(25 MHz) δ 41.37 (t), 51.6 (q), 52.54 (q), 52.78 (q), 71.20 (s), 79.40 (s), 104.84 (t), 113.40 (s), 131.90 (s), 150.12 (s), 171.0 (s). The analytical sample melted at 199 °C. Anal. Calcd for $C_{17}H_{18}O_6Cl_4$: C, 44.38; H, 3.94. Found: C, 44.82; H, 4.19.

**(b) By Direct Alkylation of 3.** Following the procedure described above, a solution of the diester **3** (204 mg, 0.5 mmol) in THF (1.5 mL) was treated with a suspension prepared by adding MeI to a cooled (−78 °C) solution of LDA [from diisopropylamine (0.18 mL, 1.28 mmol) and *n*-BuLi (0.68 mL, 1.28 mmol)] and 3-chloro-2-(chloromethyl)propene (75 mg, 0.6 mmol) in the presence of HMPA (0.2 mL, 1.15 mmol) to afford **7** (190 mg, 85%), mp and mixed mp with the sample prepared above 199 °C.

**2,6-Bis(hydroxymethyl)-7,7-dimethoxytricyclo[5.2.1.0$^{2,6}$]-dec-8-ene (1c).** A solution of the diester **1a** (200 mg, 0.44 mmol) in THF (10 mL) was treated with $LiAlH_4$ (150 mg, 3.9 mmol) with magnetic stirring at rt for 3.5 h. The reaction mixture, on cooling with ice, was quenched by dropwise addition of saturated aqueous $Na_2SO_4$ solution. The precipitated solid was filtered out, and the filtrate was dried ($Na_2SO_4$) and concentrated to afford the dihydroxy compound (160 mg, 91%). Without further purification this was subjected to the following reduction.

To magnetically stirred liquid $NH_3$ (40 mL) (distilled from sodium) was added sodium (150 mg, 6.5 mg atom) in small pieces. The blue solution was cooled to −78 °C, and a solution of the dihydroxy compound (200 mg, 0.51 mmol) obtained as above in anhydrous THF (1.5 mL) containing ethanol (60 mg, 1.3 mmol) was added dropwise. After being stirred at this temperature for 5 min, the reaction mixture was quenched by addition of powdered $NH_4Cl$. Ammonia was then allowed to evaporate. The residual mass was treated with water (5 mL). The organic mass was extracted with ether (3 × 15 mL) (NaCl) and dried ($Na_2SO_4$). Removal of solvent afforded a liquid (120 mg, 92%) which was purified by column chromatography [ether–petroleum ether (1:4)] to give pure **1c**, mp 125 °C; IR 3280, 1280, 1120 cm$^{-1}$; $^1H$ NMR (100 MHz) δ 1.52–2.36 (m, 6 H), 2.50 (br s, 2 H), 2.66 (t, $J$ = 2 Hz, 2 H), 3.1 (s, 3 H), 3.2 (s, 3 H), 3.42 (s, 4 H) and 6.22 (t, $J$ = 2 Hz, 2 H). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11, H, 8.72. Found: C, 66.36; H, 8.66.

**2,6-Bis(hydroxymethyl)-7,7-dimethoxy-4-methylenetricyclo[5.2.1.0$^{2,6}$]dec-8-ene (1d).** A solution of the diester **1b** (180 mg, 0.4 mmol) in THF (10 mL) was reduced with $LiAlH_4$ (150 mg, 4 mmol) as above to produce the corresponding diol (150 mg, 95%) which without further purification was reduced with Na (200 mg, 8.7 mg atom) in liquid $NH_3$ (40 mL) as above to afford after column chromatography [ether–petroleum ether (1:4)] **1d** (70 mg, 71%), mp 89 °C: IR 3420, 1290, 1125 cm$^{-1}$; $^1H$ NMR (60 MHz) δ 2.73 (m, 6 H), 3.13 (s, 3 H), 3.21 (s, 3 H), 3.26 (br, partly under the singlet at 3.21, 2 H), 3.43 (s, 4 H), 4.70 (m, 2 H) and 6.20 (t, $J$ = 2 Hz, 2 H). Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.16; H, 8.57.

