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A NOVEL CYCLISATION REACTION OF ALKYLTHIODIPHENYLCYCLOPROPENIUM IONS WITH 1,3-DIKETONES TO GIVE CYCLOPENTADIENOLS

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Alkylthiodiphenylcyclopropenium ions reacted with 2,4-pentanedione or ethyl acetoacetate to give cyclopentadienol derivatives by ring expansion, while triphenylcyclopropenium perchlorate yielded substituted cyclopropenes.

Cyclopropenium ions with phenyl-, amino-, and alkylthio- groups as substituents condense with nitrogen nucleophiles such as hydrazine, aliphatic amines, and azides to give 5- or 6-membered nitrogen heterocycles,[1-4] whereas the 3-ethoxy-1,2-diphenylcyclopropenium cation reacts with 1,3-diketones yielding fulvenes.[5,6] In the course of our studies on the chemistry of cyclopropenone derivatives,[7,8] we found a novel cyclisation reaction of 3-alkylthio-1,2-diphenylcyclopropenium salts 1 with 2,4-pentanedione 2a or ethyl acetoacetate 2b affording the cyclopentadienols 3.

Diphenylcyclopropenethione readily reacted with alkyl halides, such as methyl bromide, ethyl iodide, and benzyl bromide, in benzene to give the corresponding cyclopropenium salts 1.[9] A mixture of 1, 2, and triethylamine in a molar ratio of 1:1:2 was stirred in benzene at room temperature for 20 min. Column chromatography of the reaction product on silica gel afforded pale

Table 1. The Reaction of 1 or 5 with 2.

Product	Reactants		R	R'	Yield/%	M.p./°C
3a	1a	2a	Me	Me	73	105-106
3b	1a	2b	Me	EtO	36	96-97
3c	1b	2a	Et	Me	71	107-107.5
3d	1b	2b	Et	EtO	45	62-63
3e	1c	2a	$PhCH_2$	Me	65	116-117
3f	1c	2b	$PhCH_2$	EtO	14	120-121
6a	5	2a	--	Me	73	135-137
6b	5	2b	--	EtO	61	133-134

yellow crystals of the cyclopentadienols 3 (Table 1).

Although many isomeric structures are mechanistically possible as products, the ^{1}H- and ^{13}C-NMR, and mass spectra of the compounds did not permit clear choice to be made.[10]

The cyclopentadienol structure for 3a was however unambiguously established by an X-ray crystallographic analysis (Fig. 1).

