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2-PHENYLSULFINYLMETHYL-1,3-BUTADIENE IN THE THERMAL DIELS-ALDER REACTION

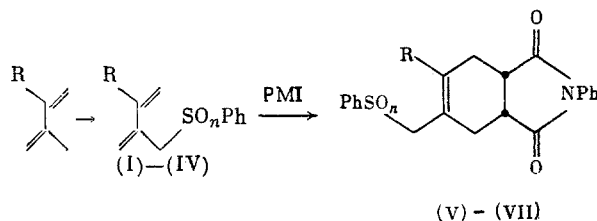
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The Diels-Alder reaction is an efficient method for constructing a variety of carbocyclic and heterocyclic structures, including those of natural origin, and recent advances in this area are due to the use of functional derivatives of 1,3-dienes [1-4]. Of special interest are those in which simple operations enable intermediate substituted cyclohexenes to be converted into compounds inaccessible by the direct diene synthesis. We here discuss the use for this purpose of the isoprene sulfoxide (I) described by us previously [5], as exemplified by the synthesis of some oxygenated monoterpenes of the carane and p-menthane series.

The ability of (I) to undergo diene condensation was first shown in its reaction with N-phenylmaleimide (PMI) as a reactive dienophile. The same reaction has been carried out with the diene (III) [5] and its methyl analog (IV), obtained from the sulfoxide (II), first synthesized by an ene-type reaction of PhSOCl with 2,3-dimethylbutadiene. It was found that all the dienes (I), (III), and (IV) reacted smoothly at ~25°C over 60-150 h to give the adducts (V)-(VII), the structures of which were confirmed spectrally. In addition, the bicyclic sulfoxide (V) is selectively oxidized by m-chloroperbenzoic acid (MCPBA) to the sulfone (VI).

The reaction of (I) with such a moderately reactive symmetrical dienophile

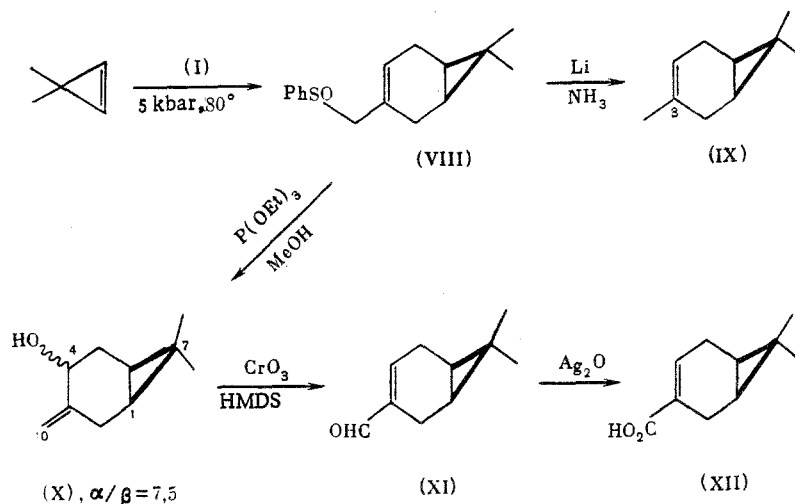


R = H, n = 1(I), (V); R = Me, n = 1(II); R = H, n = 2(III), (VI); R = Me, n = 2(IV), (VII).

as dimethylcyclopropene was found to be of low efficiency under the usual conditions. Furthermore, it was not possible to accelerate the reaction in the presence of Lewis acids or thermally, as a result of the lability of the starting materials. The use of high pressure techniques [6] however gave good yields of the [4+2]-cycloadduct (VIII). The latter, like (V), was a mixture (~1:1) of diastereoisomers, as shown by the doubling of the signals in the PMR spectra for the CH₂C=CH fragment adjacent to the sulfoxide group, and by the single signal for one of the CH₃ groups of the gem-dimethylcyclopropane residue in (VIII). Reductive desulfurization gives the difficultly-accessible racemic Δ³-carene (IX).

