The 8.35-g. product fraction had λ_{max}^{EtOH} 227 mμ with ε 11,300 (based on II), indicating that this material was 91% II. However, v.p.c. analysis showed only one peak. A small shoulder at 280 mμ, possibly due to 6-hydroxy-1-tetralone,[1] was the only indication of the possible nature of a contaminant. The 1.95-g. product fraction had λ_{max}^{EtOH} 227 mμ with ε 9600 (based on II) and thus was 77% pure. Therefore, the yield of II, based on these ultraviolet spectra, was 70%.

V.p.c. analysis and an infrared spectrum of the 3.82 g. of material in the first trap indicated that it was essentially pure acetic acid. This trap material gave a 90% yield of piperazonium 1,4-diacetate, m.p. 208–209°,[3] which was identical with a sample prepared from known acetic acid. On the basis of its odor, the 0.23 g. in trap 2 was considered to be acetic acid, making the total yield 4.05 g. (79%).

In another pyrolysis experiment, the effluent vapors were collected over mercury and analyzed on a 5A Molecular Sieve column at 100°.[11] Carbon monoxide was found as the only gas present (other than oxygen and nitrogen) by comparison of its retention time to that of a known sample.

When the glass packing of the pyrolysis column was evenly interspersed with a total of 1 g. of 6–14-mesh activated charcoal and the pyrolysis of I was conducted under the same general conditions described above, there was obtained only 25% of II (by ultraviolet spectral analysis of a yellow distillate equivalent in weight to 41% of II). The material in both traps 1 and 2 had the characteristic odor of methyl vinyl ketone (as well as that of acetic acid). Decomposition of the material in the pyrolysis flask to a dark tar was more rapid when the carbon was present.

2-(3-Oxobutyl)cyclopentanone (III).—To 1.795 g. (7.48×10^{-3} mole) of II in 35 ml. of ethyl acetate was added 0.6 g. of 10% palladium on carbon and the mixture was hydrogenated at atmospheric pressure and room temperature for 30 min. The mixture was filtered and the filtrate was evaporated to give 1.803 g. of an oil which had λ_{max} 5.75 and 5.84 μ and showed one sharp peak upon v.p.c. analysis. This oil afforded a bissemicarbazone derivative which melted at 228–229° (lit.[4] m.p. 229°).

5,6,7,8-Tetrahydroindanone-5 (IV).—A mixture of 1.00 g. (6.5×10^{-3} mole) of hydrogenation product III and 0.6 ml. (7×10^{-3} mole) of pyrrolidine in 50 ml. of benzene was refluxed for 8 hr. A solution of 1.6 ml. of acetic acid, 1.6 ml. of water, and 0.9 g. of sodium acetate was then added and heating was continued for an additional 4 hr. Separation of the layers, extraction of the aqueous layer with benzene, and washing the combined extracts with 3 *M* hydrochloric acid and then saturated sodium bicarbonate solution gave, after removal of the benzene, a dark oil which was clarified by quick chromatography on acid-washed alumina to afford 0.63 g. (71%) of oil which had an infrared spectrum identical with that of a known sample of IV.[5] The material prepared from II *via* III had λ_{max}^{EtOH} 236 mμ (ε 13,400), lit.[5] λ_{max}^{EtOH} 233 mμ (ε 12,700), and formed a 2,4-dinitrophenylhydrazone, m.p. 197–198° (from methanol–chloroform), and a semicarbazone, m.p. 230–231° (from 1-butanol). The authentic sample of IV formed a 2,4-dinitrophenyhydrazone, m.p. 197–199°, and a semicarbazone, m.p. 230–231° (lit.[4] m.p. 214–219°). The respective mixture melting points were undepressed.

Treatment of II with either pyrrolidine and acetic acid in refluxing benzene or with a solution of sodium hydroxide in methanol yielded products which gave no spectral indication of containing any phenolic material, such as VI. These products were not characterized further, but a strong ultraviolet absorption maximum at 343 mμ in the product from the pyrrolidine–acetic acid treatment can tentatively be ascribed to the conjugated pyrrolidine enamine derived from the α,β,γ,δ-unsaturated ketone which would be formed by aldol cyclization–dehydration of II.

