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Synthesis and Reactions of 7,10-Methano-7,8,9,10,11,11-hexachloro-7,10-dihydrofluoranthene[1]

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The synthesis of 7,10-methano-7,8,9,10,11,11-hexachloro-7,10-dihydrofluoranthene (3) is reported and its properties are studied. The absorption spectrum of this orange substance shows an enhanced K band that may reflect an intramolecular charge-transfer process. When 3 is irradiated with 360-nm light, no quadricyclene is detected nor does 3 show any other photochemical reaction at 360 nm. The reaction of 3 with methoxide, ethoxide, and isopropoxide nucleophiles occurs in a stereospecific manner to produce 7,10-methano-6b-alkoxy-7,8,9,10,11,11-hexachloro-6b,7,10,10a-tetrahydrofluoranthene.

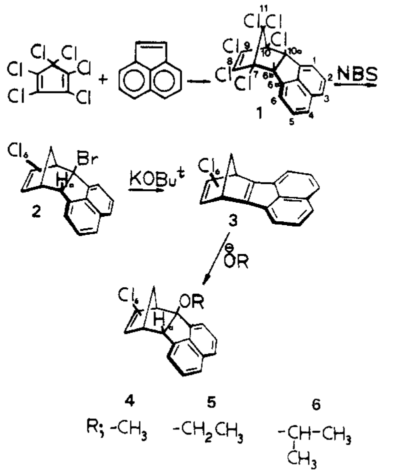
We synthesized a quantity of 7,10-methano-7,8,9,10,11,11-hexachlorofluoranthene (**3**) as a compound for photochemical study. A molecule containing a norbornadiene moiety fused through the 1,2-bridge of acenaphthylene seemed a potentially rich source of photochemical intrigue.[4] It was hoped that such a substance would exhibit photochemistry similar to that of norbornadiene-1,2-dicarboxylic acid anhydride[5] and thus be convertible to a quadricyclene derivative.[6] The bright orange crystals of **3** have currently resisted a variety of photolytic ring-closing conditions. However, we have found some interesting ground-state chemistry associated with **3**.

The study of the ground-state properties of **3** described herein has its genesis in our early attempts to synthesize **3**. During these initial studies, by-products were isolated that suggested that alkoxy groups were incorporated into the structure. Thus, the recent report by Davies and Adams[8] concerning the reaction of nucleophiles with chlorine-substituted norbornadienes stimulated us to explore in detail the similar reaction upon **3**.

Results and Discussion

The synthesis of **3** involves the thermal [4 + 2] cycloaddition of hexachlorocyclopentadiene to acenaphthylene to form *endo*-7,10-methano-7,8,9,10,11,11-hexachloro-6b,7,10,10a-tetrahydrofluoranthene (**1**).[9,10] This compound was treated with NBS in refluxing carbon tetrachloride to form the crude monobrominated derivative **2**. Subsequent treatment of crude **2** with warm potassium *tert*-butoxide in *tert*-butyl alcohol produced **3** in good yield. The mass spectrometric examination of **3** showed the expected isotopic cluster for a six chlorine atom containing molecule at M^+ of 420 through 426. The base peak at *m/e* 387 (M − 35) showed the isotopic clustering characteristic of five chlorine atoms.[13] A minor M − 105 grouping occurred at *m/e* 315, 317, and 319, suggesting a fragment with three chlorine atoms lost. The NMR spectrum of **3** showed only the typical aromatic resonances at 7.2–7.8 ppm.

The UV–visible spectrum of a cyclohexane solution of **3** is shown in Figure 1 as compared to acenaphthylene dissolved in the same solvent. The feature of major interest is the bathochromic shift and hyperchromic modification of the absorption band of acenaphthylene between 400 and 450 nm. This band has been classified as a K transition by Michl[14] and theoretical CI-SCF-P-P-P calculations indicate that this transition involves substantial intramolecular charge transfer from the peri bridge to the naphthalene chromophore. The enhancement of the K band in **3** may represent additional charge transfer involving homoconjugation of the remote dichloroethene π system with the peri bridge of the acenaphthylene unit. The recent synthesis and characterization of 8*H*-cyclopent[*a*]acenaphthylene as orange needles[15] casts some doubt on the existence of this proposed homoconjugative interaction because the remote double bond at position 8 and 9 is saturated in this molecule. We hope that studies now in progress will clarify the spectral interpretations.