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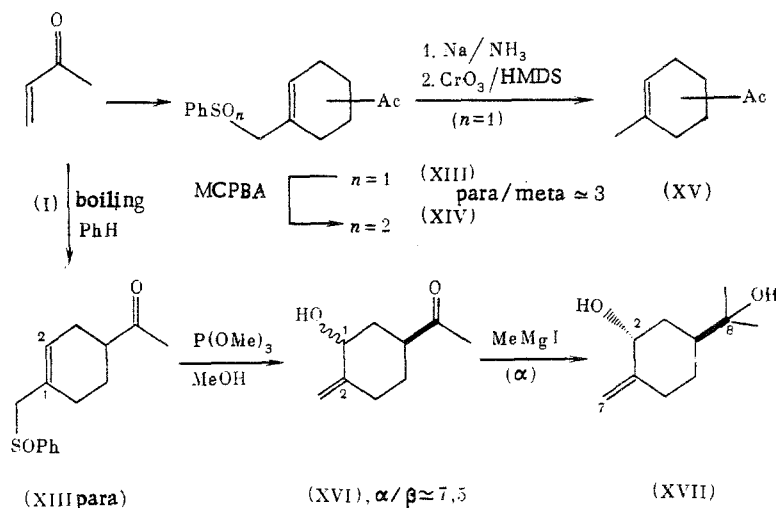
A characteristic of (VIII) is that it can be transformed directly by the sulfoxide-sulfenate rearrangement into the difficultly-accessible $\Delta^{3(10)}$ -careneol (X) in 85% yield. The PMR spectra of the alcohols (X) obtained by this method, which are readily separated chromatographically, described previously in the optically active form [7], differs markedly in the signal



at $\delta \approx 4.1$ ppm for the allyl proton at C⁴ (br.d.d., $J = 11.5$ and 6.5 Hz for the minor component, and br. t., $J = 4$ Hz for the major). With these facts in mind, and also the preferred anti-boat conformation of 7,7-disubstituted bicyclo-[4.1.0]heptanes [8], the principal rearrangement product is assigned the trans stereochemistry ($X\alpha$), with a quasi-axial OH group.

Oxidation of ($X\alpha$) with bistrimethylsilyl chromate (BTC) reagent [9] occurs with complete allyl isomerization of the intermediate allyl chromate, as with other Cr(VI) oxidants [10], to give the highly volatile (\pm)- Δ^3 -carenal (XI), which is then further converted into the (\pm)-form of natural chaminoic acid (XII) [10]. This three-stage synthesis of the latter from the [4+2]-cycloadduct (VIII) is equivalent to the use of the extremely thermolabile 1,3-butadiene-2-carboxylic acid [2] in the Diels-Alder reaction with dimethylcyclopropene.

Determination of the composition of the products of the condensation of (I) with the unsymmetrical dienophile methyl vinyl ketone (MVK) enables the contribution of this diene to the regiochemical control of the reaction to be found, this reaction giving a mixture of diastereoisomeric para- and meta-sulfoxides (XIII) in a ratio of $\sim 3:1$. This ratio was found by comparing the integral intensities of the signals for CH_2S ($\delta \approx 3.7$ ppm) in the PMR spectrum of the sulfones (XIV) obtained by the selective oxidation of the total mixture of adducts (XIII) with MCPBA. This ratio was confirmed by GLC analysis of the methylacetylcyclohexenes (XV) obtained by successive treatment of the mixture of ketosulfoxides (XIII) with excess sodium in liquid ammonia and oxidation of the resulting secondary alcohols with BTC reagent.



The para/meta ratio measured in this way is also characteristic of the thermal [4+2]-cycloaddition of MVK to isoprene and some of its derivatives functionalized with electronegative substituents at the CH₃ group [2-4].

