10 ft, 185°) to give 118 mg of the methyl ether **7a** (R = CH_3): mp 51–53°; nmr ($CDCl_3$) δ 1.46 (s, 6 H), 2.78 (t, 2 H, J = 0.8 Hz), 3.81 (s, 3 H), 3.87 (s, 3 H), 7.38 ppm (s, broad, 2 H).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.90; H, 7.32. Found: C, 70.99; H, 7.33.

The decoupling experiments are described in the text.

Decomposition of the Diazonium Salt 11 in the Presence of Copper Bronze.—The amino acid **3a** (2.38 g) was dissolved in glacial acetic acid (15 ml), and the solution was cooled in an ice–salt bath until it solidified. The solid was added in portions to a solution of sodium nitrite (0.70 g) in concentrated sulfuric acid (6 ml) and cooled in an ice–salt bath. Lumps which formed in the mixture were crushed. After the mixture was stirred for 15 min, it was poured onto ice. After stirring for 15 min, unreacted starting material (0.56 g) was removed by filtration. The filtrate, still at 0°, was divided into two equal portions which were treated with copper bronze under different conditions.

To one portion was added copper bronze (0.3 g) and the mixture was heated at 65° on the steam bath for 10 min whereupon it showed a negative diazonium test with β-naphthol. The mixture was cooled to 0° and the solids were removed by filtration. Washing these solids with dry methanol removed the organic material, and the methanol solution was treated with dry hydrogen chloride and allowed to stand for 16 hr. Ether was added, and this solution was washed with sodium bicarbonate solution and dried. Removal of the solvent left 0.38 g of crude methyl ester which was purified by chromatography on silica using chloroform as the eluent to yield 0.18 g of benzocyclobutene **2b** (20% yield considering recovered starting material), mp 135–136°. The second half of the original diazonium compound gave an 18% yield of **4b** when the decomposition in the presence of copper bronze was done for 16 hr at 20°.

Decomposition of the Diazonium Salt 11 in the Presence of Ultraviolet Light.—A filtered solution of the diazonium salt was prepared as in the preceeding section from the amino acid **3a** (1.19 g). The filtrate was cooled to 0° in a quartz vessel and stirred while it was irradiated for 6 hr with ultraviolet light from a Nester-Faust source (2537 Å). A white precipitate was removed by filtration and treated with methanol and dry hydrogen chloride to yield 0.22 g of crude methyl ester. Chromatography of this product on silica gel gave 95 mg of the benzocyclobutene **4b** (12%). The above aqueous filtrate was heated at 65° for 10 min, and 67 mg of a precipitate was removed and converted with the crude methyl ester **4b**. Chromatography on silica gel gave an additional 45 mg of **4b** for a total yield of 18%, mp 135–136°. The infrared spectra of each of the samples of this methyl ester obtained in the four runs were identical.

Registry No.—**3a**, 28538-59-2; **4a**, 28538-60-5; **4b**, 28538-61-6; **5**, 28538-62-7; **6**, 28538-63-8; **7a**, 28538-64-9.

Halogenated Ketenes. XVIII. The Stereochemistry of Some Unsymmetrical Arylketene Cycloadditions[1,2]

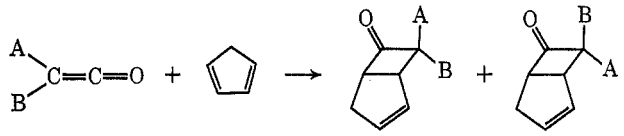
WILLIAM T. BRADY,* FRED H. PARRY, III,[3] AND JAMES D. STOCKTON

