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Diene-Transmissive Diels-Alder Reaction of $\alpha,\beta:\alpha',\beta'$-Unsaturated Thioketones

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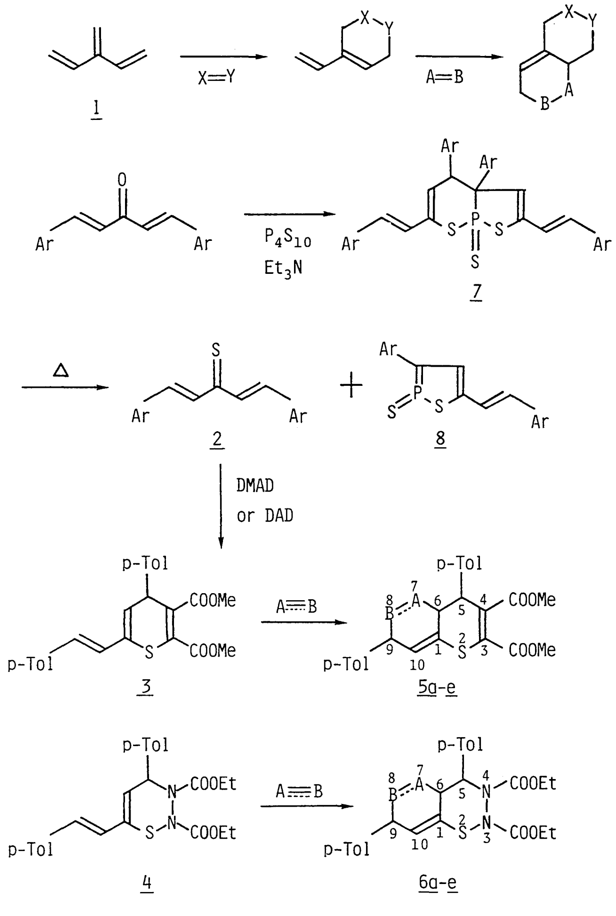
Synopsis. Diene-transmissive Diels–Alder reaction of 1,3-bis(*p*-tolylmethylene)-2-propanethione has been investigated. The cycloadducts obtained by the reaction of the thione with dimethyl acetylenedicarboxylate and diethyl azodicarboxylate underwent Diels–Alder reaction further with various dienophiles to give sulfur-containing polycyclic compounds.

The double cycloaddition reaction called domino,[1] timed,[2] tandem,[3] and diene-transmissive[4,5] Diels–Alder reactions are useful methods for the syntheses of polycyclic compounds. Among them, diene-transmissive Diels–Alder reaction consists of two sequential intermolecular Diels–Alder reactions of cross-conjugated trienes **1** with dienophiles X=Y and A=B.

Previously, we reported the first example of generation of cross-conjugated heterotrienes, viz. $\alpha,\beta:\alpha',\beta'$-unsaturated thioketones **2**, which were trapped by 2-norbornene, dimethyl acetylenedicarboxylate (DMAD), diethyl azodicarboxylate (DAD), and acrylonitrile as monocycloadducts.[6] As a continuation of the work, sequential Diels–Alder reactions of the remaining diene moiety in these adducts have been examined in the present study.[7]

The yield of the adduct with acrylonitrile was low,[6] whereas the second cycloaddition reaction of the mono adduct with norbornene was found to be very difficult to proceed probably due to steric hindrance of the norbornane ring. Therefore, cycloaddition reactions of the mono adducts with DMAD (**3**) and DAD (**4**) with various dienophiles were examined. The reactions of **3** and **4** with tetracyanoethylene (TCNE) and DAD proceeded rapidly in boiling benzene except in the case



Scheme 1.

