The Wittig Synthesis. I. Use of Certain Aliphatic Aldehydes As Intermediates in the Synthesis of Olefins[1]

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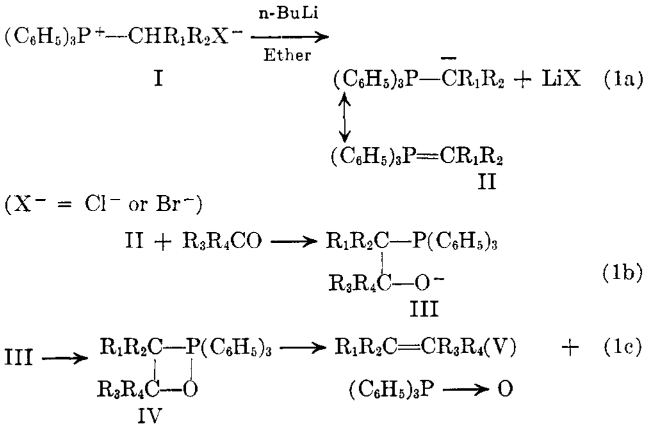
The Wittig method of olefin synthesis has been extended to include aliphatic aldehydes as the carbonyl function. Both gaseous and paraformaldehyde, acetaldehyde, propionaldehyde, *n*- and isobutyraldehyde, *n*-hexaldehyde, 4-pentenal, acrolein, and methacrolein have been utilized for preparation of a number of olefins containing ethylene, butadienyl and isoprenyl linkages. It is shown that these reactions tend to be quite rapid and may be carried out under very mild thermal conditions by use of aqueous quenching solutions. The *cis* isomer predominated in the preparation of both 2-octene and 4-octene. Qualitative evidence has been obtained for a halogen anion effect upon the rate of condensation of formaldehyde with benzylidenetriphenylphosphorane (II. R_1 = H; R_2 = —C_6H_5). Two diterminal olefins have been prepared by condensation of the appropriate biphosphoranes with formaldehyde.

Although more than one hundred and fifty articles[2] relating to olefin synthesis *via* the "Wittig" reaction (equation 1) have appeared in the literature since the initial paper by Wittig and Schöllkopf[3] in 1954, the synthesis of olefins by this method employing simple aliphatic aldehydes and more reactive aldehydes such as acrolein has remained essentially untouched. Bohlmann and Mannhardt[4] reported less than 1% yield of the polyene derived from reaction of acrolein with the ylide produced from 2,8-decadiene-4,6-diyneyltriphenylphosphonium bromide. During the course of this work, Trippett and Walker[5] reported on the reaction of pure phosphobetaines, $(C_6H_5)_3P{=}CHR$, in which R = $CONH_2$ or —CHO, with *n*-heptaldehyde and 2,7-dimethyl-2,6-octadiene-4-ynedial, an α,β-unsaturated dialdehyde. However, these phosphobetaines, isolated as pure crystalline compounds, are stable to hydroxylic solvents at room temperature, indicating their weakly basic character. Such weakly basic compounds would not be expected to catalyze aldol-type condensations as a competing reaction in the case of such aldehydes, as appears to be the case with the more strongly basic phosphoranes.



$$\underset{\text{I}}{(C_6H_5)_3P^+{-}CHR_1R_2X^-} \xrightarrow[\text{Ether}]{\text{n-BuLi}} (C_6H_5)_3P{-}\overset{-}{C}R_1R_2 + LiX \quad (1a)$$
$$\updownarrow$$
$$\underset{\text{II}}{(C_6H_5)_3P{=}CR_1R_2}$$

$(X^- = Cl^- \text{ or } Br^-)$

$$\text{II} + R_3R_4CO \longrightarrow \underset{\text{III}}{\begin{matrix} R_1R_2C{-}P(C_6H_5)_3 \\ | \\ R_3R_4C{-}O^- \end{matrix}} \quad (1b)$$

$$\text{III} \longrightarrow \underset{\text{IV}}{\begin{matrix} R_1R_2C{-}P(C_6H_5)_3 \\ |\quad\quad| \\ R_3R_4C{-}O \end{matrix}} \longrightarrow \begin{matrix} R_1R_2C{=}CR_3R_4(V) & + \\ (C_6H_5)_3P \longrightarrow O & \end{matrix} \quad (1c)$$

The Wittig reaction has also seen extensive use in the preparation of compounds possessing exocyclic methylene groups *via* condensation of methylidenetriphenylphosphorane (II. $R_1 = R_2$ = H) with carbonyl-containing compounds. However, no investigation has yet been conducted with regard to the syntheses of this type of olefin by the converse of the above reaction sequence; that is, by condensation of various phosphoranes (II. R_1 and R_2 = H, aliphatic or aromatic) with formaldehyde as the carbonyl-containing species. Organic halides are, on occasion, more readily accessible than are the corresponding carbonyl derivatives. Therefore, facile substitution of a methylene group at the position of the halogen atom in such halides would enhance the versatility of the Wittig method as a synthetic tool.

It is not readily apparent whether this absence of literature reports on use of such carbonyl compounds as intermediates in the Wittig synthesis is due to failure of these compounds to function normally, or to the fact that such experiments have not been carried out. Efforts in these laboratories to utilize such reactive aldehydes employing the normal conditions failed.

Procedures involving long reflux periods (24 hours) in ethylene glycol dimethyl ether and in ether were unsuccessful when the reactants were (1) the ylide from 5-hexenyltriphenylphosphonium bromide and acrolein and (2) the ylide from allyltriphenylphosphonium bromide and 5-hexenal. Similar experiments using the ylide from allyltriphenylphosphonium bromide and *n*-butyraldehyde were also unsuccessful.

This was tentatively attributed to the pronounced tendency for aldehydes containing one or more alpha-hydrogen atoms to undergo aldol and related reactions in the presence of strong bases such as butyl lithium, which was used in excess to generate the phosphorus ylide, or even the ylide itself. It is also known that α,β-unsaturated aldehydes, such as acrolein, are subject to extensive polymerization in presence of such strong bases. These facts could account for the essential absence of reported use of these compounds in this synthesis. The possibilities that formation of the reactive complex (III) constitutes a very rapid step, and that immediate quenching, resulting in collapse of this intermediate to the olefin and triphenylphosphine

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[1] (a) This work was supported by the National Science Foundation, grant no. NSF-G-10011, by the Petroleum Research Fund, American Chemical Society (PRF grant 470-A), and by the Aeronautical Systems Division, U.S. Air Force, under contract no. AF 33(616)-6887; (b) C. F. Hauser and G. B. Butler, Abstracts of Combined Southwest-Southeast Regional Meeting, New Orleans, La., December 7–9, 1961, p. 46. C. F. Hauser, M. L. Miles, and G. B. Butler, Abstracts of Papers, Division of Organic Chemistry, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–14, 1962, p. 59Q.

[2] J. Levisalles, *Bull. soc. chim. France*, 1021 (1958); (b) U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959); (c) R. C. Slagel, Illinois Seminar, November 17, 1960, pp. 92–101; (d) S. Trippett, "Advances in Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1960, pp. 83–102.

[3] G. Wittig and U. Schollkopf, *Ber.*, **87**, 1318 (1954).

[4] F. Bohlmann and H. J. Mannhardt, *ibid.*, **88**, 1330 (1955).

[5] S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1266, 2130 (1961).

