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THERMAL REARRANGEMENT OF 2-(BUTA-1,3-DIENYL)-2H-AZIRINES: FORMATION OF VINYLPYRROLES INSTEAD OF AZEPINES*

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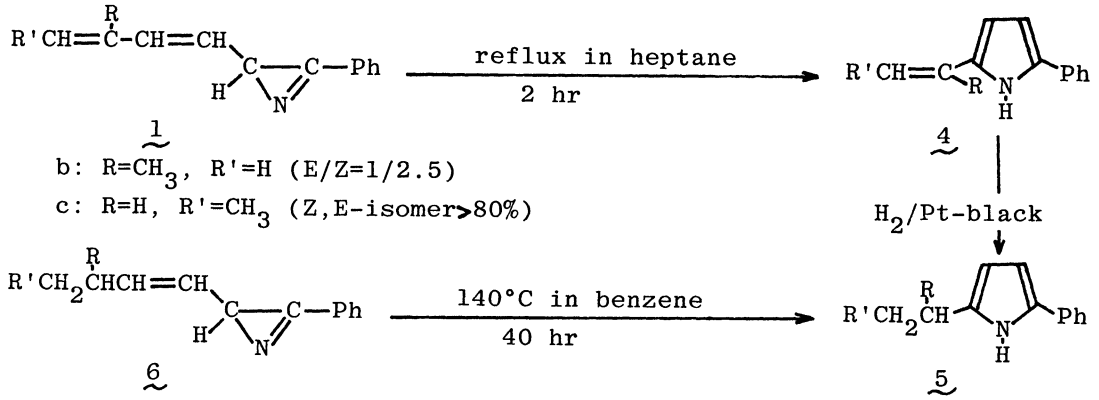
Thermal rearrangement of 2-(buta-1,3-dienyl)-2H-azirines, 1a, 1b, and 1c, afforded 2-vinylpyrroles, 4a, 4b, and 4c. The main product alleged as an azepine 2 was revealed to be a 2-vinylpyrrole 4a and evidence for the formation of the azepine 2 was not obtained.

Our early studies established that 2-aryl- and 2-styryl-2H-azirines thermally rearranged into indoles and pyrroles, respectively, via vinyl nitrene intermediates, which were produced by C-N bond fission.[1] Thermal rearrangement of 2H-azirines forming five-membered ring was exemplified by many authors[1,2,3] and is now considered as the general pathway in thermal reaction of 2H-azirines, which bear an unsaturated group at their 2-position.[2g,f] In thermal rearrangement of 2-styryl-2H-azirines, in which benzazepines and pyrroles might be the possible products, we could not obtain benzazepines but pyrroles quantitatively. On the other hand, photoreaction of Z-2-styryl-3-phenyl-2H-azirine gave a benzazepine via nitrile ylide formed by C-C bond fission.[2f] Recently, Padwa and his co-workers claimed that thermal reaction of 2-(4-carbomethoxybuta-1,3-dienyl)-3-phenyl-2H-azirine 1a afforded 2-carbomethoxy-7-phenyl-1H-azepine 2, instead of a pyrrole 4a.[3] Their results prompted us to investigate the thermal reactions of 2-(buta-1,3-dienyl)-2H-azirines 1, in detail. We found that thermal reaction of 1 gave exclusively 2-vinylpyrroles instead of azepines and confirmed that the structural assignment of the Padwa's azepine was incorrect.

2-(3-Methylbuta-1,3-dienyl)-3-phenyl-2H-azirine 1b was prepared by treating 2-formyl-3-phenyl-2H-azirine 3 with 2-methyl-2-propenylidene-1-triphenylphosphorane in ether at 0°C, and purified by molecular distillation (35∿45°C/0.05mmHg). The azirine structure was determined on the basis of NMR[4] and IR spectra ($\nu_{C=N}$, 5.75 μ). The ratio of E- to Z-isomer (E/Z) was determined to be 1/2.5 by the NMR signals of the vinyl protons situated β to the azirine ring, which were observed as doublets at δ 6.35 and 5.92.[4] Thermal rearrangement of this E,Z-mixture of 1b by heating in heptane under reflux for 2 hr was found to give colourless plates 4b, mp 80∿82°C, as a sole product. The structure of 4b was assigned as 2-phenyl-5-(2-propenyl)pyrrole by analytical and spectral results.[5] The confirmation of 4b was accomplished by catalytic hydrogenation into 2-phenyl-5-(2-propyl)pyrrole 5b, mp 53∿54°C, which was identical with the pyrrole prepared independently by thermal reaction of 2-(3-methylbut-1-enyl)-3-phenyl-2H-azirine 6b.

