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STUDIES ON DIELS-ALDER CYCLOADDITIONS OF VINYLKETENE DITHIOACETALS

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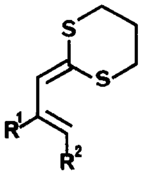
Abstract: The Diels-Alder cycloadditions of the acyclic and cyclic vinylketene dithioacetals 4 prepared from the corresponding oxoketene dithioacetals 2, either by 1,2-addition of methylmagnesium iodide and subsequent dehydration or by Wittig reaction, were studied. Thus 4a-e and 4h-i underwent facile [4+2] cycloaddition with maleic anhydride followed by elimination of methylmercaptan and subsequent aromatization through dehydrogenation to give 5-aryl/methyl -3-methylthiophthalic anhydrides (9a-e), the corresponding tetrahydronaphthalene (13) and dihydrophenanthrene (14) derivatives in good yields. The vinylketene dithioacetals 4f and 4g derived from higher alkylketones, on the otherhand, underwent sequential [4+2] cycloadditions with two moles of maleic anhydride to afford bicyclic adducts 10a and 10b respectively, while the cycloadditions of dithioacetals 4a and 4f with dimethylacetylene dicarboxylate afforded the corresponding substituted phthalates 12a and 12b in good yields. The dienes 4a-i were found to be unreactive towards weaker dienophiles like acrylonitrile, ethylacrylate and methylvinyl ketones.

The utilization of heterosubstituted dienes in Diels-Alder cycloadditions has been an area of great synthetic activity in the recent years[1]. Sulphur substituted dienes have broad synthetic potential because of the versatility of sulphur in organic synthesis and the ease of sulphur removal through desulphurization from the product adducts. A number of acyclic and cyclic sulphur containing dienes have been synthesized and shown to exhibit enhanced reactivity in cycloadditions as compared with their oxygen analogs[2]. On the other hand, the vinylketene dithioacetals derived from 1,3-dithiane are found to be rather unreactive in Diels-Alder reactions. Thus Carey and Court[3] have synthesized a number of alkylated allylidene 1,3-dithanes, of which only 1a was found to react with maleic anhydride to give the corresponding cycloadduct. Apparently, the activation of dienes by two sulphur atoms is not sufficient to overcome the steric hindrance due to rigid and bulky dithiane group. Similarly, the corresponding 2-(2-methoxyallylidene)-1,3-dithiane (1b) is reported to react with highly electrophilic dienophiles by Michael pathway, while [4+2] cycloadditions were observed with less electrophilic olefins such as methylvinylketone[4]. However, the vinylketene dithioacetals 4 should differ in their reactivity as dienes due to their structural differences from 1a involving terminally unsubstituted carbon and conformationally mobile bismethylthio groups, which might minimize the ring constraints displayed by allylidene 1,3-dithianes[5]. Besides, 4 should prove to be useful dienes to yield directly the dihydrobenzene derivatives, which can



