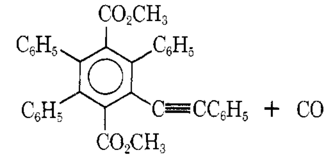
also indicated that II was the predominant species; the very weak resonances expected for III could not be discerned. In the solid state, a complex infrared absorption pattern indicated a variety of carbonyl groups. Medium and strong bands at 1703 and 1719 cm^{-1} could be ascribed to the ring carbonyl[1] and ester carbonyl,[3] respectively, in II, while absorptions at 1742, 1738, 1719, and 1675 cm^{-1} were within the expected ranges for the bridged carbonyl, saturated esters, unsaturated ester, and cyclopentenone, respectively, in III.

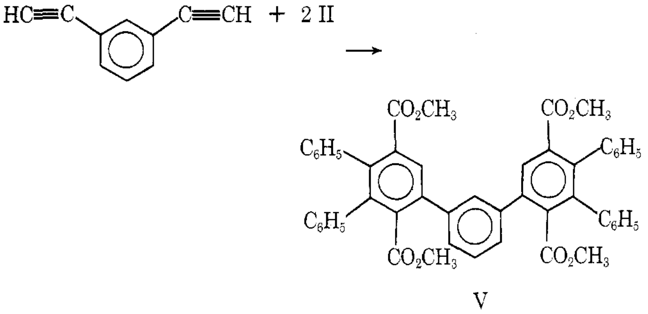
Most 3,4-diarylcyclopentadienones exist in the dimeric state at 25° if substituents in the 2 and 5 positions are small, whereas they are monomeric if the 2 and 5 substituents are bulky.[1] Apparently, the predominantly monomeric nature of II is due to the added resonance stabilization afforded by the ester groups and to the moderate extent of their steric bulk.

The intermediate reactivity toward dimerization is reflected in the reactivity of II with acetylenes. With diphenylbutadiyne the monoadduct IV was isolated in 70% yield. The reaction temperature of 180° was almost 50° lower than the temperature normally used for tetraphenylcyclopentadienone,[4] yet 50° above the temperature needed for 2,5-dimethyl-3,4-diphenylcyclopentadienone.[5]



IV

The formation of a diadduct is illustrated by the addition to *m*-diethynylbenzene to furnish the tetraester V in 65% yield.



V

Experimental Section

All melting points were measured on a Leitz hot-stage microscope and are uncorrected: ^1H nmr spectra were measured in $CDCl_3$ *vs.* TMS; ^{13}C nmr spectra were measured in acetone-d_6 *vs.* TMS.

2,5-Dicarbomethoxy-4-hydroxy-3,4-diphenylcyclopenten-2-one (I). Benzil (21.0 g, 0.1 mol), dimethyl acetonedicarboxylate (Aldrich Chemical Co., 17.4 g, 0.1 mol), and potassium hydroxide (1.0 g) in 250 ml of ethanol under nitrogen were stirred for 20 hr at 25° and then poured into water. The crystals which formed were collected on a filter, washed with water, and dried: weight 26.0 g (71%); mp (recrystallized from benzene) 136-140°; nmr of I δ 3.80 and 3.81 (OCH_3's), 5.07 (OH), 7.33 (complex multiplet, aryl H's); the δ 5.07 peak and two peaks corresponding to partial enolization of the ring H at δ 3.23 (0.1 H) and 3.88 (0.9 H) disappeared when exchanged with D_2O.

Anal. Calcd for $C_{21}H_{18}O_6$: C, 68.8; H, 5.0. Found: 69.2; H, 4.9.

Compound I was also prepared in methanol; however, the yield was lower (66%) and the work-up initially led to oils.