Acknowledgment.—This investigation was supported in part by Public Health Service Research Grant AM-05014. S. W. B. was a National Science Foundation Undergraduate Research Participant, 1963–1964. The authors are grateful to Professor K. L. Williamson for determining and discussing the n.m.r. spectrum.

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[11] G. Kyryacos and C. E. Boord, *Anal. Chem.*, **29**, 787 (1957).

Steric Requirements at Phosphorus in the Wittig Reaction

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The stereospecificity of the Wittig reaction of stable or quasi-stable ylids has been explained in terms of preferential formation and decomposition of the betaine from which the *trans* olefin is derived.[1] It has been reported[2] that tricyclohexylphosphoranes, in their reaction with aldehydes, yield the *trans* olefins as exclusive products and that carbethoxymethylenetributylphosphorane gives 95% of *trans*-ethyl cinnamate in its reaction with benzaldehyde.[1] The limited amount of data available suggests that trialkylphosphoranes react with aldehydes in a more stereospecific manner than do their triarylphosphorane counterparts and this phenomenon has been explained by the ability of the alkyl groups (which are more electron donating than phenyl) to retard decomposition of the betaine to olefin and phosphine oxide.[1,2]

In connection with some other work, the Wittig reaction of a series of ylids of type I, in which the size of the groups bound to phosphorus was varied systematically, has been studied.

$$R_3P{=}CHCO_2C_2H_5$$

I

The aim of this work was to determine if an increase in the size of the groups around phosphorus would affect the *cis–trans* ratio of ethyl cinnamates derived from the reactions of I with benzaldehyde, reasoning that as the steric requirements of the alkyl groups became greater, they could conceivably outweigh the preferential formation and decomposition of the *trans*-betaine thereby resulting in a loss of stereospecificity.

Since the trialkylphosphoranes, in most cases, are nonisolable, the ylids were prepared and used *in situ* from the corresponding phosphonium salts. As the long-chain alkyl phosphonium bromides were oils, the tetraphenylborates were utilized in order to obtain crystalline derivatives. These were treated with sodium ethoxide in ethanol under nitrogen with subsequent addition of benzaldehyde.

The olefin ratio was determined by g.l.p.c. and Table I contains the product ratio data obtained from several of these ylids. In the two cases in which the phosponium bromides were solids (*n*-butyl and cyclohexyl), the product ratio data were compared with those obtained from the tetraphenylborates. In addition, effect of reaction temperature upon product ratios was studied in two cases and the product ratios obtained from two triarylphosphoranes were determined.

As is obvious from the data in Table I, none of the factors studied significantly alters the stereochemical outcome of the Wittig reaction of the ylids considered. With the exception of the trioctylphosphorane, the

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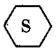
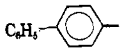
[1] (a) A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 1888 (1963); (b) A. J. Speziale and D. E. Bissing, *ibid.*, **85**, 3878 (1963).

[2] H. J. Bestmann and O. Kratzer, *Ber.*, **95**, 1894 (1962).

TABLE I

$R_3P^+—CH_2CO_2C_2H_5X^- + C_6H_5CHO$ ($NaOC_2H_5$, C_2H_5OH)

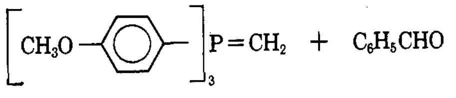
R	X	Temp., °C.	—Olefin, mole %— cis	trans
n-C_4H_9	$B(C_6H_5)_4$	25	4.0	96.0
n-C_4H_9	Br	25	4.6	95.4
n-C_4H_9	Br	78	5.0	95.0
	Br	25	0.6	99.4
	$B(C_6H_5)_4$	25	0	100
n-C_6H_{13}	$B(C_6H_5)_4$	25	1.9	98.1
n-C_8H_{17}	$B(C_6H_5)_4$	25	19.5	80.5
n-C_8H_{17}	$B(C_6H_4)_4$	78	22.3	77.7
n-$C_{10}H_{21}$	$B(C_6H_5)_4$	25	4.0	96.0
CH_3O	$B(C_6H_5)_4$	25	16.0	84.0
	Br	25	15.0	85.0
C_6H_5	Br	25	15.0	85.0

cis–trans ratio remains surprisingly constant and it must be concluded that the increased size of the alkyl groups has little effect upon the stereospecificity of the reaction. If we consider the straight-chain alkyl derivatives, stereospecificity actually increases from butyl to hexyl then decreases for octyl and increases once more for the tridecylphosphorane. The tricyclohexylphosphorane yields the lowest *cis–trans* ratio, no *cis* olefin being detected with the ylid derived from the tetraphenylborate.