Department of Chemistry, North Texas State University, Denton, Texas 76201

Received June 3, 1970

The (2 + 2) cycloadducts of cyclopentadiene and phenylchloro-, phenylbromo-, phenylmethyl-, phenylethyl-, phenoxymethyl-, and phenoxyketenes were prepared in good yield. The cycloadditions were stereoselective to produce only the *endo*-phenyl or *endo*-phenoxy isomer of the cycloadduct with the exception of phenoxymethylketene which yielded only the *endo*-methyl isomer of the cycloadduct. The cycloadducts of phenylmethylketene and ethyl vinyl ether, dihydropyran, cyclohexene, and cyclooctene were also prepared. Two cycloadduct isomers were formed with each of these olefins with only a small predominance of the *endo*- or *cis*-phenyl isomer. These results are interpreted to suggest that cyclopentadiene may be novel as a cycloaddition partner in ketene cycloadditions when a large difference exists between the size of the ketene substituents.

The ($_\pi2_s + _\pi2_a$) cycloaddition of ketenes and olefins is allowed to be a thermally concerted process whereby the ketene participates in an antarafacial role.[4] When the cycloaddition is effected with unequally substituted ketenes with unsymmetrical olefins, such as cyclopentadiene, the (2 + 2) cycloadduct may be a mixture of geometrical isomers. Recently, the stereochemistry of the cycloaddition of some unequally substituted ketenes



with cyclopentadiene has been described and revealed a most gratifying correlation with this principle of the conservation of orbital symmetry.[5–8] The results indicate a strong preference for endo specificity for the larger ketene substituent; *i.e.*, the isomer with the larger ketene substituent in the endo position has been found to be very strongly sterically preferred. In fact, this isomer has even been formed to the exclusion of the exo isomer when a large difference in size exists between the two ketene substituents.

We now wish to describe the stereochemistry of the cycloaddition of some unsymmetrical arylketenes with cyclopentadiene and also the stereochemistry of the cycloaddition of phenylmethylketene with a variety of olefinic compounds. A preliminary report of this work has appeared.[9]

Results

Phenylchloro- and phenylbromoketenes were prepared by the dehydrochlorination of α-chloro- and α-bromophenylacetyl chlorides at room temperature. The ketenes could not be isolated but could be trapped by heating the dehydrohalogenation mixtures with cyclopentadiene to produce the (2 + 2) cycloadducts in good yield. The best yields of cycloadducts are obtained by conducting the dehydrochlorinations at room temperature and then refluxing the reaction mixtures to

(1) Paper XVII: W. T. Brady and L. Smith, *Tetrahedron Lett.*, 2963 (1970).

(2) Abstracted in part from the Ph.D. thesis of F. H. P., North Texas State University, May 1970.

(3) NDEA, Title IV Fellow.

(4) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(5) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, **92**, 4618 (1970).

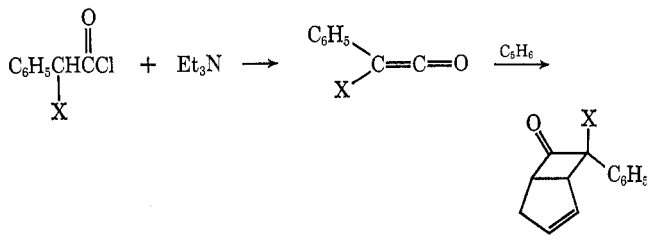
(6) T. DoMinh and O. P. Strausz, *ibid.*, **92**, 1766 (1970).

(7) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chem. Acta*, **53**, 417 (1970).

(8) W. T. Brady, E. F. Hoff, R. Roe, Jr., and F. H. Parry, III, *J. Amer. Chem. Soc.*, **91**, 5679 (1969).

(9) W. T. Brady, F. H. Parry, III, R. Roe, Jr., and E. F. Hoff, *Tetrahedron Lett.*, 819 (1970).

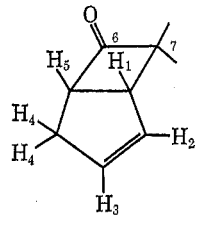
effect cycloaddition. The cleanest preparations are achieved employing acetonitrile as the solvent, al-



I, X = Cl
II, X = Br

though benzene and hexane also give good yields. Numerous attempts to isolate phenylchloroketene resulted in a tarry polymer of the ketene.

