

Reaction of Diazoindenothiophenes with Mono- and Dibenzoylacetylenes

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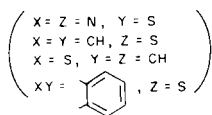
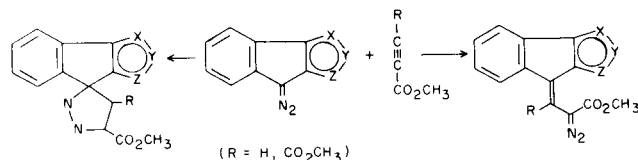
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Reaction of diazoindenothiophenes (**1** and **2**) with benzoyl acetylene (**4**) afforded the rearrangement products (**6a** and **b**) of the initial adducts. The major product of the reaction of diazo indenothiophene (**3**) with **4** was butadiene derivative **8a**. Reaction of **1** with dibenzoylacetylene (**5a**) gave the rearranged pyrazole (**12**), while the reaction of **2** and **3**, afforded the butadiene derivatives (**8b-d**).

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Recently, we have reported (1,2) that the reaction of 4-diazoindeno[2,3-*c*]-1,2,5-thiadiazoles and diazoindenothiophenes (**1-3**) with acetylenic esters afforded pyrazolines or ring-opened diazoalkenes depending upon the



bulkiness of the fused heterocycles and the substituents of the acetylenes: (i) when Z = CH, pyrazolines or its rearranged pyrazoles were formed exclusively, and no formation of diazoalkenes was observed; (ii) when Z = S, pyrazolines were formed in the reaction with acetylenic diester, while diazoalkene-formation was observed in the reaction with methyl propiolate; (iii) in the reaction of diazoindeno[2,3-*c*]-1,2,5-thiadiazoles (Z = N), diazoalkenes were formed.

As an extension of the above, the reaction of diazoindenothiophenes (**1-3**) with benzoyl substituted acetylenes (**4** and **5**) is described in the present paper.

Results and Discussion.

The reaction of diazoindenothiophenes (**1-3**) with benzoyl acetylene (**4**) was carried out at room temperature in ether or benzene. The reaction proceeded more smoothly in benzene than in ether and the results are summarized in Table I and Scheme 1. The reaction of **1** and **2** with **4** afforded the Van Alphen-Hüttel rearrangement products (**6a** and **b**) of the initially formed pyrazolines, and a considerable amount of corresponding azines (**7a** and **b**) were formed in these reactions. On the other hand, in the reac-

tion of **3** with **4** in benzene, the compound **8a** was obtained as a major product in 57% yield, and corresponding pyrazole **6c** was obtained in 7% yield. The compound **8a** was the sole product in the reaction carried out in ether, though the yield of **8a** slightly decreased. The compound **8a** was deduced to possess a butadiene structure on the basis of analysis and spectral data, however, the stereochemistry of **8a** could not be clarified.

Table I

Diazo compound	Solvent	Reaction Time	
		(hours)	Products %
1	ether	24	6a (24), 7a (5)
1	benzene	8	6a (18), 7a (16)
2	ether	24	6b (12), 7b (38)
2	benzene	8	6b (12), 7b (43)
3	ether	24	8a (48)
3	benzene	24	8a (57), 6c (7)

In the pmr spectra of **9** and **10**, Ha-(δ 8.7-8.9 ppm) and Ha'-proton (δ 9.3-9.4 ppm) appeared in the lower region than Hb-(δ 8.5-8.6 ppm) and Hb'-proton (δ 8.5-8.6 ppm) did because of the presence of benzoyl and ester group, respectively. In the pmr spectra of **6a** and **6b**, and their related compound **11a** and **11b**, such a down-field shift