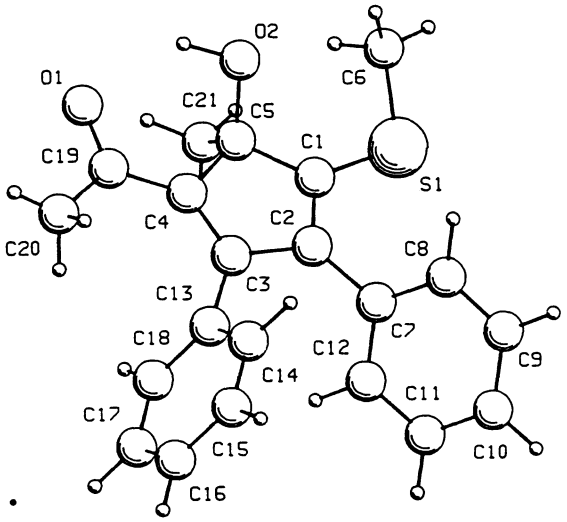
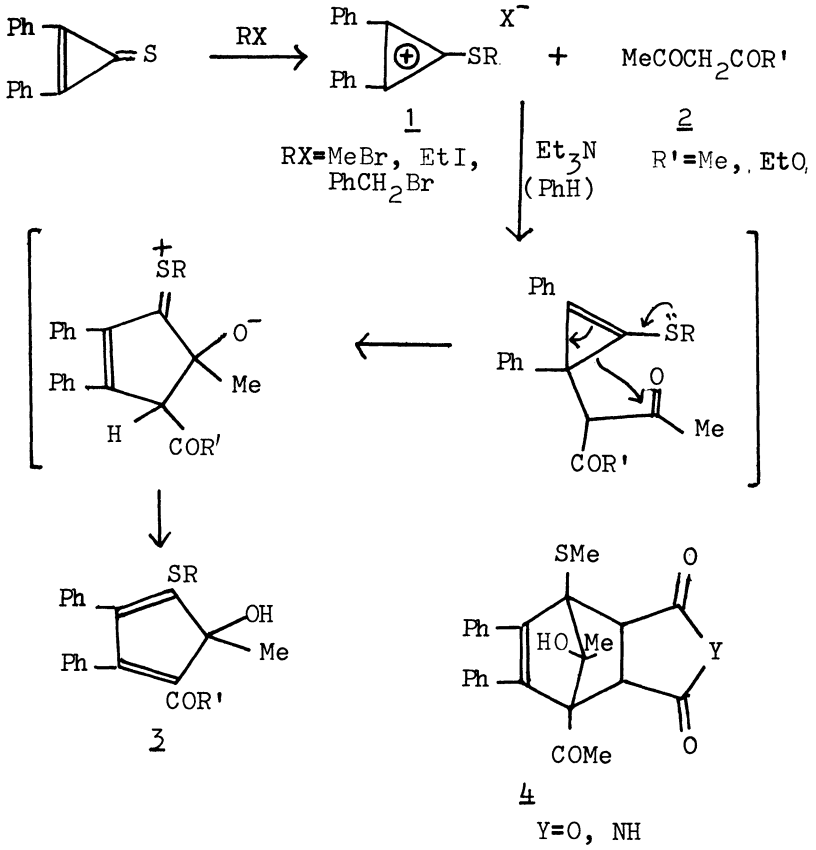


Fig. 1.

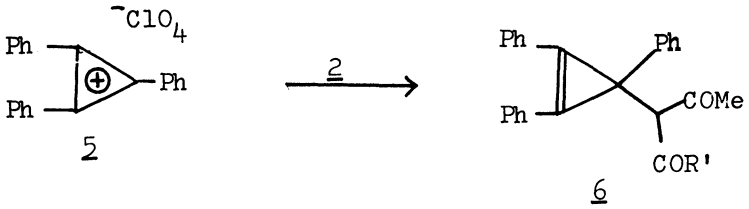
Crystal data: $C_{21}H_{20}SO_2$, Mr 336.5, monoclinic, $P2_1/n$, a=10.365(4), b=24.659(8), c=14.394(5)Å, ß=101.63(3)°, U=3603.4Å^3, Z=8, D_c=1.25g cm^{-3}, μ=0.19mm^{-1} (MoKa), R=0.053 for 2225 observed reflections.[11] The other compounds listed in Table 1 and given similar structures have similar spectra.

In agreement with the dienol structure, 3a underwent the Diels-Alder reaction with maleic anhydride and maleimide even at room temperature in benzene to give the adducts 4a and 4b in 81 and 66% yields and both showed characteristic AB quartets due to the two methine protons in their ^{1}H-NMR spectra.[12]

In contrast, analogous reactions of triphenylcyclopropenium perchlorate 5 with 2 and triethylamine in benzene produced the triphenylcyclopropenes 6 (Table 1). Their structures are clear from their ^{1}H-NMR (one proton exchanged by NaOD) and IR (2000-1700 cm^{-1} due to the cyclopropene ring) spectra.[13]



Scheme 1



The marked difference in reaction products between 1 and 5 may be ascribed to the electron releasing properties[14] of the alkylthio grouping of 1. The exact mechanism for the formation of 3 is not clear but must involve an initial nucleophilic attack of the carbanion generated from 2 on the cyclopropene ring of 1 as occurs in the reaction of 5 with 2 to form 6, follwed by ring expansion (Scheme 1).