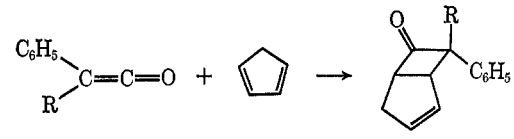
Both the *endo*- and *exo*-phenyl isomers were expected for I and II, since both isomers of the alkylhaloketene–cyclopentadiene cycloadducts are produced.[10] However, distillation and subsequent vpc and nmr analysis indicated that the distillate contained only one isomer, and furthermore this was the *endo*-phenyl isomer. We have previously reported the cross-ring deshielding effect of a halogen in the exo position on C-7 of bicyclo[3.2.0]hept-2-en-6-ones.[5] The assignment of I and II as both being the *endo*-phenyl isomer was made on the basis of the chemical shift of H_5 in I and II, δ 4.35



and 4.36, respectively (see Table I). Further evidence that this assignment is correct is the resonance of the vinyl protons. An *endo*-phenyl substituent in the bicyclo[3.2.0]hept-2-en-6-ones causes a multiplet or pair of multiplets for the vinyl protons which are considerably shielded (δ 5.5) from the vinyl absorption in similar compounds without a phenyl substituent in the endo position (δ 5.8–5.9).

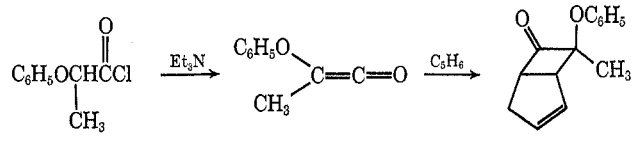
The vinyl region of the nmr spectra was split into two multiplets at δ 5.7 and 5.35 for I and δ 5.78 and 5.41 for II. Decoupling at the frequency of the H_4 resonance collapsed the upfield portion of the vinyl resonance into a doublet, while the downfield portion became a pair of doublets. It seemed apparent that H_2 was responsible for the downfield portion of the total vinyl resonance and that the upfield portion was due to H_3. The coupling constants $J_{H_1-H_2}$ and $J_{H_2-H_3}$ could be seen to be 2.0 and 6.5 Hz, respectively.

In an effort to determine if this stereoselectivity was general for unequally substituted arylketenes, phenylmethyl- and phenylethylketenes were prepared and purified by distillation. The cycloadditions with cyclopentadiene took place very smoothly to give a good yield of only one isomer. The vinyl resonances indicated an *endo*-phenyl isomer. Moreover, the methyl resonance for III was consistent only with an *exo*-methyl group.[11] Furthermore, bromination of III resulted in a methyl resonance shift of only δ 0.02.[10]



III, R = CH_3
IV, R = C_2H_5

To determine the effect on the stereochemistry of moving the phenyl substituent away from the ketene functionality, phenoxymethylketene was prepared and allowed to undergo *in situ* cycloaddition with cyclopentadiene. The cycloaddition was observed to proceed stereoselectivity as evidenced by only one singlet (δ 1.26) for the methyl substituent in the nmr spectrum. The chemical shift of the methyl group indicated an *endo*-methyl, which was further verified by observing a downfield shift of the methyl resonance of δ 0.30 upon bromination of V.[10]



V

Due to this unexpected reversal in the stereochemistry of the phenoxymethylketene cycloaddition, the adduct of phenoxyketene and cyclopentadiene (VI) was produced to aid in elucidating the role of the phenoxy group on the stereochemical outcome of the cycloaddition. The nmr spectrum revealed a pair of doublets for H_7 with coupling constants of $J_{H_1-H_7}$ = 8.0 Hz and $J_{H_5-H_7}$ = 3.0 Hz, which could only be reconciled with a system of all three cis hydrogens on the four-membered ring.[12] The absence of any absorption about δ 0.5 farther upfield further indicated a stereospecific cycloaddition. While the 3.0-Hz cross-ring coupling is probably consistent with either isomer of the cycloadduct, the vicinyl coupling of 8.0 Hz could only be the result of two hydrogens which were very nearly in the same plane.

