The Wittig Reaction with Five- and Six-Membered Cyclic Ketones and Their Benzylidene Derivatives[1]

G. Witschard and C. E. Griffin

Department of Chemistry, University of Pittsburgh, Pittsburgh 13, Pennsylvania

Received September 26 1963

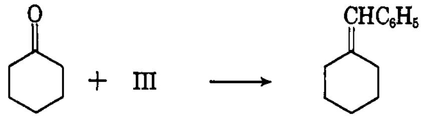
A number of benzylidenecycloalkanes have been prepared utilizing the reaction of benzylidenetriphenylphosphorane and the corresponding cycloalkanone or benzylidenecycloalkanone. Mono-, 1,2-di-, and 1,2,3-tribenzylidenecyclohexane, mono- and 1,2-dibenzylidenecyclopentane, and 1-benzylideneindane were prepared successfully; attempted reactions with 2,5-dibenzylidenecyclopentanone, 1-tetralone, 2-benzylideneindanone-1, and 2-benzylidenetetralone-1 were unsuccessful. In reactions of cyclopentanones, anion formation and base-catalyzed condensations constitute major competitive reactions. In the attempted reaction with 2-benzylidene-indanone, a dimer was formed by a base-catalyzed aldol process.

The formation of the synthetically important mono- (I) and polyalkylidenecycloalkanes (II) has been achieved by a number of conventional procedures, primarily alcohol dehydration[2] and amine N-oxide[3] and carboxylate[4] pyrolyses. However, each of these procedures is limited in application and utility. Double bond migration has been commonly observed in both alcohol dehydrations[2] and amine N-oxide pyrolyses[3]; thus, dehydration of 1-benzylcyclopentanol leads to the predominant formation of 1-benzylcyclopentene rather than the *exo* isomer.[2a] The formation of II from alkylidenecycloalkanones by Grignard procedures is complicated by the occurrence of 1,4-additions. Although the pyrolysis of carboxylates is reported to proceed without double bond migration,[4a] aromatization often occurs at the high temperatures necessary for gas-phase pyrolyses.[4b] In an effort to develop a more generally applicable route for the formation of I and II, a study of the Wittig reaction[5] with cycloalkanones and benzylidenecycloalkanones has been carried out. The potential advantages of the Wittig reaction for these syntheses are the specific double bond placement observed with this reaction[5] and the ready availability of the starting ketones.

While no extensive study of the formation of I and II by means of the Wittig reaction has been carried out previously, a number of simple compounds of type I have been prepared by this procedure. Benzylidenecyclohexane,[6,7] methylenecyclopentane,[8] -heptane,[9] and -octane,[9] ethylidenecycloheptane,[10] and ethyl cyclohexylidene acetate[11] are representative examples. Although Wittig reactions have been carried out with a wide variety of α,β-unsaturated ketones,[5,12] only three isolated examples of 1,4-additions have been reported.[12-14] In the only reported example of a Wittig reaction with an alkylidenecycloalkanone, Inhoffen has shown that 2-methylenecyclohexanone undergoes 1,4-addition.[13] In the present study, benzylidenecycloalkanes were chosen as model compounds, since it was felt that the occurrence of 1,4-addition would be less likely than with simpler alkylidenecycloalkanones.

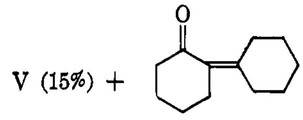
Results

Benzylidenecyclohexanes.—The results of the reactions of a number of cyclohexanones and benzylidenetriphenylphosphorane (III) are summarized in the following equations; unless otherwise noted, the phosphorane was generated by the action of ethanolic sodium ethoxide on benzyltriphenylphosphonium chloride in absolute ethanol.

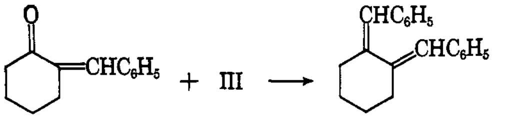


IV V (66%)[15]

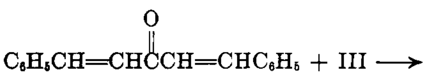
IV + III (n—C$_4$H$_9$Li generation) ⟶



VI (<1%)

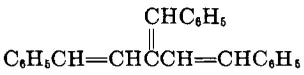


VII VIII (37.5%)



$$C_6H_5CH{=}CH\overset{O}{\overset{\|}{C}}CH{=}CHC_6H_5 + III \longrightarrow$$

IX



$$C_6H_5CH{=}CH\overset{CHC_6H_5}{\overset{\|}{C}}CH{=}CHC_6H_5$$

X (46%)[16]

In the reaction of XIII, triphenylphosphine oxide (70.4%) was isolated, indicating that a Wittig reaction had probably occurred; however, none of the anticipated product (XV) could be isolated by column chro-

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[1] This study was supported in part by a grant (G-11280) from the National Science Foundation.

[2] (a) E. L. Eliel, J. W. McCoy, and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1957); (b) H. J. Schaeffer and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 124 (1956).

[3] A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *ibid.*, **79**, 4729 (1957).

[4] (a) W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, **27**, 3476 (1962); (b) W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

[5] U. Schollkopf, *Angew. Chem.*, **71**, 260 (1959).

[6] G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955).

[7] U. Schollkopf, Dissertation Thesis, Tubingen, 1955; cited in ref. 5.