Fractional crystallization of the mixture (XIII) readily affords the principal regioisomer (XIII-para), sulfoxide-sulfenate rearrangement of which gives high yields of a mixture of the hitherto unknown ketols (XVI), in which, as in the case of (X), the trans isomer (XVI α) predominates. This stereochemistry was assigned from the signals for HC¹ in the PMR spectra of the pure isomers isolated by fractional crystallization, which in the case of the major component is characteristic of an equatorial proton, being seen as a broadened triplet with J = 5 Hz at $\delta \approx 4.4$ ppm, whereas in the minor component this signal is shifted by $\Delta\delta \approx 0.25$ ppm to higher field, and seen as an unresolved multiplet with $\Delta\nu_{1/2} \approx 25$ Hz. Finally, treatment of (XVI α) with MeMgI gives (\pm)- $\Delta^{1(7)}$ -menthene-2,8-diol (XVII), in the PMR spectrum of which the signal for HC² is similar to that of HC¹ in its precursor, and in addition, the spectrum itself is similar to that for the optically active form of (XVII) obtained from α -terpineol [11].

Hence, the isoprene phenyl sulfoxide (I) is a reactive component in the thermal Diels-Alder reaction, is similar in its regiochemical character to isoprene itself, and provides a simple means of converting a dienophile into vicinal exomethylenecyclohexanols, including terpenes.

EXPERIMENTAL

Melting points were measured on a Kofler block. IR spectra were obtained on a UR-20 instrument, the UV spectra of alcoholic solutions on a Specord UV-VIS, and PMR spectra of solutions in CDCl₃ relative to TMS on Tesla BS-497 (100 MHz) and Bruker WM-250 spectrometers. Mass spectra were obtained on a Varian MAT CH-6 at 70 eV. R_f values are given for bound layers of Silufol SiO₂. GLC was carried out on an LKM-8MD instrument with a glass capillary column with OV-17, at 120°C.

2-Phenylsulfinylmethyl-3-methyl-1,3-butadiene (II). To a stirred solution of 5.25 g (32.7 mmoles) of PhSOCl and 5.40 g (74.9 mmoles) of 2,3-dimethylbutadiene in 40 ml of n-PrNO₂ was added at -60°C under argon 4.5 g (33.0 mmoles) of ZnCl₂. After 1.5 h, the mixture was warmed to 0°C, then treated with water and ether. The aqueous layer was separated, neutralized with NaHCO₃, and extracted with ether. The combined organic layers were washed with water, dried over MgSO₄, evaporated under reduced pressure, and the residue (5.9 g) chromatographed on 150 g of silica. Gradient elution from hexane to ether (up to 50% of the latter) gave 4.18 g (62%) of (II) as a colorless oil, R_f 0.43 (ether), bp 126-128°C (0.07 mm), n_D²⁰ 1.5760. IR spectrum (CHCl₃, ν , cm⁻¹): 900, 915, 1000, 1040, 1070, 1085, 1120, 1235, 1310, 1370, 1400, 1445, 1465, 1480, 1600, 1630, 2860, 2930, 3000, 3060, 3095. UV spectrum (λ_{\max} , nm, (ϵ)): 209 (34400), 218 (31000), 237 (21300). PMR spectrum (δ , ppm): 1.87 br. s (3H, CH₃), 3.58 AB (2H, CH₂S, J_{AB} = 12 Hz, $\Delta\delta$ 0.18), 4.8-5.3 m (4H, HC=C), 7.4 m (5H, C₆H₅). Found: S 15.20%; M⁺ 206. C₁₂H₁₄OS. Calculated: S 15.54%; Mol. wt. 206.3.

