values would be expected to be due to the presence of nitrogen. It seems unreasonable that the presence of an *n*-butyl side chain could cause the difference noticed in this case. Evidence that the effect is related to the change in cation type is seen by comparing the Ag<sup>+</sup> results with those of Na<sup>+</sup>. The log  $K_1$  values for complexation of Na<sup>+</sup> with 1 and 7 are comparable (3.22 and 3.30, respectively), whereas the log  $K_1$  value for Ag<sup>+</sup>:1 interaction is much greater than that for Ag+:7 interaction. Furthermore, K+ shows a smaller log  $K_n$  value in its complexation with 1 than with 7.  $Ag^+$  is intermediate between  $Na^+$  and  $K^+$  in ionic radus,<sup>22</sup> so the observed changes in  $\log K$  cannot be attributed to size effects. The effect of donor atom type on equilibrium constant is discussed in detail by Lamb et al.22

**Cation Effects.** Among the alkali metal cations,  $\log K_1$ decreases with increasing ion size when the host contains nitrogen in the macrocycle ring. A possible exception to this is the binding of the cations by 6 where  $\log K_1$  for binding of K<sup>+</sup> is large and not determined accurately. For the lariat ether hosts that contain only oxygen donor atoms, the largest log  $K_1$  values are found in the case of K<sup>+</sup> and the smallest in the case of Cs<sup>+</sup>.

Of the cations studied, K<sup>+</sup> and Ca<sup>2+</sup> showed the greatest propensity to form 1:2 complexes with the macrocycles studied. In some cases, principally those for  $Ca^{2+}$  reacting with 1 and 7,  $\log K_2$  rivals  $\log K_1$  in magnitude. The largest cation, Cs<sup>+</sup>, formed well-defined 1:2 complexes only with 5 and 4. In the remaining cases, either the reactions with Cs<sup>+</sup> could not be well characterized as including 1:2 complexes or  $K_2$  was at least 2 orders of magnitude less than  $K_1$ . The reaction of Cs<sup>+</sup> with 3 could not be characterized at all. Examining the plots of heat produced vs. titrant volume showed them to be practically superimposable. In

this case, the problem is not run to run inconsistency in the calorimeter output but in the theory applied to explain the shape of the enthalpogram.

### Conclusions

In comparable cases, enlarging the ring size from 15 to 18 atoms results in increased log K values. The inclusion on the aza-15C5 ring of a side chain bound to nitrogen and having an oxygen atom in the number 3 position (compound 2) improves the stability of the complexes formed with the cations studied here by about an order of magnitude. These results indicate that the side chain is involved in the binding although it is not clear by what mechanism the improved stability is achieved. Lengthening the side chain and including more donor atoms in it has little if any perceptible effect on the binding with the 18-crown-6 variety of macrocycles. Finally, the effect on the equilibrium constant produced by appending side chains to a carbon pivot atom of 7 is small. Such a gross structural variation must result in some alteration of the characteristics of the molecule. Possibly, an enlarged set of cations might include one which could "see" the difference in the ligands. Organic ammonium cations with groups that could interact with the donor atoms on the side chain would be an obvious choice.

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# 4,4'-Methylenebis(benzyne) [4,4'-Methylenebis(1,2-didehydrobenzene)] Equivalent

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The aprotic diazotization of 5.5'-methylenebis(anthranilic acid) (4) by isoamyl nitrite in refluxing 1,2-dichloroethane functions as a 4,4'-methylenebis(benzyne) (5) equivalent. 5 undergoes Diels-Alder reaction with tetraphenylcyclopentadienone, anthracene, and 2,5-dimethylfuran and [2 + 2] cycloaddition with trans-1,2dichloroethylene to give the corresponding bis-adducts in moderate to low yields. Reactions of 5 with iodine, carbon disulfide, and ethyl phenyl sulfide are also described.