We have recently examined the cycloaddition of methylchloro- and methylbromoketenes with a variety of olefins and found that not only were two isomers produced but the isomer distributions were nearly independent of the olefin structure.[13] Since all of the reports on the stereochemistry of the cycloaddition of unsymmetrical ketenes, where a large difference exists between the size of the ketene substituents, have been with cyclopentadiene, it seemed desirable to determine if the endo specificity observed was general for all olefins. Consequently, the cycloaddition of phenylmethylketene with several olefins was effected. The cycloadditions were accomplished by the addition of this pure isolable ketene to an excess of olefin and refluxing the resultant solution. The results are shown in Table II. Both *endo*- or *cis*-methyl and *exo*- or *trans*-methyl isomers were produced with all four olefins.

(10) W. T. Brady and B. M. Holifield, *Tetrahedron*, **23**, 4251 (1967).

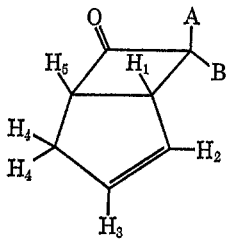
(11) W. T. Brady, R. Roe, Jr., E. F. Hoff, Jr., and F. H. Parry, III, *J. Amer. Chem. Soc.*, **92**, 146 (1970).

(12) (a) I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967); (b) B. Braillon, *J. Mol. Spectrosc.*, **27**, 313 (1968).

(13) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, **93**, 1662 (1971).

TABLE I

NMR SPECTRA OF PHENYLHALO- AND ARYLALKYLKETENE CYCLOADDUCTS OF CYCLOPENTADIENE



Compd	A (exo)	B (endo)	Registry no.	H_1	H_2	H_3	H_4	H_5
I	Cl	C_6H_5		4.05	5.70	5.35	2.55	4.35
II	Br	C_6H_5		4.05	5.78	5.41	2.55	4.36
III	CH_3 (1.61)	C_6H_5		3.49		5.52	2.52	3.93
IV	C_2H_5	C_6H_5		3.50		5.46	2.45	3.86
V	C_6H_5O	CH_3 (1.26)		3.86		5.83	2.53	4.05
VI	H (5.19)[a]	C_6H_5O		3.48		5.76	2.53	3.86
	C_6H_5	C_6H_5	5452-28-8	4.23	5.71	5.45	2.67	3.78
	Cl	Cl	5307-99-3	4.08		5.9	2.68	4.25
	CH_3 (1.28)	CH_3 (0.93)	767-85-1	3.15		5.8	2.70	3.95
	CH_3 (1.77)	Cl	13363-88-7	3.62		5.9	2.65	3.95
	Cl	CH_3 (1.47)	13363-87-6	3.65		5.9	2.64	4.28

[a] $J_{H_1-H_7} = 8.0$; $J_{H_6-H_7} = 3.0$.

TABLE II

CYCLOADDUCTS OF PHENYLMETHYLKETENE

Compd	Olefin	*exo*- or *trans*/*endo* or *cis*-methyl ratio
VII	Ethyl vinyl ether	2.3
VIII	Dihydropyran	1.7
IX	Cyclohexene	2
X	Cyclooctene	1.1

The isomer distributions for the adducts with cyclohexene and cyclooctene were determined by vpc and the ratio of methyl singlets in the nmr spectra. The distinction between isomers was made on the basis of the chemical shift of the methyl singlet.