The reaction of **3** with various alkoxides was pursued analogous to the procedure in prior studies[8] by refluxing an alcoholic mixture of **3** with the appropriate sodium alkoxide. We observed that there were qualitative rate differences and that the reaction of **3** with alkoxides occurred in the order $CH_3O^- > CH_3CH_2O^- > (CH_3)_2CHO^- >>> (CH_3)_3CO^-$. Methoxide and ethoxide addition proceeded smoothly. The addition of isopropoxide proceeded with difficulty, and some

Table I. Proton NMR Data, δ Values

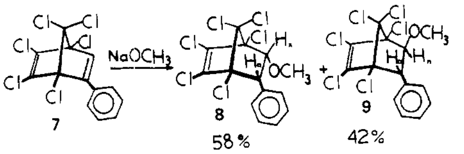
Compd	Registry no.	H_a	CH	CH_2	CH_3
1	63784-80-5	4.80			
2	63784-81-6	5.05			
4	63784-83-8	4.18			2.92 (s)
5	63784-84-9	4.18		3.00 (q)	1.15 (t)
6	63784-85-0	4.20	3.30 (m)		0.83, 0.95 (d)
8[a]	37053-27-3	4.48			3.16
9[b]	36964-07-5	4.71			3.51

[a] H_x = 3.98. [b] H_n = 3.22.

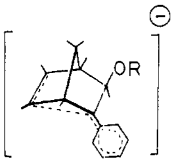
decomposition was found. Within the limits of detection we could not find any addition of *tert*-butoxide to **3**.

All reactions showed a high degree of stereospecificity with the major isomer being the only product that was isolated. GLC analysis of the crude product mixture verified that the total percentage of minor components was always less than 10%. Of the minor components detected, about 30% seemed to be one isomer.

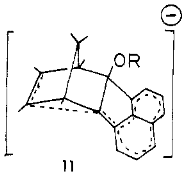
The selectivity of the reaction that produces the major stereoisomer is supported by several observations. The alkoxy adduct is a pure white crystalline substance indicating that the ethylene bridge common to acenaphthylene and norbornadiene is now saturated. The elemental analysis of the product is indicative of the retention of all six chlorine atoms. If alkoxide were to add at the dichloroethene bridge, β elimination of HCl would be anticipated and this is not found. The addition of methoxide to 5-phenylhexachloronorbornadiene (**7**) is also selective with the phenyl-substituted double bond being the site of reaction.[8]



The factors that contribute to the selectivity of alkoxide addition to **3** are analogous to those that cause more exo product than is normally found when **7** is subjected to nucleophilic substitution. The transition states leading to the alkoxy derivatives of **3** are likely stabilized by significant resonance delocalization in the acenaphthylene group as suggested in **11**. Since the π system of acenaphthylene can stabilize negative charge through resonance, the alternative addition of alkoxide to the dichloroethylene bridge of **3** is expected to have a greater activation energy because chlorine will not be as effective in stabilizing negative charge when compared to acenaphthylene. Thus, the selectivity is readily rationalized and supported by analogy to the transition state **10** for reaction of **7**.



10



11

Discrete rather than nonclassical carbanions have been proposed for the Birch reduction of benzonorbornadiene.[16] Therefore, it is probable that **3** may also form such intermediates.

The endo or exo geometry adopted by the attacking nucleophile upon **3** is subject to both steric and electronic demands made in the transition state. Careful study of molecular models allows no clear decision as to which stereoisomer is produced during these reactions.[17]