Although diaryne synthons have been sporadically described in the literature,<sup>1-3</sup> it is in recent years that their synthetic utility has attracted much attention. Hart and co-workers showed that 1,2,4,5- and 1,2,3,4-tetrahalobenzenes are synthetically useful diaryne (1 and 2)equivalents.<sup>4</sup> For example, when they are treated with 2 equiv of an organolithium reagent in the presence of a receptor diene, they form products which correspond formally to bis-adducts of 1 and 2. 1,5-Naphthodiyne (3) synthon was recently utilized for the preparation of chrysenes.<sup>5</sup> Very recently it was shown that oxidation of

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diaminobenzo[1,2-d:4,5-d']ditriazole with 2 equiv of lead tetraacetate is an excellent 1,4-diaryne (1, R = H) equivalent.<sup>6</sup> In these cases, two formal triple bonds of 1-3 are introduced into the same benzene or naphthalene ring probably in a stepwise manner. As far as we know, no report has appeared on a diaryne intermediate which has two formal triple bonds in two different benzene rings connected by a methylene chain. Herein we report the generation of a formal 4,4'-methylenebis(benzyne) (5) and its reactions.

A variety of methods are currently available for generation of arynes.<sup>7</sup> Among them the aprotic diazotization of anthranilic acid by isoamyl nitrite provides a clean source of benzyne.<sup>7,8</sup> Fortunately 5,5'-methylenebis(anthranilic acid) (4) is commercially available at a reasonable price. We therefore examined the aprotic diazotization of 4 with the expectation of generating 5. Tetraphenylcyclopentadienone is one of the most efficient receptors of benzyne.<sup>7,8</sup> Thus, to a stirred and refluxed solution of tetraphenylcyclopentadienone and isoamyl nitrite in 1,2dichloroethane was added a solution of 4 in dioxane. Chromatographic workup of the reaction mixture satisfactorily afforded the expected twin Diels-Alder adduct 6 in 51% yield.



Since it has now been established that 4 functions as a precursor of 5, reactions of 5 with several substrates were next examined. Anthracene smoothly reacted with 5 to give 2,2'-methylenebis(triptycene) (7) in 46% yield.<sup>9</sup> By the way, the physicochemical properties of 7 are worthy of mention. Bartlett was the first to synthesize triptycene and suggested the existence of the transannular interaction between the three benzene rings of triptycene,<sup>10</sup> though it still remains a subject of controversy. In the electronic absorption spectrum, triptycene shows two maxima at 271 and 278 nm, with log  $\epsilon$  3.66 and 3.56, respectively, and a



shoulder at about 263 nm with log  $\epsilon$  3.25.<sup>10b</sup> On the other hand, in compound 7 two weak maxima appear at 310 (log  $\epsilon$  1.85) and 324 nm (log  $\epsilon$  1.91) in addition to two maxima at 273 (log  $\epsilon$  3.91) and 280 nm (log  $\epsilon$  3.98) and a shoulder at 282 nm (log  $\epsilon$  3.96) which correspond to the absorptions observed with triptycene. We tentatively ascribe the origin of these weak absorptions to the charge-transfer interaction between the three benzene rings of the one triptycene nucleus and those of the other triptycene nucleus. Another interesting feature of 7 is its strong tendency to form solvated crystals with organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, benzene, and acetonitrile. Further investigation on these topics is under way in our laboratory.

2,5-Dimethylfuran also undergoes Diels-Alder reaction with 5 to give the adduct 8 in 61% yield.<sup>11</sup> Compound 8 was converted to the naphthalene derivative 9 by treatment with low valent titanium. Benzyne reacts with carbon disulfide to produce 1,3-benzodithiol-2-ylidenecarbene and in the presence of alcohols 2-alkoxy-1,3benzodithioles are obtained as the final products.<sup>12</sup> Thus, when 5 was allowed to react with carbon disulfide in the presence of isoamyl alcohol, the dithiole 10 was obtained in 19% yield. Iodine adds to 5 to give the tetraiodo compound 11 in 29% yield.<sup>18</sup> Benzyne reacts with ethyl phenyl sulfide to yield diphenyl sulfide with elimination of ethylene.<sup>14</sup> Thus 5 reacts with ethyl phenyl sulfide to

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give an isomeric mixture 12 in 21% yield.