1a, $R^1=R^2=Me$

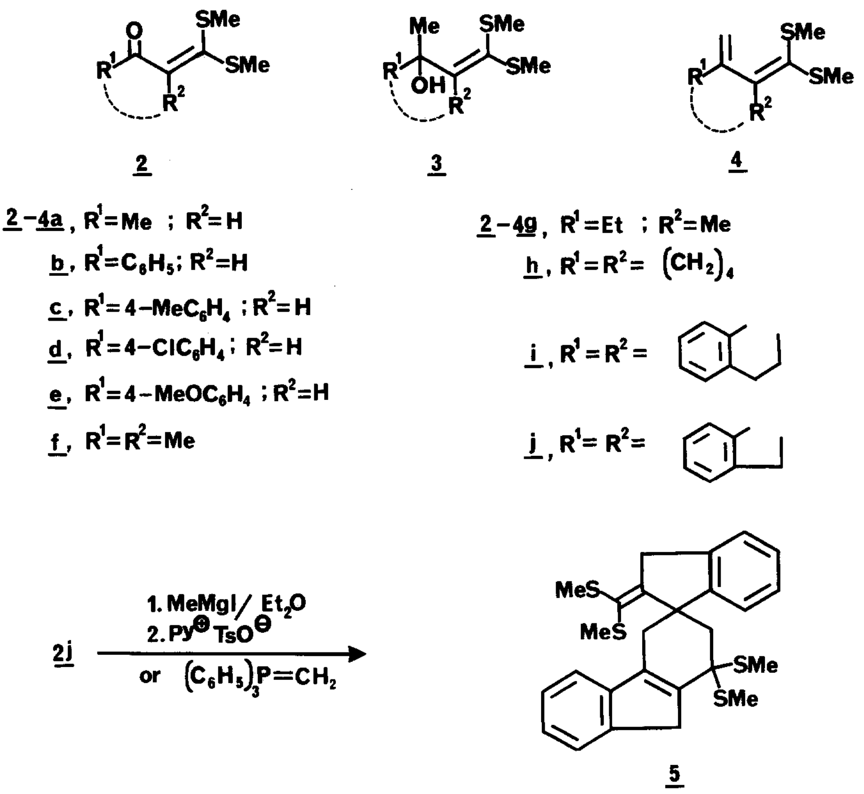
1b, $R^1=MeO, R^2=H$

easily transform into fully aromatic systems, since the elimination of the methylmercaptan is imminently facile. From our literature survey, we found that Thuillier and coworkers[6] have reported the preparation of a few of these dienes by Wittig Reaction on oxoketene dithioacetals, however, their reactivity as dienes in the light of above considerations remains unexplored.

In the course of our programmed studies on α-oxoketene dithioacetals[7], we had reported a facile 1,2-addition of methylmagnesium iodide to give the corresponding carbinolacetals 3 in high yields which on boron trifluoride etherate assisted methanolysis afforded the corresponding β-methyl-α,β-ene esters[8]. We further considered these carbinolacetals 3 as useful precursors for dienes 4 under appropriate dehydration conditions. We herein report the new route for the preparation of 4 and their cycloaddition studies under Diels-Alder conditions.