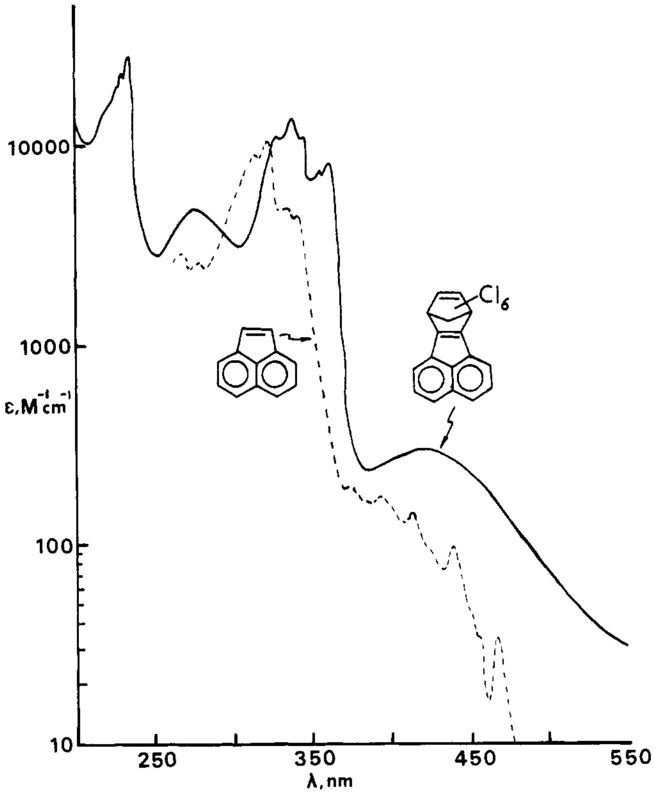


Figure 1. The ultraviolet–visible absorption spectrum of acenaphthylene and 7,10-methano-7,8,9,10,11,11-hexachloro-7,10-dihydrofluoranthene.

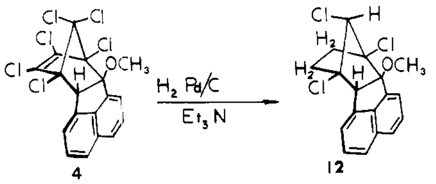
We attempted to synthesize structures **4**, **5**, and **6** by an alternate route. We envisaged that a Diels–Alder reaction between 1-methoxyacenaphthylene and hexachlorocyclopentadiene would produce the desired compound whose stereochemistry would be predictable from the Alder Rule.[11] Unfortunately, the reactions studied to date have not satisfactorily produced the product we desire.

The ^1H NMR spectra of the various compounds are recorded in Table I. The chemical shifts for proton H_a are consistent for the compounds **4**, **5**, and **6**, suggesting identical geometry for all the adducts. We have tried to find other model systems for a comparison of chemical shifts in the hope that NMR data would indicate a trend that would allow us to make stereochemical assignments. The H_a protons for **8** and **9** resonate at lower field and differ substantially in their environment from adducts **4**, **5**, and **6**. The [4 + 2] endo adduct derived from tetrachlorocyclopentadienone and acenaphthylene shows a chemical shift for H_a of 4.35 ppm while the analogous exo adduct has a shift for H_a of 4.49 ppm.[18] The endo and exo [4 + 2] products derived from the reaction of acenaphthylene and cyclopentadiene show chemical shifts of 4.04 and 3.52 for H_a, respectively.[19] These bridge protons show nonsystematic behavior, and consequently are not reliable indicators of endo or exo stereochemistry.

The chemical shifts and multiplicities of the various alkoxy compounds are those expected for these substituents. The NMR spectrum of isopropoxy adduct **6** shows clear evidence of the diastereotopic relationship of the two methyl groups. The quasitriplet at a field width of 500 Hz is resolved upon scale expansion into a set of close-lying doublets, J = 4.8 Hz. We have also observed that scale expansion of the proton resonance for H_a in **4**, **5**, and **6** shows a perturbation of this signal. We surmise that some weak long-range coupling is occurring. Perhaps the closest ortho hydrogen to H_a undergoes a weak spin–spin interaction with H_a.

We are currently studying reductive dehalogenation of the structures **3**, **4**, **5**, and **6** and wish to report an initial experiment. We initiated these studies in the hope that the reduced products would lead to a prediction of the endo or exo geometry of the alkoxy substituent. The results are interesting but not definitive.

When methoxy compound **4** is treated with hydrogen over Pd/C in the presence of triethylamine (TEA) and the hydrogenation interrupted early in the reaction, NMR analysis of the crude product shows the presence of one hydrogen atom at δ 3.75. as well as H_a at δ 4.0. We suggest that the chlorine at the 11 position anti to the dichloroethene bond is first to be removed by virtue of homoconjugative assistance from the 8,9 π bond. Subsequent attack by hydrogen is then anti to the π bond. Further reduction occurs at the dichloroethene bond to form compound 12.



4 **12**

Dissolving metal reductions have been shown to selectively substitute the anti-chlorine with hydrogen in 1,2,3,4,7,7-hexachloro-5-*endo*-acetoxybicyclo[2.2.1]2-heptene.[20] However, when these same investigators used TEA and H_2/Pd/C they found that chlorine removal from the geminal position did not occur in competition with saturation of the ethene bridge.

Our results are contrary to this observation but seem internally consistent if the peri-fused naphthalene is endo to the 8,9 π bond of **4**. This endo position would add some steric interference to catalytic hydrogenation of the 8,9 π bond of **4** allowing the rate of hydrogenation of the 11-geminal chlorine group to become competitive as enhanced by homoconjugative assistance.