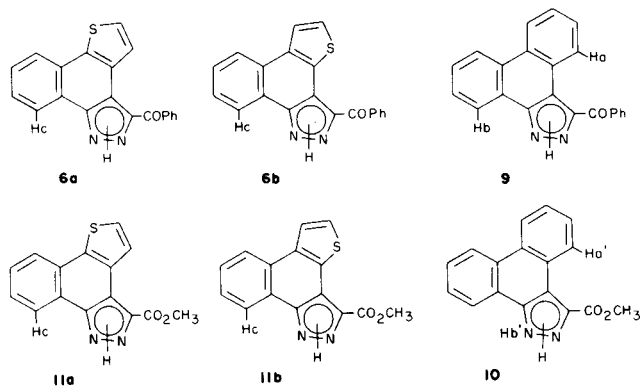


Table 2

¹³C-NMR Spectral Data for 2-Oxotetrahydropyridines **4** and **6**

Product	2-C	3-C	4-C	5-C	6-C	
4a	171.5 (s)	30.2 (t)	20.7 (t)	102.1 (d)	137.4 (s)	
4b	170.2 (s)	30.1 (t)	27.5 (t)	109.8 (s)	135.6 (s)	
4f	174.4 (s)	34.6 (d)	29.0 (t)	101.6 (d)	135.4 (s)	
4g	173.2 (s)	36.0 (d)	34.5 (t)	109.7 (s)	135.6 (s)	
6b	172.0 (s)	34.1 (t)	27.2 (t)	123.7 (s)	136.3 (s)	173.2 (s, C=O)

Table 3

Microanalytical, IR and ¹H-NMR Spectral Data for 2-Oxotetrahydropyridines **4** and **6**

Compound	Formula	Molecular weight	Analysis			ν max (Nujol)/cm ⁻¹	¹ H-NMR (δ from TMS)
			Found	Calcd.			
			C	H	N		
4a	C ₁₁ H ₁₁ NO	173.11	76.51 (76.31)	6.37 (6.35)	8.12 (8.08)	1690 (CO) 3200 (NH)	2.55 (d, t, 3H), 5.50 (m, H), 7.30-8.00 (m, HAr, NH)
4b	C ₁₂ H ₁₃ NO	187.11	77.22 (77.02)	7.04 (6.94)	7.39 (7.48)	1690 (CO) 3210 (NH)	1.75 (s, 3H), 2.20-2.60 (m, 4H), 7.00-7.50 (m, HAr, NH)
4c	C ₁₃ H ₁₅ NO	201.13	77.42 (77.62)	7.29 (7.45)	6.94 (6.96)	1690 (CO) 3200 (NH)	1.00 (t, 3H), 2.10 (q, 2H), 2.35-2.50 (m, 3H), 7.00-7.50 (m, HAr, NH)
4d	C ₁₂ H ₁₂ NOCl	221.57	65.14 (65.04)	5.37 (5.41)	6.33 (6.81)	1670 (CO) 3160 (NH)	1.70 (s, 3H), 2.30-2.70 (m, 4H), 7.10-7.50 (m, HAr, NH)
4e	C ₉ H ₁₃ NO	151.09	71.59 (71.54)	8.58 (8.60)	9.30 (9.26)	1680 (CO) 3190 (NH)	1.40-2.60 (m 12H), 8.40 (m, NH)
4f	C ₁₂ H ₁₃ NO	187.11	77.22 (77.02)	6.85 (6.94)	7.45 (7.48)	1670 (CO) 3180 (NH)	1.20 (d, 3H), 2.10-2.70 (m, 3H), 5.40 (m, H), 7.20-7.60 (m, HAr), 7.90 (m, NH)
4g	C ₁₃ H ₁₅ NO	201.13	77.72 (77.62)	7.39 (7.45)	6.88 (6.96)	1690 (CO) 3260 (NH)	1.25 (d, 3H), 1.80 (s, 3H), 2.10-2.80 (m, 3H), 6.90-7.50 (m, HAr, NH)
4h	C ₁₀ H ₁₅ NO	165.10	72.77 (72.74)	9.17 (9.08)	8.57 (8.47)	1680 (CO) 3200 (NH)	1.20 (d, 3H), 1.30-2.30 (m, 11H), 7.90 (m, NH)
6a	C ₁₃ H ₁₃ NO ₂	215.13	72.67 (72.57)	6.14 (6.04)	6.45 (6.50)	1710 (CO)	2.20-2.80 (m, 6H), 5.60 (dd, H), 7.10-7.50 (m, HAr)
6b	C ₁₄ H ₁₅ NO ₂	229.14	73.26 (73.37)	6.45 (6.54)	6.09 (6.11)	1710 (CO)	2.20 (s, 3H), 2.60-3.20 (m, 6H), 7.50-8.00 (m, HAr)
6h	C ₁₄ H ₁₅ NO ₂	229.14	73.33 (73.37)	6.59 (6.54)	6.21 (6.11)	1720 (CO)	1.60 (d, 3H), 2.45-3.15 (m, 6H), 6.15 (dd, H), 7.50-7.80 (m, HAr)