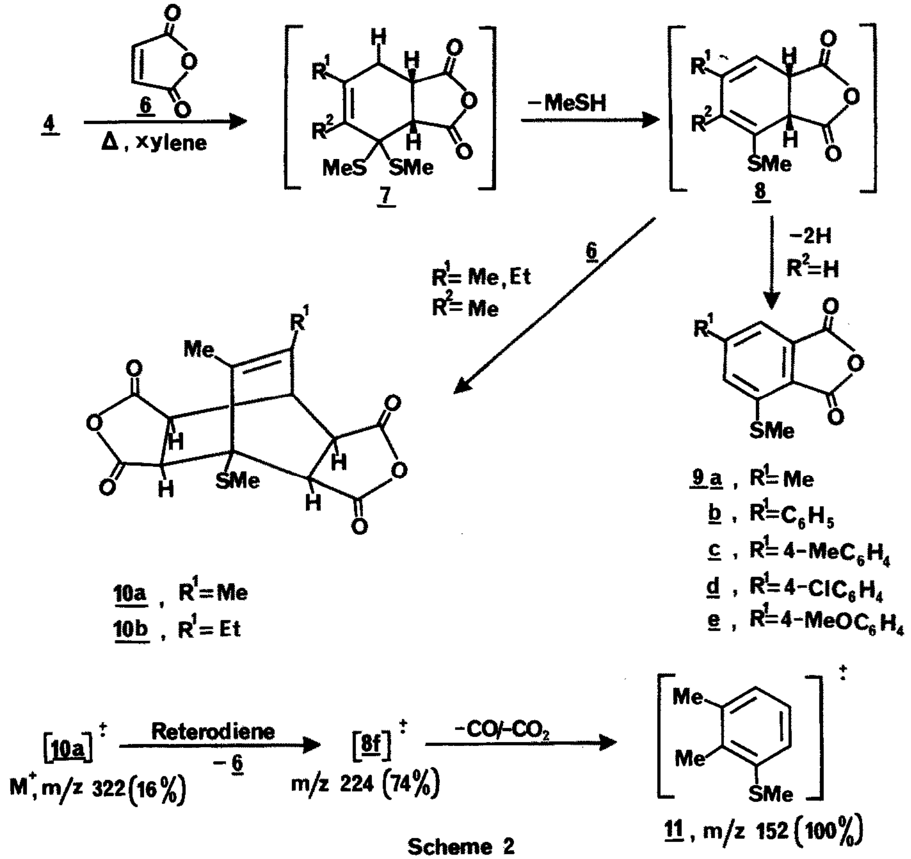
RESULTS AND DISCUSSION

The vinylketene dithioacetals 4a-f and 4i were prepared by 1,2-addition of methylmagnesium iodide to the respective oxoketene dithioacetals (2a-f,2i) and subsequent dehydration of the resulting carbinolacetals 3 in the presence of pyridinium tosylate. The dienes 4g and 4h were on the otherhand obtained by Wittig reaction[6], since the dehydration method in these cases gave the mixtures of isomeric dienes. The attempted preparation of 4j from oxoketene dithioacetal 2j derived from indanone, by either of the methods gave only the dimeric adduct 5(Scheme 1). The purified dienes 4a-i were characterized with the help of spectral data (IR and ^{1}H NMR) whereas the analytically pure samples could be obtained only in the case of dienes 4a,4f-i, since the attempted purification of 4b-e for elemental analysis resulted in their polymerization and decomposition. In a typical cycloaddition studies, when 4a was reacted with maleic anhydride in refluxing xylene in the presence of a trace of hydroquinone, the reaction mixture after work-up yielded a product(68%), which was characterized as 5-methyl-3-methylthiophthalic anhydride 9a on the basis of spectral and analytical data. Apparently the reaction has gone through initial 1,4-cycloaddition of 4a and 6 to give the adduct 7a, which on elimination of methylmercaptan and subsequent dehydrogenation of the resulting diene 8a under experimental conditions affords the fully aromatic 9a(Scheme 2). Cycloadditions of other acyclic vinylketene dithioacetals 4b-e and 6 similarly yielded the corresponding 5-aryl-3-methylthiophthalic anhydrides 9b-e in 62-72% overall yields. Interestingly, when the dithioacetal 4f derived from ethylmethyl ketone was reacted with maleic anhydride under identical conditions,



Scheme 1

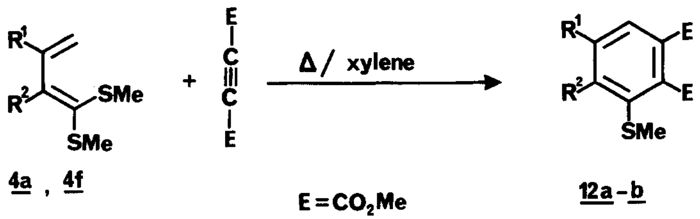
the product isolated after work-up was characterized as bicyclic anhydride 10a (45%), which was obtained in improved yield (88%), when 4f was reacted with excess of maleic anhydride. The structure of 10a was confirmed with the help of spectral and analytical data. Thus 10a was analyzed for $C_{15}H_{14}O_6S$, while its mass spectrum exhibited molecular ion peak at m/z 322 (16%) along with two prominent peaks at m/z 224 (74%) and m/z 152 (100%) due to the fragment ions 8f and 11 respectively (Scheme 2). The IR spectrum (KBr) of 10a showed characteristic anhydride carbonyl peaks at 1785 and 1858 cm^{-1} respectively. In the ^1H NMR spectrum (DMSO-d_6) of 10a, the absorptions due to two methyl and methylthio groups were present at δ 1.60, 1.63 and 2.23 (3H each) respectively, while the signals due to bridgehead and four methine protons appeared at δ 3.30(brs,1H) and 3.60(s,4H) respectively. The ^{13}C NMR spectrum of 10a confirmed its symmetrical structure and showed signals at δ 10.57($\underline{C}H_3$); 13.88($\underline{C}H_3$); 18.47 (S$\underline{C}H_3$); 38.94(bridgehead $\underline{C}H$), 44.37, 45.57($\underline{C}H$), 52.85(-$\underline{C}$-SMe), 131.43, 132.75(olefinic $\underline{C}$) and 168.18, 171.87($\underline{C}O$) respectively. The reaction of the corresponding 2-methyl-3-ethyl