2-Phenylsulfonylmethyl-3-methyl-1,3-butadiene (IV). To a stirred solution of 0.43 g (2.1 mmoles) of (II) in 10 ml of CH₂Cl₂ was added at -20°C under argon 0.5 g (2.9 mmoles) of MCPBA, the mixture stirred for 1 h at -20°C, warmed to 25°C over 30 min, evaporated under reduced pressure, and the residue (1 g) chromatographed on 25 g of alumina (grade II activity). Elution with ether-hexane (1:1) gave 0.38 g (82%) of (IV), mp 44.5-45°C (ether-hexane). IR spectrum (CHCl₃, ν , cm⁻¹): 890, 920, 1085, 1155, 1225, 1310, 1320, 1450, 1585, 1600, 2950, 2980, 3020, 3060, 3090. UV spectrum (λ_{\max} , nm) (ϵ): 220 (14400), 237 (7600), 259 (7000), 265 (7000), 273 (5500). PMR spectrum (δ , ppm): 1.80 br. s (3H, CH₃), 4.02 s (2H, CH₂S), 4.8-5.4 m (4H, HC=C), 7.2-7.9 m (5H, C₆H₅). Found: C 64.53; H 6.31; S 14.17%; M⁺ 222. C₁₂H₁₄O₂S. Calculated: C 64.83; H 6.35; S 14.42%; mol. wt. 222.3.

N-Phenyl-cis-4-phenylsulfinylmethylcyclohex-4-ene-1,2-dicarboximide (V). A solution of 0.26 g (1.5 mmoles) of (I) and 0.52 g (3.0 mmoles) of PMR in 3 ml of benzene was kept at 25°C for 60 h, evaporated under reduced pressure, and the residue (0.8 g) chromatographed on 30 g of SiO₂. Gradient elution from hexane to ether, then acetone (up to 10% of the latter) gave 0.49 g (89%) of (V) as an oil, R_f 0.56 (ether-acetone, 4:1). IR spectrum (CHCl₃, ν , cm⁻¹): 900, 920, 950, 1045, 1090, 1160, 1190, 1315, 1390, 1450, 1505, 1600, 1710, 2860, 3010, 3040. PMR spectrum (δ , ppm): 2.2-2.8 m (4H, CH₂), 3.3 m (2H, HC¹, HC²), 3.5 m (2H, CH₂S), 5.82 and 5.96 br. s (1H, HC⁵), 7.2-7.7 m (10H, C₆H₅). Mass spectrum (m/z): 365 (M⁺), 349, 257, 250, 240, 218, 212, 185, 173, 154, 141, 126, 119, 109, 91.

N-Phenyl-cis-4-phenylsulfonylmethylcyclohex-4-ene-1,2-dicarboximide (VI). To a stirred solution of 0.1 g (0.27 mmole) of (V) in 3 ml of CH_2Cl_2 was added 0.07 g (0.41 mmole) of MCPBA at -20°C , the mixture stirred for 30 min at -20°C , evaporated under reduced pressure, and the residue crystallized from a mixture of THF and ether to give 0.09 g (87%) of (VI) as colorless needles, mp $139-140^\circ\text{C}$. IR spectrum (KBr, ν , cm^{-1}): 830, 910, 1090, 1125, 1150, 1180, 1220, 1250, 1305, 1375, 1450, 1500, 1600, 1715, 2840, 2890, 2950, 2975, 3060. PMR spectrum (δ , ppm): 2.2-2.8 m (4H, CH_2), 3.2 m (2H, HC^1 , HC^2), 3.76 br. s (2H, CH_2S), 5.70 br. s (1H, HC^5), 7.1-7.9 m (10H, C_6H_5). Found: C 65.94; H 5.02; N 3.84; S 8.33%. M^+ 381. $\text{C}_{21}\text{H}_{19}\text{NO}_4\text{S}$. Calculated: C 66.12; H 5.02; N 3.67; S 8.40%; mol. wt. 381.5.

A solution of 0.12 g (0.58 mmole) of (III) and 0.1 g (0.58 mmole) of PMI in 5 ml of benzene was kept at 25°C for 150 h, then evaporated under reduced pressure. Crystallization of the residue gave 0.14 g (63%) of (VI), mp $138-139.5^\circ\text{C}$ (ether-THF), identical with the sample of (VI) described above.