TABLE I[a]

OLEFINS SYNTHESIZED FROM SIMPLE ALIPHATIC ALDEHYDES, ACROLEIN AND METHACROLEIN

Reaction no.	Olefin	Phosphorane (II)	Aldehyde	Yield, %	B.p.
1	$CH_3CH=CH(CH_2)_4CH_3$	$R_1 = H; R_2 = -(CH_2)_4CH_3$	CH_3CHO	69	124–125°
2	$CH_3(CH_2)_2CH=CH(CH_2)_2CH_3$	$R_1 = H; R_2 = (CH_2)_2CH_3$	$CH_3(CH_2)_2CHO$	82	121–122°
3	$CH_3CH(CH_3)CH=CH(CH_2)_2CH_3$	$R_1 = H; R_2 = (CH_2)_2CH_3$	$CH_3CH(CH_3)CHO$	67	110–111°
4	$CH_3CH_2C(CH_3)=CH(CH_2)_2CH_3$	$R_1 = CH_3; R_2 = -CH_2CH_3$	$CH_3(CH_2)_2CHO$	68	120–121°
5	$C_6H_5CH=CHCH_2CH_3$	$R_1 = H; R_2 = -C_6H_5$	CH_3CH_2CHO	78	92–93°/23 mm.
6[b]	$CH_2=CH-CH=CH(CH_2)_2CH_3$	$R_1 = H; R_2 = -CH=CH_2$	$CH_3(CH_2)_2CHO$	28 (52)	99–100°
7a	$CH_2=CH-CH=CH(CH_2)_4CH_3$	$R_1 = H; R_2 = -(CH_2)_4CH_3$	$CH_2=CHCHO$	34	70–71°/44 mm.
7b		$R_1 = H; R_2 = -CH=CH_2$	$CH_3(CH_2)_4CHO$	30	70–71°/44 mm.
8a	$CH_2=C(CH_3)-CH=CH(CH_2)_4CH_3$	$R_1 = H\ R_2 = -(CH_2)_4CH_3$	$CH_2=C(CH_3)CHO$	38	74–77°/25 mm.
8b		$R_1 = H; R_2 = -C(CH_3)=CH_2$	$CH_3(CH_2)_4CHO$	14	74–77°/25 mm.
9a	$CH_2=CH-CH=CH-(CH_2)_2-CH=CH_2$	$R_1 = H; R_2 = -(CH_2)_2CH=CH_2$	$CH_2=CHCHO$	24	124–125°
9b		$R_1 = H; R_2 = -CH=CH_2$	$CH_2=CH-(CH_2)_3CHO$	12	124–125°
10	$CH_2=CH-CH=CH-(CH_2)_3-CH=CH_2$	$R_1 = H; R_2 = -(CH_2)_3CH=CH_2$	$CH_2=CHCHO$	17	68–69°/43 mm.
11[c]	$CH_2=CH-CH=CHCH_2CH=CH-CH=CH_2$	$(C_6H_5)_3P=CHCH_2CH=P(C_6H_5)_3$	$CH_2=CHCHO$	6 (12)	52°/20 mm.
12[c]	$CH_2=CH-CH=CH(CH_2)_3CH=CH-CH=CH_2$	$(C_6H_5)_3P=CH(CH_2)_3CH=P(C_6H_5)_3$	$CH_2=CH-CHO$	6 (12)	71–73°/2 mm.

[a] Boiling ranges uncorrected. [b] Phosphorane derived from the allylphosphonium bromide afforded olefin in 28% yield; phosphorane derived from phosphonium chloride afforded olefin in 52% yield. [c] Tetraene isolated in 6% yield with diethyl ether solvent; 12% yield with diglyme as solvent.

TABLE II[a]

OLEFINS SYNTHESIZED FROM GASEOUS FORMALDEHYDE OR PARAFORMALDEHYDE

Reaction no.	Olefin (IV)	Phosphorane (II)	Aldehyde	Yield, %	B.p.
1	$CH_2=CH(CH_2)_4CH_3$	$R_1 = H; R_2 = -(CH_2)_4CH_3$	CH_2O	47	93–94°
2	$CH_2=CH(CH_2)_5CH_3$	$R_1 = H; R_2 = -(CH_2)_5CH_3$	$(CH_2O)_n$	42	121–122°
3a	$C_6H_5CH=CH_2$[a]	$R_1 = H; R_2 = -C_6H_5$	CH_2O	64	52–53°/27 mm.
3b	$C_6H_5CH=CH_2$[b]	$R_1 = H; R_2 = -C_6H_5$	$(CH_2O)_n$	65	52–53°/27 mm.
3c	$C_6H_5CH=CH_2$[c]	$R_1 = H; R_2 = -C_6H_5$	$(CH_2O)_n$	75	52–53°/27 mm.
4	$CH_2=C(CH_3)(CH_2)_5CH_3$	$R_1 = CH_3; R_2 = -(CH_2)_5CH_3$	$(CH_2O)_n$	52	142–143°

[a] Boiling ranges are uncorrected; yields based upon gas-liquid chromatography analysis of distillation fractions over a somewhat wider range than recorded. [b] Phosphorane prepared from benzyltriphenylphosphonium bromide. [c] Phosphorane prepared from benzyltriphenylphosphonium chloride.

oxide, could overcome the difficulty postulated above, lead to the work reported here. Following this approach, it has been found that this method of olefin synthesis can readily be extended to include aldehyde types such as formaldehyde, either gaseous or paraformaldehyde, *n*-butyraldehyde, acrolein and methacrolein for the preparation of a large number of olefins containing ethylene, butadienyl, and isoprenyl linkages. Moreover, these olefins may be prepared under considerably milder reaction conditions than those normally employed in Wittig syntheses.

A number of mono- and polyolefins have been prepared by use of these types of aldehydes, the results of which are presented in Table I. The olefins possessing only one double bond were generally isolated in good yields, ranging from a high of 82% of theoretical for 4-octene (2) to a low of 67% for 2-methyl-3-heptene (3). In contrast, however, the yields of polyenes were somewhat lower, varying from a low of 6% of theoretical for 1,3,6,8-nonatetraene and 1,3,9,11-dodecatetraene (11 and 12, respectively) to a high of 52% for 1,3-heptadiene (6). These yields, although somewhat less than may be desired, are nevertheless quite satisfactory in consideration that the majority of these polyenes are at best only difficultly accessible by other means. Indeed, it is entirely possible that the mild thermal conditions employed for the olefins shown in Table I allowed the isolation of the two tetraenes (11 and 12, respectively).

Two supplements to the data presented in Table I should be mentioned. First, the yield of 1,3-heptadiene appeared to be directly dependent upon the kind of halide ion (chloride *vs.* bromide) associated with the phosphonium halide salt from which allylidenetriphenylphosphorane (II. $R_1 = H$, $R_2 = -CH=CH_2$) was derived (6). In particular, the phosphorane derived from allyltriphenylphosphonium chloride afforded the diene in 52% yield, whereas only a 28% yield was obtained when the phosphorane was derived from allyltriphenylphosphonium bromide. Second, the reported yields of olefins were obtained *via* condensation of two equivalents of aldehyde with one equivalent of phosphorane. Better yields seem to have resulted from a 2:1 ratio of aldehyde to phosphorane than were obtained from a 1:1 ratio.

Four olefins possessing a single terminal methylene group have subsequently been prepared from readily accessible organic halides and formaldehyde. The results of these preparations are presented in Table II. Reasonably good yields of olefin products were obtained, ranging from a high of 75% of theoretical for styrene, (3c) to a low of 42% for 1-octene (2). The use of paraformaldehyde, *vs.* gaseous formaldehyde, appeared to have little adverse effect upon the yields of olefins but offered the advantage of a more simplified experimental procedure.