**Acknowledgment**. Financial support from Department of Science and Technology, Government of India is gratefully acknowledged. G.S. thanks CSIR for a Senior Research Fellowship.

**Registry No.** *exo*-**1a**, 144270-78-0; *endo*-**1a**, 144270-83-7; *exo*-**1b**, 144270-84-8; *endo*-**1b**, 144270-85-9; *exo*-**1c**, 144270-86-0; *endo*-**1c**, 144270-87-1; *exo*-**1d**, 144270-88-2; *endo*-**1d**, 144270-89-3; *exo*-1 ($R^1$ = Cl, $R^2$ = $CH_2OH$, $R^3$ = $H_2$), 144270-90-6; *endo*-1 ($R^1$ = Cl, $R^2$ = $CH_2OH$, $R^3$ = $H_2$), 144270-91-7; *exo*-**1** ($R^1$ = Cl, $R^2$ = $CH_2OH$, $R^3$ = $CH_2$), 144270-92-8; *endo*-1 ($R^1$ = Cl, $R^2$ = $CH_2OH$, $R^3$ = $CH_2$), 144270-93-9; **2**, 142743-08-6; **3**, 144270-79-1; **4**, 144370-44-5; **5X**, 144270-80-4; **5N**, 144270-94-0; **6**, 144270-81-5; **7**, 144270-82-6; allyl bromide, 106-95-6; 3-chloro-2-(chloromethyl)propene, 1871-57-4; 1,3-dibromopropane, 109-64-8.

**Supplementary Material Available:** Tables 1–5 listing positional and thermal parameters, bond lengths and bond angles, including estimated standard deviations, details of the X-ray analysis, and the ORTEP plot of **5X** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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# Dimerization of Substituted 1,3-Diarylallenes

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*Received May 15, 1992*

The regio- and stereoselectivity observed in thermal dimerization of allenes has usually been interpreted[3] on the basis of the bis-allyl diradical intermediate, **2**, but it has been shown that a concerted $[_\pi 2_s + (_\pi 2_s + _\pi 2_s)]$ mechanism can also explain the results in many instances.[4] Other calculations for allene indicate that a 1,1′-bis-allyl diradical intermediate corresponds to the smallest energy barrier for formation of 1,2-dimethylenecyclobutane.[5] Dehmlow[6] found that 1,3-diphenylallene, **1a**, gave **3a**, **4a**, and **5a** in approximately equal amounts. Optically active allene gave inactive dimers, and neither of the possible dimers having both phenyl groups inward on the exocyclic double bonds was formed. This result is in contrast to that with many other substituted allenes, which give dimers having the exocyclic substituents in the hindered inward positions as major products. We therefore dimerized 1,3-bis(*p*-chlorophenyl)allene and 1,3-bis(*p*-bromophenyl)allene to establish the generality of Dehmlow's results.

Dimerizations were carried out in refluxing benzene. Pure samples of the dimers **3b** and **3c** were obtained by precipitation from hexane and recrystallization from hexane–toluene. The other more soluble dimers were chromatographed on acidic alumina and recrystallized with difficulty from 95% ethanol. **1b** and **1c** gave similar products. **1b** gave only **3b**, **4b**, and **5b** in a ratio of 1.9:1.3:1 in 90–95% total yield. **1c** gave only **3c**, **4c**, and **5c** in a ratio of 2.1:1.4:1.

The identity of the products was determined principally by $^1H$, 60-MHz NMR spectroscopy (see Table I) and is consistent with UV and IR data. Mass spectroscopy confirmed the dimeric nature of the compounds. X-ray crystallographic studies on **3b** confirmed the structure shown.

