HETEROCYCLES, Vol. 55, No.10, 2001, pp. 1859 - 1872, Received, 13th July, 2001

THERMAL REARRANGEMENTS OF 3,3-SPIROALKYLATED PYRAZOLES: RING EXPANSION AND NOVEL CASES OF SEQUENTIAL 1,5-SHIFTS

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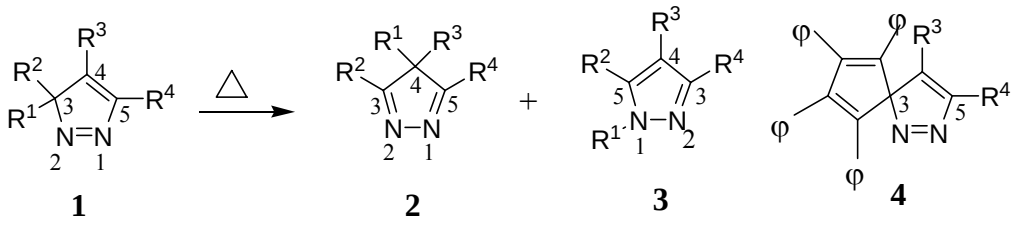
Abstract - A 3,3-spiro-(cyclopentyl)pyrazole containing electron withdrawing ester groups undergoes readily ring expansion in the form of the van Alphen-Huettel rearrangement. Subsequent post van Alphen-Huettel rearrangement involved a sequence of 1,5-shifts different from that suggested earlier. Reactive intermediates have been isolated and identified. The corresponding phenyl analog does not exhibit post van Alphen-Huettel rearrangement. A rationale for the different behavior is offered. X-Ray crystallography has been applied to differentiate between structurally similar product.

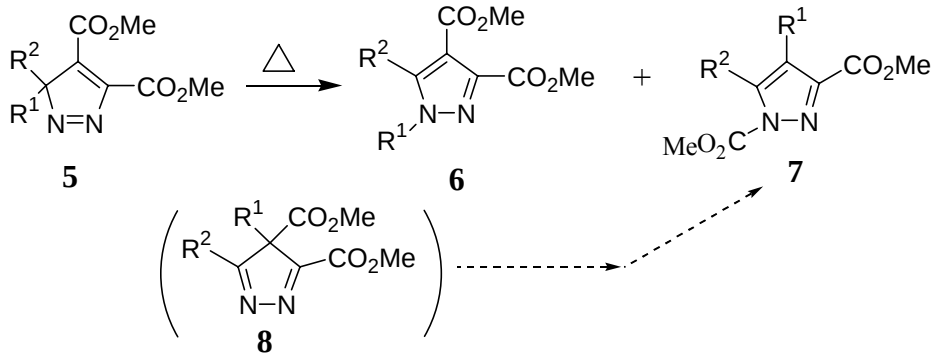
INTRODUCTION

1,5-Sigmatropic rearrangement of cyclopentadiene is a well known reaction that occupies an important chapter in symmetry correlation reactions.[1] Pyrazoles are hetero-cyclopentadienes; hence, their propensity in undergoing 1,5-shift is also well known and continued to be of an interest.[2] Such reactions, first studied by van Alphen, later were investigated in more detail by Huettel and coworkers.[3] Henceforth, the common alkyl rearrangements of 3-hydrogen or 3-alkylated pyrazoles (**1**) to the adjacent C or N centers giving respectively the 4*H*-pyrazoles (**2**) or the 1*H*-pyrazoles (**3**) are known as the van Alphen-Huettel rearrangements.[4]



1 **2** **3** **4**

Recent works,[4] particularly those of Warkentin and coworkers,[4] have shown that relative importance of the two1,5-rearrangements and in some cases of possible formation of further rearrangement products is a sensitive balance between the structure and electronic properties of the substituents. Hence, it was shown that for 3-acyl-3-alkylpyrazoles, the acyl migration to the adjacent N-center is the exclusive process taking place below room temperature[5] while corresponding migration of an alkyl group usually happens at >150℃. The 1,5-shift was shown to take place preferentially around the pyrazole ring rather than the cyclopentadiene ring in the 3,3-spiro-pyrazole (**4**).[6] And thermal rearrangement of **5** gave an unexpected product (**7**) in addition to the expected alkylated product (**6**) (corresponding to **3**).[2k] Since **7** was formed at the apparent expense of the C-alkyated product (**8**) (corresponding to **2**), it was suggested without proof that formation of **7** was achieved *via* two subsequent 1,5-shifts originating from **8** (a post van Alphen-Huettel rearrangement). The involvement of ion-pair intermediates for cases capable of forming stable carbocation added a new dimension to the rearrangement.[7]