The [2+2] cycloaddition of benzyne with olefins is the most intensively investigated reaction from a mechanistic point of view. When 5 was allowed to react with a large excess of trans-1,2-dichloroethylene, two isomeric [2 + 2]cycloadducts were isolated by column chromatography in a ratio of about 3:1. Although the total yield of the adduct 13 was very low (ca. 3%), the results are truly reproducible. The major product (mp 121-137 °C) shows only one singlet at  $\delta$  5.14 as an absorption due to cyclobutyl hydrogens, while the minor product (mp 149-159 °C) exhibits two singlets at  $\delta$  5.14 and 5.57 in the <sup>1</sup>H NMR spectra with CCl<sub>4</sub> as solvent. The [2 + 2] cycloaddition of benzyne with trans-1,2-dichloroethylene occurs with moderate loss of the original stereochemistry, thus yielding trans- and cis-1,2dihydro-1,2-dichlorobenzocyclobutenes in a ratio of about 4:1.<sup>15</sup> The cyclobutyl hydrogens of the trans isomer appear at  $\delta$  5.26 as singlet and those of the cis isomer at  $\delta$  5.66. The observed isomer ratio and the chemical shift data, therefore, clearly indicate that for the major compound two pairs of chlorines are trans each other, while for the minor compound one pair is trans and the other is cis each other. However, note that, as their less sharp melting points show, each compound is still a mixture of isomers (for example for the trans-trans compound, see structures 14a-c).

In summary, every type of reaction that benzyne can undergo is reproducible with 5. Thus the aprotic diazotization of 4 enables one-pot preparation of many structurally interesting compounds which are otherwise difficult to obtain. Although yields are generally moderate to low, this will be fully compensated by the ready availability of the starting 4.

### **Experimental Section**

General Remarks. Melting points were determined on a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a JASCO IRA-2 spectrometer. <sup>1</sup>H NMR spectra were obtained on a JEOL PNM-PMX 60 spectrometer or on a JEOL FX 90Q spectrometer. High-resolution mass spectra were determined on a Hitachi M-80B spectrometer. UV spectra were recorded on a Hitachi 340 spectrometer. All column chromatography was executed with silica gel (Merck type 60, 70-230 mesh ASTM) or Florisil (100-200 mesh). 5,5'-Methylenebis(anthranilic acid) (4) was purchased from Tokyo Kasei Kogyo Co., Ltd. and recrystallized from dioxane. Isoamyl nitrite<sup>16</sup> and tetraphenylcyclopentadienone<sup>17</sup> were prepared according to the literature methods. 1,2-Dichloroethane was distilled and dried over molecular sieves and dioxane was used as purchased. All other chemicals were reagent grade and used without further purification.

6,6'-Methylenebis(1,2,3,4-tetraphenylnaphthalene) (6). To a stirred and gently refluxed solution of 1.92 g (5 mmol) of tetraphenylcyclopentadienone and 0.70 g (6 mmol) of isoamyl nitrite in 100 mL of 1,2-dichloroethane was added dropwise a solution of 0.72 g (2.5 mmol) of 5,5'-methylenebis(anthranilic acid) (4) in 12 mL of dioxane over a period of 20 min. The mixture was refluxed for an additional 30 min. The solvent was evaporated on a rotary evaporator. The resulting solid residue was chromatographed over silica gel (150 g) eluting with CCl<sub>4</sub> to give 0.85 g (38.5%) of pure 6 and 0.43 g of a mixture of 6 and tetraphenylcyclopentadienone. Rechromatography of the mixture part gave 0.27 g (12.1%) of pure 6. Recrystallization from  $CCl_4$ /hexane gave analytically pure 6 as white granules: mp 290.5-292.5 °C; IR (KBr) 1603, 1498, 1445, 1370, 1069, 1022, 742, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.01 (s, 2 H, methylene), 6.82 (s, 20 H, aromatic), 7.0-7.6 (m, 26 H, aromatic). Anal. Calcd for  $C_{69}H_{48}$ : C, 94.48; H, 5.52. Found: C, 94.08; H, 5.62.

2,2'-Methylenebis(triptycene) (7). Anthracene (13.37 g, 75 mmol) was dissolved in 450 mL of hot 1,2-dichloroethane, and to this was added a solution of 3.51 g (30 mmol) of isoamyl nitrite in 50 mL of 1,2-dichloroethane. The reslting mixture was stirred and gently refluxed, and to this was added a solution of 3.58 g (15 mmol) of 4 in 60 mL of dioxane over a period of 45 min. The mixture was refluxed for 1 h, cooled, and filtered to remove insoluble tarry materials. The filtrate was evaporated, and the residue was mixed with 14.7 g of maleic anhydride and 300 mL of xylene. The mixture was refluxed for 1 h and cooled below 100 °C and to this was added 300 mL of a 10% aqueous KOH solution. The mixture was stirred for 15 min. The aqueous layer was discarded and the organic layer was washed with aqueous 10% KOH (100 mL) and with water several times, and dried over MgSO<sub>4</sub>. The solvent was evaporated to leave 5.61 g of an orange solid, which was chromatographed on a silica gel column (200 g). Elution with  $CCl_4$  afforded 1.51 g of pure 7 and 2.71 g of 7 contaminated with unidentified materials. Rechromatography of the latter gave 1.47 g of pure 7. Total yield, 2.98 g (46%).