The cyclobutyl protons in **3b** are shifted to lower field than those in **4b** or **5b** by about 1 ppm. Models indicate that when the ring is trans substituted, the hydrogens are located in the shielding cone of the adjacent aryl group. When ring stereochemistry is cis, no such effect is operative and hydrogen resonance appears at lower field. Dimers **3b** and **5b** appear to have their aryl groups on the double bond directed outward since there is no mutual shielding as expected for aryl groups pushing against each other. The unsymmetrical structure of **4b** is revealed by its more complex NMR. Proton decoupling located the δ 7.22 signal within the aromatic multiplet. Similar reasoning was used in the assignment for **3c**, **4c**, and **5c** although aromatic

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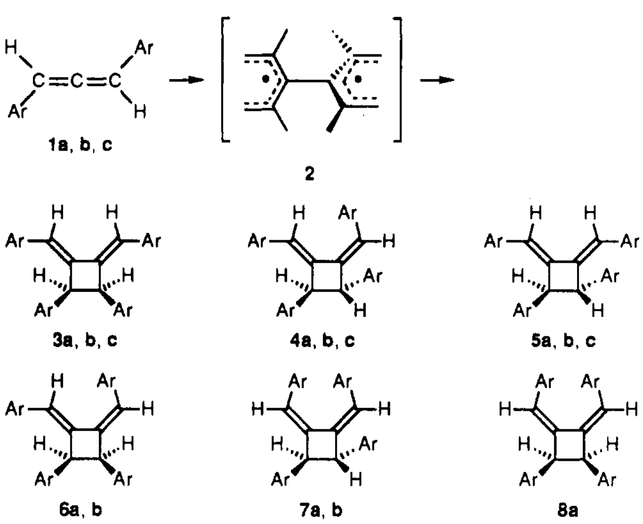
0022-3263/92/1957-7346$03.00/0

**Scheme I**[a]



[a] Key: (a) Ar = $C_6H_5$; (b) Ar = $p$-$C_6H_4Cl$; (c) Ar = $p$-$C_6H_4Br$.

**Table I. NMR Shifts**[d] **(δ, in $CDCl_3$)**

| compd | olefinic H | benzylic H |
|---|---|---|
| **3a**[a] | *b* | 5.03 |
| **3b** | 6.96s | 4.97s |
| **3c** | 6.91s | 4.92s |
| **4a**[a] | 6.20d, 6.85d | 3.99dd, 4.35dd |
| **4b** | 6.10d, 7.22d | 3.90dd, 4.25dd |
| **4c** | 6.08d, 7.20[c] | 3.80dd, 4.14dd |
| **5a**[a] | *b* | 4.34 |
| **5b** | 7.00s | 4.24s |
| **5c** | *b* | 4.21s |
| **6a**[a] | 6.05m, *b* | 4.67m |
| **6b** | 6.15m, *b* | 4.75m |
| **7a** | 6.26 | 4.66 |
| **7b** | 6.34s | 4.75m |
| **8a**[a] | *b* | 5.29 |

[a] In $CCl_4$. [b] Buried in the aromatic signal. [c] Multiplicity difficult to determine (within aromatic region). [d] All values were at 60 MHz; the values for **3b** and **4b** were verified by spectra at 300 MHz.

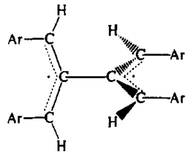
signals for the $p$-chlorophenyl group often appeared as singlets whereas the $p$-bromophenyl group never was this simple to interpret.

A kinetic study of the dimerization reaction was carried out on **1b** in benzene at 80.1° and 72.5°. The second-order reaction had $\Delta H^{\ddagger}$ = 18 kcal/mol and $\Delta S^{\ddagger}$ = −28 cal/$K^{-1}$ $mol^{-1}$. The rate of dimerization was followed by monitoring the decrease in the concentration of the allene by NMR using the δ 6.21 band of the olefinic hydrogens.

Dehmlow[6] irradiated a solution of dimer **3a** in ether and isolated the three dimers which were not produced in the thermal dimerization. We have carried out preliminary experiments on the photolysis of dimers **3b** and **4b**. A small amount of dimer **6b** was isolated, and there was NMR evidence that another chromatographic fraction contained mainly **7b**.