5 **6** **7** **8**

In this paper, we would like to describe a study of thermal rearrangement and ring-expansion of 3,3-spiro-(cyclopentyl)pyrazoles. Because of our ability to isolate and identify the intermediates involved in secondary rearrangements in one system, we ascertained a new reaction pathway involved in the post van Alphen-Huettel rearrangement. These results are described below.

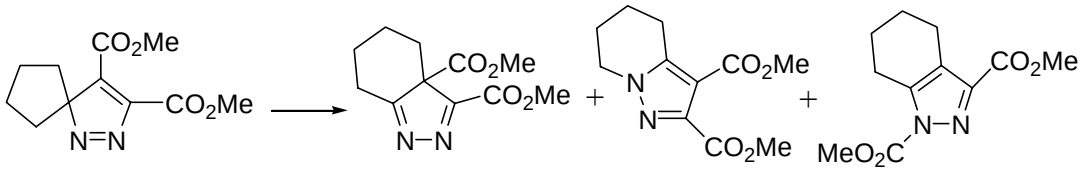
RESULTS AND DISCUSSION

Spiro-3*H*-pyrazoles (**9a-c**) were prepared following the procedure described in the literature.[8] Each of

the three pyrazoles in benzene solution (2.40×10^{-2}M) was degassed and sealed in Pyrex tubes and heated in an oil bath. Product formation was monitored using analytical HPLC. The kinetic data (Table 1, EXPERIMENTAL) followed unimolecular processes rigorously. For structural characterization, products were isolated by column chromatography from mixtures obtained from scaled up runs and identified by comparison of GC-MS, IR , ^{1}H NMR and ^{13}C NMR with those of authentic or similar, known compounds, supplemented by X-Ray crystallography (see Figures 1-5). Compound (**9a**) was studied in most detail. Its results were discussed first.

The diester spiral analog (9a). Compound (**9a**) was found to rearrange cleanly within the temperature range of 64-92℃ with an activation energy of 26.3 ± 0.1 kcal/mol and a log A value of 12.8 ± 0.1. In a preparative run, after heating a sample at 90℃ for 40 min, the reaction was found to be complete. Only one major product (**10a**) was isolated in 70 % yield. Its structure was characterized by comparison of spectral data with other van Alphen-Huettel rearranged products and by its X-Ray crystal structure (Figure 1). A trace amount of a minor product (0.4 %) was also detected which was subsequently characterized to be **11a** (see below). These products are those expected from the van Alphen-Huettel rearrangement involving ring expansion of the spiro-cyclopentyl ring. At 190℃ (60 min), the rearranged product mixture was found to contain, again, primarily a single, but different product (**12a**, 69 % isolated yield) at the complete expense of **10a** while the amount of **11a** increased to 8 % (Scheme 1 and Table 2).

Scheme 1



9a **10a** **11a** **12a**

Table 2. Experimental Reaction Conditions and Product Yields of the Thermal Reactions of Spiro-3*H*-Pyrazole (**9a**)

Condition		Yield (%) 10a	11a	12a
90 ℃	40 min	70	0.4	-
190 ℃	60 min	-	8	69

We were able to crystallize both of the isolated **11a** and **12a**. Their X-Ray crystal structures (Figures 2-3) removed any ambiguity in differentiating between them. Furthermore, the relative bond lengths clearly reflect the delocalized nature of the pyrazole rings for these two compounds, expectedly different from the localized structure of the isomeric (**10a**). Thus, that **11a** and **12a** are at the energy minima of the potential surface for 1,5-shifts can be readily rationalized by aromatic resonance stabilization.

