The precipitate from the original reaction mixture was treated with water and filtered. The filtrate was acidified with concd. hydrochloric acid and purged with nitrogen gas through a washing bottle containing 100 ml. of saturated barium hydroxide solution for 15 min. No precipitate of barium carbonate appeared in the barium hydroxide solution.

Di-p-phenylbenzoylethylene (*trans*). Twelve grams of fumaryl dichloride, b.p. 44–45° (3 mm.), was added to a tenfold excess of diphenyl in carbon disulfide under standard conditions for a Friedel-Crafts reaction with anhydrous aluminum chloride as the catalyst. The crude reaction product was dried, powdered, and washed with hot petroleum ether. The orange residue was recrystallized three times from benzene to give 10 g. (33%) of *trans*-di-*p*-phenylbenzoylethylene as yellow needles, m.p. 248–250° (lit.[18] m.p. 247.5–248°), ultraviolet spectrum in ethyl acetate, λ_{max} 318 mμ, ϵ 24,070.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.60; H, 5.18. Found: C, 86.43; H, 5.42.

The *trans*-di-*p*-phenylbenzoylethylene reacted slowly with 2,4-dinitrophenylhydrazine reagent to give a small amount of colored precipitate after standing overnight and slowly absorbed bromine in chloroform solution.

The reaction of 500 mg. of *trans*-di-*p*-phenylbenzoylethylene with 1.0 g. of dried sodium hydroxide in 500 ml. of anhydrous ether as previously described gave no material corresponding to Fraction B but did give a very small amount of *p*-phenylbenzoic acid, m.p. 224–226°.

Acknowledgment. The authors wish to thank Dr. W. W. Kaeding and Dr. A. W. Baker for the infrared analyses. Partial financial support of this investigation by the California Wine Advisory Board is also gratefully acknowledged.

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[COMMUNICATION NO. 2214 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK CO.]

Addition of Ethylenic Compounds to Tetracyclones

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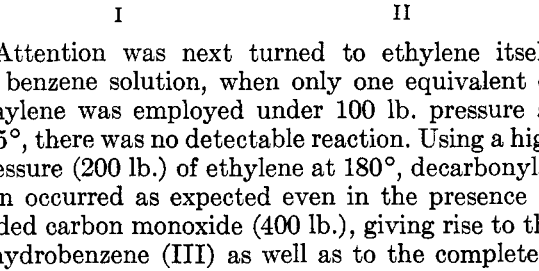
Received July 25, 1961

Ethylene and simple vinyl esters add to cyclopentadienones without accompanying decarbonylation, provided a low temperature is employed. An excess of the ethylenic component is essential for good yields. Anhydrous aluminum chloride catalyzes the addition of ethylene. The same catalyst also brings about a rearrangement of 1,2,3,4-tetraphenylbenzene to the 1,2,4,5-isomer, but the rate is too slow to be a complicating factor.

It has long been known that unsaturated compounds having the double bond activated by conjugation will add to cyclopentadienones.[2a,2b] Less attention has been devoted to simpler ethylenes such as allyl and vinyl compounds. Abramov and his group[3-8] described products obtained by heating cyclones and ethylenes in sealed tubes at 150–200°. As would have been expected, the conditions were so drastic that decarbonylation and aromatization usually occurred. However, adducts were obtained in six instances from allyl compounds and acecyclone and from vinyl ethers and esters and the very reactive phencyclone.

Since it seemed likely that the conditions employed previously had been too severe, a temperature of 100° was tried in these Laboratories fifteen years ago. After 24 hr., it was found that vinyl acetate added smoothly and quantitatively to tetracyclone and to the dissociating dimer of dimethyldiphenylcyclopentadiene,[9] giving the adducts I and II.