Scheme 2

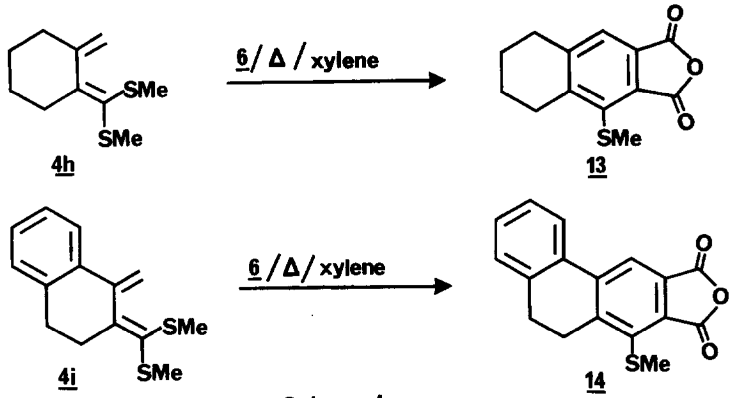
derivative 4g with 6 similarly afforded 10b in 86% yield. The structure of 10b was in conformity with its analytical and spectral data. The bicyclic adducts 10a and 10b are apparently formed by further [4+2] cycloaddition of the corresponding intermediate dienes 8f and 8g with maleic anhydride. The dehydrogenation of 8f and 8g is not favoured probably due to steric constraints in the resulting trisubstituted phthalic anhydrides. The dienes 4a and 4f also reacted with dimethylacetylene dicarboxylate under similar conditions to yield the corresponding substituted phthalates 12a and 12b in 74% and 67% yields respectively (Scheme 3). However 4a-g were found to be unreactive towards weaker dienophiles like acrylonitrile, ethyl acrylate and methylvinyl ketone.

The cycloadditions of cyclic vinylketene dithioacetals 4h-i with 6 was next examined. Thus 4h and 4i yielded the expected cycloaromatized tetrahydronaphthalene (13) and dihydrophenanthrene (14) derivatives in 71% and 76% yields respectively (Scheme 4). The structures of 13 and 14 were confirmed with the help of spectral and analytical data.



4a , 12a , R^1=Me ; R^2=H
4f , 12b , R^1=R^2=Me

Scheme 3



Scheme 4

In conclusion, it can be stated that vinylketene dithioacetals are inert towards weaker dienophiles like their 1,3-dithiano counterparts, while their reaction with highly activated dienophile like maleic anhydride provides a facile one step elaboration of benzene ring in the form of substituted phthalic anhydrides.

EXPERIMENTAL SECTION

Melting points were determined on a Thomas Hoover Apparatus and are uncorrected. The IR spectra were obtained on a Perkin Elmer 297 spectrophotometer. ^{1}H NMR spectra were recorded on Varian EM 390, 90MHz spectrometer while ^{13}C NMR spectra on Varian XL-300, 75MHz spectrometer and are reported in δ units downfield from Me_4Si. Mass spectra were obtained on Jeol JMS D-300 spectrometer.

General Procedure for the Preparation of Carbinolacetals 3a-f and 3i-j. The reaction of 2a with methylmagnesium iodide is representative. To an ice cooled (-5°C-0°C) suspension of methylmagnesium iodide [15 mmol, prepared from 0.36g(0.015 g atom) of magnesium turnings and 2.10 g (15 mmol) of methyl iodide] in dry ether (50 ml), a solution of 2a (1.60g,10 mmol) in dry benzene (25 ml) was gradually added (5 min.) and the reaction mixture was stirred at room temperature for 30 min. It was then poured into satd. NH_4Cl solution (100 ml), extracted with ether (3x50 ml), the combined extracts were washed with water, dried (Na_2SO_4) and evaporated to give carbinol 3a (1.6g, 90%) as light yellow oil; IR ν_{max}(neat) 3200-3500 cm^{-1}. All the carbinols 3a-f and 3i-j thus obtained in nearly quantitative yields were used as such for subsequent dehydration.