N-Phenyl-cis-4-phenylsulfonylmethyl-5-methylcyclohex-4-ene-1,2-dicarboximide (VII). As described for (VI), from 0.21 g (0.94 mmole) of (IV) and 0.17 g (0.98 mmole) of PMI there was obtained 0.26 g (70%) of (VII), mp $121-121.5^\circ\text{C}$ (THF-ether). IR spectrum (KBr, ν , cm^{-1}): 905, 920, 1090, 1110, 1155, 1190, 1230, 1310, 1320, 1385, 1450, 1500, 1600, 1715, 2860, 2940, 3025, 3040, 3080. PMR spectrum (δ , ppm): 1.42 br. s (3H, CH_3), 2.5 m (4H, CH_2), 3.2 m (2H, HC^1 , HC^2), 3.83 AB (2H, CH_2S , $J_{\text{AB}} = 14$ Hz, $\Delta\delta$ 0.33), 7.0-7.9 m (10H, C_6H_5). Found: C 66.80; H 5.45; N 3.47; S 7.92%. M^+ 395, $\text{C}_{22}\text{H}_{21}\text{NO}_4\text{S}$. Calculated: C 66.82; H 5.35; N 3.54; S 8.11%; mol. wt. 395.5.

(±)-10-Phenylsulfinylcar-3-ene (VIII). A solution of 1.75 g (9.1 mmoles) of (I) and 2.1 g (30.8 mmoles) of dimethylcyclopropane in 8 ml of CH_2Cl_2 was kept at 80°C in a teflon ampul at 5000 atm for 7 h, then evaporated under reduced pressure and the residue (2.1 g) chromatographed on 60 g of SiO_2 . Gradient elution from hexane to ether (up to 50% of the latter) gave 1.5 g (63%) of (VIII) as a pale yellow oil, R_f 0.48 (ether-hexane, 3:2). IR spectrum (CHCl_3 , ν , cm^{-1}): 910, 1040, 1090, 1240, 1390, 1470, 1580, 1670, 2840, 3060. PMR spectrum (δ , ppm): 0.5-0.7 m (2H, HC^1 , HC^6), 0.71, 0.74, and 1.0 s (6H, CH_3), 1.8-2.4 m (4H, CH_2), 3.32 and 3.37 AB (2H, CH_2S , $J_{\text{AB}} = 13.5$ Hz, $\Delta\delta$ 0.11 and 0.13), 5.37 and 5.43 br. s (1H, HC^4), 7.4-7.6 m (5H, C_6H_5). Found: C 73.30; H 7.73; S 12.13%. $\text{C}_{16}\text{H}_{20}\text{OS}$. Calculated: C 73.80; H 7.74; S 12.31%.

(±)-3-Carene (IX). To a vigorously stirred solution of 0.4 g (57.7 mg·atom) of lithium in 40 ml of ammonia at -50°C was added a solution of 1.5 g (5.76 mmoles) of (VIII) in 10 ml of ether. The mixture was stirred for 1 h at -50°C , then decomposed with an excess of ammonium chloride, the ammonia evaporated, and the residue treated with water and extracted with ether. The usual workup of the extract gave 0.8 g of material which was chromatographed on 25 g of silica. Elution with pentane gave 0.6 g (76.5%) of (IX), bp $84-87^\circ\text{C}$ (50 mm), n_D^{20} 1.4690 (lit. values [12] for (-)-(IX), bp $166-167^\circ\text{C}$, n_D^{20} 1.4684). PMR spectrum (δ , ppm): 0.6-0.8 m (2H, HC^1 , HC^6), 0.78 s, 1.04 s, and 1.62 br. s (9H, CH_3), 1.7-2.5 m (4H, CH_2), 5.3 m (1H, HC^4).