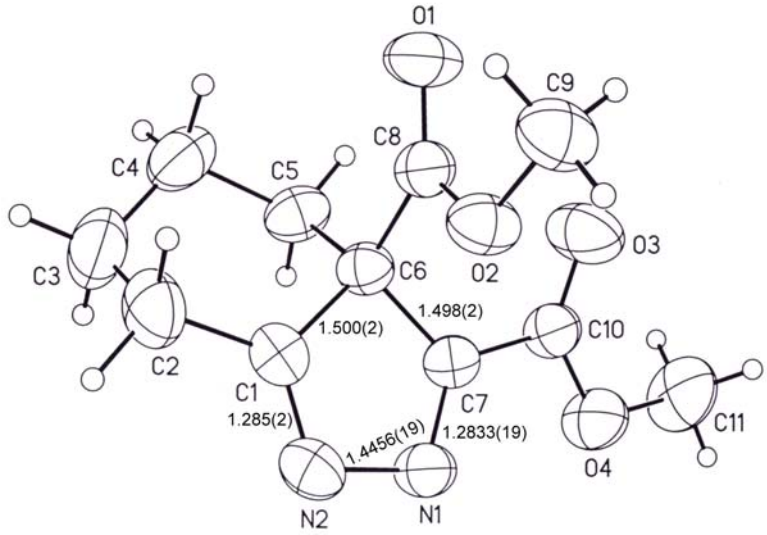


Figure 1. ORTEP Plots of Dimethyl 4,5,6,7-tetrahydro-3a*H*-indazole-3,3a-dicarboxylate (**10a**)

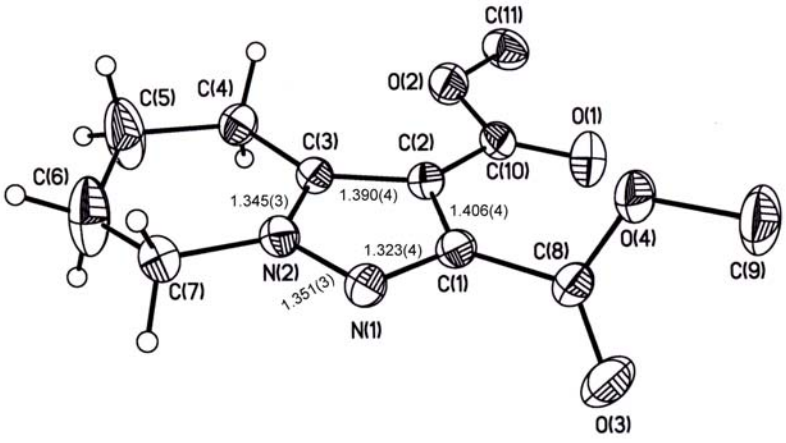


Figure 2. ORTEP Plots of Dimethyl 4,5,6,7-tetrahydropyrazolo-[1,5-*a*]pyridine-2,3-dicarboxylate (**11a**)

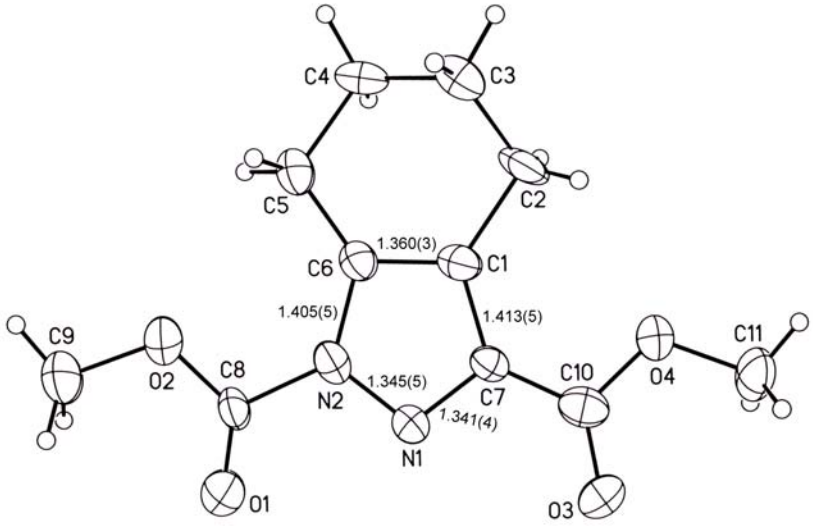
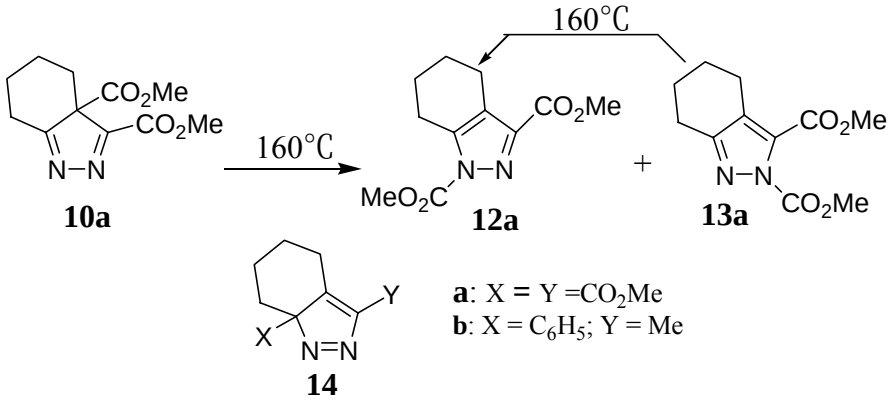