General Procedure for Dehydration of Carbinolacetals 3; Preparation of Vinylketene Dithioacetals (4a-f, 4i).- Dehydration of 3a is representative. A solution of 3a(1.76g, 10 mmol) and pyridinium tosylate (2.50g, 10 mmol) in CCl_4 (150 ml) was refluxed for 15 min. and the reaction mixture after cooling was filtered, washed with water (2x100 ml), dried (Na_2SO_4) and evaporated to give crude 4a which was further purified by passing through neutral alumina column using hexane as eluent. The pure 4b-e and 4i were obtained in this manner.

1,1-Bis(methylthio)-3-methyl-1,3-butadiene (4a); colourless viscous liquid (88%); IR ν_{max} (neat) 1605 cm^{-1}; ^{1}H NMR(CCl_4): 1.98(d,3H,J=1.5Hz,CH_3); 2.24(s,3H,SCH_3); 2.28(s,3H,SCH_3); 5.00(brs,2H,CH_2); 6.30(s,1H,H-2); (Found: C,52.74; H,7.82; Calc. for $C_7H_{12}S_2$: C,52.45; H,7.54%).

1,1-Bis(methylthio)-3-phenyl-1,3-butadiene (4b); colourless liquid (86%); IR ν_{max}(neat) 1600 cm^{-1}; ^{1}H NMR(CCl_4): 2.26(s,3H,SCH_3); 2.36(s,3H,SCH_3); 5.32(brs,1H,H-4); 5.46(s,1H,H-4); 6.44 (s,1H,H-2); 7.15-7.44(m,5H,ArH).

1,1-Bis(methylthio)-3-(4-methylphenyl)-1,3-butadiene (4c); yellow viscous oil (92%); IR ν_{max} (neat) 1605 cm^{-1}; ^{1}H NMR(CCl_4): 2.20(s,3H,CH_3); 2.28(s,6H,SCH_3); 5.20(brs,1H,H-4); 5.46(brs, 1H,H-4); 6.32(s,1H,H-2); 6.84-7.14(m,A_2B_2,4H,ArH).

1,1-Bis(methylthio)-3-(4-chlorophenyl)-1,3-butadiene (4d); yellow viscous liquid (90%); IR ν_{max}(neat) 1590 cm^{-1}; ^{1}H NMR(CCl_4): 2.24(s,3H,SCH_3); 2.32(s,3H,SCH_3): 5.28(brs,1H,H-4); 5.52(brs,1H,H-4); 6.35(s,1H,H-2); 7.08-7.46(m,4H,ArH).

1,1-Bis(methylthio)-3-(4-methoxyphenyl)-1,3-budadiene (4e); yellow viscous liquid (92%); IR ν_{max}(neat) 1600 cm^{-1}; ^{1}H NMR(CCl_4): 2.24(s,3H,SCH_3); 2.32(s,3H,SCH_3); 3.70(s,3H,OCH_3);5.12 (brs,1H,H-4); 5.48(brs,1H,H-4); 6.40(s,1H,H-2); 6.70(d,2H,J=9Hz,ArH); 7.26(d,2H,J=9Hz,ArH).

1,1-Bis(methylthio)-2,3-dimethyl-1,3-butadiene (4f); yellow oil (89%); IR ν_{max}(neat) 1642 cm^{-1}; ^{1}H NMR(CCl_4): 1.90(brs,3H,CH_3): 2.10(s,3H,CH_3); 2.21(s,3H,SCH_3); 2.30(s,3H,SCH_3);4.18 (brs,1H,H-4); 4.91(brs,1H,H-4); (Found: C,55.40; H,8.35; Calc. for $C_8H_{14}S_2$: C,55.12; H,8.09%).