2,5-Dicarboxymethyl-3,4-diphenylcyclopentadienone (II). Compound I (22 g, 0.06 mol) was added at 25° to 40 ml of acetic anhydride containing 3 drops of concentrated sulfuric acid. The mixture was heated with stirring until the solid dissolved and then allowed to stand for 0.5 hr without additional heating. The solution was added to 450 ml of water with stirring. When the crystals had settled they were filtered off, washed thoroughly with water, and dried at 50° (10 Torr). Orange crystals, weight 20 g (98%), were obtained: mp 162-167° (recrystallized from acetic acid, mp 162-164°); ^1H nmr δ 3.75 (OCH_3), 6.92-7.33 (complex multiplet, ArH's); very weak resonances of equal intensity from III were noted at δ 3.38, 3.51, 3.81, and 3.83; ^{13}C nmr δ 51.4 (CH_3), 118.6 (C-2), 126.7 (C-3), 126.8, 128.0, 129.2, and 130.0 (phenyl C's), 161.5 and 161.7 (carbonyls); ir (KBr) 1742 (s, shoulder), 1738 (s), 1719 (s), 1703 (m), 1675 cm^{-1} (w); uv (EtOH) λ_{max} 292 nm (ϵ 13,500), 360 (1220); mass spectrum *m/e* 348 (rel abundance 100).

Anal. Calcd for $C_{21}H_{18}O_5$: C, 72.4; H, 4.6. Found: C, 72.0; H, 4.5.

Dimethyl 2,3,5-Triphenyl-6-phenylethynylterephthalate (IV). A mixture of II (1.74 g, 0.005 mol) and diphenylbutadiyne (1.01 g, 0.005 mol) was heated with an oil bath at 180° for 2 hr. The melt was cooled to 80° and ethanol was added with stirring. The crystalline product was filtered off, washed with ethanol, dried, and then recrystallized from chloroform: yield 1.82 g (70%); mp 209-210°; nmr δ 3.20 (4-carbomethoxy), 3.63 (1-carbomethoxy), 7.17 (complex multiplet, 2,4 and 5 phenyl H's), 7.33 (phenylethynyl).

Anal. Calcd for $C_{34}H_{26}O_4$: C, 82.7; H, 5.0. Found: C, 82.5; H, 5.0.

2,2'',5,5''-Tetracarbomethoxy-3,3'',4,4''-tetraphenyl-*m*-terphenyl (V). *m*-Diethynylbenzene (0.63 g, 0.005 mol) was added dropwise to a solution of II (3.48 g, 0.01 mol) and 10 ml of Arochlor 1221 (chlorobiphenyl, Monsanto) at 200° over a 3-min period. After 10 min, gas evolution had ceased and the reaction mixture was cooled to 100°. Hexane was added to the viscous mixture. After cooling to 25°, crystals formed which were filtered off and washed with hexane: weight 2.5 g (65%); recrystallized from benzene-methanol (1:4), 2.0 g; mp 201-202°; nmr δ 3.27 and 3.50 (methyl H's), 7.00 (2,2'',5,5''-phenyl H's), 7.35 (3' and 4' H's), 7.48 (6'-H), 7.73 (6 and 6'' H's).

Anal. Calcd for $C_{50}H_{38}O_8$: C, 78.3; H, 5.0. Found: C, 78.0; H, 5.1.

Registry No.—I, 16691-78-4; II, 16691-79-5; III, 16691-80-8; IV, 51175-84-9; V, 51175-85-0; benzil, 134-81-6; dimethyl acetondicarboxylate, 1830-54-2; diphenylbutadiyne, 886-66-8; *m*-diethynylbenzene, 1785-61-1.

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(2) W. Ried and D. Freitag, *Chem. Ber.*, **99**, 2675 (1966); W. Ried and K. Bonnighausen, *ibid.*, **93**, 1769 (1960).
(3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, pp 181-182.
(4) M. A. Ogliaruso and E. I. Becker, *J. Org. Chem.*, **30**, 3354 (1965).
(5) Heating the dimer of 2,5-dimethyl-3,4-diphenylcyclohexadienone with diphenylbutadiyne at 130° produced the monoadduct, 2,5-dimethyl-3,4,6-triphenyltolane, in 92% yield: D. M. White, unpublished results.

