After the addition of 100 ml of water the reaction solution was extracted with chloroform. The chloroform extracts were dried and rotoevaporated. The residue was distilled under reduced pressure.

3-Methoxy-10-methylbicyclo[7.2.0]undec-1-en-11-one (II). The methoxy substitution product was distilled at 83–85° (0.005 mm): yield 80%; ir 1760 (C=O) and 1660 cm^{-1} (C=C); nmr δ 1.2 (d, 3 H), 1.5 (m, 11 H), 3.2 (s, 3 H), 3.4 (m, 1 H), and 5.6 (m, 2 H).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 75.00; H, 9.62. Found: C, 74.68; H, 9.58.

4-Isopropylidene-2-methoxy-2,3,3-trimethylcyclobutanone (IV). This methoxy substitution product was isolated in 80% yield at 60° (0.5 mm): ir 1760 (C=O) and 1660 cm^{-1} (C=C); nmr δ 1.20 (s, 3 H), 1.22 (s, 3 H), 1.24 (s, 3 H), 1.8 (s, 3 H), 2.02 (s, 3 H), and 3.4 (s, 3 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.53; H, 9.89. Found: C, 72.09; H, 10.00.

This methoxy substitution product was also obtained from the corresponding bromocyclobutanone.

Hydrolysis of 2-Chloro-4-isopropylidene-2,3,3-trimethylcyclobutanone (III). 2-Hydroxy-4-isopropylidene-2,3,3-trimethylcyclobutanone (V) and 4,4,6-Trimethyl-5-heptene-2,3-dione (VI). A 10-g portion of III was treated with 100 ml of 20% aqueous sodium carbonate at reflux with stirring for 20 hr. Upon cooling, the reaction mixture was extracted with chloroform and the extracts were dried over anhydrous calcium chloride. The solvent was removed by rotoevaporation and the residue was vacuum distilled. Two major fractions were obtained.

(1) The first fraction (VI) was a deep yellow colored liquid at 38–40° (0.8 mm): ir 1710 (C=O) and 1650 cm^{-1} (C=C); nmr δ 1.3 (s, 6 H), 1.5 (s, 3 H), 1.7 (s, 3 H), 2.24 (s, 3 H), and 5.3 (s, 1 H); mass spectrum parent peak at *m/e* 168 (theory 168) and major peaks at *m/e* 97 and 125 due to the loss of $CH_3C{=}O$ and $(H_3C({=}O)C{=}O$ and another at *m/e* 55 which is due to $-CH{=}C(CH_3)_2$.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.59; H, 9.82.

(2) The second fraction (V) distilled at 85° (0.08 mm): ir 3400 (OH), 1740 (C=O), and 1660 cm^{-1} (C=C); nmr δ 1.3 (s, 6 H), 1.4 (s, 3 H), 1.9 (s, 3 H), 2.15 (s, 3 H), and 4.4 (s, 1 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.12; H, 9.38.

The total yield was 80% but the distribution of V and VIa was very dependent upon the reaction time. Under the conditions described, the distribution was a 20% yield of VIa and a 60% yield of V.

Hydrolysis of V. The hydroxy compound upon treatment with aqueous sodium carbonate as described above was converted to the yellow liquid, VIa.

Hydrolysis of 2-Chloro-2-ethyl-4-isopropylidene-3,3-dimethylcyclobutanone (VII). 2-Ethyl-2-hydroxy-4-isopropylidene-3,3-dimethylcyclobutanone (VIII) and 5,5,7-Trimethyl-6-octene-3,4-dione (IX). The same procedure was employed as described above. Two fractions were obtained as follows.

(1) The first fraction (IX) was a deep yellow colored liquid at 50° (0.15 mm): ir 1710 (C=O) and 1650 cm^{-1} (C=C); nmr δ 1.0 (t, 3 H), 1.3 (s, 6 H), 1.5 (s, 3 H), 1.7 (s, 3 H), 2.6 (q, 2 H), and 5.3 (s, 1 H); mass spectrum parent peak at *m/e* 182 (theory 182), with major peaks at *m/e* 97 and 125 due to loss of $CH_3CH_2C{=}O$ and $CH_3CH_2C({=}O)C{=}O$ and also at *m/e* 55 and 57 due to $-CH{=}C(CH_3)_2$ and $CH_3CH_2C{=}O$.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 9.8. Found: C, 72.37; H, 9.92.

(2) The second fraction (VIII) was collected at 90–92° (0.08 mm): ir 3400 (OH), 1740 (C=O), and 1660 cm^{-1} (C=C); nmr δ 1.0 (t, 3 H), 1.28 (s, 3 H), 1.36 (s, 3 H), 1.6 (q, 2 H), 1.84 (s, 3 H), 2.05 (s, 3 H), and 4.15 (s, 1 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 9.8. Found: C, 72.23; H, 9.78.

Acknowledgments. The authors wish to express appreciation to the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund for support of this investigation.

Registry No.—I, 42915-23-1; II, 51270-76-9; III, 42915-13-9; IV, 51270-77-0; V, 51270-78-1; VIa, 51270-79-2; VII, 42915-15-1; VIII, 51270-80-5; IX, 51270-81-6; 2-bromo-4-isopropylidene-2,3,3-trimethylcyclobutane, 42915-14-0.