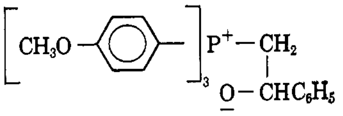
The nature of the anion also has little effect upon the stereospecificity of the Wittig reaction. It has been reported[3] that the *cis–trans* olefin ratio may be increased for unstable ylids by the addition of Lewis bases such as Br^-, I^-, or amines. If the presence of a single equivalent of bromide ion can cause an increase in the *cis–trans* olefin ratio, it might be expected that the ylids derived from the phosphonium tetraphenylborates would react in a more stereospecific manner than those derived from the bromide since it is unlikely that the tetraphenylboron anion could be an effective Lewis base. However, only very minor stereochemical differences were observed for the ylids derived from the two phosphonium salts. It was also observed[3] that stereochemical outcome of the Wittig reaction of stable ylids shows little or no dependence upon the presence of added bases and, while the ylids dealt with in the present study are nonisolable, they must be classified as quasi-stable[4] rather than unstable.

The stereochemistry of the Wittig reaction of these quasi-stable ylids are also surprisingly temperature insensitive. An increase in temperature should cause a decrease in stereospecificity; however, in the two cases studied (n-butyl and n-octyl), one showed a negligible temperature effect while the other showed a measurable, though minor, decrease in stereospecificity with increasing temperature.

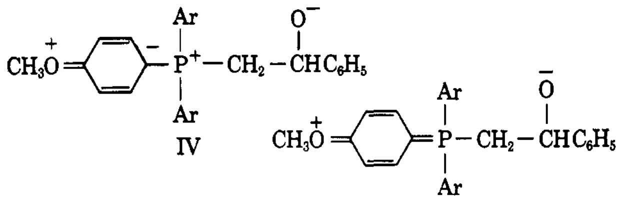
Wittig[5] found that methylenetris-p-anisylphosphorane (II) is very sluggish in its reaction with benzaldehyde, tending to stop at the intermediate betaine (III) which could be protonated and isolated in good yield. This observation was explained by Wittig in terms of the ability of the electron-donating anisyl group to reduce the effective positive charge at phosphorus thereby retarding betaine decomposition. It has been suggested, however,[6] that there are no direct resonance interactions between the π-orbitals of the benzene ring and the d-orbitals of phosphorus. If this is true, any interaction between phosphorus and substituents on the benzene ring must be inductive. Consequently, the electron-withdrawing inductive characteristics of the methoxy group would be expected to destabilize the positive charge at phosphorus, thereby increasing the rate of betaine decomposition. Since this is not observed experimentally, structures such as IV, if not V, must contribute significantly to the structure of the intermediate.



II



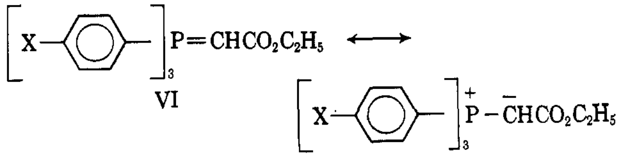
III



IV

V

Since the trialkylids react in a more stereospecific manner than do the triphenylids, it might be expected that electron-donating substituents on the benzene ring would increase the stereospecificity of the Wittig reaction of triarylylids. Although no general conclusions can be drawn from the last two entries in Table I, it appears that such substitution on the benzene ring does not significantly affect the stereochemical course of the Wittig reaction of stable ylids. The rate of betaine formation as well as that of betaine decomposition would be affected by electron density of the ring. By analogy with the work of Wittig,[4] electron-donating substituents in the ylid should enhance its nucleophilicity (thereby decreasing stereospecificity) because of increased contribution of structures such as VII. Similar substitution would decrease the rate of betaine decomposition (thereby increasing stereospecificity).