## Discussion

A clear explanation for the stereochemistry of the dimers from triphenylallene has been given[3d] assuming that the reaction proceeds through an orthogonal diradical, that the approach of the two allene molecules to form the diradical occurs in the least sterically hindered manner, that closure of this diradical occurs before any rearrangement to other diradicals can occur, and that the 1,2-dimethylenecyclobutanes are formed by conrotation and under kinetic control.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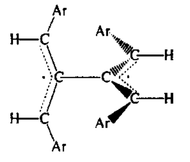
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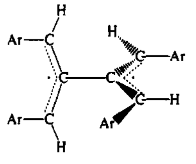
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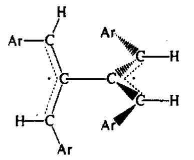
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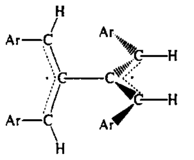
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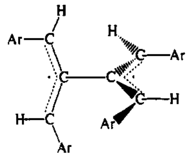
14

For dimerization of 1,3-disubstituted allenes that have identical substituents six diradicals are possible (**9**–**14**). An attempt to account for exclusive formation of stereoisomers **3**–**5** by making the same assumptions as were made for triphenylallene showed that such an explanation would be valid only if the diradicals were formed more readily from reaction of an $R$ allene with an $S$ allene than from $R + R$ or $S + S$. Dehmlow's experiments[6] with an optically active allene show that this approach is incorrect. He dimerized ($S$)-(+)-1,3-diphenylallene in carbon tetrachloride at 60° and observed that the dimerization occurred at the same rate as with racemic allene, that the mixture of dimers was the same in both experiments, and that the dimer mixture was optically inactive. The ($S$)-(+)-1,3-diphenylallene recovered after 3 half-lives had the same optical activity as the starting material. This experiment shows that formation of the diradical is irreversible. Dehmlow also reported that a thermal rearrangement of the dimers could not be observed and that by long heating resinification occurred. We refluxed a sample of dimer **4b** in deuteriobenzene for 40 h, the conditions of the original dimerization. None of the other dimers could be detected by NMR after this treatment, and dimer **4b** remained essentially unchanged. These experiments show that the ring closure of the diradical is also irreversible at the temperature employed. Dehmlow suggested that the increased stability of the phenyl-substituted diradicals allows time for their interconversion before ring closure occurs. This is clearly the simplest explanation for the results. However, it seems to us that there is no reason to assume that all of the dimers formed thermally come from a single diradical. Dehmlow assumes this, chooses **14** as the diradical, and assumes that both conrotation and disrotation occur. We believe that by conrotation only dimers **5**–**7** can form. Disrotation would give either **3** or **4**. If one assumes that several of the diradicals give dimers and that only conrotation occurs, the final mixture of dimers must depend on both the relative rates of ring closure of the different diradicals and on their relative concentrations. Diradical **9** with all aryl groups out can give only **5**, the least plentiful dimer, but models seem to indicate that this diradical is the most hindered so its concentration should be small. Diradical **10** with all aryl groups in appears to permit a conformation in which all aryl groups are in conjugation, but closure to a dimer from this conformation appears to be very difficult. It can give only dimer **7**. Diradical **11** can give dimers **3** or **4**, diradical **12** can give **4** or **8**, and diradical **13** can give only **6**. For our explanation to be valid more than half of the ring closures must occur from diradical **11**, but some must occur from diradical **9** or **14** to yield dimer **5**.

Examination of molecular models suggests that the stabilities of the dimers are in the order **5** > **3** > **4** > **6** > **7** > **8**. Molecular mechanics calculations (MM3)[7] confirm

**Table II. Energies of Isomers of 3b Estimated by Geometry Optimization with MM3**[7]

| isomer | structure | steric energy, kcal mol$^{-1}$ | steric and electronic energy, kcal mol$^{-1}$ |
|---|---|---|---|
| out-out-trans | **5b** | 26.0 | -3292.48 (= 0) |
| out-out-cis | **3b** | 26.5 | 0.4 |
| in-out-trans | **4b** | 28.3 | 1.8 |
| in-out-cis | **6b** | 28.8 | 2.7 |
| in-in-cis | **8b** | 30.7 | 3.8 |
| in-in-trans | **7b** | 31.1 | 4.4 |