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(2) W. T. Brady, J. D. Stockton, and A. D. Patel, *J. Org. Chem.*, **39**, 236 (1974).

(3) The methoxide ion could attack the unsymmetrical bicyclobutanone at either bridgehead carbon, but attack at the one indicated produces a significantly more stable carbanion.

2,5-Dicarbomethoxy-3,4-diphenylcyclopentadienone. Synthesis and Reaction with Acetylenes

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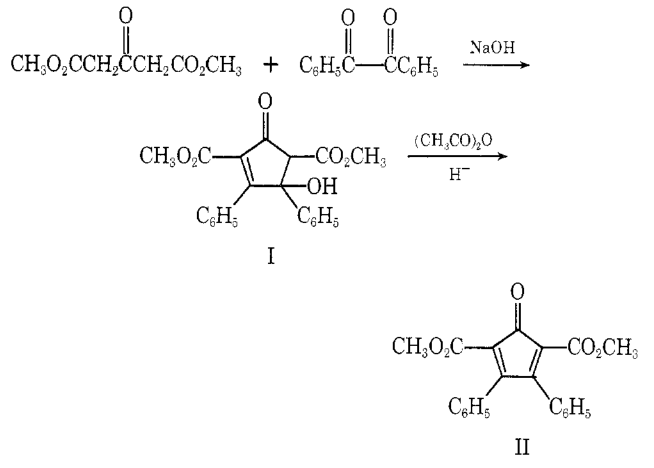
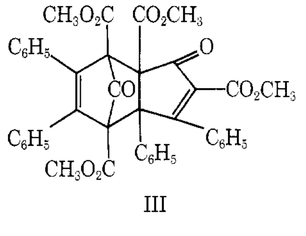
Diels-Alder additions of cyclopentadienones to acetylenes offer a convenient route to arenes.[1,2] If the cyclopentadienones contained functional groups which did not interfere with the addition reaction, useful functionality could be introduced into the products. We have found that 2,5-dicarbomethoxy-3,4-diphenylcyclopentadienone (II) does react with acetylenes to form the desired arene diesters. Compound II can be readily synthesized from available starting materials. It differs from most diphenylcyclopentadienones[1] in that at 25° it is predominantly monomeric in solution and only partially dimerized in the solid state. The synthesis and some properties of II are described below.

Base-catalyzed condensation of dimethyl acetonedicarboxylate with benzil produced the cyclopentenolone I, which appeared to be partially enolized in solution based on the nmr spectrum. Acid-catalyzed dehydration with acetic anhydride produced II, a bright-orange solid. Compound II is primarily a monomer, as shown by the strong methyl resonance in the ^1H nmr at δ 3.75. Four weak resonances of equal intensity at δ 3.38, 3.51, 3.81, and 3.83 correspond to the methyl resonances expected for III and indicate a molar ratio of II to III of *ca.* 30:1. The ^{13}C nmr





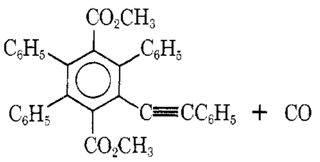
III

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.

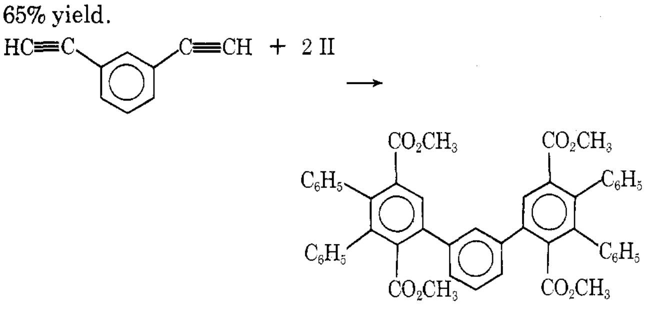
The intermediate reactivity toward dimerization is reflected in the reactivity of II with acetylenes. With diphenylbutadiyne the monoadduct IV was isolated in 70% yield. The reaction temperature of 180° was almost 50° lower than the temperature normally used for tetraphenylcyclopentadienone,[4] yet 50°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

$$\text{II} + C_6H_5C{\equiv}CC{\equiv}CC_6H_5 \longrightarrow$$



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: ^{1}H 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°); ^{1}H 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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(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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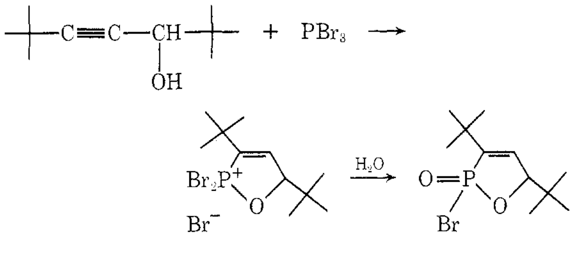
In connection with our recent findings[1] that certain propargyl alcohols react with phosphorus tribromide (PTB) to yield phosphorus–oxygen heterocycles and related compounds (eq 1), we attempted to enter isomeric manifolds



(1)