[8] C. H. Collins and G. S. Hammond, *J. Org. Chem.*, **25**, 1434 (1960).

[9] A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **84**, 3164 (1962).

[10] A. C. Cope and J. K. Hecht, *ibid.*, **85**, 1780 (1963).

[11] G. Fodor and I. T. Tomoskozi, *Tetrahedron Letters*, **16**, 579 (1961).

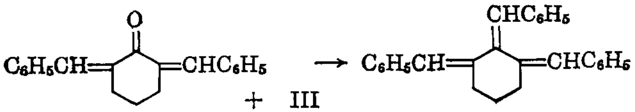
[12] F. Bohlmann, *Chem. Ber.*, **89**, 2191 (1956).

[13] H. H. Inhoffen, K. Bruckner, G. F. Domagk, and H. Erdmann, *ibid.*, **88**, 1415 (1955).

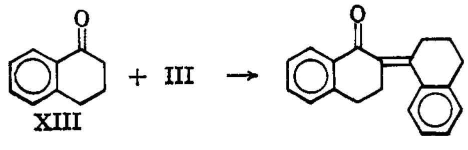
[14] J. P. Freeman, *Chem. Ind.* (London), 1254 (1959).

[15] Previously prepared by Wittig and Haag[6] in 60% yield by an identical procedure.

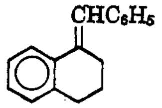
[16] Previously prepared by Bohlmann in unspecified yield by a Wittig procedure.[12]



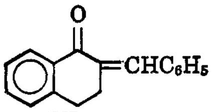
XI + III → XII (33.5%)



XIII + III → XIV (6.6%)



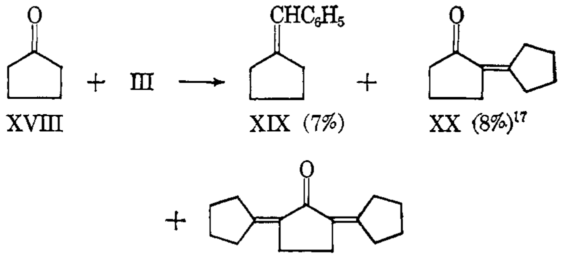
XV



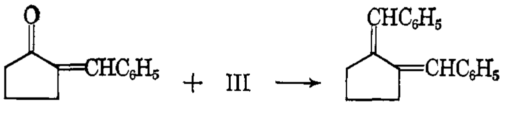
XVI

matography and no evidence for its formation was obtained. In addition to the phosphine oxide and recovered XIII, the condensation product (XIV) of XIII was the only material isolated. Attempted reaction of XVI and III led to the recovery of XVI; no evidence for the formation of the expected product, 1,2-dibenzylidenetetralin (XVII), was obtained.

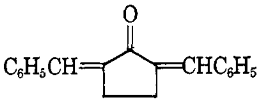
Benzylidenecyclopentanes.—In an attempt to prepare XXV, four separate reactions of III and XXIV



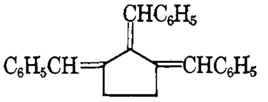
XVIII + III → XIX (7%) + XX (8%)[17] + XXI (21%)



XXII + III → XXIII (16.8%)



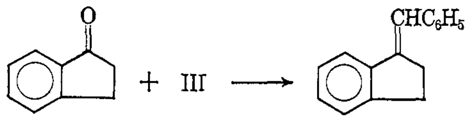
XXIV



XXV

were carried out using both sodium ethoxide and phenyllithium as bases for the generation of the phosphorane. In no case was any evidence obtained indicating the formation of XXV or triphenylphosphine oxide; only the starting phosphonium salt (37–47%) and XXIV (43–80%) were isolated. In each reaction, addition of III to XXIV led to the formation of a deep red solution indicating carbanion formation; an attempted trap of the carbanion by alkylation was unsuccessful.

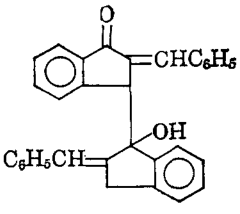
By analogy with the 1-tetralone (XIII) reaction, base-catalyzed condensation of XXVI was anticipated, but no 2-(1-indanylidene)indanone-1 was detected in the reaction products. XXVII had been previously reported as the product from the reaction of indene and



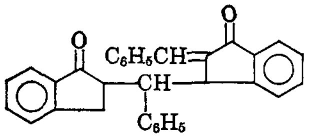
XXVI + III → XXVII (9.1%)

sodium benzylate in the presence of nickel in benzyl alcohol.[18]

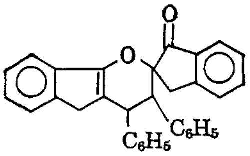
In the attempted formation of 1,2-dibenzylideneindane by reaction of III and 2-benzylideneindanone (XXVIII), the only product isolated (74–87%) was a dimer (XXIX) formed as a result of base-catalyzed self-addition of XXVIII. Elemental analyses and molecular weight determinations indicated the compound to be a simple dimer rather than any dehydrated product. Four dimeric structures were considered: the simple aldol (XXIXa), the Michael adduct (XXIXb), and two isomeric Diels–Alder or cyclized



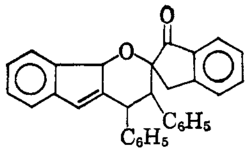
XXIXa



XXIXb



XXIXc



XXIXd

Michael adducts (XXIXc and d).[19] Evidence for the mode of formation of the dimer was obtained from its preparation in near quantitative yield by treatment of XXVIII with sodium hydride in refluxing glyme. Attempted dehydration of the dimer with iodine in refluxing xylene was unsuccessful; however, the failure of this reaction is not unexpected since there would be a marked steric barrier to the dehydration of XXIXa to the corresponding fulvalene.