Some very interesting observations have arisen from the above work. Of particular interest was the observation that the kind of halogen anion (chloride or bromide) present in the benzyltriphenylphosphonium compounds (I. $R_1 = H$, $R_2 = —C_6H_5$) from which benzylidenetriphenylphosphorane (II. $R_1 = H$, $R_2 = —C_6H_5$) was derived appeared to play a significant role in the rate with which II ($R_1 = H$, $R_2 = —C_6H_5$) reacted with formaldehyde. Indeed, a qualitative study (Table III) of the rates with which paraformaldehyde decolorized ethereal suspensions of the phosphorane derived from benzyltriphenylphosphonium chloride (A) *vs.* those derived from benzyltriphenylphosphonium bromide (B) revealed (A) to be an order of magnitude faster than (B). At a concentration of phosphorane of 0.17 *M* and a temperature of 34°, the average time required for decolorization of (A) was found to be thirty minutes, whereas the average time required for decolorization of (B) was three hundred and thirty minutes. These two reaction series, which were conducted under similar conditions, apparently differed from one another only in the type of halogen anion (chloride *vs.* bromide) associated with each of the subject benzyltriphenylphosphonium salts. It would seem, therefore, that some sort of halogen anion effect is operative in these cases.

TABLE III[a]

QUALITATIVE RATE STUDIES OF BETAINE FORMATION AS A FUNCTION OF THE PHOSPHORANES DERIVED FROM BENZYLTRIPHENYLPHOSPHONIUM CHLORIDE *vs.* BROMIDE

Reaction no.	Phosphonium halide	Decolorization time, min.	Styrene yield, %[b]
1	Bromide	390	78
2	Bromide	270	82
3	Bromide	330	75
4	Chloride	27	79
5	Chloride	32	82
6	Chloride	28	80

[a] All reactions conducted at 34°; phosphorane concentration of 0.17 *M* (0.02 mole in a total of 100 ml. of anhydrous ether and 18 ml. of anhydrous hexane). [b] Styrene yields determined by gas–liquid chromatography analysis.

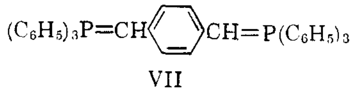
Another interesting observation arising from the work presented in Table II is the difference in rates of decolorization by formaldehyde, either gaseous or paraformaldehyde, of ethereal suspensions of the two *n*-alkylidinetriphenylphosphoranes *vs.* the rate of decolorization of ethereal suspensions of benzylidenetriphenylphosphorane. Paraformaldehyde appeared to decolorize suspensions of benzylidenetriphenylphosphorane (3b) several times more rapidly than it decolorized suspensions of *n*-heptylidenetriphenylphosphorane (2). Moreover, suspensions of the former phosphorane seemed to have been decolorized several times more rapidly by gaseous formaldehyde (3a) than those of *n*-hexylidenetriphenylphosphorane (1).

It may have been expected that the powerful carbanions of the *n*-alkylidenephosphoranes would have reacted more rapidly with formaldehyde to form betaine structures than would have the relatively weak carbanion of the benzylidenephosphorane. The observed order of reaction, contrary to this expectation, may have arisen by way of greater resonance stability offered by the benzal moiety during the bentaine formation step than could be offered by the alkyl moieties.

Attention, thus far, has been given only to the addition of a single formaldehyde moiety to certain monophosphoranes (II). However, it has now been shown that two formaldehyde units may be added to biphosphoranes of the types VI and VII, by a procedure analogous to that described earlier[3] for the addition of acrolein to similar biphosphoranes, to afford a convenient route to the corresponding symmetrical dienes.

$(C_6H_5)_3P{=}CH(CH_2)_nCH{=}P(C_6H_5)_3$

VI



VII

The two diterminal olefins, 1,6-heptadiene and *p*-divinylbenzene, were obtained in reasonable yields of 45% and 42%, respectively. Although 1,6-heptadiene was synthesized by way of gaseous formaldehyde and *p*-divinylbenzene by way of paraformaldehyde, it is conceivable that similar results would be obtained upon reversal of the respective modes of addition of formaldehyde to the two biphosphoranes. These results are recorded in Table IV.

The mechanism of the Wittig olefin synthesis has been proposed[3] as one involving a nucleophilic attack of a phosphorane (II) upon the carbonyl carbon of an aldehyde or ketone (equation lb) with formation of a zwitterionic intermediate or betaine (III). The betaine could thus be decomposed, *via* a four-membered cyclic intermediate (IV), by heat or prolonged standing at room temperature with subsequent splitting out of triphenylphosphine oxide and formation of the olefinic product (V).

During the synthesis of each of the olefins presented in Table I, it was observed that, in similarity with some earlier literature reports,[6] the intense color of the ethereal phosphorane solution or suspension was discharged immediately upon addition of aldehyde to produce a heavy, cream-colored mixture. This phenomenon was observed even at 10° for all cases (although at −10° propionaldehyde required a finite length of time to decolorize a suspension of benzylidenetriphenylphosphorane), which implied a rapid conversion of reactants into betaine-type intermediates (III) or indeed into olefin products and triphenylphosphine oxide. The reaction mixture of *n*-butylidenetriphenylphosphorane with *n*-butyraldehyde (2) has been shown to be approximately two-thirds complete, without quenching, within a condensation period of thirty minutes at 10°. (See Experimental.) In this example, at least, the reaction appears to proceed quite swiftly through the intermediate stages to afford the olefin, whereas the intermediate species of certain other condensations may be less prone to undergo rapid decomposition into products.

In any case, however, the decomposition of intermediate species into olefins and triphenylphosphine oxide, or perhaps reverse decomposition into reactants, may be brought about or at least more rapidly completed for the olefins mentioned in this text by the addition of a quenching solution to the heavy, cream-colored con-

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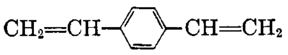
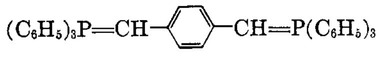
(6) (a) F. Bohlmann, *Ber.*, **90**, 1519 (1957); (b) G. Wittig and U. Schöllkopf, *ibid.*, **87**, 1318 (1954).

TABLE IV[a]

POLYENES SYNTHESIZED FROM FORMALDEHYDE INTERMEDIATE

	Polyene	Biphosphorane (VI)	Aldehyde	Yield, %	B.p.
1	$CH_2{=}CH(CH_2)_3CH{=}CH_2$	$(C_6H_5)_3P{=}CH(CH_2)_3CH{=}P(C_6H_5)_3$	CH_2O	45	89–90°
2			$(CH_2O)_n$	42	62–63°/6 mm.

[a] Boiling ranges are uncorrected.

densation mixtures. The yields of olefins reported in Table I are those obtained by water decomposition of the reaction mixtures following a five-minute condensation period at 10°. In each instance the addition of water almost immediately transformed the heavy, ethereal mixture into clear water and ether layers (a small amount of amorphous solid usually remained in the water layer) from which the olefin product could easily be isolated. Reaction times considerably in excess of five minutes did not appear detrimental to the yields of olefins derived from the aliphatic aldehydes presented in Table I. However, longer reaction times did appear to decrease the yields of olefins derived from acrolein and methacrolein.

In a test case the yield of 4-octene was observed to be dependent upon the nature of the quenching solution. The olefin was produced in 82%, 75% and 55% yields upon quenching of the particular reaction mixture with water, in aqueous ammonium chloride solution, and in aqueous hydrochloric acid solution, respectively.

The preparation of stilbene (V. $R_1 = R_3 = H$, $R_2 = R_4 = {-}C_6H_5$) *via* condensation of benzylidenetriphenylphosphorane (II. $R_1 = H$, $R_2 = {-}C_6H_5$) with benzaldehyde has been reported, after allowing the reaction mixture to stand at room temperature for two days, to afford the olefin in 82% yield.[3] By contrast of conditions, however, a condensation of the same phosphorane with benzaldehyde at 10° for five minutes followed by decomposition of the reaction mixture with water, afforded stilbene in a similar yield of 78%.