Reaction of Phosphorus Tribromide with a Conjugated Ketone. Locked Conformations in Acyclic Molecules

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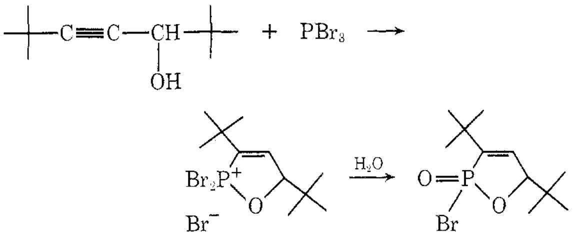
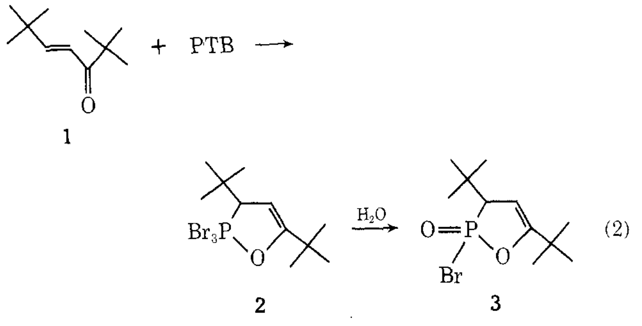
In connection with our recent findings[1] that certain propargyl alcohols react with phosphorus tribromide (PTB) to yield phosphorus-oxygen heterocycles and related compounds (eq 1), we attempted to enter isomeric manifolds

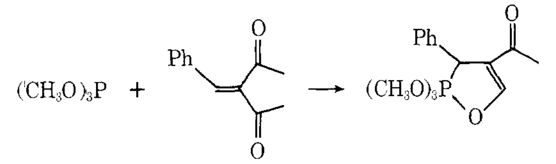


(1)

through the reaction of PTB with conjugated ketones (eq 2).



Reactions similar to eq 2 are not without precedent. Triethyl phosphite is known to react with 3-acetyl-4-phenyl-3-buten-2-one to yield an oxaphospholene.[2]



Similar reactions involving phosphorus trichloride (PTC) and related compounds have been sporadically reported over the last 55 years.[3] We have, however, been unable to locate reports of such reactions using PTB.

At least three mechanistic alternatives can be advanced for the cycloaddition of phosphorus(III) compounds to conjugated ketones: concerted (symmetry-allowed) 1,4-chelatropic addition (eq 3), preliminary nucleophilic attack by phosphorus at the β position of the enone, followed by cyclization (eq 4), or attack by phosphorus at the carbonyl carbon with subsequent rearrangement and ring closure (eq 5).[4] The relative favorability of each mechanism would depend on the steric requirements at the various sites of nucleophilic attack on the substrate, as well as on the nature of X, its steric bulk, and its nucleophilicity-increasing electronic effects. Because bromine is larger, slightly less electronegative, and a better leaving group (important during hydrolysis) than chlorine, it was of interest to determine if PTB functioned as well as PTC in such chelatropic reactions.

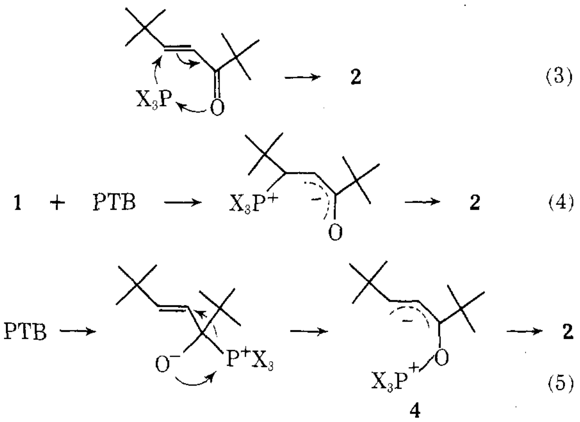
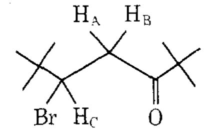


Table I
Best Fit Spectral Data for the ABC System of 5

ω, Hz[a]	$\|J\|$, Hz
H_A 162.9 ± 0.2	AB 17.7 ± 0.2
H_B 195.3 ± 0.2	AC 1.85 ± 0.23
H_C 262.9 ± 0.1	BC 9.96 ± 0.22

[a] Downfield from internal TMS at 60 MHz, carbon tetrachloride solution, ambient temperature.