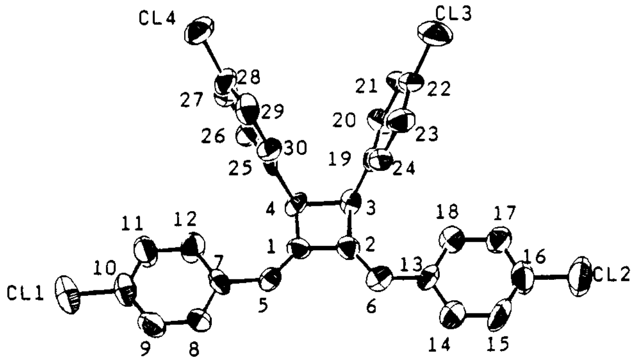

**Figure 1.** ORTEP[8] drawing of **3b**. Thermal ellipsoids enclose 50% probability; H atoms have been omitted.

this (Table II). Thus, only the three most stable dimers are formed. If the transition states for the ring closures are late the relative stabilities of the dimers would be very important. However, it is still difficult to understand why **5b**, the most stable dimer, is formed in lowest amount. Perhaps only those diradicals having at least three aryl groups out exist in high enough concentration and close rapidly enough to yield dimers. Then all of **5b** must come from **9** that appears from models to be the most hindered, so it is in lower concentration than **11**. This requires that most of the dimer mixture is formed from **11**. Further work is needed to verify these suggestions.

**Crystal Structure of 3b and Calculations.** Figure 1 shows the atomic numbering; selected distances and angles are given in Table III. The geometry of this dimer contrasts sharply with that of the dimers in ref 3a, both of which have aromatic substituents directed "in" at C5 and C6 and which have *trans*-chloro substituents at C3 and C4. The *cis*-*p*-chlorophenyl substituents at C3 and C4 in **3b** have lengthened the bond in the cyclobutane ring to 1.60 Å. The outward *p*-chlorophenyl substituents at the methylene carbons in **3b** are nearly coplanar (maximum deviation 0.14 Å) with the butadiene moiety; the molecules pack in the crystal with the $\pi$-system planes stacked along the *c* axis. The cyclobutane ring is also nearly planar in **3b**, in agreement with the microwave results for unsubstituted 1,2-dimethylenecyclobutane.[9]

Energy minimization using MM3[7] (with standard sp$^2$ and sp$^3$ potentials for the cyclobutane atoms) reproduces the molecular geometry of **3b** quite closely, except that MM3 gives a longer C1–C2 bond (1.49 vs 1.46 Å) and a shorter C3–C4 bond (1.58 vs 1.60 Å). Input coordinates for estimating the relative energies of the isomers of **3b** (Table II) were prepared by appropriate rotations and substitutions. It is evident that the "out-out" geometry, with a nearly planar extended $\pi$-system and less crowding at C5 and C6, is significantly less strained than "in-out" and "in-in", while cis or trans substitution at C3–C4 plays a minor role.

## Experimental Section

**1,3-Bis(*p*-chlorophenyl)propyne, 15.** (*p*-Chlorophenyl)-acetylene[10,11] was converted to (*p*-chlorophenyl)ethynylmagnesium bromide in THF and treated dropwise with *p*-chlorobenzyl bromide.[12] After 2 h of refluxing a small amount of CuCl was added and refluxing continued for 48 h. Addition of water, evaporation to dryness, and extraction with ether gave a mixture of unreacted *p*-chlorobenzyl bromide, 1,2-bis(*p*-chlorophenyl)-ethane, and **15**. Recrystallization from ethanol gave **15** in 40% yield, mp 59.5–60.5 °C: IR 2200 cm$^{-1}$ w; $^1$H NMR ($CCl_4$, 60 MHz) $\delta$ 3.74 s (2 H), 7.27 s (8 H); mass spectrum *m*/*e* 260 (2 chlorine isotope cluster). Anal. Calcd for $C_{15}H_{10}Cl_2$: C, 68.99; H, 3.86. Found: C, 69.01; H, 3.84. If the length of the reflux period before addition of CuCl was not adhered to or if ether was employed as solvent, the major product was 1,2-bis(*p*-chlorophenyl)ethane.