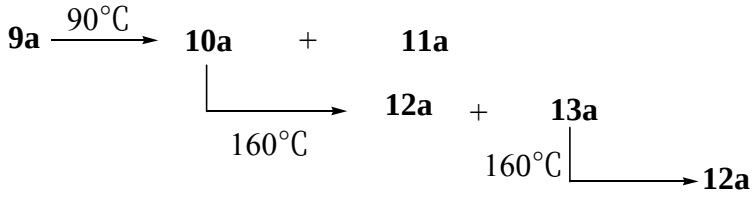
Figure 3. ORTEP Plots of Dimethyl 4,5,6,7- tetrahydro-indazole-1,3-dicarboxylate (**12a**)

To test whether **12a** originated from **10a** or not, we heated a sample of **10a** at a lower temperature (160 ℃ for 5 h). While we readily confirmed that **12a** (isolated yield 66 %) indeed originated from **10a**, much to our surprise, another isomer of pyrazole was also formed (**13a**, 19 %) (Scheme 2). But **13a** was an oil, thus its structure could not be elucidated by X-Ray crystallography. Fortunately, its spectral data were most informative. Its ^{13}C NMR spectrum exhibits three vinyl signals at 124.4, 132.5 and 149.6 ppm and two carbonyl ester carbons at 153.9 and 161.1 ppm, linked respectively to N and C-atom. These data are consistent with **13a** and not with the alternative structure (**14a**). The latter should have one C-signal at <100 ppm as in the structurally similar 5,6,7,7a-tetrahydro-3-methyl-7a-phenyl-4*H*-indazole (**14b**). [9] Finally with an isolated sample of **13a**, we found that upon heating (>160℃ for 5 h), it was cleanly converted to **12a** (89% yield).

Scheme 2



The sequence of reactions shown below summarizes the thermal reactions of **9a**. Indeed similar to that proposed previously,[2k] the unexpected product (**12a**) originated from the van Alphen-Huettel product (**10a**). However, the course of this post van Alphen-Huettel rearrangement is apparently two consecutive 1,5-shifts to **13a**[10] followed by another N,N-1,5-shift to **12a**. This is different from the proposed mechanism[2k] involving two 1,5-shifts with compound (**14a**) being the reactive intermediate.

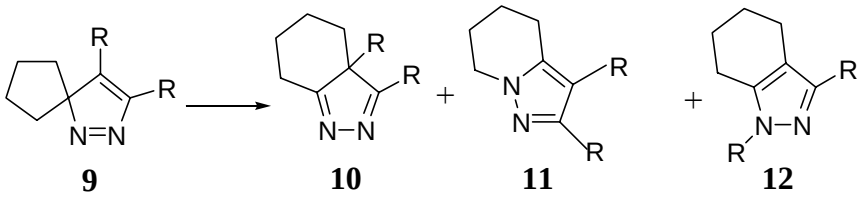


It is interesting that **10a** prefers the longer pathway of three 1,5-shifts to reach the final product. We suspect that the preference for the three consecutive "clockwise" 1,5-shifts rather than the two consecutive "counterclockwise" 1,5-shifts for the **10a** to **12a** is not controlled by thermal stability (or the lack of it) of the intermediate (**14a**) of the latter process. Rather, it is controlled by the conformation of the six-membered ring which makes 1,5-shifts across the ring-junction (the first step of the "counterclockwise" sequence) more difficult than the alternative "clockwise" 1,5-shift. However, it should be emphasized that the isolation of intermediate (**13a**) does not exclude a parallel route involving the unisolable **14a**, especially in other analogous systems.