The isomer distributions for the adducts with ethyl vinyl ether and dihydropyran were established in a similar manner. However, in these cycloadducts the resonance of the methinyl proton adjacent to the ether linkage was also significant. The isomer distributions could be confirmed by the ratio of these triplets in the ethyl vinyl ether adduct and a ratio of the doublets in the dihydropyran cycloadduct.

Discussion

In each of the six arylketene cycloadducts with cyclopentadiene, a stereoselective cycloaddition was observed.[14] In all but one instance, the larger ketene substituent was found to be in the endo position of the cycloadduct. These stereochemical results fit a now well-established pattern,[5-8] and, as expected, the methyl substituent is effectively larger than the phenoxy.[15]

The results obtained from the cycloaddition of phenylmethylketene with ethyl vinyl ether, dihydropyran, cyclohexene, and cyclooctene were totally unexpected. These data reveal that there is very little preference for the *endo*- or *cis*-phenyl isomer. Therefore, the obvious conclusion is that cyclopentadiene appears to be novel as a cycloaddition partner in ketene cycloadditions where a large difference exists between the size of the ketene substituents. Presumably the planarity of the olefin is a determining factor in these cycloadditions. It will indeed be ironic if cyclopentadiene is an anomaly since all of the initial work in this area has been with this olefin.

(14) The cycloadditions were stereoselective to the extent that only one isomer was observed. The limits of detection were <5%.

(15) R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

Experimental Section

Nmr spectra were obtained on a Varian A-60, Varian A-60A, or Varian T-60 nuclear magnetic resonance spectrometer, employing tetramethylsilane as the internal standard at 25°. All solvents were dried and purified by distillation from calcium hydride and subsequently stored over molecular sieves 4A. α-Chloro-α-phenylacetyl chloride was prepared from mandelic acid by the method of Walden.[16] α-Phenylpropionic acid was obtained by the silver oxide oxidation of the commercially available adehyde and converted to α-phenylpropionyl chloride with thionyl chloride.[17] All of the other acid halides were obtained from commercially available acids and thionyl chloride by standard procedures. The preparation of the cycloadduct of phenylchloroketene and cyclopentadiene (I) has been previously described.[18] Phenylethylketene was prepared by the dehydrochlorination of α-phenylbutyryl chloride with triethylamine.[18] Phenylmethylketene was obtained in an analogous manner by the dehydrochlorination of α-phenylpropionyl chloride.

General Method for *in situ* Cycloadditions.—A 0.2-mol portion of triethylamine in 50 ml of dry hexane was added dropwise and with stirring to a solution containing 0.2 mol of the acid halide and 0.9–1.0 mol of fresh cyclopentadiene in 250 ml of hexane at room temperature. After 1 hr of stirring, the reaction mixture was refluxed for 6 hr before filtration of the salt. Concentration of the filtrate and vacuum distillation of the residue afforded the substituted bicyclo[3.2.0]hept-2-en-6-ones. All of the cycloadditions were also run in acetonitrile as the solvent to check the stereochemistry in a more polar solvent. In no case was the stereochemistry effected, but in most cases about a 10% increase in the yield was noted.

***exo*-7-Bromo-*endo*-7-phenylbicyclo[3.2.0]hept-2-en-6-ones (II).**—II was prepared in 53% yield: bp 110° (0.8 mm); ir 1801 (C=O) and 1610 cm^{-1} (C=O).

(16) P. Walden, *Ber.*, **28**, 1287 (1895).

(17) N. Rabjohn, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 919.

(18) W. T. Brady, E. D. Dorsey, and F. H. Parry, III, *J. Org. Chem.*, **34**, 2846 (1969).

Anal. Calcd for $C_{13}H_{11}BrO$: C, 59.4; H, 4.18. Found: C 59.7; H, 4.08.

endo-7-Methyl-*exo*-7-phenoxybicyclo[3.2.0]hept-2-en-6-one (V).—V was prepared in 69% yield: bp 118° (0.2 mm); ir 1776 (C=O) and 1597 cm^{-1} (C=C).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.5; H, 6.54. Found: C, 78.68; H, 6.85.