(±)-cis-(X β) and (±)-trans-3(10)-Carene-4-ol(X α). A solution of 1.0 g (3.84 mmoles) of (VIII), 1.66 g (10 mmoles) of $\text{P}(\text{OEt})_3$ and 0.73 g (10 mmoles) of diethylamine in 15 ml of methanol was heated under argon for 10 h at 55°C , then evaporated under reduced pressure and the residue treated with ether and water. The aqueous layer was separated, neutralized with 50% sulfuric acid, and extracted with ether. The combined organic layers were washed with water, dried over MgSO_4 , evaporated under reduced pressure, and the residue (1.5 g) chromatographed on 50 g of silica. Gradient elution from hexane to ether (up to 10% of the latter) gave 0.06 g (10%) of (X β) as colorless prisms, mp $39-40^\circ\text{C}$ (pentane) (lit. values [7] for (+)-(X β): bp 87°C (2 mm)) and 0.44 g (75%) of (X α) as colorless needles, mp $34-35^\circ\text{C}$ (pentane) (lit. value [7] for (-)-(X α), mp $55-56^\circ\text{C}$).

PMR spectrum of (X β) (δ , ppm): 0.6 and 0.8 m (2H, HC^1 , HC^6), 0.95 and 0.99 s (6H, CH_3), 1.2-2.6 m (4H, HC^2 , HC^5), 4.10 d.d (1H, HC^4 , $J = 6.5$ and 11.5 Hz), 4.8 and 4.9 m (2H, HC^{10}).

PMR spectrum of (X α) (δ , ppm): 0.7 and 0.8 m (2H, HC^1 , HC^6), 0.97 and 1.0 s (6H, CH_3), 1.5-2.7 m (4H, HC^2 , HC^5), 4.08 t (1H, HC^4 , $J = 4$ Hz), 4.7 and 4.8 m (2H, HC^{10}).

(±)-3-Carene-10-ol (XI). To a solution of the BTC reagent, freshly-prepared from 0.62 g (6.2 mmoles) of CrO_3 , 1.01 g (6.3 mmoles) of HMDS, and 5 ml of CH_2Cl_2 [9] was added at 25°C a solution of 0.47 g (3.1 mmole) of (X α) in 5 ml of CH_2Cl_2 . The mixture was stirred at 25°C

for 1 h, then diluted with 150 ml of ether and filtered through a layer of silica (~5 cm). The filtrate was evaporated under reduced pressure, and the residue (0.7 g) chromatographed on 20 g of silica. Gradient elution from pentane to ether (up to 5% of the latter) gave 0.23 g (49%) of (XI), bp 119°C (22 mm), n_D^{20} 1.5030 (lit. values [10] for (-)-(XI): bp 104°C (12 mm), n_D^{20} 1.5077).

(±)-Chaminic Acid (XII). To a vigorously stirred solution of 0.7 g (4.12 mmoles) of AgNO_3 in 3 ml of water was added at 25°C a solution of 0.29 g (1.93 mmoles) of (XI) in 4 ml of methanol, followed after 40 min by 8 ml of 1 M NaOH. The mixture was stirred at 25°C for 3 h, and the precipitate filtered off and washed on the filter with water and ether. The aqueous layer was treated with 10% HCl to pH ~2, and extracted with ether. The combined organic layers were dried over MgSO_4 , evaporated under reduced pressure, and the residue (0.4 g) chromatographed on 15 g of silica. Gradient elution from hexane to ether (up to 10% of the latter) gave 0.15 g (47%) of (XII), mp 106-106.5°C (hexane) (lit. mp 104-105.5°C [13]).