Table 1. Reaction of the Adduct **3** with Dienophiles

Dienophile	Molar ratio	Reaction time	Product	Yield[a)]	Mp
	Dienophile/**3**			%	°C
TCNE	1.2	5 min	**5a**	100	165—166
DAD	1.2	30 min	**5b**	68	Orange oil
MA	5.0	20 h	**5c**	72	141—142
MI	5.0	21 h	**5d**	53	262—263
DMAD	5.0	51 h	**5e**	73	Orange oil

Table 2. Reaction of the Adduct **4** with Dienophiles

Dienophile	Molar ratio	Reaction time	Product	Yield[a)]	Mp
	Dienophile/**4**			%	°C
TCNE	1.2	10 min	**6a**	73	140—141
DAD	1.2	21 h	**6b**	74	166—167
MA	5.0	41 h	**6c**	52	193—195
MI	1.2	40 h	**6d**	47	Yellow oil
DMAD	5.0	100 h	**6e**	Trace	

a) Yields were based on the adduct **3** or **4**.

of **4** with DAD and the bis-adducts **5a,b** and **6a,b** were obtained in good yields. The reactions with DMAD, maleic anhydride (MA) and with *N*-(*p*-methoxyphenyl)maleimide (MI) were very slow under the same reaction conditions, then large excess of the dienophiles were used to promote the reaction. Attempted reaction at higher temperatures (boiling xylene) caused considerable decomposition of the product.

The structure of the product was readily determined by mass spectra, elementary analyses, IR and NMR spectra. ^{1}H NMR analysis reveals that the anhydride ring of the adducts **5c** and **6c** has an exo configuration. The other adducts with MA and MI (**5d** and **6d**) also seem to have exo configuration but their ^{1}H NMR spectra were somewhat ambiguous. All the adducts have trans relationship with respect to H_5 and H_6.[8]

It is considered that large difference between the reactiviy of -C=C-C=S- group in **2** and -C=C-C=C- group in **3** and **4** as dienes makes possible to isolate the mono-adduct under the thermolysis conditions of the phosphorus-containing precursor **7**.[9] Consequently, crossed diene-transmissive Diels–Alder reaction of the thioketone **2** was carried out easily and the results have wide application for the syntheses of various sulfur-containing polycyclic compounds.

Experimental[8]

All the melting points are uncorrected. IR spectra were measured on a Hitachi Model 270-30 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer in $CDCl_3$ solution using Me_4Si as an internal standard unless otherwise specified. Mass spectra were recorded on a Hitachi double-focusing mass spectrometer Model RMU-7M operating at an ionizing potential of 70 eV. Elementary analyses were performed using a Yanaco MT-3 CHN corder.

General Procedure for the Reaction of the Mono-Adduct (3 or 4) with Dienophiles. A solution of the mono-adduct (**3** or **4**) (1.0 mmol) and a dienophile (1.2 mmol or 5.0 mmol) in dry benzene (5.0 ml) was refluxed under a nitrogen atmosphere until the mono-adduct was completely consumed. The benzene was removed and the residue was chromatographed on a column of Wakogel C-200 with ethyl acetate–hexane (1:3) (for **5a,c,d,6b,c** and **d**) or ethyl acetate–hexane (1:4) (for **5b,e** and **6a**) as an eluent. The solid product was recrystallized from ethyl acetate–hexane.

7,7,8,8-Tetracyano-3,4-bis(methoxycarbonyl)-5,9-di-*p*-tolyl-2-thiabicyclo[4.4.0]deca-3,10-diene (5a): IR(KBr) 2256 (very weak, C≡N), 1740 cm^{-1} (C=O); ^{1}H NMR δ=2.36 (s, 3H), 2.40 (s, 3H), 3.40 (s, 3H), 3.81 (s, 3H), 3.94 (ddd, H-6, $J_{6,9}$=2.0, $J_{6,10}$=2.0, $J_{5,6}$=10.7 Hz), 4.40 (dd, H-9, $J_{6,9}$=2.0, $J_{9,10}$=4.3 Hz), 4.51 (d, H-5, $J_{5,6}$=10.7 Hz), 6.36 (dd, H-10, $J_{6,10}$=2.0, $J_{9,10}$=4.3 Hz), 7.10—7.47 (m, 8H); ^{13}C NMR δ=21.25(q), 41.72(s), 44.74(s), 46.59(d), 47.18(d), 47.52(d), 52.30(q), 53.37(q), 108.10, 109.66, 110.19, 111.02 (s, C≡N), 163.03(s), 165.17(s); MS *m/z* 420 (M$^+$ −TCNE, 41). Found: C, 68.10; H, 4.44; N, 9.91%. Calcd for $C_{31}H_{24}N_4O_4S$: C, 67.87; H, 4.41; N, 10.21%.