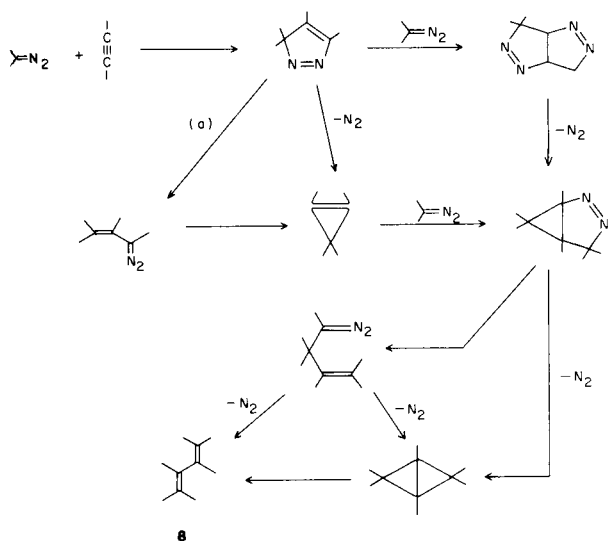
tetrahydropyridines were obtained through the formation of the corresponding adduct of *N*-alkylation. On the contrary, other unsaturated esters such as methyl cinnamate led to 2-oxotetrahydropyridines **5** which resulted from the intermediate product of *C*-alkylation (**6**).

The reaction of **1** with acrylamide and methacrylamide gave rise to the unequivocal formation of *N*-nonsubstituted 2-oxotetrahydropyridines **4**. For its simplicity and high yields, the procedure described in this paper should be the method of choice for the synthesis of heterocycles **4**. On

The pathway shown in Scheme 3 is proposed for the formation of butadiene derivatives in the reaction of diazo compound with acetylenes (3).

Although the formation of diazoalkene was not observed in the reactions of **1-3** with benzoylacetylenes **4** and **5**, it is interesting to note that diazoindenothiophenes **2** and **3**, which gave a rise to the formation of diazoalkenes in the reaction with acetylenic esters (2), afforded the butadiene derivatives **8**. Thus, the pathway (a) involving the intermediate formation of diazoalkenes is preferable for the formation-route of **8a-d**.

Scheme 3



EXPERIMENTAL

All melting points are uncorrected. Ir spectra were measured on a Nippon Bunko A-102 spectrophotometer as potassium bromide pellets. The pmr and cmr spectra were determined at 100 MHz on a Nippon Denshi JEOL FT-100 using TMS as an internal standard in deuteriodimethylsulfoxide unless otherwise stated. Mass spectra were obtained on a Nippon Denshi JMS-O1SG-2 mass spectrometer at 75 eV using a direct inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300).

Reaction of **1** and **2** with **4**.

To a stirred solution of **1** or **2** (100 mg) in a solvent (10 ml) was added dropwisely at room temperature a solution of **4** (65 mg) in a solvent (10 ml) and the mixture was stirred at room temperature for a reaction time given in Table 1. Solvent was evaporated *in vacuo* and the residue was column chromatographed. Compound **7** was eluted with benzene and then **6** with chloroform.

4-Benzoylbenzo[*g*]thieno[3,2-*e*]indazole (**6a**).

This compound was obtained as colorless needles (methanol), mp 220-224°; ir: ν NH 3350, ν CO 1640 cm^{-1} ; ms: *m/e* (relative intensity) 328 (M^+ , 100); pmr: δ 7.55-7.75 (m, 5H), 7.90 (d, 1H, $J = 5$ Hz), 8.10-8.20 (m, 3H), 8.43 (d, 1H, $J = 5$ Hz), 8.50-8.60 (m, 1H), 14.86 ppm (s, 1H).