Compound 7 forms solvated crystals with organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, benzene, and acetonitrile. Material crystallized from CH<sub>2</sub>Cl<sub>2</sub> melts at 311-315 °C and material from acetonitrile at 305–307 °C. The material crystallized from  $CH_2Cl_2$ /hexane and dried for a long period of time in vacuo still showed the absorption due to CH<sub>2</sub>Cl<sub>2</sub> in the <sup>1</sup>H NMR spectrum and gave the following analysis results. Found: C, 92.40; H, 5.20. Calcd for C<sub>41</sub>H<sub>28</sub>: C, 94.58; H, 5.42. The material crystallized from acetonitrile and dried for 10 h at 100 °C in vacuo gave the following analysis results showing the inclusion of acetonitrile: C, 94.10; H, 5.14; N, 0.36.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.78 (s, 2 H, methylene), 5.33 (s, 2 H, bridgehead), 5.37 (s, 2 H, bridgehead), 6.65-7.47 (m, 22 H, aromatic); IR (KBr) 1470, 1455, 1195, 1185, 1015, 790, 740, 615 cm<sup>-1</sup>; UV (CHCl<sub>3</sub>)  $\lambda_{max}$  ( $\epsilon$ ) 273 (8150), 280 (9540), 282 (sh, 9170), 310 (71), 324 nm (80); high-resolution mass spectrum calcd for  $C_{41}H_{28}$ m/e 520.2192, found m/e 520.2171, calcd for C<sub>21</sub>H<sub>15</sub> m/e 267.1175, found m/e 267.1210, calcd for C<sub>20</sub>H<sub>13</sub> m/e 253.1018, found m/e253.0989.

6,6'-Methylenebis(1,4-dihydro-1,4-dimethyl-1,4-epoxynaphthalene) (8). To a stirred and mildly refluxed solution of 1.44 g (15 mmol) of 2,5-dimethylfuran and 0.70 g (6 mmol) of isoamyl nitrite in 100 mL of 1,2-dichloroethane was added a solution of 0.72 g (2.5 mmol) of 4 in 12 mL of dioxane over a period of 20 min. The mixture was refluxed for 1 h, cooled, and filtered to remove insoluble polymeric materials. The filtrate was washed with aqueous 5% NaHCO<sub>3</sub> ( $2 \times 30$  mL) and water ( $2 \times 50$  mL) and dried. The solvent was evaporated to leave a red oil, which was chromatographed over Florisil. Elution with CH2Cl2 afforded 0.54 g (61%) of 8 as a viscous and nearly colorless oil: IR (thin film) 1480, 1440, 1382, 1305, 1152, 1136, 856, 670 cm<sup>-1</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>) § 1.72 (s, 12 H, methyl), 3.77 (s, 2 H, methylene), 6.5-7.1 (m, 10 H, aromatic H and olefinic H).

Deoxygenation of 8 to 9 was done by using low valent titanium prepared from TiCl<sub>4</sub> and LiAlH<sub>4</sub> in THF according to the procedure described in the literature.<sup>18</sup> Thus, when the experiment began with 0.30 g of 8, 0.16 g (59%) of 6,6'-methylenebis(1,4dimethylnaphthalene) (9) was obtained: mp 143.5-144 °C (from hexane); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  2.58 (s, 6 H, methyl), 4.30 (s, 2 H, methylene), 7.0-8.0 (m, 10 H, aromatic). Anal. Calcd for  $C_{25}H_{24}$ : C, 92.54; H, 7.46. Found: C, 92.64; H, 7.47.