2,3-Bis(ethoxycarbonyl)-8,9-bis(methoxycarbonyl)-4,10-di-*p*-tolyl-7-thia-2,3-diazabicyclo[4.4.0]deca-5,8-diene (5b): IR (neat) 1745, 1730 cm^{-1} (C=O); ^{1}H NMR δ=1.00 (t, 6H, J=7.0 Hz), 2.30 (s, 3H), 2.34 (s, 3H), 3.40 (s, 3H), 3.78 (s, 3H), 3.93 (q, 4H, J=7.0 Hz), 4.20—4.40 (m, 2H), 5.17 (bs, 1H), 5.78 (bs, 1H), 6.96—7.32 (m, 8H); ^{13}C NMR δ=14.14 (q), 21.24 (q), 48.62 (d), 52.01 (q), 53.12 (q), 60.08 (d), 60.37 (d), 62.01 (t), 63.07 (t), 155.79 (s), 164.33 (s), 166.09 (s); MS *m/z* 594 (M$^+$, 4), 562 (M$^+$ −S, 13), 420 (M$^+$ −DAD, 31), and 419 (100). Found: *m/z* 594.2040. Calcd for $C_{31}H_{34}N_2O_8S$: M, 594.2037.

11,12-Bis(methoxycarbonyl)-7,13-di-*p*-tolyl-4-oxa-10-thiatricyclo[7.4.0.0^{2,6}]trideca-8,11-diene-3,5-dione (5c): IR (KBr) 1779, 1732 cm^{-1} (C=O); ^{1}H NMR (recorded on a JEOL JNM-GSX 500 spectrometer) δ=2.35 (s, 6H), 2.97 (dddd, H-1, $J_{1,7}$=1.8, $J_{1,8}$=2.4, $J_{1,2}$=4.9, $J_{1,13}$=11.0 Hz), 3.31(dd, H-2, $J_{1,2}$=4.9, $J_{2,6}$=9.2 Hz), 3.40 (dd, H-6, $J_{2,6}$=9.2, $J_{6,7}$=8.6 Hz), 3.41 (s, 3H), 3.70 (ddd, H-7, $J_{1,7}$=1.8, $J_{6,7}$=8.6, $J_{7,8}$=3.1 Hz), 3.80 (s, 3H), 4.75 (d, H-13, $J_{1,13}$=11.0 Hz), 6.40 (dd, H-8, $J_{1,8}$=2.4, $J_{7,8}$=3.1 Hz), 7.07—7.36 (m, 8H); ^{13}C NMR δ=21.05 (q), 42.99 (d), 43.62 (d), 44.79 (d), 46.11 (d), 46.50 (d), 52.10 (q), 53.08 (q), 162.88 (s), 166.73 (s), 169.02 (s), 170.29 (s); MS *m/z* 518 (M$^+$, 1.3), 486 (M$^+$ −S, 100) and 420 (M$^+$ −MA, 12). Found: C, 67.20; H, 5.10%. Calcd for $C_{29}H_{26}O_7S$: C, 67.17; H, 5.05%.

11,12-Bis(methoxycarbonyl)-4-(*p*-methoxyphenyl)-7,13-di-*p*-tolyl-10-thia-4-azatricyclo[7.4.0.0^{2,6}]trideca-8,11-diene-3,5-dione (5d): IR (KBr) 1738, 1710 cm^{-1} (C=O); ^{1}H NMR (CD_2Cl_2) δ=2.32 (s, 3H), 2.34 (s, 3H), 3.02—3.36 (m, 3H), 3.42 (s, 3H), 3.62—3.74 (m, 1H), 3.77 (s, 6H), 4.92 (d, H-13, $J_{1,13}$=8.8 Hz), 6.44 (dd, H-8, $J_{1,8}$=2.5, $J_{7,8}$=3.7 Hz), 6.81—7.38 (m, 12H); ^{13}C NMR δ=21.20 (q), 43.04 (d), 44.11 (d), 46.15 (d), 46.35 (d), 52.20 (q), 53.22 (q), 55.71 (q), 163.71 (s), 166.73 (s), 174.58 (s), 175.46 (s); MS *m/z* 623 (M$^+$, 1.2), 591 (M$^+$ −S, 61), and 419 (M$^+$ −MI-1, 100). Found: C, 69.26; H, 5.48; N, 2.12%. Calcd for $C_{36}H_{33}NO_7S$: C, 69.32; H, 5.33; N, 2.25%.