2-Bis(methylthio)methylene-1-methylene-1,2,3,4-tetrahydronaphthalene (4i); yellow viscous liquid (90%); IR ν_{max}(neat) 1645, 1698 cm^{-1}; ^{1}H NMR(CCl_4): 2.22(s,3H,SCH_3); 2.31(s,3H,SCH_3); 2.66-3.02(m,4H,CH_2); 5.28(s,1H,olefinic); 5.74(s,1H,olefinic); 6.98-7.30(m,3H,ArH); 7.36-7.64(m,1H,ArH); (Found: C,67.48; H,6.78; Calc. for $C_{14}H_{16}S_2$: C,67.69; H,6.49%).

Dehydration of carbinolacetal 3j gave the dimer 5; colourless solid (EtOAc-Hexane); (88%); m.p.205-206°C; IR ν_{max}(KBr) 1630 cm^{-1}; ^{1}H NMR(CCl_4): 1.71-2.0(m,2H,CH_2); 2.00(s,6H,SCH_3); 2.29(s,3H,SCH_3); 2.43(s,3H,SCH_3);2.81-3.03(m,2H,CH_2);3.52(brt,2H,J=1.5Hz,CH_2); 4.28(s,2H, CH_2); 7.02-7.45(m,8H,ArH); (Found: C,66.41; H,6.27; Calc. for $C_{26}H_{28}S_4$: C,66.62; H,6.02%).

1,1-Bis(methylthio)-2-methyl-3-ethyl-1,3-butadiene (4g) was prepared by Wittig reaction on dithioacetals 2g according to the reported procedure^{6}; yellow oil (86%); IR ν_{max}(neat) 1634 cm^{-1}; ^{1}H NMR(CCl_4): 1.00(t,3H,J=7Hz,CH_3CH_2); 2.03(s,3H,CH_3); 2.17(s,3H,SCH_3); 2.20(s,3H,SCH_3); 2.23(q merged with SCH_3 and CH_3 signals, 2H,CH_2); 4.61(brs,1H,H-4); 4.83(brs,1H,H-4);(Found: C,57.64; H,8.85; Calc. for $C_9H_{16}S_2$: C,57.39; H,8.56%).

1-Bis(methylthiomethylene)-2-methylene cyclohexane (4h) was prepared by Wittig reaction according to the reported procedure^{6}; IR ν_{max}(neat) 1635, 1440 cm^{-1}; ^{1}H NMR(CCl_4): 1.40-1.83(m, 4H,CH_2); 2.15(s,3H,SCH_3); 2.22(s,3H,SCH_3); 2.42-2.80(m,4H,CH_2); 4.70(brs,1H,olefinic); 4.91 (brs,1H,olefinic); (Found: C,60.23; H,8.32; Calc. for $C_{10}H_{16}S_2$: C,59.95; H,8.05%).

Cycloadditions of Vinylketene Dithioacetals with Maleic Anhydride (6); General Procedure.- Cycloaddition of 4a with 6 is representative. A solution of 4a (1.60g,10 mmol), maleic anhydride (1.0g, 10.2 mmol) and a trace of hydroquinone in dry xylene (50 ml) was refluxed for 30 hr (monitored by t.l.c.) till starting materials were disappeared. Xylene was removed under reduced pressure and the residue was subjected to column chromatography over silica gel using EtOAc-hexane(1:20) as eluent to give pure anhydride 9a. The phthalic anhydrides 9b-e, 13 and 14 and the bicyclic adducts 10a-b were obtained in the similar manner.

5-Methyl-3-methylthiophthalic anhydride (9a); light yellow crystals (EtOAc-hexane); (68%); m.p. 201-202°C; IR ν_{max} (KBr) 1830, 1766 cm^{-1}; ^{1}H NMR(CDCl$_3$); 2.50(s,3H,C$\underline{H}_3$); 2.56(s,3H, SC$\underline{H}_3$); 7.36(brs,1H,Ar$\underline{H}$); 7.42(brs,1H,Ar$\underline{H}$); (Found: C,57.89; H,4.06; Calc. for $C_{10}H_8O_3S$: C,57.68; H,3.87%); m/z 208(70%); 164(70%); 136(100%).