When *trans*-2,2,6,6-tetramethyl-4-hepten-3-one (1) was allowed to react with a 15% excess of PTB in ether, a single crystalline product could be isolated after aqueous work-up. Its mass spectrum and elemental analysis (Experimental Section) indicated a molecular formula of $C_{11}H_{21}OBr$, resulting formally from the addition of HBr to . The isolated yield was 55%. The infrared spectrum of the product was unexceptional, save for an intense carbonyl absorption at 1715 cm^{-1}. Its pmr spectrum, however, was extremely interesting (Figure 1). In addition to two nine-proton *tert*-butyl singlets (δ 1.08 and 1.13), there appeared three four-line multiplets (one proton each) resembling the spectrum of an ABC (or ABM) system. Computer simulation of the observed spectrum (LAOCOON III) provided the exact parameters shown in Table I. The only structure consistent with the *chemical shifts* is 5-bromo-2,2,6,6-tetramethyl-3-heptanone (5), a new compound. However, this assignment requires that geminal protons H_A and H_B are anisochronous to the extent of 0.54 ppm, one of the largest geminal proton chemical shift nonequivalences to be observed in an acyclic system.[5,6] Certainly it is the chirally substituted C_5 which renders H_A and H_B diastereotopic; yet the magnitude of the effect suggests that other factors also contribute. An accurately scaled CPK space-filling molecular model of 5 provides an explanation. A representation of this is shown in C_4–C_5 Newman projection 6. One finds that the steric bulk of



5

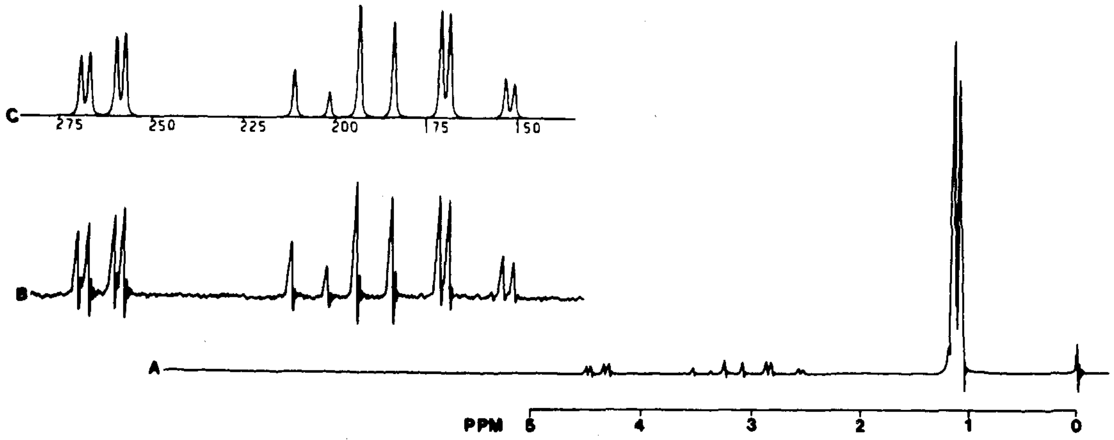
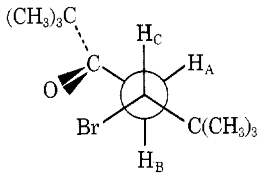


Figure 1. Pmr (60 MHz) spectrum of 5: (A) sweep width 500 Hz; (B) sweep width 250 Hz, increased amplitude, zero offset; (C) spectrum simulated with values in Table I.



