Synthesis of Dicyclopropylideneethane and Its Reaction with Some Dienophiles

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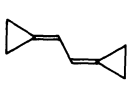
Synopsis. Preparation of dicyclopropylideneethane in three steps from 3-dimethylaminosulfolane and its reaction with some dienophiles are reported.

Dicyclopropylideneethane, **1**, a conjugated diene constituted of two highly strained, reactive methylenecyclopropanes, is of considerable interest in its physical as well as chemical properties. In particular, [4+2] cycloaddition products of **1** with acetylenic dienophiles, namely dispiro[2.2.2.2]deca-4,9-diene derivatives, **2**, will serve as the valuable substrate to synthesize variously-substituted [8]-paracycloph-4-enes and [4.2]paracyclophanes, as demonstrated previously in our laboratory.[1]



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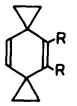

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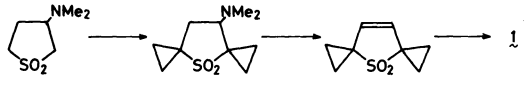
In 1972, Heinrich and Lüttke[2] have reported the formation of **1** as a minor component in the reaction of biallenyl with diazomethane. Since this approach will hold no preparative potential, it is desirable to explore proper synthetic routes for **1**. Paquette *et al.* have recently reported the synthesis of **1** from 1-trimethylsilylcyclopropanecarbaldehyde in several steps.[3] We independently prepared **1** from readily accessible 3-dimethylaminosulfolane[4] in three steps. By our hands, **1** reacted smoothly with some representative dienophiles and the yields of the adducts were substantially better than those reported by Paquette *et al.*[3]

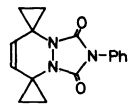
Results and Discussion

3-Dimethylaminosulfolane, **3**, was dicyclopropanated in one pot. Thus, the successive treatment of **3** in the presence of 2 equiv of oxirane with 2 equiv of *n*-BuLi, 2 equiv of benzenesulfonyl chloride, and 2 equiv of lithium diisopropylamide (LDA) afforded **4** in 40% yield. Oxidation of the amine, **4**, with 30% H_2O_2 followed by the thermal decomposition of the resulting *N*-oxide gave **5** in 80% yield.[5] Reduction of **5** with $LiAlH_4$ in refluxing THF afforded **1**[6] (50% yield by GLC; 28% yield by the isolation). The dicyclopropanated sulfolene, **5**, was thermally fairly stable and the attempted thermolysis (up to 250°C) failed to give appreciable amount of **1**.[7] Dicyclopropylideneethane, **1**, could be isolated as colorless crystals by preparative GLC, though **1** was liable to polymerize readily at room temperature.



3 **4** **5**

1,1,4,4-Tetrasubstituted butadienes are generally reluctant to undergo [4+2] cycloaddition because of the difficulty to attain *s-cis* conformation requisite for the reaction.[8] The diene, **1**, however, proved to be a fairly reactive one. Relief of the strain appears to contribute to the enhanced reactivity of **1**. The reaction of **1** with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (PTAD) was instantaneous at room temperature in benzene and the adduct, **6**, was obtained in 90% yield. The reaction with dimethyl acetylenedicarboxylate (DMAD) was much slower and required heating of a mixture of **1** and DMAD for 2 h at 80°C. Chromatographic purification of the product afforded **7** as colorless crystals in 35% yield. The addition of tetracyanoethylene (TCNE) to **1** smoothly proceeded at room temperature in dichloromethane. Chromatographic separation of the product mixture afforded **8** in 43% yield together with a 25% yield of **9**. It has recently been shown that some [2+2] adducts of TCNE to 1,3-butadienes relatively readily rearrange to the corresponding cyclohexene derivatives.[9] The latter product, **9**, however, showed no tendency to isomerize to **8** under the reaction conditions.