Bromine was added slowly, cautiously, and dropwise from a small syringe to a 30% solution of V in CCl_4 in an nmr tube. This addition was done intermittently and continued until the nmr spectrum revealed no resonance for the vinyl protons. During the addition, the methyl singlet at δ 1.26 began to decrease in intensity and a new singlet at δ 1.56 began to appear. Eventually, only the new methyl singlet was present.

endo-7-Phenoxybicyclo[3.2.0]hept-2-one (VI).—Concentration of the filtrate and recrystallization from hexane afforded a 65% yield of VI: mp 55–56°; ir 1789 (C=O) and 1597 cm^{-1} (C=C).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 78.00; H, 6.00. Found: C, 78.12; H, 6.06.

Cycloadditions of Phenylmethyl- and Phenylethylketenes with Cyclopentadiene.—A 0.2-mol portion of the ketene in 50 ml of dry hexane was added dropwise to a 0.8-mol portion of fresh cyclopentadiene in 200 ml of hexane. After the addition was complete, the reaction mixture was heated to reflux until the yellow color of the ketene disappeared (6–10 hr). Concentration and recrystallization from ether afforded the pure cycloadducts.

exo-7-Methyl-*endo*-7-phenylbicyclo[3.2.0]hept-2-en-6-one (III).—III was obtained in 85% yield: mp 26–30°; ir 1773 (C=O) and 1603 cm^{-1} (C=C).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.85; H, 7.13. Found: C, 84.9; H, 7.16.

Bromination in an nmr tube of III, as described above, resulted in the disappearance of the vinyl proton resonance but produced no change in the methyl singlet. However, on an expanded portion of the spectrum, the methyl resonance at δ 1.61 could be seen to disappear and a new singlet appear at δ 1.63.

exo-7-Ethyl-*endo*-7-phenylbicyclo[3.2.0]hept-2-en-6-one (IV).—An 83% yield of IV was obtained with mp 43.5–44°; ir 1761 (C=O) and 1592 cm^{-1} (C=O).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.9; H, 7.55. Found: C, 85.2; H, 7.67.

General Procedure for Phenylmethylketene Cycloadditions.—A solution of 0.06 mol of phenylmethylketene in 0.5 mol of olefin was refluxed overnight. The unreacted olefin was removed on a rotoevaporator. The isomer distribution was determined by nmr and vpc after mixing the reactants during the reflux period and after concentration of the reaction solution. The isomer distributions were the same in all three determinations in every instance. The concentrated reaction solution was fractionally distilled under reduced pressure. The yields were based on the total *endo*- and *exo*-methyl isomers.

2-Methyl-2-phenyl-3-ethoxycyclobutanone (VII).—An 82% yield was obtained at 95° (0.6 mm): ir 1780 cm^{-1} (C=O): nmr (CCl_4) (both isomers) δ 0.8 (t, 2.1 H), 1.15 (t, 0.9 H), 1.39 (s, 1 H), 1.4 (s, 2 H), 3.0 (m, 4 H), 3.8 (t, 0.7 H), 4.1 (t, 0.3 H), and 6.95 (m, 5 H).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.5; H, 7.84: Found: C, 76.37; H, 7.79.

8 Methyl-8-phenyl-2-oxabicyclo[4.2.0]octan-7-one (VIII).—A 77% yield was obtained at 110° (at 0.3 mm): ir 1765 cm^{-1} (C=O); nmr (CCl_4) (both isomers) δ 1.5 (m, 7 H), 1.4 and 1.55 (two singlets out of multiplet corresponding to *endo*- and *exo*-methyl isomers respectively; 1.7 *exo*-/*endo*-methyl ratio), 3.4 (m, 3 H), 4.2 (d, 0.6 H), 4.35 (d, 0.4 H), and 7.1 (m, 5 H).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.8; H, 7.42. Found: C, 77.67; H, 7.67.