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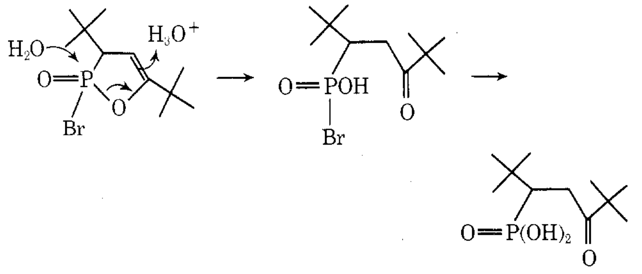
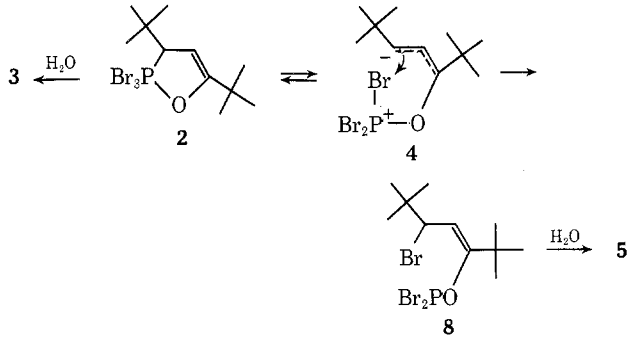
the bromine atom and the front *tert*-butyl group prevent all but the most limited rotation around the C_4–C_5 single bond (and to lesser extents, the rotation around the C_3–C_4 and C_5–C_6 bonds). Further, the model suggests that the preferred conformation is almost perfectly staggered, and may be essentially static. Evidence to support this conclusion can be adduced from the magnitudes of J_{AC} and J_{BC} (1.85 and 9.96 Hz, respectively) as would be expected for fixed dihedral angles of *ca.* 59 and 180°,[7] which are not affected by rotational averaging. Moreover, the ordering of the coupling constants requires that the higher field geminal proton (H_A) must also be the one more isolated from the deshielding influence of the bromine atom, as shown in **6**. This might have been predicted for a proton essentially s-trans to the bromine. Analogous arguments, invoking single conformations in certain acyclic molecules, have been advanced to explain the unusually large geminal chemical shift nonequivalence and long-range coupling constants in compounds bearing several halogen atoms and methyl groups.[6]

Compound **5** can arise in at least two ways. The most obvious is the Markovnikov addition of HBr, liberated from the partial hydrolysis of PTB, to **1**. Indeed, the reaction of **1** in ether with gaseous HBr provided **5** in virtually quantitative yield. However, even when carefully dried reagents and solvent were used, and aqueous work-up omitted, the pmr spectrum of the crude product showed that 40–75% (variations from different runs) of the material was **5**. The remainder of the crude product mixture was another compound which exhibited *tert*-butyl singlets at δ 1.13[8] and 1.20, as well as doublets of doublets at δ 2.75[8] (J_{HH} = 3.5, J_{PH} = 15.5 Hz) and 5.24 (J_{HH} = 3.5, J_{PH} = 38.7 Hz), exactly as would be expected[1,2] for heterocyclic structures such as **2** or **3**. Isolation by centrifugal removal of undissolved **5** provided an oil whose pmr spectrum matched the one above (integration ratio 9:9:1:1, respectively), while its ^{31}P nmr spectrum (δ −53.0, J_{PH_1} = 38.5 ± 0.5, J_{PH_2} = 15 ± 1 Hz) and ir and mass spectra (Experimental Section) provided compelling evidence for structure **3**. Not unexpectedly, **3** was fairly sensitive toward hydrolysis, and its yield was strongly affected by the nature of the work-up. Hydrolysis of **3** presumably involves ring opening to ketone **5** (*vide infra*) and/or acid **7**, as shown by the slow increase in an infrared band at 1710 cm^{-1}. Such hydrolytic instability has been previously noted in the case of related chloro compounds,[9] whereas the heterocyclic double bond isomer shown in eq 1 is much more stable toward hydrolysis.[1] The ease of hydrolytic ring opening of **3** must derive from both the increased basicity of C_4 (owing to resonance with the oxygen lone pairs) and to the heat of formation of the carbon-oxygen double bond.