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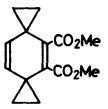

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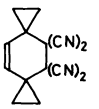

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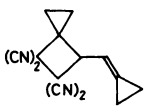

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Therefore, the observed product distribution is a kinetically controlled result. The formation of [2+2] adduct, **9**, is at variance with the result of Paquette *et al.*, who carried out the reaction in carbon tetrachloride and isolated **8** in 27% yield, but none of **9**.[3] [2+2] Cycloaddition of TCNE to unsaturated compounds is generally accepted as a two-step process by way of zwitterion[9,10] and hence accelerated in polar solvents. The observed difference in the product compositions may be accounted for at least partly by the solvent polarity effect.

The preparation of **1** described above is simple and the reaction of **1** with dienophiles provides a convenient route to variously-substituted dispiro-[2.2.2.2]decene and -decadiene derivatives. The present methodology may also be extended to the preparation of related tetrasubstituted butadienes.

Experimental

Melting points are uncorrected. NMR spectra were

obtained at 100 MHz. Mass spectra were recorded at an ionizing voltage of 70 eV; ions of each spectrum were normalized to the spectrum's most intense ion set equal to 100.

Dicyclopropanation of 3. A solution of 3-dimethylaminosulfolane[4] (2.0 g, 12 mmol) and oxirane (1.5 ml, *ca.* 30 mmol) in 30 ml of THF was treated with 10 ml of 2.5 mol dm^{-3} hexane solution of *n*-BuLi (25 mmol) at 0—−10°C. After 20 min, a solution of benzenesulfonyl chloride (4.4 g, 24 mmol) in 10 ml of THF was added at −20—−30°C. The resulting mixture was stirred for 20 min at the above temperature, then treated with 25 mmol of LDA in 30 ml of THF below −40°C, and slowly warmed up to room temperature. After removal of solvent *in vacuo*, 9 ml of water was added and the product was extracted with five 50 ml portions of ether. The extracts were combined, dried with $MgSO_4$, and concentrated. The residual oil was distilled *in vacuo* to give 1.1 g of **4** (40%), bp 115—125 °C/10^{-3} mmHg (1 mmHg = 133.3 Pa), which solidified on standing and when crystallized from hexane had mp 71—72°C. NMR($CDCl_3$): δ=0.8—1.1 (m, 3H), 1.2—1.6 (m, 5H), 1.94 (dd, J=7.5 and 13.5 Hz, 1H), 2.29 (s, 6H), 2.48 (dd, J=7.5 and 13.5 Hz, 1H), 3.44 (t, J=7.5 Hz, 1H). IR (KBr): 1290, 1150, 1110, 1060, 1045, 1040, 690 cm^{-1}. MS *m/z*: 215 (M^+, 4), 136 (19), 110 (23), 96 (100), 82 (33), 71 (28), 44 (28), 42 (26). Found: C, 55.70; H, 7.99; N, 6.47; S, 14.95%. Calcd for $C_{10}H_{17}O_2NS$: C, 55.78; H, 7.96; N, 6.61 S, 14.89%.

Preparaion of 5. To a solution of 4 (4.35 g, 20.2 mmol) in 2.6 ml of methanol was added 2.2 ml of 30% aq H_2O_2. After 2 d at room temperature, a small amount of platinum black was added to destroy excess H_2O_2 and the mixture was stirred until evolution of gas had almost ceased. After removal of the catalyst, the solution was concentrated *in vacuo* and the residual oil was heated at 110°C/0.1 mmHg. Pungent gas evolution which ceased after 5 min was observed. The product sublimed and crystallized on the upper cold glass wall of the apparatus. The crude product was collected and sublimated at 110—120°C/14 mmHg giving 2.77 g of **5** (80%). Crystallization from methanol gave **5** melting at 123.5—124.5°C. NMR ($CDCl_3$): δ=1.1—1.8 (AA'XX' m, 8H), 5.67 (s, 2H). IR (KBr): 1290, 1135, 955, 730 cm^{-1}. UV(EtOH) max: 206.5 nm (ε, 10,600). Found: C, 56.45; H, 5.88; S, 18.93%. Calcd for $C_8H_{10}O_2S$: C, 56.45; H, 5.92; S, 18.83%.

