathway-*a*, the carbon C_7 migrates toward the pyrazole ring to give (2) and (4) through (10) and (12), respectively, while (3) is given from (7) and (8) through (11) by an alternative pathway-*b*. Above results together with additional evidence that irradiation of (7) did not afford (2) but (3) and (8)[11] accompanying (9) instead of (4) at the early stage of irradiation should suggest low efficiency of pathway-*a* both in (7) and (8). These selectivities are of interest as compared with opposite directional selectivities in 6-cyano and 6-carbomethoxybenzonorcaradienes[2] which force the carbon migrations only toward the benzene ring through pathway-*a*. The structures of the pyrazolonorcaradienes (7) and (8) were determined by comparisons of their nmr spectra with those of benzoates (13) and (14) shown in Table I.

Table I. NMR Spectra[a] of (7), (8), (13) and (14)

Compd	C(1)	C(4)	C(5)	C(6)	C(7)
(7)[c,d]	2.50 J_{17},7.8(*exo*) J_{17},5.6(*endo*) J_{16},7.9	6.63	6.32 J_{45},10.0 J_{56},5.0	1.79 J_{67},8.0(*exo*) J_{67},5.6(*endo*)	*exo* 1.38 *endo* 0.15 J_{ab},4.0
(7)[b,e]	2.51	6.23	6.23	1.9	exo 1.5 endo 0.03
(13)[b,d]	2.53 J_{17},6.5 J_{16},7.0	7.23 J_{45},10.0	6.44 J_{56},5.0	2.05 J_{67},6.5	0.82
(8)[b,e]	2.31	6.54	6.00	1.98	exo 1.38 endo 0.08
(14)[b,d]	3.34 J_{17},7.0 J_{16},7.5	6.45 J_{45},10.0	6.12 J_{56},5.0	2.19 J_{67},7.0	0.91

[a] Chemical shifts in δ units; coupling constant in Hz. [b] in $CDCl_3$.
[c] in C_6D_5. [d] 100 MHz. [e] 60 MHz.



(R_1=C_6H_5; R_2=COC_6H_5)

The benzoyl group in (13) shifts the C_4 hydrogen appearing at δ 6.23 in (7) to δ 7.23, while in (14) the C_1 hydrogen is shifted to δ 3.34 from δ 2.31 in (8). Additional differences were also observed in the chemical shifts of the cyclopropane methylene hydrogens. In (7) and (8) the *exo*- and *endo*-C_7 hydrogen appear separately, while in benzoates (13) and (14) two hydrogens come together at δ 0.82 and 0.91, respectively. These suggest the occurences of the tropilidene-norcaradiene valence isomerizations both in (13) and (14) even at room temperature. In fact, coalescence temperatures both for (7) and (8) (85°C) were found to be much higher than those for (13) and (14) (-36 °C) by temperature dependent nmr analyses.[12] Thus, activation parameters, $E\mathrm{a} = 10.6 \pm 2.1$ Kcal/mol; $\log A = 11.38 \pm 2.0\ \mathrm{sec}^{-1}$ for (13) (-38° ~ -103°C) and $E\mathrm{a} = 12.4 \pm 2.0$ Kcal/mol; $\log A = 13.3 \pm 2.1\ \mathrm{sec}^{-1}$ for (14) (-43° ~ -100°C), were obtained. The significantly low activation energies observed for (13a) $\rightleftarrows$ (13b) and (14a) $\rightleftarrows$ (14b) relative to that for benzonorcaradiene ($E\mathrm{a} = 19.4$ Kcal/mol)[3] could be accounted for mainly by the difference of resonance energies between benzene (36 Kcal/mol) and pyrazole (29.3 Kcal/mol).

REFERENCES

1 Dedicated to Professor Tetsuo Nozoe on the occasion of his 77th birthday. Organic Photochemistry 44. Part 43: K. Okada and T. Mukai, *J. Am. Chem. Soc.*, in press.

2 For example, J. S. Swenton, K. A. Burdett, D. M. Madigan, T. Johnson, and P. D. Rosso, *J. Am. Chem. Soc.*, **97**, 3428 (1975). References cited therein.

3 For example, E. Vogel, D. Wendish and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).

4 Satisfactory elemental analyses were obtained for all new compounds in this report.

5 J. A. Blair and C. J. Tate, *J. Chem. Soc. (C)*, 1592 (1971).

6 B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *J. C. S. Dalton*, 456 (1972).

7 The corresponding pyrazolotropilidene without $Fe(CO)_3$ has been prepared in low yield by several steps starting from tropilidene and diazomethane. K. Takatsuki, Ph.D. thesis, Tohoku University, Sendai, Japan, 1972.

8 The λ_{max} of (**2**) appears at 313 nm when (**2**) is adsorbed on silica gel suspended in cyclohexane. This suggests the structural change of (**2**) on the surface of silica gel.

9 NMR spectra of pyrazolotropilidenes (in $CDCl_3$): (**2**) (100 MHz), δ 11.28 (s, 1H), 7.25-7.55 (5H), 6.45 (dd, 10.8, 1.0 Hz), 6.10 (ddd, 10.8, 6.0, 1.5 Hz), 5.93 (ddd, 10.0, 6.0, 1.0 Hz), 5.63 (ddd, 10.0, 6.0, 1.5 Hz), 3.23 (d, 2H, 6.0 Hz); (**3**) (100 MHz), δ 12.20 (s, 1H), 7.2-7.8 (5H), 6.56 (d, 9.5 Hz), 6.30 (d, 9.5 Hz), 5.54 (dd, 9.5, 6.0 Hz), 5.38 (dd, 9.5, 6.0 Hz), 2.60 (dd, 6.0 Hz, 2H); (**4**) (60 MHz), δ 11.0 (s, 1H), 7.3-7.7 (5H), 6.7-7.0 (m, 1H), 5.9-6.4 (m, 2H), 5.2-5.8 (m, 1H), 3.1 (d, 6.0 Hz, 2H); (**6**) (100 MHz), δ 10.60 (s, 1H), 7.06 (s, 1H), 5.45 (dd, 9.0, 5.0 Hz), 5.36 (dd, 9.0, 5.0 Hz), 3.74 (d, 9.0 Hz), 3.47 (d, 9.0 Hz), 3.04 (dd, 19.0 Hz), 2.82 (dd, 19.0 Hz).

10 J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **88**, 2494 (1966).

11 The ratios of products (**3**) and (**8**) *vs.* irradiation time: 30 min, 86% (**3**), 14% (**8**); 60 min, 70% (**3**), 25% (**8**), 5% (**9**); 120 min, 57% (**3**), 33% (**8**), 10% (**9**).

12 H. S. Gutowsky and C. H. Holm, *J. Chem. Physics*, **25**, 122 (1956).

Received, 31st August, 1978