7

The isolation of **3** and inability to suppress formation of **5** suggest that both may arise from a common mechanistic path. The most economical interpretation of our results would simply involve the formation of **4** (eq 5), which could then be partitioned between **2** and enol phosphite **8** (expected to be even more hydrolytically reactive than **2** or **3**, since it is noncyclic).



Clearly, PTB is at least as effective as PTC in these oxaphospholene-forming reactions. Whether **2** arises exclusively from **4** (eq 5), or whether it is formed independently (eq 3 or 4) and serves as the *source* of **4**, is not yet clear. Reactions 4 and 5 both require nucleophilic attack at neopentyl-like centers, and this should be retarded for a nucleophile as large as PTB. Further work to clarify these points is underway.

Experimental Section

General. The instruments and methods used in this study were exactly similar to those previously described.[1] Microanalyses were performed by Chemalytics, Tempe, Ariz. PTB was distilled immediately before use, bp 169–169.5° (729 mm).

Reaction of 1 with HBr. Gaseous HBr was bubbled gently through a solution of 0.40 g (2.4 mmol) of 1[10] in 20 ml of ether at 0° for 1 hr. The solvent was removed *via* rotary evaporation, leaving 0.61 (100% crude yield) of crystalline material: mp 73.0–74.5° after recrystallization from heptane and sublimation at 70° (1 mm); mass spectrum (70 eV) *m/e* 248 and 250 ($M\cdot^+$),[11] 169 (M − Br, 22%), and 57 [base peak, $(H_3C)_3C^+$]; ir (chloroform) 2970 (vs), 1715 (vs), 1480 (s), 1395 (m), 1370 (s), 1295 (m), 1240 (m), 1155 (m), 1088 (s), 1058 (m), 993 (m), 940 (m), 920 (m), 862 (m), 790 (vs), 653 cm^{-1} (m). The pmr spectrum is described in the text.

Anal. Calcd for $C_{11}H_{21}OBr$: C, 53.01; H, 8.50. Found: C, 52.90; H, 8.74.

Reaction of 1 with PTB. Dry argon was bubbled through a solution of 965 mg (3.57 mmol) of PTB in 50 ml of dry ether. Over a period of 15 min a solution of 563 mg (3.35 mmol) of **1** in 30 ml of ether was added dropwise. Stirring was continued at room temperature for 14 hr, with the argon flow rate maintained at *ca.* 2 ml/sec. A 1-ml aliquot was removed and evaporated, and the semisolid product was examined by pmr (ratio of **3**:**5** 1.0:1.0).[12] To the remaining solution was added 320 mg (4 mmol) of pyridine in 1 ml of water. The hydrolysis was exothermic, and the initially milky suspension clarified after stirring for 15 min. The aqueous phase was separated, and the ether phase was washed with 5 ml of water. The combined aqueous phases were extracted with 5 ml of ether, and then the combined ether solutions were dried over molecular sieve. Rotary evaporation left 968 mg (including aliquoted material) of a pale yellow semisolid, still exhibiting the 1:1 composition (106% crude yield). The most satisfactory separation[13] of **3** from **5** was accomplished by transfering the crude product mixture to a Craig tube and allowing it to sit at −20° overnight. The tube was centrifuged and the liquid portion was transferred to another Craig tube. The remaining solid was **5**, which could be purified as described above. Two more cycles of the cooling–centrifugation sequence provided **3** as a pale yellow oil containing *ca.* 5% of **5**. Distillation (60°, 0.1 mm) left the oil unchanged. The isolated yields were a function of the purity desired, and normally fell near 25% for 95% pure **3**, and 40% for >99% pure **5**; total isolation was 65% based on starting ketone.[14] Spectral data for **3** follow: mass spectrum (70 eV) *m/e* (rel abundance)[15]