The NMR spectrum of **12** is complex with a series of overlapping multiplets occurring in the range δ 2.0–3.05 and overlapping the methoxy protons at δ 2.92. Two perturbed singlets occur at δ 3.35 and 3.75. We tentatively conclude that the δ 3.75 signal is associated with the 11-bridge proton and that the perturbation of this singlet results from long-range W coupling with the endo protons now at positions 8 and 9. The perturbed singlet at δ 3.35 is therefore assigned to bridge proton H_a whose chemical shift is affected by the loss of the unsaturation and chlorine atoms and whose perturbation results from weak W coupling[21] with the exo bridge protons at positions 8 and 9 as well as with the ortho hydrogen on the aromatic ring.

We shall report in future publications the results of continuing studies on the synthesis of complex strained-ring derivatives of 3 as well as their attendant chemistry.

Experimental Section[22]

Materials. Acenaphthylene (Tech) was repeatedly crystallized from methanol and treated with charcoal. Hexachlorocyclopentadiene (Aldrich) was vacuum distilled. *N*-Bromosuccinimide was recrystallized from water and dried. Fresh potassium *tert*-butoxide was used directly from the bottle.

***endo*-7,10-Methano-6b-bromo-7,8,9,10,11,11-hexachloro-6b,7,10,10a-tetrahydrofluoranthene (2).** A mixture of 8.5 g (0.02 mol) of 1,[9] 150 mL of carbon tetrachloride, 0.10 g of azobis(isobutyronitrile) and 7.12 g (0.04 mol) of *N*-bromosuccinimide was refluxed by the radiant energy from a 150-W sun lamp for 26 h. At 6-h intervals an additional 0.1 g of AIBN was added. The cooled, brown solution was suction filtered, the filtrate was treated with decolorizing carbon, and after a second filtration the filtrate was subjected to vacuum rotary evaporation. The resulting pale yellow solid was recrystallized from cyclohexane to produce 6.3 g (70%) of off-white crystals: mp 185–190 °C; IR (KBr) 3035, 2945, 1590 cm^{-1}; NMR (CCl_4)δ 7.3–7.8 (ArH), 5.05 (ArCH) ppm.

7,10-Methano-7,8,9,10,11,11-hexachloro-7,10-dihydrofluoranthene (3). A solution of 40.5 g (0.08 mol) of **2** and 10.2 g (0.09 mol) of potassium *tert*-butoxide in 750 mL of dried *tert*-butyl alcohol was heated to 50 °C and magnetically stirred under a nitrogen atmosphere for 6 h. After cooling to room temperature, the excess alkoxide was destroyed by adding 20 mL of ice water. The solution was then made neutral by the addition of cold 6 N HCl and the solids were collected by filtration. The filtrate was vacuum rotary evaporated yielding an orange solid. All collected solids were combined and suspended in boiling hexane which was filtered hot to remove inorganic salts. The filtrate upon cooling to −10 °C for 24 h produced orange crystals: mp 169.4–169.9 °C (90%); $\lambda_{max}^{C_6H_{12}}$ nm (ϵ, M^{-1} cm^{-1}) 281 (5600), 340 (14 000), 357 (7200), 363 (7200), 400 (300); IR (KBr) 3045, 1580 cm^{-1}; NMR δ 7.3–7.95 (ArH); mass spectrum, 70 eV, *m/e* (relative intensity) 426 (3), 425 (1), 424 (6), 423 (1), 422 (8), 421 (1), 420 (3), 391 (21), 390 (13), 389 (70), 388 (20), 387 (100), 386 (13), 385 (64), 342 (2), 340 (6), 338 (5), 319 (6), 318 (3), 317 (20), 316 (3), 315 (20).

Anal. Calcd for $C_{17}H_6Cl_6$: C, 48.27; H, 1.43; Cl, 50.29. Found: C, 48.37; H, 1.35; H, 1.35; Cl, 50.30.