VI

VII

It has been shown[1] that both steps are important in determining the stereochemical ratio of olefin in the Wittig reaction, and it appears that in the case of meth-

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[3] L. D. Bergelsen and M. M. Shemyakir, *Tetrahedron*, **19**, 149 (1963).

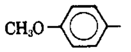
[4] The ylids with which we are concerned, though containing a group through which the negative charge at carbon may be delocalized, are nonisolable; hence they are termed "quasi-stable."

[5] G. Wittig, H. Weizmann, and M. Schlosser, *Ber.*, **92**, 676 (1961).

[6] (a) H. H. Jaffé, *J. Phys. Chem.*, **58**, 185 (1954); (b) H. H. Jaffé, *J. Chem. Phys.*, **44**, 1430 (1954); (c) C. N. R. Rao, J. Ramachandran, M. S. C. Iah, S. Somasekharo, and T. V. Rajakumar, *Nature*, **183**, 1475 (1959).

TABLE II

$R_3P^+{-}CH_2CO_2C_2H_5X^-$

R	X	M.p., °C.	Calcd., % C	Calcd., % H	Calcd., % B	Calcd., % Br	Calcd., % P	Found, % C	Found, % H	Found, % B	Found, % Br	Found, % P	Crystn. solvents
n-C_4H_9	Br	99–100	52.00	9.28	..	21.63	8.39	52.01	9.35	..	22.00	8.40	Methylene chloride–ether
n-C_4H_9	$B(C_6H_5)_4$	190–191	79.00	8.95	1.77	...	5.09	78.76	9.33	2.08	...	5.11	Methylene chloride–hexane
	Br	148–150	59.10	9.02	...	17.85	6.92	58.87	8.92	...	17.97	6.81	Methylene chloride–ether
	$B(C_6H_5)_4$	193–194	80.50	8.82	1.58	...	4.51	80.27	8.72	1.59	...	4.45	Ethanol
n-C_6H_{13}	$B(C_6H_5)_4$	124–125	79.80	9.61	1.56	...	4.41	80.05	9.71	1.84	...	4.40	Methylene chloride–hexane
n-C_8H_{17}	$B(C_6H_5)_4$	79–81	80.42	10.12	1.39	...	3.98	80.91	10.31	1.44	...	4.00	Methylene chloride–hexane
n-$C_{10}H_{21}$	$B(C_6H_5)_4$	72–73	81.00	10.53	1.26	...	3.51	81.46	10.35	1.23	...	3.64	Methylene chloride–hexane
	$B(C_6H_5)_4$	148–149	77.65	6.38	1.42	...	4.08	77.68	6.48	1.60	...	4.09	Methylene chloride–hexane

oxy substitution the two effects cancel one another for little change in *cis–trans* olefin ratio is observed.

Experimental[7]

Phosphines.—Triphenylphosphine was purchased from M and T Chemicals and recrystallized from hexane. Tributylphosphine was purchased from K and K Laboratories, Inc., and distilled prior to use. Tricyclohexylphosphine was prepared according to the procedure of Issleib.[8] Trihexylphosphine and trioctylphosphine were prepared as described by Jackson.[9] Tridecylphosphine was prepared from n-decylmagnesium bromide and phosphorus trichloride, and the crude phosphine was used for preparation of the phosphonium salt. Tris-p-anisylphosphine was synthesized as described by Mann and Chapplin.[10]

Phosphonium Salts.—The phosphonium salts were prepared by heating a benzene solution of equivalent amounts of the phosphine and ethyl bromoacetate overnight at reflux. In most cases the phosphonium bromides resisted all attempts at crystallization. The tetraphenylborates are solids and were prepared by dissolving the oily phosphonium bromides in ethanol and adding an equivalent amount of sodium tetraphenylborate in ethanol. The tetraphenylborates, insoluble in cold ethanol, were collected by filtration and recrystallized. The physical constants and analyses data are presented in Table II.