**1,3-Bis(*p*-chlorophenyl)allene, 1b.** A solution of 5.0 g of **15** in 100 mL of anhyd ether was rearranged by rapid passage through 44 g of dried, basic alumina in a 250-mL separatory funnel (mild air pressure). The alumina became blue, but the color faded as 100 mL of ether was forced through the alumina. The total eluate was then passed through the alumina a second time and an additional 100 mL of ether used to complete the elution. Evaporation of the eluate gave 5.0 g of crude **1b**, mp 72–75 °C. This was recrystallized from pentane to give 4.0 g (80%) of **1b**, mp 78.5–79 °C: $^1$H NMR ($CCl_4$, 60 MHz) $\delta$ 6.46 s (2 H), 7.20 s (8 H); IR 1930 cm$^{-1}$; mass spectrum *m*/*e* 260 (2 chlorine isotope cluster). Anal. Calcd for $C_{15}H_{10}Cl_2$: C, 68.99; H, 3.86. Found: C, 69.08; H, 3.84.

**Dimerization of 1b.** A solution of **1b** (3.8 g) and a little hydroquinone in benzene (30 mL) was refluxed for 24 h. Solvent was removed, and the residue was boiled in 150 mL of pentane. The solid that remained (1.30 g) was dimer **3b**, mp 194.5–195 °C, unchanged by recrystallization from toluene–hexane. The pentane solution was concentrated and chromatographed to yield **4b** and **5b**. Recrystallization from ethanol gave pure **4b**, mp 129–130 °C, and **5b**, mp 209–210 °C. TLC showed each of the dimers to be homogeneous. Anal. Calcd for $C_{30}H_{20}Cl_4$: C, 68.99; H, 3.86. Found for **3b**: C, 68.91; H, 3.80. For **4b**: C, 68.90; H, 3.78. For **5b**: C, 68.83; H, 3.88. Mass spectra for all these dimers: M$^+$ *m*/*e* 520 (4 chlorine isotope cluster).

For **3b**: $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 4.97 s (2 H), 6.81 d ($J$ = 7.1 Hz, 4 H), 6.94 d ($J$ = 7.1 Hz, 4 H), 6.96 s (2 H), 7.04 d ($J$ = 7.4 Hz, 4 H), 7.08 d ($J$ = 7.4 Hz, 4 H); $^{13}$C 53.45, 119.51, 128.10, 128.52, 129.78, 129.90, 132.20, 132.91, 133.97, 134.66, 141.93.

For **4b**: $^1$H NMR ($CDCl_3$, 300 MHz) 3.90 dd ($J$ = 2.2, 4.5 Hz, 1 H), 4.25 dd ($J$ = 2.2, 4.5 Hz, 1 H) 6.10 d ($J$ = 1.7 Hz, 1 H), 6.97 d ($J$ = 7.1 Hz, 2 H), 7.09 d ($J$ = 7.0 Hz, 2 H), 7.15 d ($J$ = 7.1 Hz, 2 H), 7.22 d (1 H), 7.25 d ($J$ = 7.0 Hz, 2 H), 7.34 d ($J$ = 7.0 Hz, 2 H), 7.45 d ($J$ = 7.0 Hz, 2 H), 7.50 ($J$ = 7.0 Hz, 2 H), 7.54 d ($J$ = 7.0 Hz, 2 H); $^{13}$C 56.08, 57.84, 123.24, 124.63, 128.22, 128.41, 128.69, 128.72, 128.94, 129.02, 129.60, 130.01, 132.58, 132.77, 133.10, 133.26, 133.76, 135.15, 139.29, 140.73, 140.93, 143.47.

For **5b**: $^1$H NMR ($CDCl_3$, 60 MHz) $\delta$ 4.24 s (2 H), 7.00 s (2 H), 7.10 s (8 H), 7.27 s (8 H).

NMR showed these three dimers to be the only ones present in the original dimerization mixture. The ratio of **3b**:**4b**:**5b** was 1.9:1.3:1 based on NMR after 20 h at 80 °C in benzene-$d_6$. The relative ratio of dimers did not change as the reaction proceeded, and no transient NMR signals were evident. The conversion of allene to dimers was 91.5%. A known mixture of dimers in benzene-$d_6$ with a known amount of 1,2-bis(*p*-chlorophenyl)ethane as internal standard remained unchanged for 3 days at 80 °C.