Initial evidence favoring structures XXIXa, c, and d was obtained from the infrared spectrum of the dimer which showed a single unsplit carbonyl absorption at 1701 cm.$^{-1}$ (five-membered cyclic ketone[20]). Structure XXIXb would be expected to possess either a doublet or two carbonyl absorptions. The dimer was converted to its oxime which analyzed satisfactorily for a monooxime rather than the bisoxime to be expected from XXIXb; the infrared spectrum of the oxime lacked carbonyl absorption providing further support for the elimination of structure XXIXb. Weak absorption at 3580 cm.$^{-1}$ was also observed, but the band was not sufficiently strong to make more than a tentative hydroxyl (XXIXa) assignment. The carbonyl stretching frequency (1701 cm.$^{-1}$) observed for XXIX is significantly lower than that observed for 1-indanone (1722

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[17] The mixture of XIX and XX could not be separated by distillation, but the components were identified and estimated by quantitative g.l.c.

[18] S. S. Hirsch, D. H. Lorenz, and E. I. Becker, *J. Org. Chem.*, **23**, 1829 (1958).

[19] We are indebted to the referee for suggesting structures XXIXc and d for the dimer.

[20] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 148–149.

TABLE I

P.M.R. SPECTRA[a]

Compound	Chemical shifts (τ)			
	α-CH_2	β,γ-CH_2	Vinyl	Aromatic
V	7.75 m (3.9)	8.45 m (1.9)	3.80 s (1.0)	2.90 s (5.0)
	7.75 m (4.0)	8.50 m (2.0)	3.78 s (1.0)	2.86 s (4.9)[b]
VIII	7.42 m (4.0)	8.37 m (4.0)	3.43 s (2.0)	2.80 s (10.0)
XII	7.30 *t* (4.0)[c]	8.25 m (2.1)	3.72 s (0.9)	2.78 m (15.0)
			3.32 d (1.9)	
XIX	7.68 m (3.9)	8.47 m (3.9)	3.72 q (1.0)[d]	2.97 m (5.0)[b]
XXVII	6.97 m[e]	6.97 m (3.9)[e]	3.12 t (1.0)	2.75 m (9.2)
XI	7.13 t (4.0)	8.20 q (1.9)	2.33 t (2.0)	2.67 m (9.9)
XVI	7.05 m[e]	7.05 m (4.0)[e]	2.27 t (1.0)	2.69 m (8.9)
XXVIII	5.95 d (2.0)[f]	. . .	*g*	2.38 m (10.0)[h]
	6.05 d (2.0)[f]	. . .	*g*	2.60 m (10.0)

[a] All spectra were recorded in CCl_4 solution (saturated) unless otherwise noted. Relative integrated intensities are noted in parentheses. Peak structures are assigned as multiplets (m), singlets (s), doublets (d), triplets (t), and quintuplets (q); chemical shift values cited represent centers of absorption. [b] As neat liquid. [c] $J_{HH} = 7.0$ c.p.s. [d] $J_{HH} = 2.4$ c.p.s. [e] Methylenes (α- and β-) coincident. [f] Geminal $J_{HH} = 3.0$ c.p.s. [g] Vinyl hydrogens obscured by aromatic protons. [h] In acetone-d_6 solution.

cm.$^{-1}$),[21] but is similar to that observed for 2-benzylideneindanone (1697 cm.$^{-1}$),[21] supporting a tentative assignment of structure XXIXa and providing evidence against structures XXIXc and d.

The ultraviolet spectrum of XXIX showed maxima at 248 and 295 mμ (ϵ 25,200 and 4970). 1-Indanone absorbs at 243 mμ (ϵ 12,300),[21] while 2-benzylideneindanone absorbs at 227 and 318 mμ (ϵ 9850 and 22,500).[21] The observed spectrum is consistent with structures XXIXc and d, since it may be considered as a composite of the two isolated chromophores, 1-indanone and styrene (λ_{max} 244 mμ, ϵ 12,000). However, a molecular model of XXIXa indicates attainment of coplanarity of the benzylideneindanone system to be difficult because of bond oppositions with the hydroxyl function and the indanyl system. As a consequence of this disruption of coplanarity in the α,β-unsaturated ketone chromophore, XXIXa might be expected to show the observed absorption. Additionally, the longer wave length band (295 mμ) is consistent with structure XXIXa, but not with either XXIXc or d.