4-Acetyl-1-phenylsulfinylmethylcyclohexene (XIII-para). A solution of 3.9 g (20.3 mmoles) of (I) and 6.5 g (92.7 mmoles) of MVK in 30 ml of benzene was heated at 80°C for 5 h, evaporated under reduced pressure, and the residue (6.2 g) chromatographed on SiO_2 (180 g). Gradient elution from hexane to ether gave 3.7 g (70%) of an oily mixture of (XIII), crystallization of which from ether-hexane gave 2.4 g of (XIII-para), colorless prisms, mp 72-74°C. IR spectrum (CHCl_3 , ν , cm^{-1}): 950, 1000, 1025, 1040, 1090, 1175, 1240, 1360, 1380, 1450, 1480, 1670, 1710, 2845, 2940, 3015. PMR spectrum (δ , ppm): 1.5-2.2 m (6H, CH_2), 2.13 s (3H, CH_3), 2.5 m (1H, HC^4), 3.37 AB (2H, CH_2S , $J_{AB} = 14$ Hz, $\Delta\delta = 0.12$), 5.5 m (1H, HC^2), 7.4-7.6 m (5H, C_6H_5). Found: C 68.18; H 6.99; S 11.73%. $\text{C}_{15}\text{H}_{18}\text{O}_2\text{S}$. Calculated: C 68.67; H 6.91; S 12.22%.

4-Acetyl-1-phenylsulfonylmethylcyclohexene (XIV-para). As described for (V), from 0.52 g (1.98 mmoles) of the mixture (XIII) and 0.44 g (2.55 mmoles) of MCPBA in 10 ml of CH_2Cl_2 there was obtained 1.2 g of material, which was chromatographed on SiO_2 (25 g). Gradient elution from hexane to ether gave 0.4 g (73%) of an oily mixture of (XIV), low-temperature crystallization of which from ether gave 0.18 g of (XIV-para), colorless prisms, mp 69-70°C. IR spectrum (KBr, ν , cm^{-1}): 870, 950, 1000, 1030, 1090, 1130, 1160, 1260, 1310, 1350, 1405, 1450, 1590, 1617, 1710, 2845, 2940, 3015, 3050. PMR spectrum (δ , ppm): 1.4-2.3 m (6H, CH_2), 2.17 s (3H, CH_3), 2.6 m (1H, HC^4), 3.71 s (2H, CH_2S), 5.45 m (1H, HC^2), 7.5-7.9 m (5H, C_6H_5). Found: C 65.03; H 6.73; S 11.22%. M^+ 278. $\text{C}_{15}\text{H}_{18}\text{O}_3\text{S}$. Calculated: C 64.72; H 6.52; S 11.52%, mol. wt. 278.4.

Acetylcyclohexenes (XV). To a vigorously stirred solution of 0.61 g (26.5 mg·atom) of sodium in 20 ml of ammonia was added (for 5 min) at -60°C under argon a solution of 0.66 g (2.51 mmoles) of the mixture (XIII) in 5 ml of THF. The mixture was stirred for 20 min at -60°C, decomposed with an excess of ammonium chloride, the ammonia evaporated, and the residue treated with ether and water. The aqueous layer was separated, extracted with ether, and the combined organic layers washed with 10% sodium hydroxide, neutralized with 10% sulfuric acid, dried over MgSO_4 , and evaporated under reduced pressure. The oily residue (0.31 g) was treated, as described for (XI), with the reagent obtained from 0.45 g (4.5 mmoles) of CrO_3 , 0.74 g (4.56 mmoles) of HMDS, and 4 ml of CH_2Cl_2 . There was obtained 0.28 g of product, which was chromatographed on 10 g of SiO_2 . Gradient elution from pentane to ether (up to 25% of the latter) gave 0.15 g (43%) of a mixture of (XV-para) and (XV-meta) in a ratio of ~3:1, estimated by comparison (GLC) with an authentic sample of the mixture (XV), obtained as described in [14].

cis-(XVI β) and trans-5-Acetyl-2-methylenecyclohexanol (XVI α). A solution of 2.57 g (9.8 mmoles) of (XIII-para) and 2.38 g (19.2 mmoles) of $\text{P}(\text{OMe})_3$ in 25 ml of methanol was heated at 50-60°C for 6 h, evaporated under reduced pressure, and the residue (2.8 g) chromatographed on 70 g of SiO_2 . Gradient elution from hexane to ether (up to 50% of the latter) gave 1.5 g of an oil, low-temperature crystallization of which from pentane gave 1.13 g (75%) of (XVI α), mp 49.5-50°C, and 0.16 g (10.5%) of (XVI β), mp 54-55°C.