Other spiro-3*H*-pyrazoles (9b and 9c). For the hydrogen analog (**9b**), upon heating at 140℃ for 30 min, the compound was converted completely to the final post van Alphen-Huettel product (**12b**) (95%)**.** On the other hand, for the diphenyl analog (**9c**), a much higher temperature (230℃, 2 min) was required for the van Alphen-Huettel rearrangement (activation energy = 32.1 ± 0.9 kcal/mol and log A = 13.8 ± 0.6) giving products (**10c**) and (**11c**) (Scheme 3 and Table 3). Their structures were also confirmed by their X-Ray crystal structures (Figures 4-5). The observed difference in rates (R = H > R = CO_2Me > R = C_6H_5) are clearly not a reflection of relative migratory aptitude (however, see below for additional discussion) because all these cases involved the migration of the same alkyl group. Instead, it appears to be controlled by product stability. In the phenyl case, the first step of 1,5-shift yielded a product with the loss of resonance stabilization of a stilbene unit; the diester case, the loss of conjugation of one

of the two ester functional groups; and in unsubstituted **9b,** no loss in resonance stabilization. These conclusions have since been confirmed by calculations.[11]

Scheme 3



9 **10** **11** **12**

Table 3. Experimental Reaction Conditions and Product Yields of the Thermal Reactions of Spiro-3*H*-Pyrazoles (**9b-c**)

				Yield (%)		
9	R	Condition		10	11	12
b	H	140℃	30 min	-	-	95
c	Ph	230℃	2 min	74	25	-

Furthermore, we found that prolonged heating of an isolated sample of the C-rearranged product (**10c**) at 230℃ only resulted in its complete conversion to the N-rearranged product (**11c**). Interestingly, at the mid-point of the this rearrangement (51 % conversion), we detected the presence of a small amount (0.11 %) of the spiro-reactant (**9c**). Apparently, the rearrangement of 1**0c** to **11c** involved reversion to the starting spiro structure.

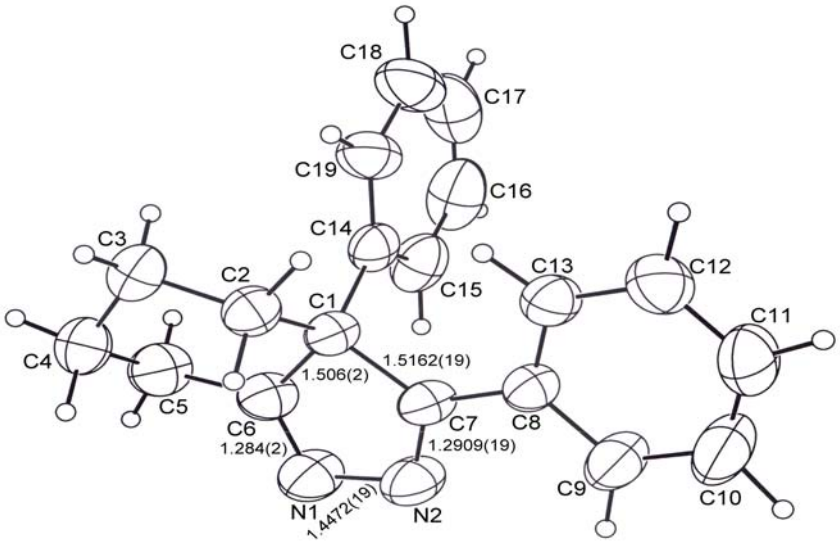


Figure 4. ORTEP plot of 3,3a-Diphenyl 4,5,6,7-tetrahydro-3a*H*-indazole (**10c**)