Unequivocal assignment of structure XXIXa to the dimer was provided by its proton magnetic resonance spectrum. In addition to a complex multiplet in the aromatic region (τ 2.0–2.7, relative intensity 19.9), signals at 7.91 (singlet, exchangeable), 5.93 (doublet, $J_{HH} = 3.0$ c.p.s.), and τ 4.68 (singlet) with relative intensities of 1.0:1.9:1.0 were observed. The intensities and chemical shift values for the three signals are consistent with their assignment as the hydroxyl, methylene, and methine protons, respectively, of XXIXa. A similar coupling constant was observed for the methylene protons in 2-benzylideneindanone (XXVIII). In XXIXa, the vinylic protons are obscured by the aromatic proton absorptions; in model structures such as XXVIII a similar shift of the vinyl proton into the aromatic region is observed. Markedly different and more complex proton spectra would be anticipated for both XXIXc and d. Structure XXIXc should show aromatic, methylene (two doublets), and methine (AB pattern) signals in the intensity ratio 18:4:2, while XXIXd should show aromatic plus vinyl, methylene (one doublet), and methine (AB plus singlet) signals with intensities 19:2:3. The observed spectrum is compatible with neither of these expectations and the dimer is consequently assigned structure XXIXa.

The physical properties of XXIXa agree with those reported for a compound obtained by the reaction of 1-indanone and benzaldehyde in the presence of alcoholic potassium hydroxide; no structure was given by the original workers, but the compound was considered to be a bisbenzylidene-1-indanone.[22]

The structures assigned to the olefins prepared in this study were substantiated by elemental analyses and infrared and ultraviolet spectra. In all cases, their proton magnetic resonance spectra were consistent with assigned structures. Integrated intensities for ring methylene protons and the absence of benzylic methylene absorptions showed the corresponding *endo* isomers to be absent, establishing specific double bond placement by these Wittig processes and lack of isomerization under the conditions of the reaction. The spectra of a number of representative compounds are summarized in Table I.[23]

Discussion

The results of this study indicate that the Wittig reaction can be applied with moderate success to the formation of I and II from cyclopentanones and cyclohexanones; the occurrence of base-catalyzed condensations of the starting ketones, particularly in the cyclopentanone series, constitutes a major limitation.

The study shows further that there is a marked difference in the behavior of five- and six-membered cyclic ketones towards III. Consistently higher yields of olefins are obtained in the cyclohexanone reactions and extensive condensation is observed only in the cyclopentanone reactions. This difference in behavior has not been reported previously in simple Wittig reactions with cycloalkanones but is readily explicable in terms of the known differences in the chemistry of these ketones and the accepted mechanism of the Wittig reaction; in particular, these results support the mechanistic conclusions of Speziale and Bissing.[24] The

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(21) A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).

(22) J. N. Chatterjea and K. Prasad, *J. Indian Chem. Soc.*, **34**, 375 (1957).

(23) A more detailed consideration of the proton spectra of these and related benzylidenecycloalkanones and -cycloalkanes with particular emphasis on couplings and *J*-values will be presented in a separate communication.

(24) A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 1888 (1963).

Wittig reaction is generally considered to proceed by the nucleophilic attack of the phosphorane carbon on the carbonyl group to produce an intermediate betaine which undergoes elimination of phosphine oxide to produce the olefinic product.[25] In this process, the carbonyl carbon atom undergoes two configurational changes: sp^2 (carbonyl) → sp^3 (betaine) → sp^2 (olefin). Speziale and Bissing[24] have shown recently that in the reactions of a stable phosphorane, carbomethoxymethylenetriphenylphosphorane, the formation of the betaine is rate determining and reversible and the second step, betaine decomposition, is rapid. Numerous previous studies have established the large differences in rates of addition to cyclopentanones and cyclohexanones[26] and have led to the generalizations of Brown[26a]; *i.e.*, an sp^2–sp^3 configurational change for a ring carbon is favored in cyclohexanones and opposed in cyclopentanones with the sp^3–sp^2 change favored in the latter ketones. The observed preference for reaction of III with cyclohexanones rather than cyclopentanones indicates that in this series, as in the reactions studied by Speziale, betaine formation is rate determining since the sp^2–sp^3 configurational change is involved in this step and is favored in cyclohexanones. If betaine decomposition (sp^3–sp^2 change) were rate determining, cyclopentanones would be expected to show a higher order of reactivity than cyclohexanones toward III. Thus, this study indicates that betaine formation may be rate determining in the reactions of unstable as well as stable[24] phosphoranes. No experiments designed to test the reversibility of betaine formation were carried out in this study.

As a partial test of this interpretation, the reaction of benzaldehyde and cyclopentylidenetriphenylphosphorane (XXX) was carried out; the expected olefin (XIX) was obtained in 34% yield as contrasted to the 7% yield obtained by the reaction of cyclopentanone and III. Since the cyclopentylidene carbon of XXX has a configuration intermediate between sp^3 and sp^2, betaine formation would be expected to be kinetically more favorable than in the cyclopentanone reaction.