Reaction of 3 with 2-butenylidene-1-triphenylphosphorane afforded 2-(pent-1,3-dienyl)-3-phenyl-2H-azirine 1c, which was found to be a mixture of more than two geometric isomers, containing the Z,E-isomer as the major component (more than 80%) by NMR spectrum.[4] Thermal reaction of 1c by the same procedure as 1b gave colourless plates 4c, mp 79∿83°C, as the exclusive thermal product. On the basis of IR and NMR spectra[5] 4c was assigned as a mixture of E- and Z-2-phenyl-5-propenylpyrrole, in which the E-isomer was contained in more than 80%. Catalytic hydrogenation of this E,Z-mixture of 4c gave a single product, 2-phenyl-5-propylpyrrole 5c, mp 55∿56°C, which was confirmed by comparison with the thermal reaction product of 2-(pent-1-enyl)-3-phenyl-2H-azirine 6c.



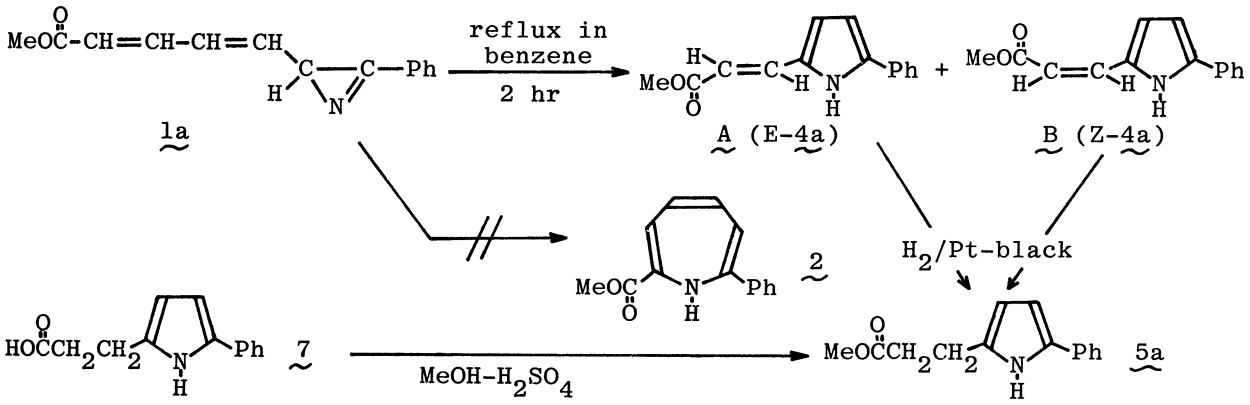
Since no azepine was detected in thermal reactions of two butadienyl azirines, 1b and 1c, we decided to reinvestigate the thermal reaction of the butadienyl azirine 1a, which was reported to afford the azepine 2.[3] The reported procedures were followed precisely. Reaction of 3 with 3-carbomethoxy-2-propenylidene-1-triphenylphosphorane in benzene at 50°C for 3 hr, followed by column chromatography on Florisil gave yellow needles A and dark oil. The dark oil was found to contain mainly isomeric mixture of 1a, as in the Padwa's case. Heating the dark oil for 8 hr[6] in benzene under reflux followed by chromatography on silica gel, gave A