3,4,7,8-Tetrakis(methoxycarbonyl)-5,9-di-*p*-tolyl-2-thiabicyclo[4.4.0]deca-3,7,10-triene (5e): IR (neat) 1730 cm^{-1} (C=O); ^{1}H NMR δ=2.29 (s, 3H), 2.36 (s, 3H), 3.04 (s, 3H), 3.30 (s, 3H), 3.53 (s, 3H), 3.75 (s, 3H), 3.90 (d, H-6, $J_{5,6}$=11.0 Hz), 4.20 (d, H-5, $J_{5,6}$=11.0 Hz), 4.26 (d, H-9, $J_{9,10}$=4.2 Hz), 6.17 (d, H-10, $J_{9,10}$=4.2 Hz), 6.96—7.32 (m, 8H); ^{13}C NMR δ=21.20 (q), 43.86 (d), 45.47 (d), 51.71 (q), 51.81 (q), 52.15 (d), 52.98 (q), 164.34 (s), 166.15 (s), 167.02 (s), 167.12 (s); MS *m/z* 562 (M$^+$, 13) and 530 (M$^+$ −S, 45). Found: *m/z* 562.1642. Calcd for $C_{31}H_{30}O_8S$: M, 562.1662.

7,7,8,8-Tetracyano-3,4-bis(ethoxycarbonyl)-5,9-di-*p*-tolyl-2-thia-3,4-diazabicyclo[4.4.0]dec-10-ene (6a): IR (KBr) 2256 (very weak C≡N), 1742, 1722 cm^{-1} (C=O); ^{1}H NMR δ=1.16 (t, 3H, J=7.2 Hz), 1.28 (t, 3H, J=7.2 Hz), 2.38 (s, 6H), 4.18 (q, 2H, J=7.2 Hz), 4.24 (q, 2H, J=7.2 Hz), 4.15—4.45 (m, 2H), 5.82(d, H-5, $J_{5,6}$=11.2 Hz), 5.92 (dd, H-10, $J_{6,10}$=2.4, $J_{9,10}$=3.6 Hz), 7.17—7.50 (m, 8H); ^{13}C NMR δ=14.13 (q), 14.23 (q), 21.25 (q), 40.45 (s), 43.33 (d), 44.69 (s), 46.89 (d), 63.70 (d), 63.85 (t), 64.63 (t), 108.05, 109.61, 110.39, 110.93 (s, C≡N), 154.01 (s), 154.21 (s); MS *m/z* 452 (M$^+$ −TCNE, 1.0) and 277 (thione−1). Found: C, 63.86; H, 4.90; N, 14.28%. Calcd for $C_{31}H_{28}N_6O_4S$: C, 64.12; H, 4.86; N, 14.47%.

3,4,7,8-Tetrakis(ethoxycarbonyl)-5,9-di-*p*-tolyl-2-thia-3,4,7,8-tetraazabicyclo[4.4.0]dec-10-ene (6b): IR (KBr) 1750, 1728 cm^{-1} (C=O); ^{1}H NMR δ=1.00 (t, 3H, J=7.2 Hz), 1.16 (t, 3H, J=7.2 Hz), 1.27 (t, 6H, J=7.2 Hz), 2.33 (s, 6H), 3.94 (q, 2H, J=7.2 Hz), 4.14 (q, 2H, J=7.2 Hz), 4.20 (q, 2H, J=7.2 Hz), 4.24 (q, 2H, J=7.2 Hz), 5.11 (bs, 1H), 5.40—5.70 (m, 3H), 7.10—7.57 (m, 8H); ^{13}C NMR δ=14.04 (q), 14.28 (q), 14.38 (q), 14.48 (q), 21.20 (q), 57.32 (d), 59.61 (d), 61.99 (t), 63.41 (t), 64.19 (t), 66.43 (d), 154.74 (s), 155.62 (s); MS *m/z* 626 (M$^+$, 5.6), 451 (M$^+$ −DAD−1, 3.0) and 277 (thione−1, 9.6). Found: C, 59.71; H, 6.07; N, 8.66%. Calcd for $C_{31}H_{38}N_4O_8S$: C, 59.41; H, 6.11; N, 8.94%.