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**Table III. Distances and Angles[a] for 3b, $C_{30}H_{20}Cl_4$**

| | | | | | |
|---|---|---|---|---|---|
| C1–C2 | 1.465 (13) | C1–C4 | 1.531 (12) | C1–C5 | 1.332 (12) |
| C2–C3 | 1.518 (12) | C2–C6 | 1.355 (13) | C3–C4 | 1.604 (12) |
| C3–C19 | 1.505 (12) | C4–C25 | 1.514 (12) | C5–C7 | 1.478 (10) |
| C6–C13 | 1.468 (11) | C10–Cl(1) | 1.722 | C16–Cl(2) | 1.717 |
| C22–Cl(3) | 1.712 | C28–Cl(4) | 1.718 | | |

| | | | |
|---|---|---|---|
| C2–C1–C4 | 92.0 (7) | C2–C1–C5 | 130.5 (9) |
| C4–Cl–C5 | 137.4 (9) | C1–C2–C3 | 93.1 (7) |
| C1–C2–C6 | 131.8 (9) | C3–C2–C6 | 135.0 (9) |
| C2–C3–C4 | 87.3 (7) | C2–C3–C19 | 118.7 (7) |
| C4–C3–C19 | 117.3 (7) | C1–C4–C3 | 87.4 (7) |
| C1–C4–C25 | 120.8 (7) | C3–C4–C25 | 118.0 (7) |
| C1–C5–C7 | 130.5 (8) | C2–C6–C13 | 129.7 (9) |
| C5–C7–C8 | 116.7 (6) | | |

Angle between planes C1–C2–C3 and C1–C4–C3: 5.3°

[a] Units of distances are Å, of angles, deg. Esd in parentheses, in units of least significant digit of the corresponding value. C–C distances and angles in phenyl rings were restrained to ideal values; all C–H distances were also restrained (see Experimental Section). An approximate esd of the C–Cl distance is 0.007 Å (taking the restraints into account).

**Photolysis.** A mixture of dimers **4b** and **5b** (200 mg) in ether was photolyzed for 2 h. Preparative TLC on silica gel gave dimer **6b**, mp 179.5–181 °C, mass spectrum $M^+$ $m/e$ 520 (4 chlorine isotope cluster). A second spot gave a glass that appeared to be mainly dimer **7b** on the basis of NMR.

For **6b**: $^1H$ NMR ($CDCl_3$, 60 MHz) $\delta$ 4.75 m (2 H), 6.15 m (1 H), 6.81–7.68 m (17 H).

For **7b**: $^1H$ NMR ($CDCl_3$, 60 MHz) $\delta$ 4.75 m (2 H), 6.34 m (2 H), 6.80–7.32 m (16 H).

**1,3-Bis(*p*-bromophenyl)propyne** was prepared from (*p*-bromophenyl)acetylene[11,13] and *p*-bromobenzyl bromide by the procedure used for **15**. The yield of pure product, mp 75.0–75.5 °C, was only 13% owing to the presence of less soluble material that was difficult to remove. No attempt was made to improve this yield: $^1H$ NMR ($CCl_4$ 60 MHz) $\delta$ 3.73 s (2 H), 7.21–7.46 (8 H, 2 overlapping p-disubstituted benzene patterns). Anal. Calcd for $C_{15}H_{10}Br_2$: C, 51.47; H, 2.88. Found: C, 51.57; H, 2.91.

**1,3-Bis(*p*-bromophenyl)allene, 1c,** mp 90–91.5 °C, was prepared in 88% yield as described for **1b**: $^1H$ NMR ($CCl_4$ 60 MHz) $\delta$ 6.47 (2 H), 7.05–7.40 (8 H, p-disubstituted benzene pattern). Anal. Calcd for $C_{15}H_{10}Br_2$: C, 51.47; H, 2.88. Found: C, 51.68; H, 2.89.