Anal. Calcd. for $C_{20}H_{12}N_2O_2S$: C, 73.16; H, 3.68; N, 8.53. Found: C, 73.16; H, 3.86; N, 8.07.

4-Benzoylbenzo[*g*]thieno[2,3-*e*]indazole (**6b**).

This compound was obtained as colorless needles (methanol), mp

185-191°; ir: ν NH 3250, ν CO 1640 cm^{-1} ; ms: *m/e* (relative intensity) 328 (M^+ , 69), 271 (17), 196 (M^+ -PhCOCHN, 31), 105 (100); pmr: δ 7.60-6.80 (m, 5H), 7.82 (d, 1H, $J = 5$ Hz), 8.26 (d, 1H, $J = 5$ Hz), 8.24-8.35 (m, 2H), 8.56-8.66 (m, 2H), 14.99 ppm (s, 1H).

Anal. Calcd. for $C_{20}H_{12}N_2OS$: C, 73.16; H, 3.68; N, 8.53. Found: C, 72.77; H, 3.78; N, 8.09.

4*H*-Indeno[1,2-*b*]thiophen-4-one Azine (**7a**).

This compound was obtained as red solid (benzene), mp 190-194°.

Anal. Calcd. for $C_{22}H_{12}N_2S_2$: C, 71.72; H, 3.28; N, 7.60. Found: C, 71.84; H, 3.31; N, 7.22.

8*H*-Indeno[2,1-*b*]thiophen-8-one Azine (**7b**).

This compound was obtained as red solid (benzene), mp 182-187°.

Anal. Calcd. for $C_{22}H_{12}N_2S_2$: C, 71.72; H, 3.28; N, 7.60. Found: C, 71.70; H, 3.20; N, 7.21.

Reaction of **3** with **4**.

To a stirred solution of **3** (100 mg) in ether (10 ml) was added dropwise at room temperature a solution of **4** (52 mg) in ether (10 ml). The reaction mixture was stirred for 24 hours at room temperature and the precipitate **8a** (55 mg) was filtered.

The reaction of **3** with **4** in benzene was carried out as described above. The precipitated **6c** (10 mg) was filtered and the filtrate was column chromatographed using benzene as an eluent to give **8a** (65 mg).

6-Benzoylbenzo[*g*]benzothieno[2,3-*e*]indazole (**6c**).

This compound was obtained as colorless solid, mp 212-214°; ir: ν NH 3250, ν CO 1640 cm^{-1} ; ms: *m/e* (relative intensity) 378 (M^+ , 100), 321 (M^+ -N₂-COH, 5), 246 (M^+ -PhCOCNH, 17); pmr: δ 7.52-6.93 (m, 7H), 8.16-8.32 (m, 3H), 8.65-8.75 (m, 1H), 8.90-9.00 (m, 1H), 9.15-9.25 (m, 1H), 14.72 ppm (s, 1H).

Anal. Calcd. for $C_{22}H_{14}N_2O_2S$: C, 76.18; H, 3.73; N, 7.40. Found: C, 76.02; H, 3.84; N, 6.96.

bis(Benzo[*b*]thieno[2,3-*e*]indenylidene)-1-benzoylthane (**8a**).

This compound was obtained as brown prisms (methanol), mp 154-156°; ir: ν CO 1670 cm^{-1} ; ms: *m/e* (relative intensity) 570 (M^+ , 53), 465 (M^+ -PhCO, 75), 464 (67), 105 (100); pmr (deuteriochloroform): δ 7.00-8.10 ppm (m).

Anal. Calcd. for $C_{39}H_{22}O_2S_2$: C, 82.08; H, 3.89. Found: C, 81.79; H, 4.09.

Reaction of **1** with **5a**.

To a stirred solution of **1** (100 mg) in benzene (10 ml) was added dropwise at room temperature a solution of **5a** (117 mg) in benzene (10 ml), then the mixture was stirred for 3 hours at that temperature. Solvent was evaporated *in vacuo* and the residue was column chromatographed using benzene as an eluent to give **12** (90 mg) and **7a** (15 mg).

4,5(or 6)-Dibenzoylbenzo[*g*]thieno[3,2-*e*]indazole (**12**).