11,12-Bis(ethoxycarbonyl)-3,7-di-*p*-tolyl-4-oxa-10-thia-11,12-diazatricyclo[7.4.0.0^{2,6}]tridec-10-ene-3,5-dione (6c): IR (KBr) 1778, 1734 cm^{-1} (C=O); ^{1}H NMR δ=1.16 (t, 3H, J=7.0 Hz), 1.31 (t, 3H, J=7.0 Hz), 2.30 (s, 3H), 2.32 (s, 3H), 2.94 (dddd, H-1, $J_{1,7}$=2.5, $J_{1,8}$=2.5, $J_{1,2}$=5.1, $J_{1,13}$=10.7 Hz), 3.09 (dd, H-2, $J_{1,2}$=5.1, $J_{2,6}$=8.0 Hz), 3.46 (dd, H-6, $J_{2,6}$=8.0, $J_{6,7}$=9.3 Hz), 3.90 (ddd, H-7, $J_{1,7}$=2.5, $J_{7,8}$=3.7, $J_{6,7}$=9.3 Hz), 4.11 (q, 2H, J=7.0 Hz), 4.28 (q, 2H, J=7.0 Hz), 5.92 (d, H-13,

$J_{1,13}$=10.7 Hz), 5.92 (dd, H-8, $J_{1,8}$=2.5, $J_{7,8}$=3.7 Hz), 6.88—7.52 (m, 8H); ^{13}C NMR δ=14.23 (q), 14.38 (q), 21.05 (q), 38.50 (d), 40.35 (d), 41.87 (d), 46.25 (d), 59.41 (d), 62.92 (t), 64.38 (t), 156.20 (s), 156.30 (s), 168.34 (s), 169.80 (s); MS *m/z* 550 (M$^+$, 24). Found: C, 63.26; H, 5.41; N, 5.05%. Calcd for $C_{29}H_{30}N_2O_7S$: C, 63.26; H, 5.49; N, 4.94%.

11,12-Bis(ethoxycarbonyl)-4-(*p*-methoxyphenyl)-7,13-di-*p*-tolyl-10-thia-4,11,12-triazatricyclo[7.4.0.0^{2,6}]tridec-10-ene-3,5-dione (6d): IR (neat) 1785, 1714 cm^{-1} (C=O); ^{1}H NMR δ=1.14 (t, 3H, *J*=7.2 Hz), 1.29 (t, 3H, *J*=7.2 Hz), 2.29 (s, 3H), 2.33 (s, 3H), 2.96—3.48 (m, 3H), 3.73 (s, 3H), 3.48—4.00 (m, 1H), 4.10 (q, 2H, *J*=7.2 Hz), 4.26 (q, 2H, *J*=7.2 Hz), 5.98 (dd, H-8, $J_{1,8}$=2.2, $J_{7,8}$=3.9 Hz), 6.21 (d, H-13, $J_{1,13}$=10.7 Hz), 6.48—7.60 (m, 12H); ^{13}C NMR δ=14.18 (q) 14.28 (q), 20.91 (q), 21.06 (q), 39.38 (d), 41.13 (d), 41.33 (d), 45.47 (d), 55.27 (q), 59.07 (d), 62.67 (t), 64.09 (t), 156.10 (s), 156.20 (s), 174.14 (s), 175.01 (s); MS *m/z* 655 (M$^+$, 0.3). Found: *m/z* 655.2356. Calcd for $C_{36}H_{37}N_3O_7S$: M, 655.2354.

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7) In the thermolysis of phosphorus-containing precursor **7**, another component **8** could be trapped by norbornene.$^{6)}$ However, **8** does not have cross-conjugated double bond and therefore can not be utilized in diene-transmissive Diels–Alder reaction.

8) In the ^{1}H NMR spectral data, unified numbering of the product shown in Scheme 1 is used for convenience. It is irrespective of the nomenclature.

9) An exception is the reaction of **7** with MA where the 2:1 adduct of MA with **7** was obtained under all of the attempted reaction conditions.