The synthesis of olefins by the Wittig reaction has generally been observed to afford mixtures of *cis* and *trans* isomers, wherein the *trans* species tends to be the predominant isomer.[2] The general predominance of *trans* is believed[2b] to arise by the path of least steric interference between R groups (See equation 1) in the four-membered cyclic transition state (IV). If, therefore, a 1,2-disubstituted ethylene (V. $R_1 = R_3 = H$, $R_2 = R_4 =$ aliphatic) were to be synthesized by appropriate choice of phosphorane (II) and aldehyde, the product would be expected to contain a predominance of the *trans* isomer. However, the preparation of both 2-octene and 4-octene (Table I, 1 and 2, respectively) afforded a predominance of the *cis*, not the *trans*, species. The assignment of geometric structures has been authenticated by comparative gas–liquid chromatography and by infrared analysis of each reaction product with authentic samples[7] of the appropriate *cis* and *trans* isomers. The chromatograms of each olefin exhibited first a smaller and then a larger peak. Mixtures of authentic *trans*-4-octene with the isomeric 4-octene obtained in Table I resulted in a proportional increase in the area of the first and smaller peak with respect to the second peak. Opposite results were obtained from mixtures of the isomeric 4-octene and the authentic *cis* isomer. Moreover, the isomeric 4-octene exhibited an infrared absorption band of medium strength in the region of 965 cm.$^{-1}$, as contrasted with the very strong band exhibited by the authentic *trans* isomer at that frequency[8] and the relatively weak band exhibited by *cis*-4-octene. Also, a broad band of moderate strength was observed for the isomeric mixture in the region of 710–690 cm.$^{-1}$, a region normally associated with *cis* olefins.[8] Similar results were obtained for the isomeric 2-octene upon analogous comparison by g.l.c. and infrared analysis with authentic samples[7] of *cis*- and *trans*-2-octene.

A study of the effects of temperature and condensation time upon the distribution of geometric isomers in 2- and 4-octene has been conducted and the results are presented in Table V. However, with the possible exception that lower temperatures tend to lessen the predominance of *cis* isomer, no conclusive results are to be drawn from the study at this time.

TABLE V

INFLUENCE OF TEMPERATURE AND CONDENSATION TIME UPON *cis:trans* ISOMER DISTRIBUTION OF 2- AND 4-OCTENE

Olefin	Temp., °C.	Time, min.	Yield, %	*cis:trans*[a] ratio
4-Octene	−15	5	76	67:33
	10	5	78	71:29
	10	0.3	82	84:16
2-Octene	−15	5	60	77:23
	10	5	69	87:13
	10	0.3	62	81:19

[a] Isomer ratio determined by gas–liquid chromatography analysis on a 10-ft., 20% Carbowax 1000 (on 42/60 firebrick) column.

The syntheses of two additional alkyl-substituted ethylenes shown in Table I, 2-methyl-3-heptene (3) and 3-methyl-3-heptene (4), may have been brought about with a predominance of the *cis* isomer. The infrared spectrum of 2-methyl-3-heptene showed a broad absorption band of moderate strength in the region of 740–700 cm.$^{-1}$ and a moderate absorption around 965 cm.$^{-1}$. An authentic sample[7] of *trans*-2-methyl-3-heptene, however, exhibited no similar absorption in the region of 740–700 cm.$^{-1}$, but showed a very strong absorption band around 965 cm.$^{-1}$. Analysis of the 2-methyl-3-heptene by g.l.c. techniques, however, on a variety of column packings produced in each case only a single, sharp peak, the retention time of which was only slightly different from that of an authentic *trans* sample. Moreover, essentially no alterations in the shapes of the chromatograms were detected when mixtures of 2-methyl-3-heptene and the authentic *trans* isomer were subjected to similar analysis.

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[7] Supplied through the courtesy of Dr. Kenneth W. Greenlee, Director of the Ohio State University Hydrocarbon Laboratory, Columbus, Ohio.

[8] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, chap. 3.

The infrared spectrum of the second olefin, 3-methyl-3-heptene exhibited very little absorption in the region of 965 cm.$^{-1}$, contrary to what may have been expected if indeed the olefin contained an appreciable quantity of the *trans* isomer. Moreover, g.l.c. analysis on several different column packings produced chromatograms in each case possessing a single, but relatively broad peak.

It would, therefore, seem that the *cis* isomers were certainly present in the reaction products of the above two olefins, although in neither case is sufficient data yet available to verify predominance or exclusive presence of either isomer.

Experimental[9]

2-Octene. A. *n*-Hexyltriphenylphosphonium Bromide.—A mixture of 458 g. (1.75 moles) of triphenylphosphorus[10] and 288 g. (1.75 moles) of *n*-hexyl bromide in 500 ml. of monochlorobenzene was refluxed with stirring for 24 hr., at which time the mixture was allowed to cool and the supernatant liquid poured away from the viscous oil in the bottom of the flask. The oil was mixed with 500 ml. of ether, whereupon the resulting pasty mass solidified after standing for several hours at room temperature. The solid was triturated several times with ether and dried *in vacuo* over phosphorus pentoxide to afford 666 g. (90% yield of theoretical) of a light tan solid of m.p. 198–200°. The *n*-hexyltriphenylphosphonium bromide was stored in a capped bottle in a desiccator.

Anal. Calcd. for $C_{24}H_{28}PBr$: C, 67.4; H, 6.6; P, 7.3, Found C, 67.3; H, 6.6; P, 7.2.

B. 2-Octene.—To a stirred suspension of 42.7 g. (0.1 mole) of *n*-hexyltriphenylphosphonium bromide in 400 ml. of dry ether under a nitrogen atmosphere was added 90 ml. of 14.90% *n*-butyllithium (0.15 mole) in hexane[11] by means of a hypodermic syringe and a syringe cap. The resulting deep red solution was cooled to 10° in a Dry Ice–acetone bath and a solution of 8.8 g. (0.2 mole) of acetaldehyde in 200 ml. of dry ether was added over a period of 1 min. while maintaining the bath temperature at 10°. A heavy, cream-colored suspension resulted almost immediately which, after stirring for a total of 5 min. at 10°, was decomposed by the addition of 250 ml. of water.

The layers were separated and the water layer extracted once with 150 ml. of ether, whereupon the ethereal fractions were combined, dried over anhydrous sodium sulfate and most of the solvent distilled away after removal of the drying agent. The resulting oil was fractionated through a 28 theoretical plate, spinning band distillation column, after which the distillation fractions were analyzed for yield by g.l.c. using a 10-ft., 20% Carbowax 1000 (on 42/60 firebrick) column.[12]

A second final work-up procedure was sometimes used wherein, after removal of the solvent from the dried ethereal solution, dry petroleum ether (b.p. 30–60°) was added to the remaining oil until precipitation ceased. The mixture was allowed to stand for 1 hr., at which time the supernatant liquid was poured away from the solid material, consisting largely of triphenylphosphine oxide, m.p. 148–152° (lit.,[3] m.p. 152.5–154.0°), and most of the petroleum ether removed. The remaining oil was subsequently fractionated through the spinning band column. Similar yields were obtained by either route.

2-Octene, b.p. 124–125° (lit.,[13] b.p. *cis*, 125.6°; *trans*, 125.0°); n^{25}_{D} 1.4092 (lit.,[13] n^{25}_{D} *cis*, 1.4139; *trans*, 1.4128), was obtained in 69% (7.7 g.) yield of theoretical[14] as based upon the *n*-hexyltriphenylphosphonium bromide.

Qualitative g.l.c. analyses[12] afforded reasonable separation of the pure product into two peaks. The area under the first and smaller peak could be increased proportionately with respect to the area under the second peak, or *vice versa*, by use of mixtures of the pure reaction product with authentic *trans*-2-octene or authentic *cis*-2-octene,[7] respectively. The *cis* isomer was thus shown to be predominant.

The predominance of *cis*-2-octene was found to vary, depending upon the reaction conditions (see Table V), from a 3:1 ratio to a 4:1 ratio with respect to the *trans* isomer.