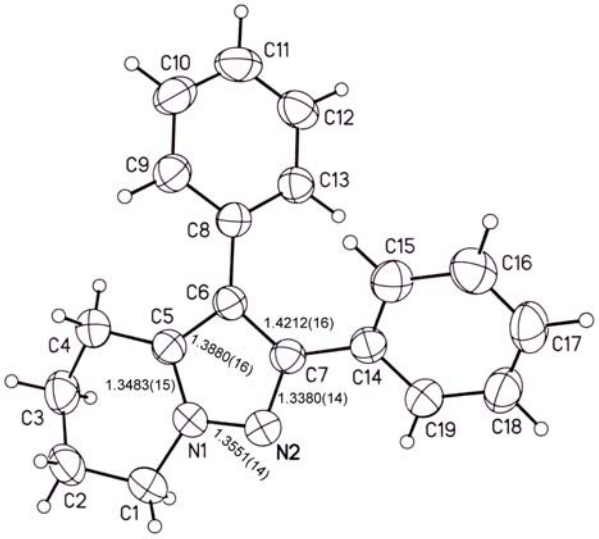
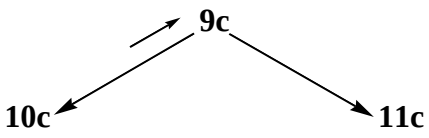
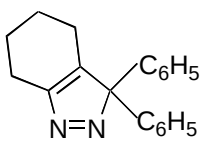


Figure 5. ORTEP plot of 2,3-Diphenyl 4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyridine (**11c**)

A few interesting points may be concluded from these observations. First, in this case no post van Alphen-Huettel rearrangement product was detected. We believe this is due to the fact that additional rearrangement would result in a further loss of resonance stabilization to give first, in the case of **10c,** compound (**15**). It is apparently too high in energy. Second, the reaction pathway for **10c** to **11c** has been clarified. Conversion of **10c** to **11c** (and also **10a** to **11a**, previous section) involves a formal 1,3-sigmatropic reaction, a symmetry forbidden process. The sequence of consecutive symmetry allowed 1,5-shifts with intermediacy of **9c** is therefore a logical alternative. The secondary rearrangement of **10c**, and related compounds, provides a good measure of the migratory aptitude of the two substituents at the quaternary carbon. In the case of **10c**, the result clearly shows the lower migratory aptitude of the phenyl group. Thus, it made reversion to the starting spiro-cyclopentyl system competitively possible. In the equivalent structure (**10a**), the ester group clearly migrates much more readily. This large difference in migratory aptitude for these two substituents is consistent with analogous examples in cyclopentadienes[12] and other pyrazoles,[5] favoring systems with electron deficient substituents.





15

In summary, because of our ability to isolate reaction intermediates in a van Alphen-Huettel rearrangement and another case of a post van Alphen-Huettel rearrangement, we were able to characterize the specific reaction pathways involved in different stages of the thermal rearrangements of the pyrazoles. A better understanding of relative product stability and migratory aptitude allowed us to rationalize the seemingly confusing and divergent pathways available to these compounds.

EXPERIMENTAL

General information. Melting point were determined on Yamaco micro melting points apparatus and are uncorrected. IR spectra were obtained on a Perkin Elmer 2000 spectrophotometer in KBr. ^{1}H NMR spectra were determined on a Bruker AC-250 spectrometer in $CDCl_3$ with TMS as an internal standard. High performance liquid chromatography (HPLC) was performed on a Dynamax Chromatograph equipped with Dynamax SD-200 pump and controller and a Water 486 detector.

Materials. The dimethyl 3,3-cyclopentyl-3*H*-pyrazole-4,5-dicarboxylate (**9a**), and 3,3-cyclopentyl-3*H*-pyrazole (**9b**) were prepared according to published procedures.[8] 3,3-Cyclopentyl-4,5-diphenyl-3*H*-pyrazole (**9c**) was prepared in sequence of reactions similar to those of 3,3-dimethyl-4,5-diphenyl-3*H*-pyrazole.[13] Hence, only characterization data are listed below.

3,3-Cyclopentyl-4,5-diphenyl-3*H*-pyrazole (9c)

Product (**9c**) was prepared following the literature[13] procedure and recrystallized from n-hexane; yield 26 %; mp 134-135℃; ^{1}H NMR ($CDCl_3$) δ: 1.86-2.02 (m, 6H), 2.28-2.35 (m, 2H), 7.13-7.43 (m, 8H), 7.70-7.74 (m, 2H); IR (KBr): 3056, 2969, 2870, 1454, 771, 710 cm^{-1}; MS m/z (%): 274 (M^+, 8), 246 (68), 218 (45), 217 (100), 203 (27), 202 (34), 178 (36); Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.21; H, 6.57; N, 10.22. Found: C, 83.33; H, 6.49; N, 10.19.