References

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9) 1a:yield 88%;mp 131-132°C. 1b:yield 62%;mp 130-132°C. 1c:yield 79%;mp 131-134°C.
10) 3a:IR(KBr) 3300-3500(OH) and 1615cm^{-1}(CO);^{1}H-NMR($CDCl_3$) δ=1.79(3H, s, MeCO), 1.82(3H, s, MeCOH), 2.39(3H, s, MeS), 4.36(1H, s, OH), and 6.9-7.5(10H, m, Ph);^{13}C-NMR($CDCl_3$) δ=15.0(q, MeS), 27.1(s, MeCOH), 29.7(q, MeCO), 87.2(s, COH), 127.7, 128.2, 128.6, 129.7, 133.4, 134.7(s), 139.6(s), 143.6(s), 154.0(s), 155.4(s), and 196.0(s, C=O);MS(m/e) 336(M^+).
3b:IR(KBr) 3300-3500(OH) and 1670cm^{-1}(C=O);^{1}H-NMR($CDCl_3$) δ=0.99(3H, t, J=7.5 Hz, $MeCH_2$), 1.78(3H, s, MeCO), 2.31(3H, s, MeS), 3.88(1H, s, OH), 4.06(2H, q, $MeCH_2$), and 7.0-7.6(10H, m, Ph);^{13}C-NMR($CDCl_3$) δ=13.6(q, MeS), 15.1(q, $MeCH_2O$), 21.6(q, MeCOH), 59.9(t, CH_2O), 86.1(s, COH), 127.1, 127.5, 128.1, 129.7, 133.5(s), 134.2(s), 134.7(s), 139.9(s), 154.2(s), 155.1(s), and 164.1(s, CO_2);MS(m/e) 366(M^+).
11) Precise studies on X-ray crystallographic analysis will be published in a forthcoming paper.
12) 4a:mp 151-165°C;IR(KBr) 3450(OH), 1855, 1770, and 1690cm^{-1};^{1}H-NMR($CDCl_3$-DMSO-d_6 1/1) δ=1.63(3H, s, MeCOH), 2.03(3H, s, MeCO), 2.22(3H, s, MeS), 3.10(1H, bs, OH), 4.33(1H, d, J=9Hz, CH), 4.83(1H, d, CH), and 6.6-7.6(10H, m, Ph);MS(m/e) 434(M^+).
4b:mp 234-238°C;^{1}H-NMR($CDCl_3$-DMSO-d_6 1/1) δ=1.01(3H, s, MeCOH), 2.14(3H, s, MeCO), 2.16(3H, s, MeS), 3.24(1H, s, OH), 3.86(1H, d, J=7.5Hz, CH), 4.52(1H, d, CH), 5.91(1H, s, NH), and 6.6-7.3(10H, m, Ph);MS(m/e) 443(M^+).
13) 6a:IR(KBr) 1810, 1730, and 1700cm^{-1};^{1}H-NMR($CDCl_3$) δ=2.07(6H, s, MeCO), 5.22(1H, s, CH), 7.0-8.1(15H, m, Ph);^{13}C-NMR($CDCl_3$) δ=31.2(q, Me), 33.0(s, C_3), 72.1(d, CH), 116.9(s), 125.9, 126.2, 128.0, 128.2, 128.3, 128.6, 128.9, 129.7, 144.3(s), and 204.2(s, CO);MS(m/e) 366(M^+).
6b:IR(KBr) 1950, 1890, 1730, and 1710cm^{-1};^{1}H-NMR($CDCl_3$) δ=0.94(3H, t, J=6.8 Hz, $MeCH_2$), 2.12(3H, s, MeCO), 3.98(2H, q, $MeCH_2O$), 4.96(1H, s, CH), and 7.1-8.0(15H, m, Ph);^{13}C-NMR($CDCl_3$) δ=13.6(q, $MeCH_2$), 30.3(q, MeCO), 32.5(s, C_3), 61.1(t, $MeCH_2$), 64.6(d, CH), 116.0(s), 116.3(s), 125.8, 126.2(s), 128.0(s), 128.2, 128.7, 129.0, 129.7, 129.8, 144.2(s), 169.1(s, CO_2), and 202.5(s, COMe);MS(m/e) 396(M^+).
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