6,6'-Methylenebis[2-(isopentyloxy)-1,3-benzodithiole] (10). To a stirred mixture of carbon disulfide (5 mL), isoamyl nitrite (0.70 g, 6 mmol), isoamyl alcohol (0.88 g, 10 mmol), and 1.2-dichloroethane (100 mL) was added a solution of 0.72 g (2.5 mmol) of 4 in 12 mL of dioxane over a period of 20 min. The mixture was refluxed for 1 h, cooled, and filtered to remove insoluble tarry materials formed. The filtrate was washed with aqueous 5% NaHCO<sub>3</sub> (2  $\times$  30 mL) and water (2  $\times$  50 mL) and dried over  $MgSO_4$ . The solvent was evaporated to leave an orange oily residue, which was chromatographed on a column of Florisil.

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Elution with  $CH_2Cl_2$  gave 0.17 g (14%) of 10 as a faint yellow oil, which solidified on standing in a refrigerator: mp 94-96 °C (from hexane); <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 0.85 (d, 12), 1.1-1.9 (m, 6 H), 3.1-3.7 (m, 4 H), 3.88 (s, 2 H), 6.89 (s, 2 H), 6.9-7.5 (m, 6 H). Anal. Calcd for C<sub>25</sub>H<sub>32</sub>O<sub>2</sub>S<sub>4</sub>: C, 60.94; H, 6.55. Found: C, 60.72; H, 6.39.

4,4'-Methylenebis(1,2-diiodobenzene) (11). To a stirred and gently refluxed solution of 1.27 g (5 mmol) of iodine, 0.70 g (6 mmol) of isoamyl nitrite in 100 mL of 1,2-dichloroethane was added a solution of 0.72 g (2.5 mmol) of 4 in 12 mL of dioxane over a period of 20 min. The mixture was refluxed for 1 h, cooled, and filtered to remove insoluble materials formed. The filtrate was washed with aqueous 5%  $\rm Na_2S_2O_4~(2\times25~mL)$  and water (2  $\times$  25 mL) and dried over MgSO<sub>4</sub>. The solvent was evaporated and the resulting solid residue was purified by column chromatography (CCl<sub>4</sub>, silica gel) to provide 0.47 g (29%) of 11 as white crystals, mp 180–182 °C (from benzene). A solution of 11 in benzene turned pink on standing at room temperature because the compound liberates molecular iodine. A satisfactory elemental analysis could not be obtained for this compound. The following is the most satisfactory among several attempts. Anal. Calcd for  $C_{13}H_8I_4$ : C, 23.24; H, 1.20; I, 75.56. Found: C, 24.26; H, 1.39; I, 74.51. IR (KBr) 1448, 1375, 1256, 1085, 1000, 896, 802 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.80 (s, 2 H, methylene), 6.8 (d, 2 H, aromatic, 7.2-8.1 (m, 4 H, aromatic).

Methylenebis[(phenylthio)benzene] (12). A solution of 0.72 g (2.5 mmol) of 4 in 12 mL of dioxane was added to a stirred and refluxed solution of 1.38 g (10 mmol) of ethyl phenyl sulfide and 0.70 g (6 mmol) of isoamyl nitrite in 100 mL of 1,2-dichloroethane over a period of 20 min. The mixture was refluxed for 1 h and then evaporated to leave a red oil. The oil was dissolved in benzene (50 mL), washed with 5% KOH ( $2 \times 30$  mL) and water  $(2 \times 30 \text{ mL})$ , and dried. The benzene was evaporated and the residual oil was chromatographed on a column of silica gel. Elution with CCl<sub>4</sub> gave a mixture of 12 and ethyl phenyl sulfide, which was subjected to fractional distillation (Kugelrohr). Ethyl phenyl sulfide was distilled at 75 °C (3 mmHg) and 12 at 200 °C (0.05 mmHg) as a viscous oil which solidified in a refrigerator: 0.20 g (21%); mp 95–102 °C (from hexane); <sup>1</sup>H NMR ( $CCl_4$ )  $\delta$  3.85 (br, C, 78.08; H, 5.24. Found: C, 77.82; H, 5.43. 4,4'-Methylenebis(1,2-dichloro-1,2-dihydrobenzocyclobutene) (13). To a stirred and gently refluxed mixture of trans-1,2-dichloroethylene (20 mL), isoamyl nitrite (0.70 g, 6 mmol), and 1,2-dichloroethane (100 mL) was added a solution of 0.72 g (2.5 mmol) of 4 in 12 mL of dioxane over a period of 20 min. The mixture was refluxed for 1 h, cooled, and filtered to remove insoluble materials formed. The filtrate was evaporated to leave an oily residue, which was chromatographed on a column of silica gel. Elution with CCl<sub>4</sub> gave 20 mg (2.2%) of the trans, trans-13 and 7 mg (0.8%) of the cis, trans-13. The reaction was repeated five times on this scale. The results are truly reproducible and the above two products were repeatedly obtained in the ratio described.