Wittig Reactions.—All experiments were performed in the same manner. The phosphonium salt (0.0045 mole) was suspended (dissolved) in 20 ml. of anhydrous ethanol under nitrogen. The bromides were soluble while the tetraphenylborates were insoluble at room temperature. Five milliliters of 0.895 M sodium ethoxide was added, whereupon the solution became homogeneous. Benzaldehyde (0.0045 mole) in 5 ml. of anhydrous ethanol was then added, and the solution was stirred under nitrogen for 16 hr. The solvent was then removed *in vacuo*, and the residue was digested with a small amount of hexane (in which the olefins are soluble) and filtered. The hexane solution was then analyzed by g.l.p.c. using a 6-ft. column of silicone rubber SE-30 on 60-80 Diatoport S and an external standard.

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[7] Melting points are uncorrected.

[8] V. K. Issleib and A. Brock, *Z. anorg. allgem. Chem.*, **277**, 258 (1954).

[9] I. K. Jackson, W. C. Davies, and W. J. Jones, *J. Chem. Soc.*, 2109 (1931).

[10] F. G. Mann and E. J. Chapplin, *ibid.*, 527 (1937).

The Stereospecificity of Amine Additions to Acetylenic Esters

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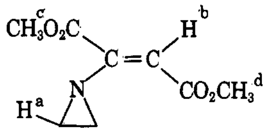
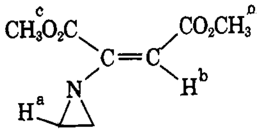
Nucleophilic addition to triple bonds has been studied from a variety of synthetic viewpoints.[1-3] The stereochemistry of additions of thiolic nucleophiles has been carefully studied by Truce who has evolved a "Rule of *trans*-Nucleophilic Addition" in such cases.[4] However, it has been previously suggested by some that the reaction of amines with acetylenic materials may involve cisoid additions[2,5] while others have favored transoid mechanisms.[3] We have been able to establish that indeed *both* types of additions are possible depending upon the nature of the solvent.

In conjunction with certain synthetic efforts we studied the reaction of aziridine with dimethyl acetylenedicarboxylate and with ethyl propiolate. Reaction of equimolar ratios of aziridine and dimethyl acetylenedicarboxylate in methanol at room temperature provides a 76% yield of a semisolid, b.p. 80–85° (0.20 mm.). Analysis of the product mixture was expedited by examination of the p.m.r. spectrum which revealed that the *trans* ester I comprised 67% of the product and the *cis* ester II, 33%.



I



II

However the reaction course in dimethyl sulfoxide under the same conditions proved to be dramatically different. The reaction product obtained in this solvent consisted of 95% *cis* ester II and only 5% of the *trans* ester I; the product mixture was obtained in 75% yield.

The pure fumarate ester I was a solid, white needles from hexane–benzene, m.p. 67–70°; the pure maleate ester II was a mobile liquid, b.p. 80–82° (0.20 mm.). We have established that neither of the esters in question isomerize to the other under the conditions of the respective reactions.

The difference in physical properties parallels the classic differences of maleates and fumarates. How-

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[1] A. W. Johnson, "Chemistry of the Acetylenic Compounds," Vol. II, Longmans, Green and Co., New York, N. Y., 1950, pp. 199–266; W. E. Truce and R. B. Kruse, *J. Am. Chem. Soc.*, **81**, 5372 (1959); E. I. Grinblat and I. Y. Postovsky, *Dokl. Akad. Nauk SSSR*, **133**, 847 (1960); H. J. Backer and A. E. Beute, *Rec. trav. chim.*, **54**, 200, 523 (1936); S. Ruhemann and A. V. Cunnington, *J. Chem. Soc.*, **75**, 954 (1899); J. B. Hendrickson, *J. Am. Chem. Soc.*, **82**, 653 (1962); G. Stork and M. Tomasz, *ibid.*, **86**, 471 (1964).

[2] E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1423 (1949).

[3] J. B. Hendrickson, R. Rees, and J. F. Templeton, *J. Am. Chem. Soc.*, **86**, 107 (1964).

[4] W. E. Truce, H. G. Klein, and R. B. Kruse, *ibid.*, **83**, 4636 (1961), and previous papers.

[5] W. E. Truce and B. F. Heine, *ibid.*, **79**, 5311 (1957), footnote 2.