Table. Physical properties of the thermal reaction products of 1a

Compound	Padwa and co-workers 2	Present study A	Present study B
mp (°C)	156∿157	159∿160	62∿63
MS (m/e)	227 (M^+)	227 (M^+)	227 (M^+)
IR (μ)	3.00, 5.92, 6.12	3.00, 5.95, 6.15, 10.16 ($\delta_{trans\text{-}HC=CH-}$)	3.11, 5.93, 6.20
NMR	3.72 (3H, s)[a]	3.78 (3H, s)	3.73 (3H, s)
(δ in $CDCl_3$)	6.30 (1H, d)	6.24 (1H, d J 16 Hz)	5.46 (1H, d J 12 Hz)
	6.60 (1H, d)	6.59 (2H, d J 3 Hz)[b]	6.50 (2H, m)[b]
	7.20∿7.80 (6H, m)	7.58 (1H, d J 16 Hz)[c]	6.67 (1H, d J 12 Hz)
		7.23∿7.73 (5H, m)	7.12∿7.71 (5H, m)
		9.36 (1H, bs)[d]	12.60 (1H, bs)[d]
UV ($\lambda^{95\%\ EtOH}_{max}$, nm)	388 (ε 29 300)	368 (ε 37 500)	376 (ε 27 500)

a) The reported NMR data were shown in τ value and lacked N-H signal. b) Coupled with N-H. c) Found by decoupling technique. d) Disappeared on addition of D_2O.

and another new yellow needles B, in 50 and 8% isolated yield, respectively. Physical properties of the azepine 2 reported by Padwa and those of A and B are shown in Table. The mp and spectral data of A almost coincide with those of 2, except the UV spectrum. The compound A was found to have trans-olefinic linkage (IR 10.16 μ. NMR δ 6.24, 7.58) and pyrrole ring (IR 3.00 μ. NMR δ 6.59, 9.36). These and the other results shown in Table demonstrate that the compound A should be E-methyl β-(5-phenyl-2-pyrrolyl)acrylate E-4a. The compound B was assigned as Z-4a, the Z-isomer of A, by spectral properties and analytical results, especially by the fact that IR and NMR spectra showed the presence of pyrrole ring (IR 3.11 μ. NMR δ 6.50, 12.60) and cis-olefinic linkage (NMR δ 5.46, 6.67). These structural assignments were further substantiated by the fact that the chemical shifts and the coupling constants of the olefinic protons are essentially identical with those reported for E- [δ 6.08 (1H, d J 16 Hz), 7.58, d J 16 Hz)] and Z-ethyl β-(2-pyrrolyl)acrylate [δ 5.02 (1H, d J 12 Hz), 7.58 (1H, d J 12 Hz)].[7] Catalytic hydrogenation reactions of A and B finally established their five-membered ring structures instead of azepine, as follows. Hydrogenation of A and B afforded a same product which was identified as methyl β-(5-phenyl-2-pyrrolyl)-propionate 5a, mp 106∿107°C, by comparison with the authentic sample prepared by esterification of the known acid 7.[8]



In this paper, we could demonstrate that three 2-(buta-1,3-dienyl)-2H-azirines also gave pyrrole derivatives by the pathway which is generally observed in thermal rearrangement of azirines bearing an unsaturated group at their 2-position. We have not yet obtained any evidence for azepine formation, although Z-1b and Z,E-1c have suitable configurations for azepine formation. Thermal azepine formation from 2H-azirine would require more compelling factors as will be described in the subsequent paper.

References and Notes

1 (a) K. Isomura, S. Kobayashi, and H. Taniguchi, Tetrahedron Lett., 3499 (1968). (b) K. Isomura, M. Okada, and H. Taniguchi, ibid., 4073 (1969). (c) K. Isomura, M. Okada, and H. Taniguchi, Chem. Lett., 629 (1972).

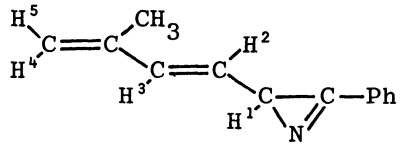
2 (a) E. F. Ullman and B. Singh, J. Am. Chem. Soc., 88, 1844 (1968). (b) H. J. Bowie and B. Nussay, Chem. Comm., 1565 (1970). (c) H. Hemetsberger, D. Knittel, and H. Weidmann, Monatsh. Chem., 101, 166 (1970). (d) H. Hemetsberger, D.