trans, trans-13: mp 121-127 °C (from hexane); white granules; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.00 (s, 2 H, methylene), 5.14 (s, 4 H, cyclobutyl H), 7.0-7.2 (m, 6 H, aromatic); MS, m/e (relative intensity) 360 (52), 358 (100), 356 (77) (M<sup>+</sup>), 323 (15), 298 (25), 296 (25), 262 (38), 251 (20), 215 (30), 191 (35), 189 (35); high-resolution mass spectrum, calcd for  $C_{17}H_{12}Cl_4$  359.9636, 357.9666, and 355.9696, found 359.9626, 357.9628, and 355.9695.

cis,trans-13: mp 149-158 °C (from hexane); white granules; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.00 (s, 2 H, methylene), 5.14 (s, 2 H, cyclobutyl H), 5.57 (s, 2 H, cyclobutyl H), 7.0-7.2 (m, 6 H, aromatic); MS, m/e (relative intensity) 360 (52), 358 (100), 356 (76) (M<sup>+</sup>), 323 (16), 285 (15), 262 (21), 249 (20), 215 (36), 189 (23); high-resolution mass spectrum, calcd for C17H12Cl4 359.9636, 357.9666, and 355.9696, found 359.9604, 357.9641, and 355.9680.

Registry No. 4, 7330-46-3; 5, 92958-37-7; 6, 92958-38-8; 7, 92958-39-9; 8, 92958-40-2; 9, 92958-41-3; 10, 92958-42-4; 11, 92958-43-5; 12, 92958-44-6; 13, 92958-45-7; Cl(CH<sub>2</sub>)<sub>2</sub>Cl, 107-06-2; trans-ClCH=CHCl, 156-60-5; TiCl4, 7550-45-0; LiAlH4, 16853-85-3; CS<sub>2</sub>, 75-15-0; I<sub>2</sub>, 7553-56-2; EtSPh, 622-38-8; isoamyl nitrite, 110-46-3; tetraphenylcyclopentadienone, 479-33-4; anthracene, 120-12-7; 2,5-dimethylfuran, 625-86-5; isoamyl alcohol, 123-51-3; dioxane, 123-91-1.

# Application of the Peterson Olefination to the Preparation of Substituted **Triafulvenes from Methoxycyclopropenylium Triflates**

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Three new unusually substituted triafulyenes were prepared by reacting methoxycyclopropenylium triflates with  $\alpha$ -silyl substituted anions. The mode of a nucleophilic attack varied, depending on the anion. Attack occurred at the methoxy substituted carbon, yielding the desired triafulvene, the methoxy methyl group, yielding the cyclopropenone and the methyl substituted anion, or the alkyl/aryl substituted carbon. The latter rearranged upon heating in CH<sub>3</sub>CN to give the desired triafulvene. These reactions are discussed in detail.

Triafulvenes represent the simplest cross-conjugated cyclic hydrocarbons and have therefore been of considerable theoretical and synthetic interest.<sup>2</sup> The recent reports by Billups<sup>3</sup> and Staley<sup>4</sup> and co-workers on the elegant synthesis of the long sought after parent triafulvene,  $C_4H_4$ , prompted us to report a new method for the preparation

of novel exocyclic substituted triafulvenes.

Although a variety of methods, prominent among them the Wittig olefination of diphenylcyclopropenone<sup>5</sup> and the condensation of activated methylene compounds such as  $(CN)_2CH_2$  with ethoxycyclopropenylium ions,<sup>6</sup> have been used for the synthesis of substituted triafulvenes, the well-known Peterson olefination<sup>7,8</sup> has, to our knowledge, not been employed. Since this method is an excellent

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<sup>(2)</sup> For a review see: Eicher, T.; Weber, J. L. Top. Curr. Chem. 1975, 57, 1

<sup>(3)</sup> Billups, W. E.; Lin, L. J.; Casserly, E. W. J. Am. Chem. Soc. 1984, 106. 3698.

<sup>(4)</sup> Staley, S. W.; Norden, T. D. J. Am. Chem. Soc. 1984, 106, 3699.

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