Synthesis of 7,10-Methano-6b-alkoxy-7,8,9,10,11,11-hexachloro-6b,7,10,10a-tetrahydrofluoranthene. A mixture of 1.0 g (2.37 mM) of **3** and 50 mL of absolute alcohol solvent containing 0.5 g (22 mM) of dissolved sodium was refluxed gently for 6 and 24 h, depending upon the alkoxide used. The bright orange diene slowly dissolved and the mixture became pale yellow to dark brown, depending upon the alcohol used. After reflux, the cooled mixture was carefully quenched with 100 mL of ice-cold 0.1 N HCl. This mixture was extracted with three 50-mL portions of dichloromethane, and the combined CH_2Cl_2 extracts were treated with decolorizing carbon, dried over anhydrous $MgSO_4$, filtered, and vacuum rotary evaporated. The resulting off-white solid was dissolved in a minimum amount of hot methanol and allowed to crystallize at 0 °C for 24 h. The methoxy, ethoxy, and isopropoxy substituents were made in this manner.

Methoxy Substituent 4: mp 132–133 °C (90%); NMR δ 2.95 (3 H, CH_3, s), 4.1 (1 H, ArCH, s), 7.35–7.9 (6 H, ArH); IR (KBr) 3045, 2940, 2925, 2810, 1595, 1190, 1155, 1110, 1040, 975, 905, 780 cm^{-1}. Anal. Calcd for $C_{18}H_{10}Cl_6O$: C, 47.51; H, 2.22; Cl, 46.53. Found: C, 47.66; H, 2.19; Cl, 46.75.

Ethoxy Substituent 5: mp 111–112 °C (25%); NMR δ 1.15 (3 H, CH_3, t), 3.0 (2 H, CH_2, q), 4.1 (1 H, s), 7.4–7.9 (6 H, ArH, m); IR (KBr) 3045, 2960, 2920, 2880, 1595, 1240, 1200, 1170, 1108, 1050, 910, 865, 775 cm^{-1}. Anal. Calcd for $C_{19}H_{12}Cl_6O$: C, 48.67; H, 2.56; Cl, 45.36. Found: C, 48.48; H, 2.77; Cl, 44.73.

Isopropoxy Substituent 6: mp 159–160 °C (10%); NMR δ 0.83 (3 H, CH_3, d), 0.95 (3 H, CH_3, d), 3.30 (1 H, (O)C(H)>, m), 4.1 (1 H, ArCH, s), 7.4–7.9 (6 H, ArH, m); IR (KBr) 3045, 2960, 2910, 1595, 1240, 1205, 1170, 1125, 1100, 1060, 1055, 950, 845, 780 cm^{-1}. Anal. Calcd for $C_{20}H_{14}Cl_6O$: C, 49.74; H, 2.90; Cl, 44.05. Found: C, 49.90; H, 2.90; Cl, 43.75.

7,10-Methano-6b-methoxy-7,10-11,trichloro-6b,7,8,9,10,10a-hexahydrofluoranthene (12). A mixture of 15 mL of absolute methanol, 0.175 g (0.38 mM) of **4**, 0.1 g (0.95 mM) of triethylamine, and 20 mg of 10% Pd/C catalyst was placed in a Parr medium-pressure hydrogenator. The system was pressurized to 50 psi with H_2 and shaken. After 2 h of agitation, an additional 20 mg of catalyst was added, and the system was repressurized to 50 psi and shaken an additional 2.5 h. The mixture was filtered and the filtrate vacuum rotary evaporated to produce a pale yellow oil. This oil was mixed with 50 mL of CCl_4 and washed with three 25-mL portions of H_2O, and the organic phase was dried over $MgSO_4$. Vacuum rotary evaporation of the dry CCl_4 solution produced an off-white crystalline substance that was vacuum dried at 1 mmHg. The solid was recrystallized from hexane to produce 0.072 g (53%) of **12**: mp 119–120 °C; NMR δ 1.95–3.05 (4 H, CH_2CH_2, m) 2.95 (3 H, OCH_3, s), 3.35 (1 H, s), 3.8 (1 H, s), 7.2–7.8 (6 H, ArH); IR (KBr) 3045, 2995, 2947, 2820, 1590, 1295, 1245, 1230, 1178, 1090, 1032, 984, 922, 875, 785, cm^{-1}. Anal. Calcd for $C_{18}H_{15}Cl_3O$: C, 61.16; H, 4.24; Cl, 30.08. Found: 61.10; H, 4.18; Cl, 29.98.

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Registry No.—**3**, 63784-82-7; **12**, 63784-86-1.

References and Notes

(1) Presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, 1976.

(2) (a) Robert A. Welch Postgraduate Fellow; (b) taken in part from the Master's Thesis of D.M.C., Trinity University, 1970.

(3) (a) NSF Undergraduate Research Participant; (b) Robert A. Welch Undergraduate Scholar.