3-Methylthio-5-phenylphthalic anhydride (9b); light yellow crystals (EtOAc-Hexane); (72%); m.p. 155-156°C; IR ν_{max} (KBr) 1843, 1762 cm^{-1}; ^{1}H NMR(CDCl$_3$): 2.66(s,3H,SC$\underline{H}_3$); 7.45-7.68(m, 5H,Ar$\underline{H}$); 7.70(brs,1H,Ar$\underline{H}$); 7.86(brs,1H,Ar$\underline{H}$); (Found: C,66.88; H,3.91; Calc. for $C_{15}H_{10}O_3S$: C,66.65; H,3.73%); m/z 270(M$^+$,100%); 226(100); 198(100).

5-(4-Methylphenyl)-3-methylthiophthalic anhydride (9c); light yellow crystals (EtOAc-Hexane); (66%); m.p. 170-171°C); IR ν_{max} (KBr) 1846, 1772 cm^{-1}; ^{1}H NMR(CDCl$_3$); 2.40(s,3H,C$\underline{H}_3$); 2.63 (s,3H,SC$\underline{H}_3$); 7.20-7.54(dd,A_2B_2,4H,Ar$\underline{H}$); 7.62(brs,1H,Ar$\underline{H}$); 7.78(s,1H,Ar$\underline{H}$); (Found: C,67.81; H,4.48; Calc. for $C_{16}H_{12}O_3S$: C,67.59; H,4.26%); m/z 284(M$^+$,100%); 240(49); 212(37).

5-(4-Chlorophenyl)-3-methylthiophthalic anhydride (9d); light yellow crystals (EtOAc-Hexane); (69%); m.p. 176-177°C; IR ν_{max} (KBr) 1850, 1767 cm^{-1}; ^{1}H NMR(CDCl$_3$); 2.60(s,3H,SC$\underline{H}_3$); 7.38(s, 4H,Ar$\underline{H}$); 7.50(brs,1H,Ar$\underline{H}$); 7.64(brs,1H,Ar$\underline{H}$); (Found: C,59.28; H,3.21; Calc. for $C_{15}H_9ClO_3S$: C,59.12; H,2.98%); m/z 306(40%); 304(M$^+$,100%); 262(25); 260(68); 234(21); 232(57).

5-(4-Methoxyphenyl)-3-methylthiophthalic anhydride (9e); light yellow crystals (EtOAc-Hexane); (62%); m.p. 165-166°C; IR ν_{max} (KBr) 1842, 1766 cm^{-1}; ^{1}H NMR(CDCl$_3$): 2.66(s,3H,SC$\underline{H}_3$); 3.86 (s,3H,OC$\underline{H}_3$); 7.00(d,2H,J=9Hz,Ar$\underline{H}$); 7.58(d,2H,J=9Hz,Ar$\underline{H}$); 7.64(brs,1H,Ar$\underline{H}$); 7.78(brs,1H,Ar$\underline{H}$); (Found: C,64.27; H,4.31; Calc. for $C_{16}H_{12}O_4S$: C,63.98; H,4.02%); m/z 300(M$^+$,100%); 256(47); 228(31).

Endo-7,8-Dimethyl-1-methylthiobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic anhydride(10a); white crystals (EtOAc-Hexane); (45%, 88% with 2 eqv. of 6);m.p. 298-299°C; spectral data described in text; (Found: C,55.67; H,4.53; Calc. for $C_{15}H_{14}O_6S$: C,55.89; H,4.38%).