This compound was obtained as colorless needles (methanol), mp 197-199°; ir: ν CO 1695, 1675 cm^{-1} ; ms: *m/e* (relative intensity) 432 (M^+ , 33), 327 (M^+ -PhCO, 5), 105 (100); pmr (deuteriochloroform): δ 7.07 (d, 1H, $J = 5$ Hz), 7.77 (d, 1H, 5 Hz), 7.50-7.80 (m, 8H), 7.86-7.96 (m, 2H), 8.02-8.20 (m, 3H), 8.40-8.50 ppm (m, 1H).

Anal. Calcd. for $C_{27}H_{16}N_2O_2S$: C, 74.98; H, 3.73; N, 6.48. Found: C, 75.19; H, 3.65; N, 6.64.

Reaction of **2** with **5a**.

A reaction of **2** (100 mg) with **5a** (117 mg) in benzene was carried out and treated as described above, affording **7b** (20 mg) and **8b** (70 mg).

bis(Thieno[2,3-*b*]indenylidene)-1,2-dibenzoylthane (**8b**).

This compound was obtained as orange prisms (benzene), mp 104-107°; ir: ν CO 1660 cm^{-1} ; ms: *m/e* (relative intensity) 574 (M^+ , 4), 469 (M^+ -PhCO, 46), 364 (M^+ -2PhCO, 9), 105 (100).

Anal. Calcd. for $C_{38}H_{22}O_2S_2$: C, 79.42; H, 3.86. Found: C, 79.33; H, 3.92.

Reaction of **3** with **5a**.

A reaction of **3** (100 mg) with **5a** (94 mg) in benzene was carried out as described above. Solvent was evaporated *in vacuo* to leave the residue which, on trituration with methanol (2 ml) and on subsequent recrystallization from benzene, afforded **8c** (95 mg).

bis(Benzo[*b*]thieno[2,3-*d*]indenylidene)-1,2-dibenzoylthane (**8c**).

This compound was obtained as dark brown prisms, mp 195-199°; ir: ν CO 1660 cm^{-1} ; ms: *m/e* (relative intensity) 674 (M^+ , 3), 5.69 (M^+ · PhCO, 23), 464 (M^+ · 2PhCO, 11), 105 (100).

Anal. Calcd. for $C_{46}H_{26}O_2S_2$: C, 81.87; H, 3.88. Found: C, 81.48; H, 4.19.

Reaction of **3** with **5b**.

A reaction of **3** (100 mg) with **5b** (105 mg) in ether was carried out as described above. Solvent was evaporated *in vacuo* to leave the residue which, on recrystallization from methanol, gave **8d** (105 mg).

bis(Benzo[*b*]thieno[2,3-*d*]indenylidene)-1,2-di-*p*-toluylethane (**8d**).

This compound was obtained as dark brown prisms, mp 221°; ir: ν CO 1660 cm^{-1} ; ms: *m/e* (relative intensity) 702 (M^+ , 6), 583 (M^+ · $\text{CH}_3\text{C}_6\text{H}_5\text{CO}$, 12), 464 (M^+ · $2\text{CH}_3\text{C}_6\text{H}_5\text{CO}$, 6), 119 (100); pmr (deuteriochloroform): δ

2.23 (s, 3H), 2.26 (s, 3H), 6.84-8.30 ppm (m, 2H); cmr (deuteriochloroform): δ 21.7, 119.1, 122.0, 122.7, 123.4, 123.5, 124.6, 124.9, 125.1, 126.1, 129.0, 129.3, 130.1, 131.9, 133.0, 133.3, 134.3, 137.6, 137.7, 138.2, 138.9, 140.0, 143.2, 145.2, 145.7, 146.5, 193.8, 195.3 ppm.

Anal. Calcd. for $C_{48}H_{30}O_2S_2$: C, 82.02; H, 4.30. Found: C, 81.60; H, 4.51.

Hydrolysis of **10**.

Compound **10** (35 mg) was heated at reflux in a mixture of concentrated hydrochloric acid (1 ml) and ethanol (4 ml) for 1 hour. The reaction mixture was poured into water (50 ml), extracted with chloroform (30 ml) and dried over sodium sulfate. Evaporation of the solvent gave **6a** (20 mg).

REFERENCES AND NOTES

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