Infrared absorption bands[8] were observed for the isomeric 2-octene at 1670, 965 and 690 cm.$^{-1}$. The band at 965 cm.$^{-1}$ was of intermediate strength as compared with the very intense absorption exhibited by the *trans* isomer and very weak absorption exhibited by the *cis* isomer in this region.[8] Moreover, the *cis*, not the *trans* isomer, showed absorption[8] in the region of 690 cm.$^{-1}$.

The following nine mono- and polyolefins were prepared by experimental procedures similar to that used for the preparation of 2-octene with the exception of the types of phosphonium halide salts and aldehydes employed.

4-Octene.—4-Octene, b.p. 121–122° (lit.,[13] b.p. *cis*, 121.7°; *trans*, 121.4°); n^{20}_{D} 1.4130 (lit.,[13] n^{20}_{D} *cis*, 1.4136; *trans*, 1.4416), was obtained in 80% yield[14] *via* condensation of the phosphorane derived from *n*-butyltriphenylphosphonium bromide[15] with *n*-butyraldehyde.

A similar result, that is a predominance of *cis* isomer, was found for the 4-octene reaction product as was found previously for 2-octene when subjected to g.l.c. and infrared analysis with authentic *cis*- and *trans*-4-octene samples.[7] The predominance of *cis* isomer with respect to *trans* isomer was found to vary from a 2:1 ratio to a 4:1 ratio depending upon reaction conditions (see Table V).

Attempted Isolation of Intermediate to 4-Octene.—To a stirred solution of *n*-butylidenetriphenylphosphorane (0.08 mole) in 300 ml. of anhydrous ether, prepared by the previously described procedure, was added at 10° a solution of 11.8 g. (0.16 mole) of *n*-butyraldehyde in 20 ml. of dry ether. The resulting cream-colored, heavy suspension was allowed to stir at 10° for 5 min., at which time the reaction flask was connected to a vacuum line by way of two Dry Ice–acetone-cooled traps. A pressure of about 15 cm. was applied to the system for 25 min. while holding the temperature at 10°, at which time the vacuum was released and the clear liquid in the trap (about 150 ml.) subsequently concentrated to a volume of 40 ml. (phase I).

The wet solid remaining in the reaction flask was filtered through a sintered-glass funnel under anhydrous conditions (within 30 min. after initial condensation) and the white solid remaining on the filter washed with dry pentane. The filtrate was poured into a separatory funnel and shaken with 200 ml. of water, whereupon some precipitate appeared but quickly reentered solution. The layers were separated and the water layer extracted once with ether. The ether extracts were combined, dried over anhydrous calcium chloride and most of the solvent distilled away after removal of the drying agent (phase II).

The white solid obtained from the above anhydrous filtration was well shaken with a mixture of 150 ml. of water and 50 ml. of pentane and let stand for several hours. The resulting mixture was filtered and washed well with water, followed by pentane. The white solid remaining on the filter was then dried to yield 15.3 g. (69%) of triphenylphosphine oxide of m.p. 147–151° and mixed m.p. 150–153° with authentic sample of m.p. 153° (lit.,[3] m.p. 152.5–154.0°). The filtrate was separated into layers and the water layer extracted once with ether. The organic extracts were combined, dried over anhydrous calcium chloride and most of the solvent distilled away after removal of the drying agent (phase III).

Phases I, II, and III were fractionated separately in a spinning band column and the distillation fractions analyzed for yield by g.l.c.[14] Phases I, II, and III contained 2%, 50% and 26% yields, respectively, of 4-octene.

2-Methyl-3-Heptene.—2-Methyl-3-heptene, b.p. 110–111° (lit.,[13] b.p. 112.0°); n^{20}_{D} 1.4103 (lit.,[13] n^{20}_{D} 1.407), was obtained in 67% yield[14] *via* condensation of the phosphorane derived from *n*-butyltriphenylphosphonium bromide[15] with isobutyraldehyde.

Anal. Calcd. for C_8H_{16}: C, 85.62; H, 14.37. Found: C, 85.61; H, 14.43.

The product exhibited characteristic infrared absorption bands[8] at 1700, 1640, 970 and 730 cm.$^{-1}$. G.l.c. analysis,[12] using 5- and 10-ft. Carbowax columns, a 10-ft. Carbowax 20 M column, and a 5-ft. Ucon polar column, showed only a single, sharp peak with no

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[9] Melting and boiling ranges are uncorrected. Analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Micro Tech Laboratories, Skokie, Ill.

[10] Obtained from Peninsular ChemResearch, Inc., Gainesville, Fla.

[11] Foote Mineral Company, Philadelphia 44, Pa.

[12] Column obtained from Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

[13] "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, pp. 58–59.

[14] The yield of product was based upon g.l.c. analysis of distillation fractions over a somewhat wider boiling range than recorded.

[15] R. Mechoulam and F. Sondheimer, *J. Am. Chem. Soc.*, **80**, 4386 (1958).

indication of splitting into *cis–trans* isomers. Subsequent efforts to separate *cis–trans* isomers of the straight-chain octenes on a 5-ft. Ucon polar column with 5% added silver nitrate were not successful.

3-Methyl-3-heptene. A. 2-Butyltriphenylphosphonium Bromide.—A pressure bottle was charged with 78.6 g. (0.30 mole) of triphenylphosphorus,[10] 43.8 g. (0.32 mole) of 2-bromobutane and 75 ml. of dry benzene. The bottle and contents were heated at 140° with shaking for 16 hr., whereupon the bottle was cooled and the supernatant liquid poured away from the amorphous material. The solid was triturated several times with benzene and recrystallized from isopropyl ether–absolute ethanol solvent pair. After drying *in vacuo* over phosphorus pentoxide, 60.0 g. (50% yield) of a white crystalline solid, m.p. 225–227°, was obtained.

Anal. Calcd. for $C_{22}H_{24}PBr$: C, 66.2; H, 6.1; P, 7.8. Found: C, 66.0; H, 6.4; P, 7.8.

B. 3-Methyl-3-heptene.—This olefin, b.p. 119–120° (lit.,[13] b.p. 121°); n^{20}_D 1.4201 (lit.,[13] n^{20}_D 1.418), was obtained in 66% yield[14] *via* condensation of the phosphorane derived from 2-butyltriphenylphosphonium bromide with *n*-butyraldehyde.

Anal. Calcd. for C_8H_{16}: C, 85.63; H, 14.37. Found: C, 85.40; H, 14.70.

The product exhibited characteristic infrared absorption bands[8] at 1660 and 836 cm.$^{-1}$. G.l.c. analysis[12] showed only a single, broad peak.

1-Phenyl-1-butene.—1-Phenyl-1-butene; b.p. *cis*, 84.0–85.0°/23 mm.; *trans*, 91.0–92.0°/23 mm. (lit.,[16] b.p. *cis*, 187.1°; *trans*, 198.7°); n^{23}_D *cis*, 1.5282; *trans*, 1.5428 (lit.,[16] n^{20}_D *cis*, 1.5284; *trans*, 1.5420), was obtained in 78% yield[14] (59% *trans*, 19% *cis*) *via* condensation of the phosphorane derived from benzyltriphenylphosphonium chloride[3] with propionaldehyde.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.60; H, 9.27.

Stilbene.[3]—Stilbene, b.p. *cis*, 135–136°/10 mm.; m.p. *trans*, 123–125° and mixed m.p. of 123–125° (lit.,[17] b.p. *cis*, 136–137°/10 mm.; m.p. *trans*, 124°); n^{25}_D *cis*, 1.6204 (lit.,[17] n^{25}_D *cis*, 1.6214), was obtained in 78% yield[14] (42% *trans;* 36% *cis*) *via* condensation of the phosphorane derived from benzyltriphenylphosphonium chloride[3] with benzaldehyde.