Endo-8-Ethyl-7-methyl-1-methylthiobicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic anhydride (10b); white crystals (ethylacetate); (86% with 2 eqv of 6); m.p. 306-307°C; IR ν_{max} (KBr) 1856, 1784 cm^{-1}; ^{1}H NMR(DMSO-d$_6$); 0.82(t,J=7Hz,3H,C$\underline{H}_3$CH$_2$); 1.60(s,3H,C$\underline{H}_3$); 2.04(q,J=7Hz,2H, CH$_3$C$\underline{H}_2$); 2.28(s,3H,SC$\underline{H}_3$); 3.45(brs,1H,bridgehead C-H); 3.67(s,4H,ring C$\underline{H}$); ^{13}C NMR(DMSO-d$_6$); 10.59($\underline{C}$H$_3$); 14.58($\underline{C}$H$_3$CH$_2$); 17.31(S$\underline{C}$H$_3$); 24.30(CH$_3\underline{C}$H$_2$): 37.35(bridgehead $\underline{C}$H); 44.81,45.35 ($\underline{C}$H); 52.59(-$\underline{C}$-SCH$_3$); 131.42, 132.01(olefinic C); 168.23,171.81($\underline{C}$O); (Found: C,57.36; H, 4.69; Calc. for $C_{16}H_{16}O_6S$: C,57.13; H,4.80%); m/z 336(M$^+$,19%); 238(96); 166(100).

1-Methylthio-5,6,7,8-tetrahydro-2,3-naphthalic anhydride (13); white crystals (EtOAc-Hexane); (71%); m.p. 110-111°C; IR ν_{max} (KBr) 1840, 1778 cm^{-1}; ^{1}H NMR(CDCl$_3$): 1.57-2.11(m,4H,C$\underline{H}_2$); 2.55(s,3H,SC$\underline{H}_3$); 2.70-3.19(m,4H,C$\underline{H}_2$); 7.56(s,1H,Ar$\underline{H}$); (Found: C,62.69; H,5.11; Calc. for $C_{13}H_{12}O_3S$: C,62.88; H,4.87%); m/z 248(M$^+$,100%); 204(44).

9,10-Dihydro-1-methylthio-2,3-phenanphthalic anhydride (14); white crystals; (EtOAc-Hexane); (76%); m.p. 171-172°C; IR ν_{max} (KBr) 1834, 1775 cm^{-1}; ^{1}H NMR(CDCl$_3$): 2.51(s,3H,SC$\underline{H}_3$); 2.78-3.07(m,2H,C$\underline{H}_2$); 3.15-3.43(m,2H,C$\underline{H}_2$); 7.11-7.40(m,3H,Ar$\underline{H}$); 7.65-7.97(m,1H,Ar$\underline{H}$); 8.24(s,1H, Ar$\underline{H}$); (Found: C,68.78;H,4.29; Calc. for $C_{17}H_{12}O_3S$: C,68.89; H,4.08%); m/z 296(M$^+$,60%); 252 (39).

Cycloaddition of 4a and 4f with Dimethylacetylene Dicarboxylate was carried out in the similar manner as described for cycloaddition of 4 with maleic anhydride by taking 10 mmol of either 4a or 4f and 1.42g (10 mmol) of dimethylacetylene dicarboxylate and refluxing in xylene (50 ml) for 24 hr. Work-up and column chromatography as described afforded 12a and 12b.

Dimethyl 5-methyl-3-methylthiophthalate (12a); yellow crystals ($CHCl_3$-Hexane); (74%); m.p. 62-63°C; IR ν_{max} (KBr) 1720, 1600 cm^{-1}; ^1H NMR($CDCl_3$): 2.38(s,3H,CH_3); 2.45(s,3H,SCH_3); 3.86 (s,3H,OCH_3); 3.92(s,3H,OCH_3); 7.36(brs,1H,ArH); 7.62(brs,1H,ArH); (Found: C,56.45; H,5.78; Calc. for $C_{12}H_{14}O_4S$: C,56.68; H,5.55%); m/z 254(M^+,89%); 223(100).

Dimethyl 4,5-dimethyl-3-methylthiophthalate (12b); yellow crystals ($CHCl_3$-Hexane); (67%); m.p. 89-90°C; IR ν_{max} (KBr) 1735, 1722 cm^{-1}; ^1H NMR(CCl_4): 2.24(s,3H,CH_3); 2.33(s,3H,CH_3); 2.56(s,3H,SCH_3); 3.85(s,3H,OCH_3); 3.95(s,3H,OCH_3); 7.76(s,1H,ArH); (Found: C,57.96; H,6.29; Calc. for $C_{13}H_{16}O_4S$: C,58.19; H,6.01%); m/z 268(M^+,23%); 237(100); 205(100).

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