297,* 295* (0.1, 0.1), 240,* 238* (10, 10), 225,* 223* (3, 3), 193, 191 (8, 8), 168 (17), 159* (7), 111* (100), 97* (5), 95* (4), 93* (9), 85 (25), 83 (18), 69 (8), 57 (38); ir (carbon tetrachloride) 2960 (s), 1665 (m), 1490 (w), 1480 (w), 1380 (w), 1272 (m), 1245 (s), 1065 (m), 860 (vs), 690 (m), 610 (w), 550 cm^{-1} (m). The ^{1}H and ^{31}P nmr spectral data for **3** are described in the text.

Acknowledgment. We appreciate the constructive criticisms offered by one of the referees. E. R. K. has been an NSF Trainee, 1970-present. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No.—**1**, 20859-13-6; **3**, 51270-67-8; **5**, 51270-68-9; HBr, 10035-10-6; PTB, 7789-60-8.

References and Notes

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(2) F. Ramirez, O. P. Madan, and S. R. Heller, *J. Amer. Chem. Soc.*, **87**, 731 (1965).

(3) See, for example, R. G. Harvey and E. R. DeSombre, *Top. Phosphorus Chem.*, **1**, 92 (1964); J. A. Miller in "Organophosphorus Chemistry," Vol. 3, The Chemical Society, London, 1972, p 44 ff; L. R. Drake and C. S. Marvel, *J. Org. Chem.*, **2**, 387 (1937), and the series of papers by J. B. Conant cited therein.

(4) This path resembles the Perkow reaction as described by I. J. Borowitz, S. Firstenberg, G. B. Borowitz, and D. Schuessler, *J. Amer. Chem. Soc.*, **94**, 1623 (1972).

(5) An excellent and detailed discussion of the general phenomenon of geminal chemical shift nonequivalence can be found in G. Binsch, *et al.*, *J. Amer. Chem. Soc.*, **95**, 175, 182, 190 (1973).

(6) To our knowledge, the only larger value was 0.6 ppm as exhibited by 1,3-dichloro-2,3-dimethylbutane: F. Schweinsberg and J. G. Traynham, *Tetrahedron Lett.*, 3809 (1970).

(7) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(8) Part of this absorption overlapped with peaks due to **5**. Locations of such lines were initially inferred from anomalous intensities.

(9) See, for example, J. B. Conant and A. A. Cook, *J. Amer. Chem. Soc.*, **42**, 830 (1920).

(10) W. Rundel, *Chem. Ber.*, **102**, 374 (1964); mp after sublimation (40°, 15 mm) 43–44°.

(11) $[M + H]^+$ peaks three times as intense as the parent ions were observed at *m/e* 249 and 251.

(12) Any variation in conditions (*e.g.*, omission of argon, more concentrated or moist solutions, etc.) which permits the buildup of HBr provided product mixtures richer in **5**, sometimes to the virtual exclusion of **3**. Another fascinating feature of this reaction, as well as those described earlier,[1] is the inability to suppress the hydrolysis of (presumed intermediate) **2** to **3**. Even under strictly anhydrous conditions without aqueous work-up, **3** was the sole heterocyclic product observed.

(13) Compounds **3** and **5** are similar enough in volatility that sublimation (0.60 mm and 40°) provides a mixture only slightly enriched in **5** (up to 65% from 50%). Nor were any chromatographic techniques, including tlc, elution, or glc, found that would allow **3** to survive.

(14) Although we have not been able to directly substantiate this by mass balance, it seems that, during the purification of **3**, the amount of **5** recovered at each stage exceeds the decrease of **5** observed in the oil. This would support the assertion that **3** can decompose to **5**, *via* an intermediate similar to **4**.

(15) Asterisks mark the peaks common to derivatives of the isomeric ring system shown in reaction 1. The appearance of weak $[M + H]^+$ ions, rather than M^+, seems to be a characteristic of these systems.[1] A single peak at *m/e* 281 (4), overlapping the $[M - CH_3]$ doublet, suggests the presence of a higher molecular weight impurity.