General Procedure for Thermal Rearrangement of 3*H*-pyrazoles (9a-c)

For preparataive purpose, thermal rearrangement was carried out by heating a solution (1.5 mL, 2.40 × 10^{-2} M) of the appropriate 3*H*-pyrazole in benzene in a sealed pyrex tube. After the rearrangement of reactant was complete (>95 %), the products were isolated by flash column chromatography on silica gel using the solvent mixtures: n-hexane/EA = 3/1 or n-hexane/EA = 5/1 for **10a** and **11a**.

Characterization data of the products are listed below.

Dimethyl 4,5,6,7-tetrahydro-3aH-indazole-3,3a-dicarboxylate (10a)

Yield 70 %; mp 94.5-95.5℃ (ethanol); ^{1}H NMR ($CDCl_3$) δ: 1.16-1.50 (m, 2H), 1.77-1.97 (m, 2H), 2.23-2.50 (m, 2H), 3.08-3.13 (m, 2H), 3.68 (s, 3H), 3.96 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 21.1, 27.5, 28.7, 35.3, 52.8, 53.1, 70.3, 159.8, 164.4, 167.6, 180.3; IR (KBr): 2955, 2860, 1754, 1720, 1562, 1443, 1367, 1219, 1091 cm^{-1}; MS m/z (%): 238 (M^+, 7), 206 (53), 179 (100), 163 (26), 147 (55), 135 (25), 119 (3), 91 (45); Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 55.61; H, 5.87; N, 11.55.

Dimethyl 4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyridine-2,3-dicarboxylate (11a)

Yield 0.4 %; mp 65-66℃ (n-hexane); ^{1}H NMR ($CDCl_3$) δ: 1.87-1.98 (m, 2H), 2.04-2.15 (m, 2H), 3.04 (t, 2H, J= 6.3 Hz), 3.83 (s, 3H), 3.94 (s, 3H), 4.19 (t, 2H, J= 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ: 19.3, 22.6, 23.1, 48.6, 51.6, 52.5, 110.5, 143.1, 144.8, 162.7, 163.0; IR (KBr) 2961, 1736, 1717, 1303, 1077 cm^{-1}; MS m/z (%): 238 (M^+, 22), 207 (94), 206 (100), 177 (22), 163 (16), 135 (10), 57 (29); Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 55.41; H, 5.84; N, 11.94

General Procedure for Thermal Rearrangement of 10a

Dimethyl 4,5,6,7-tetrahydro-3a*H*-indazole-3,3a-dicarboxylate (**10a**) (1.5 mL × 2.50 × 10^{-2} M) in benzene was degassed, sealed in pyrex tube and heated in an oil bath at 160℃ for 4 h. The reaction mixture was concentrated *in vacuo* and the products were isolated by flash column chromatography on silica gel using the solvent mixtures : n-hexane/EA = 9/1 for **12a** and **13a**. Characterization data of **12a** and **13a** are listed below.

Dimethyl 4,5,6,7-tetrahydroindazole-1,3-dicarboxylate (12a)

Yield 66 %; mp 152-154℃ (ethanol); ^{1}H NMR ($CDCl_3$) δ: 1.69-1.90 (m, 4H), 2.74 (t, 2H, J = 6.3 Hz), 2.98 (t, 2H, J = 6.1 Hz), 3.93 (s, 3H), 4.06 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 21.2, 21.9, 22.0, 24.1, 52.0, 54.7, 122.3, 143.8, 144.8, 150.3, 162.5; IR (KBr) 2955, 1767, 1730, 1442, 1312, 1257, 1205, 1139, 806, 765 cm^{-1}; MS m/z (%): 238 (M^+, 76), 206 (73), 179 (100), 147 (25), 135 (39), 59 (25); Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 55.44; H, 6.03; N, 11.69.

Dimethyl 4,5,6,7-tetrahydroindazole-2,3-dicarboxylate (13a)

Yield 19 %; bp 65℃/0.25 torr; ^{1}H NMR ($CDCl_3$) δ: 1.77-1.85 (m, 4H), 2.63 (t, 2H, J = 6.0 Hz), 2.71 (t,

2H, J = 6.3 Hz), 3.91 (s, 3H), 4.02 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 20.6, 22.2, 22.4, 23.4, 52.7, 55.0, 124.4, 132.4, 149.6, 153.9, 161.1; IR (neat) 2926, 2854, 1764, 1733, 1439, 1358, 1299, 1059, 804 cm^{-1}; HRMS calcd for $C_{11}H_{14}N_2O_4$: 238.09536. Found: 238.09545.

