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A NEW REARRANGEMENT OF SPIRO-3H-PYRAZOLES

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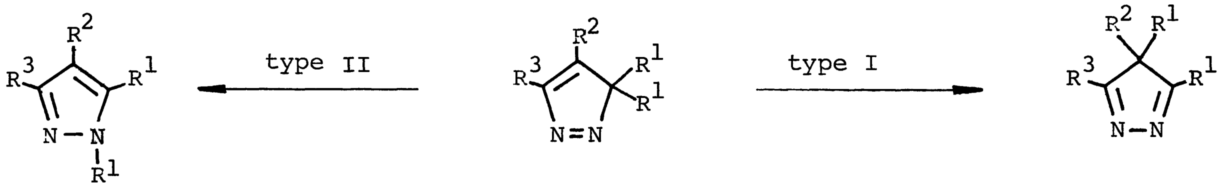
The thermally labile spiro-3H-pyrazoles obtained by the reaction of diazoindenothiophenes with dimethyl acetylenedicarboxylate rearranged into the corresponding 3H-pyrazoles which are formed via Van Alphen-Hüttel rearrangement followed by the migration of an ester group.

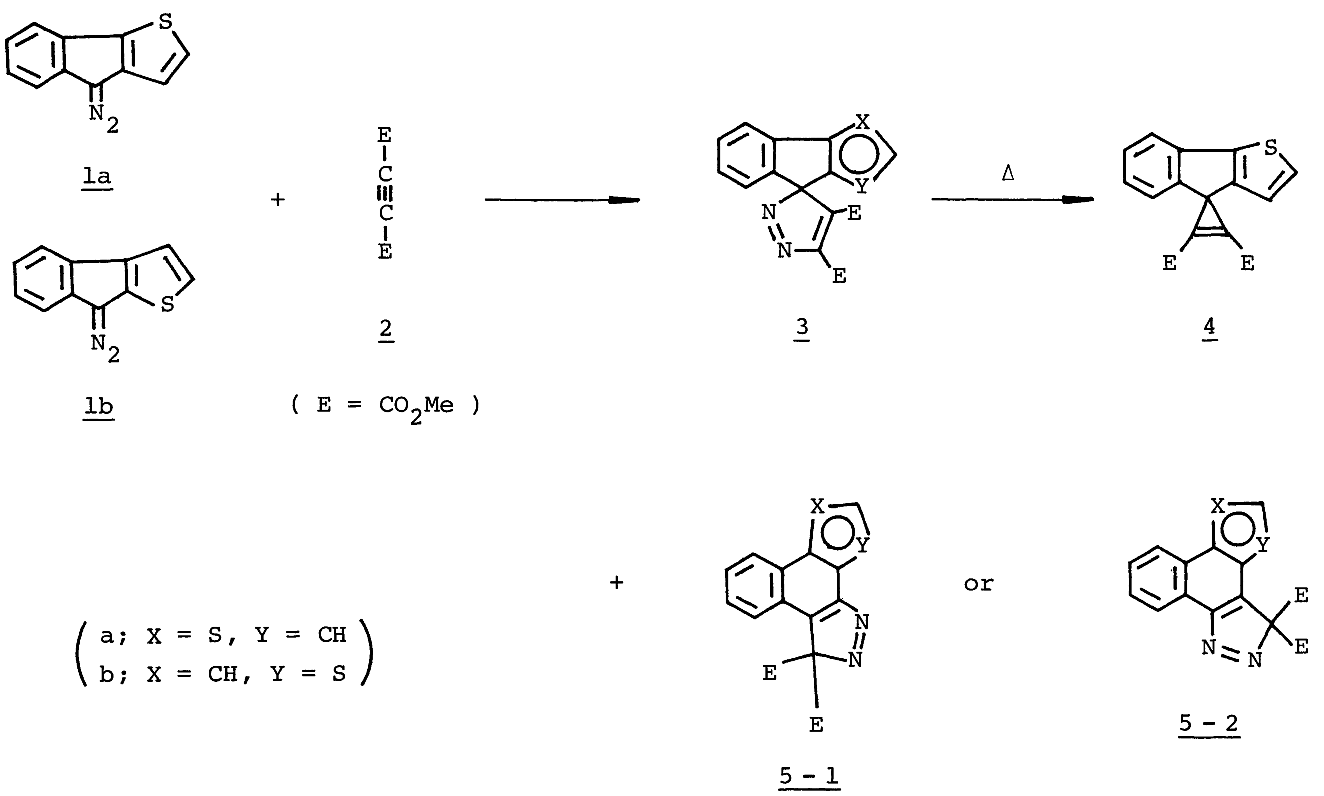
The Van Alphen-Hüttel rearrangement of 3,3-disubstituted 3H-pyrazoles is well studied[1-4] and now considered to proceed via the path way of type I and/or type II.