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(6) It has not escaped our attention that compound **3** offers potential for the storage of solar energy[7] and we are continuing our efforts to find suitable photochemical conditions for its transformation.

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(17) The diagrams we have chosen for illustration are arbitrarily illustrated with the alkoxy group in the exo position for clarity of presentation. We shall attempt to identify the correct geometry for these adducts when subsequent studies are finished.

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(22) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded in KBr pellets on a Perkin-Elmer 337 or 283. NMR spectra were obtained in dilute solutions of $CDCl_3$ or CCl_4 with internal Me_4Si on a Varian T-60. UV-visible spectra were obtained on a Cary 118C. GLC analyses were run on a Varian Hy-Fl 2400 with a flame-ionization detector and a 5 ft × 0.125 in. column of 1.5% OV-101 on Chromosorb G. Mass spectra were recorded on a Finnegan 1015 C system/150 Quadrupole spectrometer at 70 eV. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Versatile Allene and Carbon Dioxide Equivalents for the Diels–Alder Reaction

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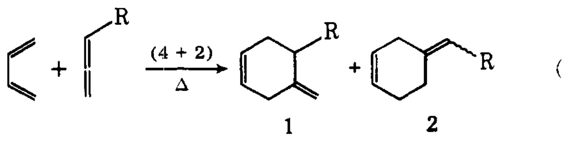
The Diels–Alder cycloaddition of vinyltriphenylphosphonium bromide (4) with a variety of 1,3-dienes generated the unsaturated cyclic phosphonium salts 3 in excellent yield. Wittig condensation of the ylides of 3 with aldehydes afforded the alkylidene derivatives. In addition, the known Diels–Alder adducts 13 were prepared from diethyl ketomalonate (12) and 1,3-dienes. These dihydropyrans could be transformed, via diacids 14, to β,γ-unsaturated valerolactones 15 by either lead tetraacetate mediated oxidative decarboxylation or by the Curtius degradation.

The Diels–Alder reaction figures prominently in the arsenal of organosynthetic reactions, and a wealth of knowledge exists concerning reactivity profiles, regioselectivity, and stereochemistry of the 4 + 2 cycloaddition reaction.[2] In recent years the construction of synthetic equivalents for unreactive dienophiles such as ketene[3] and allene[4] has extended the scope of this cyclization reaction to the production of cyclohexene systems not normally generated by this thermal process. This report relates the development of two such Diels–Alder equivalents: an allene equivalent[5] capable of introducing the $-CH_2C(=CHR)-$ group in a Diels–Alder sense, and a carbon dioxide equivalent[6] which places the $-OC(=O)-$ group into the cycloadduct.

Results and Discussion

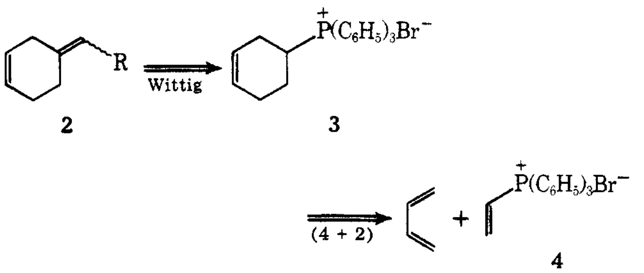
General Allene Equivalent. Two isomeric Diels–Alder products may be realized from the 4 + 2 cyclization between alkyl-substituted allenes and 1,3-dienes (eq 1).[7] It was felt that



(1)

an allene equivalent capable of producing the alkylidene moiety in **2** might be obtained from the intermediate **3** via a Wittig transformation (Scheme I). Cycloadduct **3** might then be obtained using the Diels–Alder transform, thus requiring a 1,3-diene and vinyltriphenylphosphonium bromide (**4**) as starting materials.

Scheme I



Indeed, vinyltriphenylphosphonium bromide[8] underwent smooth Diels–Alder reaction with a number of dienes at elevated temperatures to afford the desired adducts in excellent yield as shown in Table I. Cycloadducts **3a–e** were recovered as powders after recrystallization. These new phosphonium salts could be readily converted to the ylides by treatment with lithium diisopropylamide at −78 °C in tetrahydrofuran. Addition of a slight excess of aldehyde at 0 °C followed by warming to room temperature afforded the alkylidene derivatives as shown in Table II. Formaldehyde, aliphatic and aromatic aldehydes, and α,β-unsaturated aldehydes underwent condensation and the desired olefins were obtained in good yield although, in some cases, product volatility con-