Reductive Elimination of SO_2 from 5. To a suspension of 150 mg of $LiAlH_4$ (3.9 mmol) in 15 ml of THF was added 150 mg of **5** (0.88 mmol) and the mixture was refluxed. After 2 h, the sulfone had been consumed. The reaction mixture was cooled in an ice bath and treated successively with 150 µl of water, 150 µl of 15% NaOH, and 450 µl of water.[11] The resulting suspension to which a small amount of hydroquinone was added was filtered and the precipitate was washed well with pentane. The solvent was removed through a 15 cm packed column and the residue was subjected to preparative GLC (Apiezone Grease L 20% on Celite 545, 4 mm×2 m, 100 °C) giving 26 mg of **1** (28%) as colorless crystals melting at 39.5—42 °C. The yield of **1** determined by GLC with internal standard was 50%. The physical property of **1** agreed with that reported.[2,3]

Reaction of 1 with PTAD. To a solution of **1** (32 mg, 0.30 mmol) in 0.5 ml of benzene was added 50 mg of PTAD (0.29 mmol) in 0.5 ml of benzene under argon. The reaction was almost instantaneous and colorless crystals soon precipitated giving 72 mg of **6** (90%). Crystallization from benzene–hexane (1:1) gave analytically pure **6** melting at 149.5—150 °C. NMR($CDCl_3$): δ=0.7—1.3 (m, 4H), 1.9—2.5 (m, 4H), 5.25 (s, 2H), 7.47 (s, 5H). IR(KBr): 1760, 1695, 1505, 1420, 1330, 1150 cm^{-1}. MS *m/z*: 281 (M^+, 100), 254 (32), 147 (51), 135 (48), 134 (66), 119 (49), 126 (32), 91 (89), 79 (35). UV(EtOH) max: 220 (ε, 19,000), 250 nm (1200). Found: C, 68.43; H, 5.37; N, 15.02%. Calcd for $C_{16}H_{15}O_2N_3$: C, 68.31; H, 5.38; N, 14.94%.

Reaction of 1 with DMAD. A solution of **1** (24 mg, 0.23 mmol) in 150 µl of DMAD was heated at 80 °C for 2 h and then subjected to chromatography on SiO_2 with benzene elution. The fraction containing the product (R_f=0.22) was concentrated and the residue was crystallized from hexane to give 20 mg of **7** (35%) melting at 92—93 °C (lit,[3] 92.5—93 °C). UV(EtOH) max: 290 nm (ε, 6000). The NMR, IR, and MS spectra of **7** agreed with those reported.[3] Found: C, 67.92; H, 6.57%. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%.

Reaction of 1 with TCNE. A solution of 96 mg of **1** (0.87 mmol) and 145 mg of TCNE (1.13 mmol) in 30 ml of CH_2Cl_2 was stirred at room temperature for 4 d. Chromatography of the product mixture on SiO_2 with benzene elution afforded first 85 mg of **8** (43%, R_f=0.32), which showed a decomposition point of *ca.* 190 °C (lit,[3] 182 °C). Further elution with benzene produced 50 mg of **9** (25%, R_f=0.24) melting at 151.5—152.5 °C. The NMR and MS spectra of **8** agreed with those reported.[3] **8**: IR(KBr): 1640, 1440, 1410, 1270, 1035, 980, 955, 890, 760 cm^{-1}. Found: C, 71.70; H, 4.22; N, 23.89%. Calcd for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92%. **9**: ^{1}H-NMR($CDCl_3$): δ=0.8—1.7 (m, 8H), 4.32 (d, J=9 Hz, 1H), 5.9 (dm, J=9 Hz, 1H). ^{13}C-NMR($CDCl_3$): δ=2.7(t), 3.9(t), 9.5(t), 10.4(t), 33.1(s), 41.0(s), 42.3(s), 50.9(d), 108.3(d), 108.8(s), 109.1(s), 110.1(s), 137.8(s). IR(KBr): 2255, 1420, 1280, 1045, 1030, 965, 935, 855, 800 cm^{-1} MS *m/z*: 234 (M^+, 4), 233 (22), 206 (28), 91 (100), 78 (27), 51 (29), 39 (53). Found: C, 71.83; H, 4.34; N, 23.73%. Calcd for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92%.

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