In the rearrangement of type I, the followings were proposed;[5] (1) if the substituents on sp^3-carbons of 4H-pyrazoles are alkyls or aryls, the compounds are stable; (2) if R^2= H, 4H-pyrazoles isomerize into 1H-pyrazoles; (3) if R^2 is an ester group, 4H-pyrazoles afford 1H-pyrazoles under drastic conditions.

In the present communication, we now describe the first example of the isolation of 3H-pyrazoles (5a and 5b) which are formed via a thermal migration of an ester group in the rearrangement of spiro-3H-pyrazoles (3a and 3b).

The reaction of 4-diazoindeno[1,2-b]- and 8-diazoindeno[2,1-b]thiophene (1a and 1b)[6] with dimethyl acetylenedicarboxylate (2) in ether at 0 °C for 2 h gave the thermally labile 1 : 1 -adducts (3).[7] When the adduct (3a) was pyrolyzed in benzene at reflux, a cyclopropene derivative (4) and the rearranged product (5a)[8] were isolated



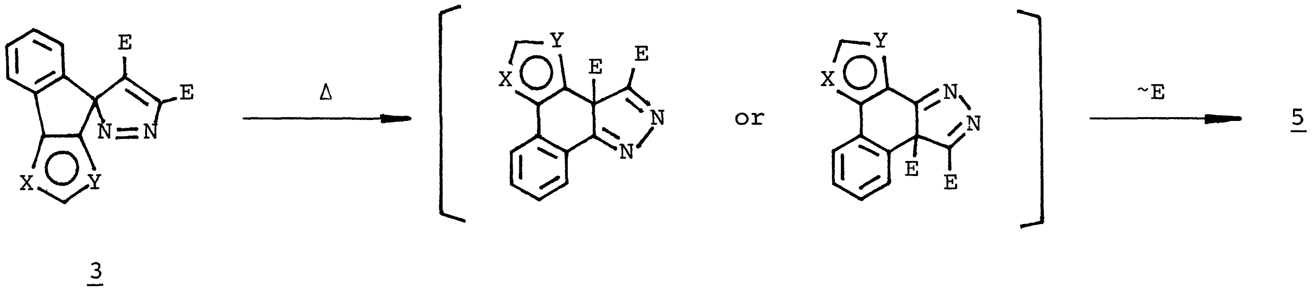
through column chromatography in 15 and 2% yields, respectively, together with a large amount of resinous materials. On being allowed to stand at room temperature in benzene or chloroform, the adducts (3) gradually rearranged into 5. After 3 days, the rearranged products (5a and 5b)[8] were obtained in the yields shown in the Table 1.

Table 1. Rearrangement of 3 into 5 at room temperature for 3 days

Product	Solvent	Yield 5 (%)
5a	$CHCl_3$	41
5a	C_6H_6	17
5b	$CHCl_3$	12
5b	C_6H_6	13

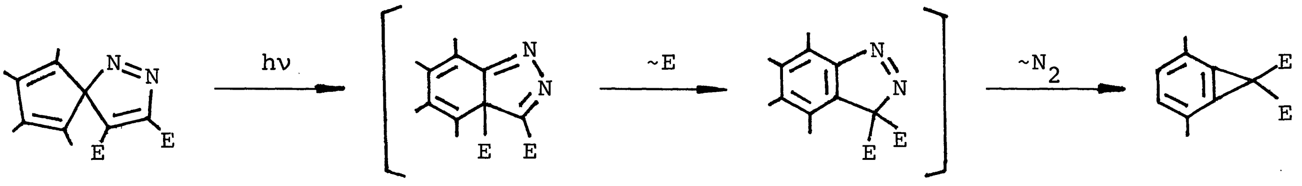
The structures of 5a and 5b were deduced from elemental analysis and spectral data.[8] However, it was not determined which structure 5-1 or 5-2 is correct based on the data at hand.