1,3-Heptadiene. A. From Allyltriphenylphosphonium Bromide.[3]—The olefin, b.p. 99.0–100.0° (lit.,[18] b.p. 100.0°); n^{20}_D 1.4417 (lit.,[18] n^{20}_D 1.4428), was obtained in 28% yield[14] *via* condensation of the phosphorane derived from allyltriphenylphosphonium bromide with *n*-butyraldehyde.

Anal. Calcd. for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.54; H, 12.67.

B. From Allyltriphenylphosphonium Chloride. 1. Preparation of Allyltriphenylphosphonium Chloride.—A mixture of 131.0 g. (0.5 mole) of triphenylphosphorus[10] and 300 ml. of allyl chloride was heated under reflux for 24 hr., at which time the resulting slurry was cooled, and the solid collected by filtration. The salt, m.p. 225–227°, was obtained in 64% yield (108.0 g.) upon subsequent washing with benzene and drying *in vacuo* at 100°.

Anal. Calcd. for $C_{21}H_{20}PCl$: C, 74.4; H, 5.9; P, 9.2. Found: C, 73.9; H, 5.9; P, 8.9.

2. **1,3-Heptadiene.**—The olefin, exhibiting a similar boiling range and refractive index as that prepared in (A), was obtained in 52% yield[14] *via* condensation of the phosphorane derived from allyltriphenylphosphonium chloride with *n*-butyraldehyde.

The infrared spectra of products (A) and (B) were mutually superimposable and exhibited characteristic bands[8] at 1650, 1600, 1000, 955, and 905 cm.$^{-1}$. A single peak was observed upon g.l.c. analysis[12] of each product and quantitative catalytic hydrogenation required two equivalents of hydrogen per equivalent of diene.

1,3-Nonadiene. A. From Acrolein.—The olefin, b.p. 72–74°/44 mm.; n^{20}_D 1.4521, was obtained in 34% yield *via* condensation of the phosphorane derived from *n*-hexyltriphenylphosphonium bromide (*vide supra*) with acrolein.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.00; H, 12.81.

B. From *n*-Hexaldehyde.—The olefin, exhibiting a similar boiling range and refractive index as that prepared in (A), was obtained in 30% yield *via* condensation of the phosphorane derived from allyltriphenylphosphonium bromide[3] and *n*-hexaldehyde.

The infrared spectra of products (A) and (B) were mutually superimposable and exhibited characteristic bands[8] at 1650, 1600, 1000, 955 and 905 cm.$^{-1}$. A single peak was observed upon g.l.c. analysis[12] of each product and quantitative catalytic hydrogenation required two equivalents of hydrogen per equivalent of diene.

2-Methyl-1,3-nonadiene. A. From Methacrolein.—The olefin, b.p. 74–77°/25 mm.; n^{20}_D *cis*, 1.4510; *trans*, 1.4600, was obtained in 38% yield *via* condensation of the phosphorane derived from *n*-hexyltriphenylphosphonium bromide (*vide supra*) with methacrolein.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: (*cis*) C, 87.18; H, 12.92; (*trans*) C, 87.12; H, 12.88.

B. From *n*-Hexaldehyde. 1. Preparation of Methallyltriphenylphosphonium Chloride.—The salt, m.p. 210–213°, was prepared in 90% yield from methallyl chloride and triphenylphosphorus[10] by a procedure similar to that described previously for the preparation of allyltriphenylphosphonium chloride.

Anal. Calcd. for $C_{22}H_2PCl$: C, 74.9; H, 6.24; P, 8.81; Cl, 10.1. Found: C, 74.87; H. 6.17; P, 8.71; Cl, 10.29.

2. **2-Methyl-1,3-nonadiene.**—The olefin, exhibiting similar boiling range and refractive indices for *cis* and *trans* isomers to those prepared in (A), was obtained in 14% yield *via* condensation of the phosphorane derived from methallyltriphenylphosphonium chloride with *n*-hexaldehyde.

Both (A) and (B) could be separated into *cis* and *trans* isomers by g.l.c. analysis on diethyleneglycol succinate supported on firebrick.[12] The *cis* isomer exhibited characteristic infrared absorption bands[8] at 1640, 1600, and 885 cm.$^{-1}$. The *trans* isomer exhibited infrared bands at 1640, 1600, 965, and 885 cm.$^{-1}$. Quantitative catalytic hydrogenation required approximately two equivalents of hydrogen per equivalent of diene.

1,3,7-Octatriene. A. From 4-Pentenal.—The olefin, b.p. 115–117°; n^{20}_D 1.4594, was obtained in 19.5% yield *via* condensation of the phosphorane derived from allyltriphenylphosphonium bromide[3] with 4-pentenal.[10]

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.48; H, 11.37.

B. From Acrolein. 1. Preparation of 4-Pentenyltriphenylphosphonium Bromide.—The salt, m.p. 134–140°, was prepared in 90% yield from 1-bromo-4-pentene[10] and triphenylphosphorus[10] by a procedure similar to that described previously for the preparation of *n*-hexyltriphenylphosphonium bromide.

Anal. Calcd. for $C_{23}H_{24}PBr$: C, 67.1; H, 5.8; P, 7.6. Found: C, 66.6; H, 6.3; P, 7.6.

2. **1,3,7-Octatriene.**—The olefin, b.p. 120–122°, n^{20}_D 1.4604, was obtained in 24% yield *via* condensation of the phosphorane derived from 4-phentenyltriphenylphosphonium bromide with acrolein.

Product (A) showed a single peak upon g.l.c. analysis[12] and exhibited characteristic infrared absorption bands[8] at 1640, 1600, 1000, and 910 cm.$^{-1}$. Product (B) showed two peaks of similar area upon g.l.c. analysis in diethyleneglycol succinate, supported on firebrick[12] and exhibited characteristic infrared absorption bands[8] at 1640, 1600, 1000, 965, and 910 cm.$^{-1}$. Quantitative catalytic hydrogenation required three equivalents of hydrogen per equivalent of triene.

1,3,8-Nonatriene. A. Preparation of 5-Hexenyltriphenylphosphonium Bromide.—The salt, m.p. 165–168°, was prepared in 95% yield from 1-bromo-5-hexene[10] and triphenylphosphorus[10] by a procedure similar to that described previously for the preparation of *n*-hexyltriphenylphosphonium bromide.

Anal. Calcd. for $C_{24}H_{26}PBr$: C, 67.9; H, 6.3; P, 7.1. Found: C, 67.6; H, 6.1; P, 7.3.

B. 1,3,8-Nonatriene.—The olefin, b.p. 68–69°/43 mm. n^{20}_D 1.4721, was obtained in 20% yield *via* condensation of the phosphorane derived from 5-hexenyltriphenylphosphonium bromide with acrolein.

The product showed a single peak upon g.l.c. analysis on diethylene glycol succinate supported on firebrick[12] and exhibited characteristic infrared absorption bands[8] at 1640, 1600, 1000, 950, 910, and 900 cm.$^{-1}$. Quantitative catalytic hydrogenation required three equivalents of hydrogen per equivalent of triene.

1,3,9,11-Dodecatetraene. A. Preparation of Hexamethylenebis(triphenylphosphonium Bromide.)—A mixture of 262 g. (1.0 mole) of triphenylphosphorus and 122 g. (0.5 mole) of hexamethylene dibromide was heated under a nitrogen atmosphere to 200° in an oil bath. The wet paste first formed into a viscous liquid and then quite suddenly solidified at 150°. The resulting salt was

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(16) A. L. Henne and A. H. Matuszak, *J. Am. Chem. Soc.*, **66**, 1649 (1949).

(17) See Heilbron, "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1953, p. 375.

(18) "Physical Constants of the Principal Hydrocarbons," 3rd ed., The Texas Company, New York, N. Y., 1942, p. 49.

allowed to cool to room temperature and then dissolved in hot chloroform. The product was precipitated by pouring the chloroform solution into 1.5 volumes of acetone, whereupon the solid was collected by filtration and dried overnight at 60° and 40 mm. pressure. A yield of 82% (297 g.) of the diphosphonium salt, m.p. 335–337°, was obtained.