The fact that the rate-determining step is kinetically slow in the reactions of cyclopentanones with III, in comparison with cyclohexanone reactions, provides an explanation for the base-catalyzed condensations observed in the former reactions. In the absence of any rapid consumption of ketone by betaine formation, either the basic phosphorane (III) or the strong base (sodium ethoxide, phenyllithium) used to generate III from the phosphonium salt could attack the α-hydrogen leading to anion formation and subsequent condensation. The reactions of cyclopentanone (XVIII) and cyclohexanone (IV) provide an excellent example of this competition. In the reaction of III with IV, betaine formation is rapid and only a small amount of condensation product is formed; in the reaction of III with XVIII, the slower rate of betaine formation leads to significant amounts of anion formation leading to condensation as the major process (80% of total products). The lack of reactivity of 2,5-dibenzylidenecyclopentanone (XXIV) can similarily be attributed to anion formation; the marked red color associated with anions was observed when this compound was treated with III or other bases. Schriesheim and co-workers have postulated that the facile formation of anions from cyclopentanes is due to the planarity of the ring system which allows a maximum p–π overlap in the transition state.[26c] In XXIV three trigonal ring carbons lead to a completely planar molecule and formation of the carbanion is facilitated. The lack of self-condensation of XXIV reflects the stability of the anion and the hindered nature of the carbonyl group. In the case of 2-benzylideneindanone (XXVIII), anion formation is facile since the methylene group is activated by both styryl and phenyl groups and the self-condensation proceeds readily since the carbonyl is less hindered than that of XXIV. No attempt to detect condensation products in the reaction of III with 2-benzylidenecyclopentanone was carried out, but in analogy with XXIV and XXVIII, it is probable that some anion formation occurs.

The lack of olefin formation and the extensive base-catalyzed condensation encountered with 1-tetralone (XIII) are anomalous; 1-indanone (XXVI), which would be expected to follow the general behavior of the cyclopentanones, gives 1-benzylideneindane and no condensation products. Other anomalous reactions of these ketones have been observed. Cook and Lawrence have shown that XIII undergoes self-condensation to produce XIV as the major product on treatment with cyclohexylmagnesium chloride,[27] and Coles and co-workers have shown that XIII polymerizes in the presence of trace amounts of nitrogen tetraoxide while XXVI forms the isonitroso ketone (50%) upon treatment with this reagent.[28]

The only other reported citation of base-catalyzed carbonyl reactions competing with normal Wittig reactions is contained in the recent work of Butler and co-workers.[29] The failure to obtain olefin formation in the reactions of *n*-butyraldehyde and 5-hexenal with simple ylides was attributed to competing aldol condensation of the aldehydes. Acrolein similarly failed to give a Wittig product, presumably because of its ability to undergo facile base-initiated polymerization.

Steric hindrance about the carbonyl group of the cyclic ketones apparently exerts little influence on the course of the Wittig reactions. Thus, both the mono- and dibenzylidene derivatives of cyclohexanone lead to the formation of the corresponding olefin in approximately equal yields, and benzylidenecyclopentanone forms the olefin in higher yield than does cyclopentanone. However, steric hindrance about the carbonyl group cannot be eliminated as a factor in promoting the competitive base-catalyzed condensations in the cyclopentanones.

The ultraviolet absorption spectra of mono- (V), 1,2-di- (VIII), and 1,2,3-tribenyzlidenecyclohexane (XII) showed the usual influence of steric disruption of coplanarity in conjugated systems, *i.e.*, shifts of absorption maxima to shorter wave lengths than observed in

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[25] For a summary of primary references regarding the mechanism of the Wittig reaction, see ref. 5 and 24.

[26] (a) H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956), and preceding papers; (b) A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *ibid.*, **79**, 4729 (1957); (c) A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962).

[27] J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 1431 (1936).

[28] H. W. Coles, R. H. F. Manske, and T. B. Johnson, *J. Am. Chem. Soc.*, **51**, 2269 (1929).

[29] C. F. Hauser, T. W. Brooks, M. L. Miles, M. A. Raymond, and G. B. Butler, *J. Org. Chem.*, **28**, 372 (1963).

coplanar model systems.[30,31] As anticipated, the spectrum of V (λ_{max} 244 mμ, ϵ 12,700) is nearly identical with that of styrene (λ_{max} 244 mμ, ϵ 11,700–12,000) indicating no deviation from coplanarity in the styryl system. As anticipated for the conjugated system, VIII absorbs at longer wave length (285 mμ, ϵ 19,000) than does V, but its absorption maximum has undergone a 47–51-mμ hypsochromic shift relative to coplanar model compounds (*trans*-1,4-diphenylbutadiene, λ_{max} 332 mμ[32]; 1,2-dibenzylidenecyclopentane, λ_{max} 336 mμ[33]). The positions of maximum absorption of VIII and 1-phenylbutadiene[30] are approximately the same, indicating that in VIII only one phenyl group is effectively conjugated with the diene system. Tribenzylidenecyclohexane (XII) absorbs at even lower wave lengths (275 mμ) than does VIII, indicating even greater deviations from coplanarity; the acyclic analog, β,β-distyrylstyrene, which presumably possesses a nearly planar structure has major maxima at 295 and 330 mμ.[12] Molecular models (Dreiding) of XII and VIII do not indicate any reasonable conformations in which phenyl–phenyl oppositions are absent and in which coplanarity is possible.

Experimental[34]

Benzylidenecyclohexane (V).—A solution of 20.0 g. (0.052 mole) of benzyltriphenylphosphonium chloride in 100 ml. of absolute ethanol was treated with 100 ml. of a 0.5 *M* solution of sodium ethoxide in ethanol with continuous stirring under an atmosphere of nitrogen; the orange color of the phosphorane (III) appeared immediately. After the solution was stirred for 10 min., 4.9 g. (0.05 mole) of cyclohexanone was added. The mixture was refluxed for 4 hr., cooled, and filtered; the filtrate was concentrated on a steam bath to precipitate unreacted phosphonium salt and sodium chloride. After removal of the precipitated salts, the filtrate was distilled to yield 2.06 g. (66%) of V, b.p. 117–121° (6 mm.), lit.[6] b.p. 124.5–126.5° (12 mm.). Extraction of the distillation residues with a chloroform-benzene mixture gave 3.4 g. (67%) of triphenylphosphine oxide. The ultraviolet spectrum of V had a maximum at 244 mμ (ϵ 12,700), lit.[6] λ_{max} 243 mμ (ϵ 12,900).