The formation of 5 from 3 is now considered to proceed via Van Alphen-Hüttel rearrangement followed by the migration of an ester group as is shown in Scheme 1.



Scheme 1

The photolysis of the substituted spiro-3H-pyrazoles was reported[9)] to afford the corresponding benzocyclopropenes and the pathway involving the migration of an



ester group bound on sp^3-carbon of 4H-pyrazoles is proposed, although no evidence of the occurrence of such migration was given. Our results mentioned above present a more direct evidence of the thermal rearrangement of the ester group bound on sp^3-carbon of 4H-pyrazoles to form 3H-pyrazoles.

The thermal rearrangement of other pyrazoles obtained by the reaction of diazocyclopentadiene derivatives with acetylenes is now in progress.

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6) Diazo compounds (1a and 1b) were prepared by the HgO-oxidation of the corresponding hydrazones. The parent ketones were prepared by the reported methods.[10-13)]

7) Analytically pure samples of 3a and 3b could not be obtained because of their

unstabilities, however, they gave satisfactory spectral data. The freshly obtained 3a was washed with hexane and submitted for elemental analysis (Found; C, 60.15, H, 3.64, N, 7.73; Calcd for $C_{17}H_{12}N_2O_4S$; C, 60.00, H, 3.55, N, 8.23).

3a: mp. 88 °C (d.); NMR: δ 3.54 (s, 3H, CH_3), 4.00 (s, 3H, CH_3), 6.50 (d, J = 5 Hz, 1H), 6.5-6.7 (m, 1H), 7.0-7.45 (m, 4H); IR (KBr): 1750, 1730 cm^{-1}.

3b: mp. 82 °C (d.); NMR: δ 3.72 (s, 3H, CH_3), 4.06 (s, 3H, CH_3), 7.1-7.7 (m, 6H); IR (KBr): 1740, 1720 cm^{-1}.

8) The compounds (4 and 5) were separated through column chromatography (Wako gel, C 300) using benzene as an eluent and purified by the recrystallization from hexane (4) or methanol (5a and 5b).

4: mp. 139-140 °C; NMR: δ 3.82 (s, 6H, CH_3), 6.93 (d, J = 5 Hz, 1H), 7.1-7.6 (m, 5H); IR (KBr): 1850, 1720 cm^{-1}; Mass: m/e (rel. int., %) 312 (M^+, 15), 281 (M^+-OCH_3, 9), 280 (M^+-HOCH_3, 32), 253 ($M^+-CO_2CH_3$, 26), 195 ($M^+-CO_2CH_3-CO_2CH_2$, 100) and 194 ($M^+-2CO_2CH_3$, 39); Anal. Found; C, 65.24, H, 3.88; Calcd for $C_{17}H_{12}O_4S$; C, 65.38, H, 3.87.

5a: mp. 159-160 °C; NMR: δ 3.82 (s, 6H, CH_3), 7.6-7.8 (m, 2H), 7.65 (d, J = 5 Hz, 1H), 7.85 (d, J = 5 Hz, 1H), 8.2-8.3 (m, 1H), 9.0-9.1 (m, 1H); IR (KBr): 1750, 1730 cm^{-1}; Mass: m/e (rel. int., %) 340 (M^+, 53), 312 (M^+-N_2, 16) and 297 ($M^+-N_2-CH_3$, 100); Anal. Found; C, 59.94, H, 3.65, N, 8.08; Calcd for $C_{17}H_{12}N_2O_4S$; C, 60.00, H, 3.55, N, 8.23.

5b: mp. 144-146 °C; NMR: δ 3.84 (s, 6H, CH_3), 7.7-7.85 (m, 2H), 7.90 (d, J = 5 Hz, 1H), 8.10 (d, J = 5 Hz, 1H), 8.4-8.5 (m, 1H), 9.0-9.1 (m, 1H); IR (KBr): 1750, 1730 cm^{-1}; Mass: m/e (rel. int., %) 340 (M^+, 90), 312 (M^+-N_2, 39) and 297 ($M^+-N_2-CH_3$, 100); Anal.Found; C, 60.17, H, 3.85, N, 7.82; Calcd for $C_{17}H_{12}N_2O_4S$; C, 60.00, H, 3.55, N, 8.23.

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