**Dimerization of 1c** was carried out as described for **1b**. From 1.4 g were obtained 0.3 g of **3c**, mp 189.5–190.5 °C, 0.2 g of **4c**, and 0.14 g of **5c**. Anal. Calcd for $C_{30}H_{20}Br_4$: C, 51.47; H, 2.88. Found for **3c**: c, 51.47; H, 3.08. For **4c**: 51.58; H, 2.91.

For **3c**: $^1H$ NMR ($CCl_4$, 60 MHz) $\delta$ 4.92 s (2 H), 6.91 s (2 H), 6.72–7.21 m (16 H).

For **4c**: $^1H$ NMR ($CCl_4$, 60 MHz) $\delta$ 3.80 dd (1 H), 4.14 dd (1 H), 6.08 d (1 H), 7.20 (1 H), 7.05–7.58 m (16 H).

For **5c**: $^1H$ NMR ($CCl_4$, 60 MHz) $\delta$ 4.21 s (2 H), 6.88–7.53 (18 H).

**X-ray Crystal Structure Analysis of 3b.** Space group *Fdd*2, $a$ = 51.101 (13) Å, $b$ = 14.450 (4) Å, $c$ = 14.015 (3) Å, $V$ = 10348 Å$^3$, $C_{30}H_{20}Cl_4$, $M_r$ = 522.27 g mol$^{-1}$, $Z$ = 16, $\rho_{calc}$ = 1.341, $\mu$(Mo K$\alpha$) = 4.21 cm$^{-1}$, 3268 measured reflections, 2820 measured reflections (2807 unique, $R_{merg}$ = 0.18) with $h$ = 0–49, $k$ = 0–18, $l$ = 0–18, 1717 of these reflections with $F > 2\sigma(F)$, 1090 considered unobserved, 270 parameters refined, isotropic secondary-extinction factor 2 × 10$^{-5}$, maximum shift/error 0.04, peaks in final difference map 0.38/−0.40 e Å$^{-3}$, $w = 1/\sigma^2$, $R$ = 0.092, $R_w$ = 0.063, GOF = 1.35. Data were taken on a Syntex P1bar diffractometer with graphite monochromator; intensities were not corrected for absorption; structure solution by SHELX86;[14] refined with a locally-modified version of SHELX76.[15] The phenyl rings were refined as rigid bodies with ideal bond lengths and angles since there were very few significant intensities. Anisotropic displacement parameters were refined for all non-H atoms. All calculations were performed on the VAX 3100 using the UCLA Crystallographic Package[16] and the SHELX, local geometry and Cambridge Structural Database[17] programs.

**Registry No.** **1b**, 143959-14-2; **1c**, 144345-78-8; **3b**, 144345-79-9; **3c**, 144408-50-4; **4b**, 144408-46-8; **4c**, 144345-80-2; **5b**, 144408-47-9; **5c**, 144408-48-0; **6b**, 144408-49-1; **7b**, 144489-50-9; **8b**, 144408-51-5; **15**, 144345-81-3; (*p*-chlorophenyl)acetylene, 873-73-4; *p*-chlorobenzyl bromide, 622-95-7; (*p*-bromophenyl)acetylene, 766-96-1; *p*-chloroacetophenone, 99-91-2; *p*-bromoacetophenone, 99-90-1.

**Supplementary Material Available:** Complete tables of atomic parameters, bond distances, angles and torsion angles, and least-squares planes for **3b** and further experimental details for preparation of the allenes and dimerization (6 pages). This material is contained in many libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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## Synthesis of $\beta$-Keto 1,3-Dithianes from Acetylenic Ketones

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*Received June 22, 1992*

$\beta$-Keto 1,3-dithianes are highly functionalized three-carbon units which are of much importance as potentially useful synthetic intermediates.[1] Procedures reported for the preparation of these compounds include $\alpha$-alkylation of carbonyl compounds with 1,3-dithiane or its derivatives,[2] nucleophilic addition of 1,3-dithiane to epoxides followed by oxidation,[3] and conjugate reduction of $\alpha$-oxo ketone dithio acetals.[4] In this paper we wish to disclose a new

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