The preparation of V was repeated using the same molar quantities of phosphonium salt and cyclohexanone in benzene with *n*-butyllithium employed for the generation of III. After a 26-hr. reaction period, a yield of 16% of V was obtained by distillation, b.p. 88–95° (0.7 mm.). A sample of the distilled material was examined by g.l.c.[34]; two peaks (retention times of 60 and 69 min.) were observed and identified as V and cyclohexylidenecyclohexanone (XX),[35] respectively, by comparison with authentic samples. Quantitative g.l.c. showed 97% of V and 3% of XX. A small sample of XX was trapped from the g.l.c. effluent; the proton spectrum of this material showed methylene absorptions in the τ 7.0–8.5 region as the only observable signals. The absence of signals in the region normally associated with vinyl protons (τ 4.0–5.0 for trisubstituted olefins[36]) confirmed the structure as XX, eliminating the isomeric 2-(1-hexenyl)cyclohexanone and 2-cyclohexyl-2-cyclohexenone[35b] as structural possibilities.

1,2-Dibenzylidenecyclohexane (VIII).—A solution of 19.9 g. (0.05 mole) of phosphonium salt and 9.3 g. (0.05 mole) of 2-benzylidenecyclohexanone[37] in 100 ml. of 0.5 *M* ethanolic sodium ethoxide was refluxed for 22 hr.; the reaction mixture was quenched with 150 ml. of water and extracted with two 100 ml. portions of ether. The combined ether extracts were dried over magnesium sulfate and concentrated on a steam bath; trituration of the residues with 50 ml. of 95% ethanol led to crystallization of the product. VIII, 3.5 g. (37.5%), was purified by washing with 200 ml. of boiling ethanol and melted at 137.5°. Concentration of the filtrates and trituration with petroleum ether (b.p. 90°) yielded 7.2 g. (51%) of triphenylphosphine oxide.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 91.99, H, 8.03.

The ultraviolet spectrum of VIII showed a band at 285 mμ (ϵ 19,000) and VIII absorbed in the infrared ($CHCl_3$) at 1626 w, 1600 s, 1575 w, 1493 s, 1445 s, 1260 w, 1136 w, 1070 m, 1028 m, 971 w, 917 m–s, 838 m, and 820 w cm.$^{-1}$.

β,β-Distyrylstyrene (X).—This preparation was carried out in the same manner as that of VIII using 0.05 *M* quantities of phosphonium salt, dibenzylideneacetone, and sodium ethoxide in 100 ml. of ethanol and a reflux period of 12 hr. Isolation of the product in the same manner as for VIII gave 7.1 g. (46%) of crude X melting at 104–107°. X was recrystallized from 95% ethanol and dried under vacuum over sulfuric acid, m.p. 106–108°, lit.[12] m.p. 110°.

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.22; H, 6.57.

The ultraviolet spectrum of X showed maxima at 237, 299, and 331 mμ (ϵ 16,400, 29,800, and 29,900). Bohlmann[12] reports maxima at 234, 295, and 330 mμ (ϵ 20,900, 33,900, and 29,500).

1,2,3-Tribenzylidenecyclohexane (XII).—The reaction of 13.7 g. (0.05 mole) of 2,6-dibenzylidenecyclohexanone,[37] 0.05 mole of phosphonium salt, and 0.05 mole of sodium ethoxide in 100 ml. of ethanol was carried out at reflux for 18 hr. The product was isolated in the same manner as VII. XII was obtained in a crude yield of 33.5% (5.3 g.), m.p. 110–111°; recrystallization from 95% ethanol gave a constant melting point of 113.5–114.5°. The ethanolic mother liquors from the isolation and purification of XII gave 5.45 g. (42.3%) of triphenylphosphine oxide and 1 25 g. of the starting ketone.

Anal. Calcd. for $C_{27}H_{24}$: C, 93.06; H, 6.94. Found: C, 93.18; H, 7.05.

XII showed a maximum in the ultraviolet at 275 mμ (ϵ 27,800) and in the infrared had bands at 1629 w, 1600 m, 1574 w, 1495 s, 1445 m–s, 1145 w–m, 1124 w–m, 1073 m, 1029 m, 917 m–s, 873 m–s, 841 w, 769 w–m, 754 w–m, 725 w, and 698 s cm.$^{-1}$.

Attempted Synthesis of 1-Benzylidenetetralin (XV).—A mixture of 7.3 g. (0.05 mole) of 1-tetralone (XIII), 0.05 mole of phosphonium salt, and 0.05 mole of *n*-butyllithium in 70 ml. of anhydrous benzene was refluxed for 21 hr., cooled, and quenched with 150 ml. of water. The aqueous layer was extracted with 150 ml. of ether and the combined organic layers were dried over sodium sulfate, and concentrated on a steam bath. Trituration of the residues with ether and petroleum ether (b.p. 30–60°) gave 7.8 g. (70%) of triphenylphosphine oxide. The filtrate was treated with 95% ethanol which led to the precipitation of 0.45 g. (6.6%) of 2-(1-tetrylidene)tetralone-1 (XIV). The product was recrystallized from 95% ethanol to give a constant melting point of 133.0–133.5°, lit.[27] m.p. 130.0–130.5°. The ultraviolet spectrum was essentially identical with that reported[38] and XIV showed a strong band at 1669 cm.$^{-1}$ (α,β-unsaturated aryl ketone).