A General Indene Synthesis *via* Cyclization of Phenyl-Substituted Allylic Cations

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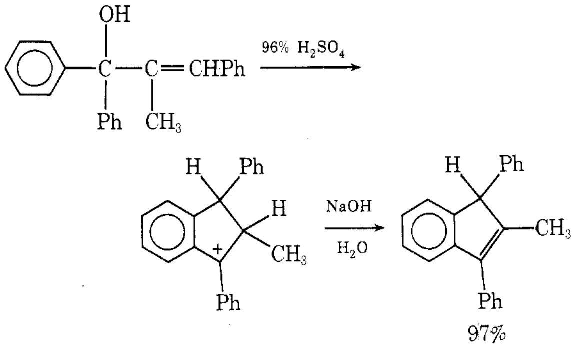
Received January 23, 1974

Indenes have been prepared by a number of cyclialkylation procedures, such as dehydration of phenyl-substituted diols and reaction of phenyl-substituted alkenes with phosphorus halides.[1-3] Recently, the reaction of *gem*-dihalocyclopropanes with benzene and aluminum chloride was used.[4] These procedures are of limited scope; so indenes have generally been prepared by treating Grignard or lithium reagents with an appropriate indanone followed by dehydration of the resulting indanol. The required indanones have usually been prepared by cyclization of β-phenyl-substituted carboxylic acids resulting from Reformatsky, Perkin, or Friedel–Crafts routes.[5,6] Overall, these routes consist of several steps with low overall yields and only moderate flexibility for the preparation of substituted derivatives.

Recently, we reported the generation of indanyl cations by dissolving phenyl-substituted allylic alcohols, of wide variety, into strongly acidic media (*i.e.*, FSO_3H, H_2SO_4, etc.).[7] Initially, acyclic allylic cations are formed. These then cyclize to give indanyl cations in the acidic media.[7] We have found that solutions of indanyl cations give good yields of the corresponding indenes when quenched into excess aqueous base. This fact, and the ease with which a variety of phenyl-substituted allylic alcohols can be prepared, make this indene synthesis a general and efficient procedure. A typical example is the cyclization of 1,1,3-triphenyl-2-methylpropenol to 1,3-diphenyl-2-methylindene in high yield (eq 1).



(1)

This method has several advantages over techniques employed previously. First, the overall yields are improved. Second, desired substitution at carbons 1, 2, and 3 is easily achieved in a few steps. For example, phenyl-substituted allylic alcohols in wide variety can be conveniently prepared by aldol condensation followed by treatment of the resulting α,β-unsaturated ketone with Grignard or lithium reagents. Alternatively, reaction of vinyl Grignard reagents with appropriate aldehydes or ketones give allylic alcohol precursors. These routes are outlined in Scheme I.

Scheme I

$$\begin{tikzcd} R_5R_4C{=}CR_3Li(MgX) + R_2COR_1 \arrow[r] & R_5R_4C{=}CR_3C(OH)R_2R_1 \\ R_5COR_4 + R_3CH_2COR_2 \arrow[r, "\text{base}"'] & R_5R_4C{=}C(R_3)COR_2 \arrow[u, "\text{hydride reduction}", "\text{or } R_1Li(MgX)"'] \end{tikzcd}$$

Another advantage of this method is that the indanyl cations can be directly observed by nmr spectroscopy, allowing one to monitor the cyclization. Also, some indanyl cations further rearrange in solution when the temperature is raised.[8] This allows two possible indenes to be generated from the same precursor alcohol simply by choosing the temperature the acid solution is permitted to reach before quenching (for examples see Scheme II).

A few cases of indenes prepared by allylic cyclodehydration, presumably *via* transient indanyl cation intermediates, have appeared.[9,10] Bergman obtained an unspecified amount of 1,2-diphenylindene on treatment of 1,2,3-triphenylpropenol with dilute sulfuric acid followed by distillation.[9] Similarly, Koelsch converted 1,1,2,3,3-penta-