4,5,6,7-Tetrahydroindazole (12b)

Yield 95%; mp 78-79℃ (petroleum ether); ^{1}H NMR ($CDCl_3$) δ: 1.69-1.80 (m, 4H), 2.52 (t, 2H, J = 5.8 Hz), 2.65 (t, 2H, J = 5.7 Hz), 7.27 (s, 1H), 11.06 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ: 20.3, 21.9, 23.0, 23.4, 114.7, 131.5, 143.0; IR (KBr) 3160, 2931, 2852, 1443, 1342, 1087, 964, 854, 796 cm^{-1}; MS m/z (%): 122 (M^+, 35), 94 (100), 81 (4), 67 (7); HRMS calcd for $C_7H_{10}N_2$: 122.0843. Found: 122.0841.

3,3a-Diphenyl-4,5,6,7-tetrahydro-3a*H*-indazole (10c)

Yield 75 %; mp 151-153℃ (ether); ^{1}H NMR ($CDCl_3$) δ: 1.47-1.64 (m, 2H), 1.80-1.91 (m, 2H), 2.13-2.26 (m, 2H), 2.91-2.99 (m, 1H), 3.17-3.24 (m, 1H), 7.09-7.38 (m, 8H), 7.70-7.74 (m, 2H); ^{13}C NMR ($CDCl_3$) δ: 21.4, 26.6, 29.5, 34.6, 67.9, 125.3, 126.5, 127.1, 127.6, 127.8, 128.4, 129.5, 129.9, 130.5, 130.8, 132.5, 179.0, 183.2; IR (KBr) 3055, 2949, 2860, 1582, 1518, 1496, 1448, 1337, 772, 693 cm^{-1}; MS m/z (%): 274 (M^+, 32), 246 (81), 217 (54), 202 (20), 170 (38), 143 (87), 129 (100), 115 (29), 103 (36), 77 (29); Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21; Found: C, 82.90, H; 6.70; N, 10.35.

2,3-Diphenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyridine (11c)

Yield 11 %; mp 142-144℃ (ether/n-hexane); ^{1}H NMR ($CDCl_3$) δ: 1.82-1.96 (m, 2H), 2.07-2.82 (m, 2H), 2.80 (t, 2H, J = 6.3 Hz), 4.28 (t, 2H, J = 6.1 Hz), 7.18-7.35 (m, 8H), 7.43-7.47 (m, 2H); ^{13}C NMR ($CDCl_3$) δ: 20.2, 22.4, 23.2, 47.9, 116.3, 124.8, 126.1, 126.7, 127.1, 127.9, 128.2, 129.6, 130.9, 133.6, 137.9, 148.2; IR (KBr) 3048, 2950, 2863, 1600, 1542, 1496, 1431, 1347, 760 cm^{-1}; MS m/z (%): 274 (M^+, 100), 273 (42), 245 (10), 115 (8); Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 82.90, H; 6.75; N, 10.09; HRMS calcd for $C_{19}H_{18}N_2$: 274.1470. Found: 274.1467.

For kinetic runs, benzene solutions of an appropriate pyrazole sealed in pyrex tubes were heated in a constant temperature bath. Aliquots were taken for periodic analysis by HPLC. Conditions for analysis were: hplc, Partisil-10 column, 25 cm × 4.6 mm, solvent hexane: ether = 3 : 1. Selected rate constants are listed in Table 1.

Table 1. Rates of Rearrangement of **9a** and **9c**

Compound	T (℃)	$10^4 \times k\ (s^{-1})$
9a	64	0.52 ± 0.01
	71	1.31 ± 0.14
	76	2.42 ± 0.05
	82	3.81 ± 0.01
	92	11.09 ± 0.52
9c	130	2.03 ± 0.11
	136	3.50 ± 0.29
	140	5.34 ± 0.32
	144	7.92 ± 0.08
	151	14.44 ± 0.30

ACKNOWLEDGMENT

The authors gratefully acknowledge the National Science Council of the Republic of China for financial support and Dr. Y. J. Lee for helpful discussions.

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10. Conceptually a single 1,3-shift could have achieved the same results. But we believe the long accepted suprafacial 1,5-shifts for cyclopentadienes should apply here.
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