The reaction was repeated using a 5-hr. reaction period at room temperature and a 1-hr. reflux period. The only materials isolated were triphenylphosphine oxide (31%), XIV (4.4%), and unreacted XIII (17%). XIII was isolated by Florisil chromatography (elution with benzene) of the petroleum ether fractions.

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(34) All melting points are uncorrected; microanalyses were performed by Galbraith Laboratories. Infrared spectra were recorded on Perkin-Elmer Model 21 and Beckman IR-8 spectrophotometers; ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer using dilute solutions in 95% ethanol. G.l.c. analyses were carried out on an F and M Model 500 gas chromatograph using a 21-ft. Apiezon L (16.9% on Chromosorb W, 110-120 mesh) column at a column temperature of 200° and a helium flow rate of 24 ml./min. Proton magnetic resonance spectra were determined with a Varian Associates A-60 spectrometer; we are indebted to Dr. B. L. Shapiro and Miss M. Gordon for assistance in the determination of proton spectra.

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2-Benzylidenetetralone-1 (XVI).—A mixture of 5.30 g. (0.05 mole) of benzaldehyde and 7.20 g. (0.05 mole) of 1-tetralone was poured into 20 ml. of 80% sulfuric acid; after the reaction mixture was stirred for 1 hr., it solidified to a red mass which was triturated with ice-water and filtered to give 10.1 g. (87%) of XVI, m.p. 103.0–103.5°. Cromwell and co-workers[39] report a melting point of 107°; the ultraviolet and infrared spectra of X agreed with reported values.[39] Attempted preparation of X by the reported method[39] was unsuccessful.

Attempted Synthesis of 1,2-Dibenzylidenetetralin (XVII).—A mixture of 0.02 mole of 2-benzylidenetetralone (XVI), 0.02 mole of phosphonium salt, and 0.02 mole of ethanolic sodium ethoxide was refluxed for 3 hr. XVI (49% recovery) and triphenylphosphine oxide (19.5%) were the only materials isolated; no evidence for the formation of XIII was observed.

Benzylidenecyclopentane (XIX). A. Reaction of Cyclopentylidenetriphenylphosphorane (XXX) and Benzaldehyde.—A mixture of 20.5 g. (0.05 mole) of cyclopentyltriphenylphosphonium bromide,[40] 5.3 g. (0.05 mole) of benzaldehyde, and 0.05 mole of *n*-butyllithium in 110 ml. of anhydrous benzene was refluxed for 3 hr., cooled, and concentrated on a steam bath. Distillation of the residues gave 2.66 g. (33.8%) of XIX, b.p. 82–84° (1 mm.), lit.[41] b.p. 85–86° (1.9 mm.). XIX had a maximum at 256 mμ (ϵ 18,700) and bands in the infrared at 3058 w, 3030 w–m, 2950 s, 2865 m, 2833 w, 1616 w, 1592 w, 1481 w–m, 1439 m, 1422 w–m, 1070 w, 1025 w, 1010 w, 950 vw, 905 w–m, 732 m, and 690 s cm.$^{-1}$.

B. Reaction of Benzylidenetriphenylphosphorane (III) and Cyclopentanone (XVIII).—A mixture of 0.05 mole of phosphonium salt, 0.05 mole of XVIII, and 0.05 mole of *n*-butyllithium in benzene was refluxed for 19 hr., cooled, and quenched with water. The aqueous layer was extracted with ether and the combined organic layers were dried over sodium sulfate and distilled at 0.7 mm. to yield two fractions: A, b.p. 75–80°, 0.60 g.; B, b.p. 140–155°, 0.75 g. Fraction A was subjected to g.l.c. analysis which showed two peaks (retention times 41 and 51 min.) which were identified as cyclopentylidenecyclopentanone[42] (XX) and XIX, respectively, by comparison of their g.l.c. behavior with authentic samples. Quantitative g.l.c. analysis indicated fraction A to consist of 53% XX and 47% XIX, total yields 8 and 7%, respectively. Fraction B was identified as dicyclopentylidenecyclopentanone (XXI) by a comparison of its infrared spectrum with that of an authentic sample. The structures of XX and XXI were confirmed by their proton spectra which showed only methylene absorptions (τ 7.0–8.5); the absence of olefinic proton signals[36] eliminated the possibility of *endo* isomeric structures for these compounds.

1,2-Dibenzylidenecyclopentane (XXIII).—A mixture of 5.0 g. (0.031 mole) of 2-benzylidenecyclopentanone,[43] 0.031 mole of phosphonium salt, and 100 ml. of 0.31 *M* ethanolic sodium ethoxide was refluxed for 5 hr., cooled, and filtered to give 0.90 g. of XXIII. An additional 0.30 g. of XXIII was obtaind by concentration of the filtrate for a total yield of 1.20 g. (16.8%). XXIII was recrystallized from a mixture of benzene and hexane and melted at 157–159°, lit.[33] m.p. 153.4–156.1°. Concentration of the ethanolic filtrate and trituration with petroleum ether (b.p. 30–60°) yielded 3.8 g. (47.3%) of triphenylphosphine oxide. XXIII has maxima at 236 and 332 mμ (ϵ 9090 and 30,500), lit.[33] λ_{max} 336 mμ (ϵ 30,600).