8-Methyl-8-phenylbicyclo[4.2.0]octan-7-one (IX).—A 43% yield was obtained at 115° (0.3 mm): ir 1780 cm^{-1} (C=O); nmr (CCl_4) (both isomers) δ 1.3 (s, *endo*-methyl, 1 H), 1.6 (s, *exo*-methyl, 2 H), 1.45 (m, 11 H, the two methyl singlets were a part of this multiplet), 2.5 (m, 1 H), 3.55 (m, 1 H), and 7.2 (m, 5 H).

Anal. Calcd for $C_{15}H_{18}O$: C, 83.7; H, 8.84. Found: C, 83.92; H, 8.34.

10-Methyl-10-phenylbicyclo[6.2.0]decan-9-one (X).—A 41% yield was obtained at 120° (0.35 mm): ir 1780 cm^{-1} (C=O); nmr (CCl_4) (both isomers) δ 1.4 (s, *endo*-methyl, 1.4 H), 1.6 (s, *exo*-methyl, 1.6 H), 1.45 (m, 16 H, the two methyl singlets were a part of this multiplet), 3.3 (m, 1 H), and 7.3 (m, 5 H).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.3; H, 9.46. Found: C, 84.1; H, 9.58.

Registry No.—I, 27849-05-4; II, 28291-19-2; III, 27849-04-3; IV, 28538-79-6; V, 28538-80-9; VI, 28538-81-0; VII (ethoxy/methyl-*cis*), 28538-82-1; VII (ethoxy/methyl-*trans*), 28538-89-8; VIII (*endo*-methyl), 28538-83-2; VIII (*exo*-methyl), 28538-90-1; IX (*endo*-methyl), 28607-65-0; IX (*exo*-methyl), 28538-91-2; X (*endo*-methyl), 28538-84-3; X (*exo*-methyl), 28607-67-2.

Acknowledgment.—Support for this investigation by the Robert A. Welch Foundation, the National Science Foundation (GP-14016), and a North Texas State University Faculty Research Grant is gratefully acknowledged.

Reactions of Phosphorus Compounds. XXIV.[1] Preparation and Reactions of Phosphonium Betaines

EDWARD E. SCHWEIZER* AND CHARLES M. KOPAY[2]

Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received October 28, 1970

A number of active methylene species (dibenzoylmethane, ethyl benzoylacetate, benzoylacetone, dimedon, ethyl acetoacetate, acetylacetone, and diethyl malonate) have been phosphonioethylated with vinyltriphenylphosphonium bromide. A correlation was observed between acidity of the active methylene moiety and ease of di- *vs.* monophosphonioethylation. The monophosphonioethylated salts obtained were converted into the corresponding betaines, on treatment with base, and isolated. Methylation of the betaines was accomplished. Fusion of the betaines produced 1,1-disubstituted cyclopropanes and/or 2,3-disubstituted 4,5-dihydrofurans.

In 1964 phosphonioethylation reactions were accomplished for the first time[3,4] by allowing compounds with replaceable protons to react with vinylphosphonium bromides (1).

$$ZH + CH_2{=}CH\overset{+}{P}R_3\ Br^- \longrightarrow ZCH_2CH_2\overset{+}{P}R_3\ Br^-$$
$$\text{1a, R = } n\text{-Bu} \quad \text{b, R = Ph} \qquad \text{2}$$

Although the adducts from acetoacetic ester and diethyl malonate were prepared and isolated as their

(1) Previous paper in this series: E. E. Schweizer and A. T. Wehman, *J. Chem. Soc. C*, in press.

(2) From the Ph.D. Dissertation of C. M. Kopay.

(3) P. T. Keough and M. Grayson, *J. Org. Chem.*, **29**, 631 (1964).

(4) E. E. Schweizer and R. D. Bach, *ibid.*, **29**, 1746 (1964).