Anal. Calcd. for $C_{42}H_{42}P_2Br_2$: C, 65.7; H, 5.5; P, 8.1; Br, 20.8. Found: C, 65.55; H, 5.73; P, 8.18; Br, 20.59.

B. 1,3,9,11-Dodecatetraene.—To a stirred suspension of 76.8 g. (0.1 mole) of hexamethylene bis(triphenylphosphonium bromide) in 700 ml. of dry ether under a nitrogen atmosphere was added 140 ml. of 14.90% *n*-butyllithium (0.22 mole) in hexane.[11] The resulting mixture was cooled to 5° in a Dry Ice–acetone bath and a solution of 35 ml. of acrolein in 200 ml. of dry ether was added over a 15-min. period while maintaining the bath temperature at 5°. The reaction was subsequently worked up in a manner similar to that described previously for the preparation of 2-octene.

The olefin, b.p. 71–73°/2 mm., n^{19}_{D} 1.5093, was obtained in 6% yield.[14] The yield could be elevated to 12% of theoretical by use of diglyme as solvent.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.80; H, 11.10. Found: C, 88.64; H, 11.13.

Quantitative catalytic hydrogenation required four equivalents of hydrogen per equivalent of tetraene.

1,3,6,8-Nonatetraene.—The olefin, b.p. 52°/20 mm., n^{29}_{D} 1.5133, was obtained in 6% yield (12% yield in diglyme solvent) *via* condensation of the biphosphorane derived from tetramethylenebis(triphenylphosphonium bromide)[19] with acrolein by a procedure similar to that described previously for preparation of 1,3,9,11-dodecatetraene.

Anal. Calcd. for C_9H_{12}: C, 90.00; H, 10.00. Found: C, 89.76; H, 10.40.

The product showed a single peak with a shoulder upon g.l.c. analysis in diethyleneglycol succinate supported on firebrick[12] and exhibited characteristic infrared absorption bands[7] at 1640, 1590, 1000, and 900 cm.$^{-1}$. Quantitative catalytic hydrogenation required four equivalents of hydrogen per equivalent of tetraene.

Styrene. Procedure A: With Gaseous Formaldehyde.—A 2-l. flask and a 200-ml. flask were connected by means of a wide bore neoprene tube and the 200-ml. flask connected to a suitable nitrogen source. After flushing the entire system with nitrogen, the smaller flask was charged with 20 g. (0.66 equivalent of formaldehyde) of paraformaldehyde (dried *in vacuo* over phosphorus pentoxide). The larger flask was charged with a mixture of 43.3 g. (0.1 mole) of benzyltriphenylphosphonium bromide[20] and 400 ml. of dry ethyl ether, to the stirred suspension of which was added 80 ml. of 14.90% *n*-butyllithium (0.13 mole) in hexane[11] by means of a hypodermic syringe and a syringe cap. The resulting brilliant orange suspension was allowed to stir for 0.5 hr., whereupon the smaller flask and contents were heated over a low flame to allow an even stream of formaldehyde and nitrogen to flow over the stirred phosphorane suspension until complete discoloration had been achieved (approximately 15 min.). The reaction was subsequently quenched by the addition of 250 ml. of water to the heavy, cream-colored suspension, at which time the layers were separated and the water layer extracted once with 150 ml. of ether. The ethereal extracts were combined, dried over anhydrous sodium sulfate and most of the solvent distilled after removal of the drying agent. The resulting oil was fractionated through a twenty-eight theoretical plates spinning band distillation column (hydroquinone used as inhibitor), after which the distillation fractions were analyzed for yield by g.l.c. analysis on diethyleneglycol succinate supported on firebrick.[12] Styrene, b.p. 52–53°/27 mm. (lit.,[21] b.p. 52–53°/28 mm.); n^{20}_{D} 1.5461 (lit.,[8] n^{20}_{D} 1.5462), was obtained in 64% yield[14] (6.65 g.).

Procedure B: With Paraformaldehyde.—A 0.1 *M* suspension of benzylidenetriphenylphosphorane was prepared by a procedure similar to that described in (A). However, 6.0 g. (0.2 equivalent of formaldehyde) of dry paraformaldehyde supported in 100 ml. of dry ether was added directly to the stirred suspension, whereupon discoloration was complete within 3.5 hr. at room temperature. Subsequent work-up of the reaction afforded styrene in 65% yield.[14]

A similar reaction between the phosphorane derived from benzyltriphenylphosphonium chloride[3] and paraformaldehyde afforded styrene in 75% yield.[14] The phosphorane suspension in this case was completely decolorized within 30 min. at room temperature. The infrared spectra of (A) and (B) were mutually superimposable and each superimposable upon the spectrum of an authentic styrene sample.

Qualitative Rate Studies of Betaine Formation as a Function of the Phosphoranes Derived from Benzyltriphenylphosphonium Chloride *vs.* Bromide. A. From Benzyltriphenylphosphonium Chloride.—A 300-ml. three-neck flask was placed in a water bath at 34° and was fitted with a mechanical stirrer, an efficient reflux condenser capped with a calcium chloride drying tube, and a syringe cap. The benzylidenetriphenylphosphorane was formed by reaction of 7.76 g. (0.02 mole) of benzyltriphenylphosphonium chloride[3] in 80 ml. of dry ether with 18 ml. of 14.90% *n*-butyllithium (0.03 mole) in hexane[11] under a nitrogen atmosphere. Dry paraformaldehyde (1.2 g., 0.04 equivalent of formaldehyde) in 20 ml. of dry ether was added to the stirred phosphorane suspension and the resulting mixture allowed to stir at 34° until complete decolorization had been achieved.

The styrene product was worked up by a procedure similar to that given previously for preparation of styrene from paraformaldehyde and analyzed for yield by quantitative g.l.c. analysis on diethyleneglycol succinate supported on firebrick.[12]

B. From Benzyltriphenylphosphonium Bromide.—The reactions were carried out in a manner similar to that described in (A), with the exception that 8.66 g. (0.02 mole) of benzyltriphenylphosphonium bromide[20] was used.

Each of the reactions in (A) and (B) were repeated twice and the results are presented in Table IV.

The following six mono- and diterminal olefins were prepared by similar procedures to those described in either procedure A or B for the synthesis of styrene, with the exception that different phosphonium salts were employed for each olefin.

1-Heptene.—The olefin, b.p. 92–93° (lit.,[22] 93.6°); n^{20}_{D} 1.4013 (lit.,[22] n^{20}_{D} 1.3998), was obtained in 47% yield[14] *via* condensation of the phosphorane derived from *n*-hexyltriphenylphosphonium bromide (*vide supra*) with gaseous formaldehyde (see Styrene; procedure A). The infrared spectrum correlated well with a spectrum of 1-hexene as shown in the literature.[23]

1-Octene. A. *n*-Heptyltriphenylphosphonium Bromide.—The phosphonium salt, m.p. 171–174°, was prepared in 74% yield from 1-bromoheptane and triphenylphosphorus by a procedure similar to that described previously for the preparation of *n*-hexyltriphenylphosphonium bromide with the exception that xylene, instead of monochlorobenzene, was used as solvent.

Anal. Calcd. for $C_{25}H_{30}PBr$: C, 68.0; H, 6.9; P, 7.0. Found: C, 68.0; H, 6.8; P, 7.3.

B. 1-Octene.—The olefin, b.p. 121–122° (lit.,[22] b.p. 121.3°); n^{20}_{D} 1.4090 (lit.,[22] n^{20}_{D} 1.4087), was obtained in 42% yield[14] *via* condensation of the phosphorane derived from *n*-heptyltriphenylphosphonium bromide with paraformaldehyde (see Styrene; procedure B).