Attempted Synthesis of 1,2,3-Tribenzylidenecyclopentane (XXV).—The reaction of 2,5-dibenzylidenecyclopentanone[44] and the phosphonium salt was attempted four times using both sodium ethoxide and phenyllithium as bases for the generation of III. The only material which was isolated was unreacted ketone (78–80%).

1-Benzylideneindane (XXVII).—A mixture of 6.6 g. (0.05 mole) of 1-indanone (XXVI), 0.05 mole of phosphonium salt, and 0.05 mole of *n*-butyllithium in 70 ml. of benzene was refluxed for 23 hr., cooled, and quenched with water. The aqueous layer was extracted with 100 ml. of ether and the combined organic layers were dried over sodium sulfate and concentrated on a steam bath. Trituration of the residue with petroleum ether (b.p. 30–60°) gave 6.25 g. (45%) of triphenylphosphine oxide. The filtrate was concentrated and triturated with hot 95% ethanol to give XXVII, 0.94 g. (9.1%); XXVII was recrystallized from 95% ethanol, m.p. 73.0–74.5°, lit.[18] m.p. 73.4–74.4°.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.17; H, 6.84. Found: C, 93.29, 93.07; H, 6.80, 6.74.

The reaction was repeated with a reflux time of 1 hr. After removal of triphenylphosphine oxide, the petroleum ether soluble material was chromatographed carefully on a Florisil column. The only materials isolated were XXVII (3%) and the phosphine oxide (13.6%) by elution with benzene and acetone, respectively.

2-Benzylideneindanone (XXVIII).—A mixture of 1.06 g. (0.01 mole) of benzaldehyde and 1.49 g. (0.011 mole) of 1-indanone was treated with 14 ml. of 80% sulfuric acid. The reaction mixture solidified to a brown mass after stirring for 30 min.; trituration with ice-water and filtration gave 1.65 g. (75%) of XXVIII, m.p. 106–109°, lit.[21] m.p. 109–111°. The ultraviolet spectrum of XXIII is identical with that reported.[21] The compound has previously been prepared by basic catalysis,[21] but consistently better results were obtained in the present study with the sulfuric acid catalyst.

Attempted Synthesis of 1,2-Dibenzylideneindane. Formation of 3-(1-Hydroxy-2-benzylidene-1-indanyl)-2-benzylideneindanone-1 (XXIXa).—A mixture of 5.50 g. (0.025 mole) of XXVIII, 0.025 mole of phosphonium salt, and 100 ml. of 0.25 *M* ethanolic sodium ethoxide solution was stirred at room temperature for 2 hr.; during this period the characteristic orange color of IV faded to yellow. The reaction mixture was quenched with 48% hydrobromic acid and was extracted with 100 ml. of chloroform. Concentration of the chloroform extract gave 4.60 g. (84%) of XXIXa, m.p. 214–221°. XXIXa was recrystallized from absolute ethanol to a constant melting point of 228–233°.

Anal. Calcd. for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49; mol. wt., 440. Found: C, 86.55, 86.65; H, 5.48, 5.57; mol. wt., 458, 468, 453.[45]

The dimer had maxima at 248 and 295 mμ (ϵ 25,200 and 4970), a shoulder at 290 mμ (ϵ 4810), and a minimum at 276 mμ (ϵ 3070). XXIX showed bands in the infrared at 3058 w, 3030 w, 3003 w–m, 2933 w–m, 1701 s, 1600 m, 1582 sh, 1490 w, 1460 w–m, 1449 w–m, 1422 w, 1323 w–m, 1280 m, 1149 w, 1116 w, 1107 w, 1010 w, 952 w, 908 w, 875 w, 762 m, 725 m, and 702 m cm.$^{-1}$ ($CHCl_3$); 3580 cm.$^{-1}$ (KBr).

XXIXa was converted to its **oxime** by refluxing a mixture of 1 g. of XXIXa, 4 g. of potassium hydroxide pellets, and 1 g. of hydroxylamine hydrochloride in 80 ml. of 95% ethanol for 2 hr.; the mixture was filtered while hot and acidified with 10% hydrochloric acid to precipitate the oxime. After recrystallization from glacial acetic acid, the oxime of XXIX melted at 266–268°. Its infrared absorption spectrum showed the absence of any carbonyl absorption.

Anal. Calcd. for $C_{32}H_{25}NO_2$ (oxime of XXIXa): C, 84.37; H, 5.53; N, 3.08. Calcd. for $C_{32}H_{26}N_2O_2$ (bisoxime of XXIXb): C, 81.67; H, 5.57; N, 5.95. Found: C, 84.02, 84.15; H, 5.69, 5.74; N, 2.69, 2.77.

XXIXa was also prepared by refluxing a 1:1 molar mixture of XXVIII and sodium hydride in glyme for 24 hr. The product separated when the reaction mixture was quenched with water; XXIXa was collected and recrystallized from 95% ethanol, m.p. 226–228° (99.5%). The material was identical in all respects with that prepared previously.

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