Knittel, and H. Weidmann, ibid., 103, 194 (1972). (e) T. L. Gilchrist, G. E. Gymer, and C. W. Rees, J. C. S. Perkin 1, 555 (1973). (f) A. Padwa, J. Smolanoff, and A. Tremper, J. Am. Chem. Soc., 97, 4683 (1975). (g) L. A. Wendling and R. G. Bergmann, J. Org. Chem., 41, 831 (1976).

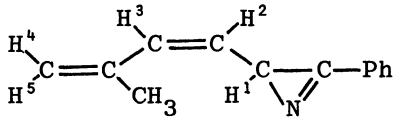
3 A. Padwa, J. Smolanoff, and A. Tremper, J. Org. Chem., 41, 543 (1976).

4 NMR spectra of 1b and 1c (δ in CCl_4).

1b Phenyl protons 7.40∿7.90. Other protons were assigned as below.



E-1b

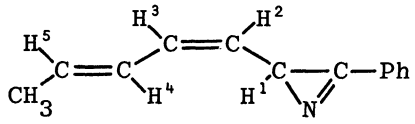


Z-1b

Methyl	1.77 s	Methyl	2.04 s
H^1	2.69 d, J 8 Hz	H^1	3.14 d, J 9 Hz
H^2	5.32 dd, J 8 and 15 Hz	H^2	4.76 dd, J 9 and 11 Hz
H^3	6.35 d, J 15 Hz	H^3	5.92 d, 11 Hz
$H^4$and H^5	4.83 bs	$H^4$and H^5	5.05 bs

1c 1.85 (3H, d), 3.05 and 2.70 (1H, d), 4.52∿7.00 (4H, m), 7.40∿8.10 (5H, m)

Aliphatic and olefinic protons in the Z,E-isomer were assigned as below.



Z,E-1c

Methyl	1.85 d, J 6.5 Hz
H^1	3.05 d, J 9.5 Hz
H^2	4.73 dd, J 9.5 and 11 Hz
H^3	6.16 t, J 11 Hz
H^4	6.63 dd, J 11 and 15 Hz
H^5	5.78 dq, J 6.5 and 15 Hz

5 Elemental analyses (EA) and spectral data of 4b and 4c.

4b EA Found C; 85.01, H; 7.25, N; 7.34%

Calcd for $C_{13}H_{13}N$ C; 85.20, H; 7.15, N; 7.64%

IR (nujol, cm^{-1}) 3450 vs. NMR (δ in $CDCl_3$) 2.07 (3H, s), 4.83 (1H, s), 5.07 (1H, s), 6.27 (1H, t J 3 Hz), 6.45 (1H, t J 3 Hz), 7.08∿7.63 (5H, m), 8.40 (1H, exchangeable bs). MS (m/e) 183 (M^+). UV [λ_{max} (ε) in 95% EtOH, nm] 320 (22 700)

4c EA Found C; 85.07, H; 7.15, N; 7.63%

Calcd for $C_{13}H_{13}N$ C; 85.20, H; 7.15, N; 7.64%

IR (nujol, cm^{-1}) 3380 vs, 950 vs. NMR (δ in CCl_4) 1.80 and 1.92 (3H, d 7 Hz), 5.3∿6.3 (4H, m) (on decoupling with methyl protons at 1.80, a doublet with a coupling constant of 18 Hz was observed at 5.8), 7.00∿7.38 (5H, m), 8.0 (1H, exchangeable bs). MS (m/e) 183 (M^+). UV [λ_{max} (ε) in 95% EtOH, nm] 320 (29000)

6 Under the same reaction conditions (heating in benzene for 1 hr under reflux) reported by Padwa,[3] only one half of 1a reacted.

7 W. Flitsh and U. Neumann, **Chem.** Ber., 104, 2170 (1971).

8 R. Robinson and W. M. Todd, J. Chem. Soc., 1743 (1939).

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