Anal. Calcd. for C_8H_{16}: C, 85.62; H, 14.37. Found: C, 85.53; H, 14.53.

The decolorization time was normally between 10–12 hr. at room temperature. The infrared spectrum correlated well with a spectrum of 1-octene as shown in the literature.[23]

2-Methyl-1-Octene. A. 2-Octyltriphenylphosphonium Bromide.—The phosphonium salt was prepared in 66% yield from 2-bromooctane and triphenylphosphorus in a pressure bottle by a procedure similar to that described previously for the preparation of 2-butyltriphenylphosphonium bromide.

Anal. Calcd. for $C_{26}H_{32}PBr$: C, 68.6; H, 7.1; P, 6.8. Found: C, 68.6; H, 7.6; P, 6.1.

B. 2-Methyl-1-octene.—The olefin, b.p. 143.0–144.0°, n^{20}_{D} 1.4197; (lit.,[24] b.p. 143°, n^{20}_{D} 1.4190), was obtained in 52% yield[14] *via* condensation of the phosphorane derived from 2-octyltriphenylphosphonium bromide with paraformaldehyde (see Styrene; procedure B).

Anal. Calcd. for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.81; H, 14.23.

The olefin exhibited characteristic infrared absorption bands[8] at 3075, 1665, 1375, and 885 cm.$^{-1}$.

1,6-Heptadiene. A. Pentamethylenebis(triphenylphosphonium Bromide).—A mixture of 104.8 g. (0.4 mole) of triphenyl-

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(19) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

(20) G. Wittig and W. Haag, *Ber.*, **88**, 1654 (1955).

(21) See Heilbron, "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1958, p. 379.

(22) Ref. 13, p. 52.

(23) "Infrared Spectral Data," compiled by the American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., October 31, 1960.

(24) Ref. 18, p. 29.

phosphorus, 46.0 g. (0.2 mole) of 1,5-dibromopentane and 250 ml. of dry dimethylformamide was refluxed with stirring under a nitrogen atmosphere for 16 hr., at which time about 130 ml. of solvent was removed by distillation. The residue was allowed to cool and then poured into 500 ml. of dry benzene. The supernatant liquid was poured away from the resulting pasty material and an additional 200 ml. of dry benzene added to the paste whereupon immediate crystallization of the product occurred. The solid was broken up and, after washing on the filter with dry benzene and dry ether, was recrystallized from ethanol–isopropyl ether solvent pair to yield 100 gm. (66% yield) of the diphosphonium salt of m.p. 240–244°.

Anal. Calcd. for $C_{41}H_{40}P_2Br_2$: C, 65.26; H, 5.34; P, 8.21. Found: C, 65.41; H, 5.38; P, 7.83.

B. **1,6-Heptadiene.**—The olefin, b.p. 89–90°, n^{18}_{D} 1.4151 (lit.,[24] b.p. 90°, n^{20}_{D} 1.4142), was obtained in 45% yield[14] *via* condensation of pentamethylenebis(triphenylphosphonium bromide) with formaldehyde (see Styrene; procedure A). The diene exhibited characteristic infrared absorption bands[8] at 1640, 990, and 910 cm.$^{-1}$.

***p*-Divinylbenzene.**—The olefin, b.p. 62–63°/6 mm. (lit.,[25] 85–86°/16 mm.), was obtained in 42% yield *via* condensation of the diphosphorane derived from *p*-xylenebis(triphenylphosphonium chloride)[26] and paraformaldehyde (see Styrene: procedure B).

Anal. Calcd. for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.92; H, 8.02.

The diene exhibited characteristic infrared absorption bands[8] at 1625, 980, and 900 cm.$^{-1}$.

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[25] Lespieau and Deluchat, *Compt. rend.*, **190**, 683 (1930).

[26] T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

β-Diketones. IV. Synthesis of Monosubstituted Benzoylcyclopentanones[1]

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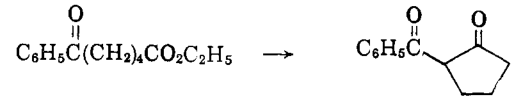
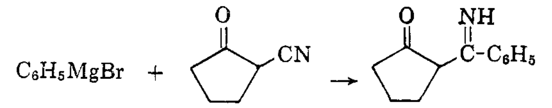
A series of seventeen monosubstituted benzoylcyclopentanones has been prepared by condensation of the pyrrolidene–enamine of cyclopentanone with substituted benzoyl chlorides. The yields ranged from 28 to 76%. In some cases, the 2,5-dibenzoylcyclopentanone was isolated. Other methods of condensation of cyclopentanone with benzoate esters were studied; larger amounts of by-products and lower yields of benzoylcyclopentanones resulted. Keto–enol equilibrium data are presented and discussed.

In a continuing study[1,3,4] of benzoylcyclanones it was desirous to prepare a number of monosubstituted benzoycylopentanones. The parent compound 2-benzoylcyclopentanone (I) was first prepared[5] by Bauer, in a Dieckmann ring closure, employing sodium amide as catalyst. Sodium ethoxide has also been used.[6] The diketone I was reported[5,6] to melt at 41–42°.

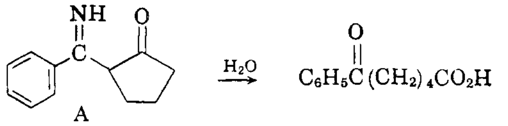


I

The reaction of 2-cyanocyclopentanone with phenylmagnesium bromide gave a product, m.p. 117°, erroneously identified[7] as I. The product melting at 117° has since been shown[8] to be the imine intermediate (structure A). Hydrolysis of A gives ring opening, rather than I. The direct benzoylation of cyclopentanone by benzoyl chloride in the presence of sodium amide was reported[9] to give I in 53% yield. When *p*-methoxybenzoyl chloride was used only a 22% yield of the diketone was formed. Self-condensation of cyclopentanone was found to occur under the reaction conditions, decreasing the yield of diketone. When methyl benzoate was employed, no diketone I was formed, and complete self-condensation occurred.[10]



A



A

The synthetic method which we found to be useful in the series of monosubstituted benzoylcyclopentanones was the condensation of N-cyclopentenylpyrrolidene with benzoyl chloride or its monosubstituted derivatives. Stork[11] reported the preparation of 2-benzoylcyclohexanone by this method, but no conditions or yield were given. Eistert[12] reported the synthesis of I in 42% yield employing N-cyclopentenylmorpholine.[13] This method was found suitable for benzoylcyclanones of larger ring size.[12]

We found it possible to prepare monosubstituted benzoylcyclopentanones in satisfactory yields, by use of the Stork enamine method.[11] Seventeen compounds prepared this way are listed in Table I with pertinent data. The reaction procedure was essentially that used by others.[11–13] The intermediate amino ketone was not isolated. It was hydrolyzed immediately to give the substituted benzoylcyclopentanone (I-XVII).

The diketone resulting from hydrolysis was isolated by three different procedures. Diketones, I, XIII, and XVII, were obtained in sufficient purity by distilling the ether extract of the hydrolysis mixture (pro-

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[1] Previous paper in this series, R. D. Campbell and H. M. Gilow, *J. Am. Chem. Soc.*, **84**, 1440 (1962). Taken in part from the M.S. thesis of W. L. H., 1962. Presented in part at the 141st National Meeting of the American Chemical Society, Washington, D.C., 1962.

[2] Monsanto Research Fellow, Summer Session, 1961.

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[5] E. Bauer, *Ann. Chim. Phys.*, 9, **1**, 393 (1914).

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[8] B. Eistert and H. Wurzler, *Ann.*, **650**, 157 (1961).

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[11] G. N. Stork, R. Terrell, and J. Szmuszkovicz, *ibid.*, **76**, 2029 (1954); see also *Chem. Abstr.*, **51**, 9703e (1957).

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