For (XVI α), IR spectrum (chloroform, ν , cm^{-1}): 920, 960, 1000, 1030, 1080, 1170, 1260, 1290, 1305, 1350, 1420, 1440, 1660, 1710, 2870, 2950, 3015, 3090, 3470, 3610. PMR spectrum (δ , ppm): 1.4-2.1 m (4H, HC^4 , HC^6), 2.18 s (3H, CH_3), 2.1-2.6 m (2H, HC^3), 3.0 m (1H, HC^5), 4.39 br. t (1H, HC^1 , $J = 5$ Hz), 4.8 and 4.9 m (2H, $\text{HC}=\text{C}$). Found: C 70.14; H 9.27; M^+ 154. $\text{C}_9\text{H}_{14}\text{O}_2$. Calculated: C 70.09; H 9.16%; mol. wt. 154.2.

For (XVI β), IR spectrum (chloroform, ν , cm^{-1}): 910, 940, 1060, 1085, 1170, 1250, 1285, 1350, 1370, 1445, 1655, 1705, 2860, 2945, 3020, 3400, 3600. PMR spectrum (δ , ppm): 1.4-2.0 m (4H, HC⁴, HC⁶), 2.19 s (3H, CH₃), 2.2-2.5 m (2H, HC³), 2.6 m (1H, HC⁵), 4.15 m (1H, HC¹), 4.8 and 5.0 m (2H, HC=C). Found: C 70.32; H 9.47%. M⁺ 154. C₉H₁₄O₂. Calculated: C 70.09; H 9.16%; mol. wt. 154.2.

(\pm)-trans-p-1(7)-Menthene-2,8-diol (XVII). To a solution of MeMgI, obtained from 6.26 g (44.1 mmoles) of MeI and 1.21 g (49.8 mmoles) of Mg in 70 ml of ether under argon, was added at 25°C a solution of 1.36 g (8.82 mmoles) of (XVI α) in 10 ml of THF. The mixture was stirred for 30 min at 25°C, and decomposed with an excess of saturated ammonium chloride solution. The aqueous layer was separated, extracted with ether, the combined organic layers washed with water, dried over MgSO₄, evaporated under reduced pressure, and the residue (1.4 g) chromatographed on 80 g of SiO₂. Gradient elution from hexane to ether (up to 50% of the latter) gave 0.19 g of (XVI α) and 1.06 g of (XVII) (82%, calculated on (XVI α) reacted), colorless needles, mp 108-109°C (ether) (lit.[11] mp, 109-110°C). IR spectrum (chloroform, ν , cm^{-1}): 840, 870, 915, 950, 985, 1000, 1040, 1080, 1140, 1200, 1250, 1290, 1375, 1420, 1440, 1460, 1660, 2900, 2940, 2980, 3015, 3070, 3420, 3605. PMR spectrum (δ , ppm): 1.1-1.9 m (4H, HC³, HC⁵), 1.18 s (6H, CH₃), 2.1 m (1H, HC⁴), 2.2-2.5 m (2H, HC⁶), 4.50 br. t (1H, HC², J = 3.5 Hz), 4.8 and 4.9 m (2H, HC=C). Found: C 70.81; H 10.93%; M⁺ 170. C₁₀H₁₈O₂. Calculated: C 70.55; H 10.65%; mol. wt. 170.3.

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CONCLUSIONS

1. The behavior of 2-phenylsulfinylmethylbuta-1,3-diene in the thermal Diels-Alder reaction with symmetrical (N-phenylmaleimide, dimethylcyclopropene) and unsymmetrical (methyl vinyl ketone) dienophiles has been examined.

2. This reaction provides a simple method of preparing exomethylene allyl alcohols of the carane and p-menthane series which are difficult to obtain by other methods.

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