I II

Attention was next turned to ethylene itself. In benzene solution, when only one equivalent of ethylene was employed under 100 lb. pressure at 105°, there was no detectable reaction. Using a high pressure (200 lb.) of ethylene at 180°, decarbonylation occurred as expected even in the presence of added carbon monoxide (400 lb.), giving rise to the dihydrobenzene (III) as well as to the completely aromatized 1,2,3,4-tetraphenylbenzene (IV). There was no appreciable reaction at 100° until anhy-

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[2] (a) C. F. H. Allen, *Chem. Revs.*, **37**, 209 (1945). (b) C. F. H. Allen, *Chem. Revs.*, *in press*.

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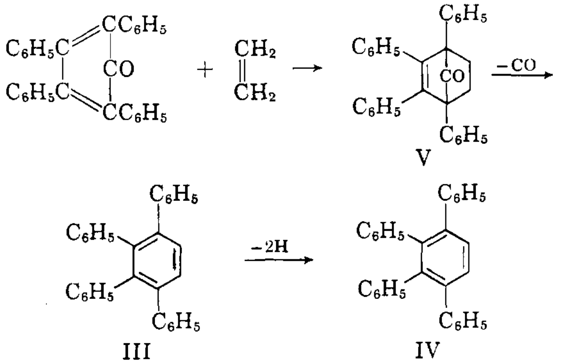
drous aluminum chloride was added as a catalyst.[10,11] With this aid, the desired adduct (V), having the carbonyl bridge (infrared band at 5.64 mμ), was readily formed.



On being heated above its melting point, decarbonylation occurs, giving rise to the dihydro compound (III) and 1,2,3,4-tetraphenylbenzene (IV).

It was essential to know that there had been no isomerization during the reaction, as the migration of phenyl groups in the presence of anhydrous aluminum chloride has been shown to occur with *o*-terphenyl.[12] It has also been found in these Laboratories that 1,2,3,4-tetraphenylbenzene in benzene solution, with anhydrous aluminum chloride, is converted partially to the 1,2,4,5-isomer; the latter separates because of its sparing solubility. 2,3-Diphenyl-*p*-xylene is likewise isomerized, but the locations of the substituents in the product were not determined. Both tetraphenylbenzenes, made by unequivocal syntheses, are known, and with specimens at hand for comparison, it was simple to show that there had been no rearrangement during the reaction with ethylene.

EXPERIMENTAL

5,6-Dihydro-1,2,3,4-tetraphenylbenzene (III). A mixture of 5 g. of tetracyclone and 150 ml. of benzene was placed in an autoclave, ethylene was added to 200 p.s.i., and the whole heated at 190°, with shaking, for 16 hr. After cooling, the benzene solution yielded a pink solid which became colorless after several recrystallizations from methyl and ethyl alcohols, using a decolorizing carbon; yield of purified product, 2.5 g. (50%) m.p., 175–176°. It shows a brilliant blue fluorescence when irradiated with a source of ultraviolet light.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.8; H, 6.3. Found: C, 93.6; H, 6.2.

When the heating was extended to 24 hr., a part of the dihydro compound was dehydrogenated to the aromatic 1,2,3,4-tetraphenylbenzene. The molecular weight was determined in the mass spectrometer.

7-Oxo-1,4,5,6-tetrahydro-1,2,3,4-tetraphenyl-1,4-methanobenzene (V) was obtained by heating a mixture of 7.7 g. of tetracyclone, 2.7 g. of anhydrous aluminum chloride, and 150 ml. of dry benzene in an autoclave, flushed with ethylene and then charged to 300 p.s.i. After 24 hr. at 100°, with rocking, the cooled reaction mixture was removed, poured upon iced hydrochloric acid and the benzene layer separated; the solvent was evaporated and replaced by methanol which, on dilution, gave 1.5 g. (18%) of a light-tan solid, m.p. 90–95°, with dec. The IR band was at 5.64 mμ.

Anal. Calcd. for $C_{31}H_{24}O$: C, 90.2; H, 5.8. Found: C, 90.0; H, 6.0.

The decarbonylation to the dihydro compound (III) and 1,2,3,4-tetraphenylbenzene is done very conveniently in the mass spectrometer. The latter compound was identified by comparing its mass spectrum with that of an authentic specimen[13]; the patterns were identical

5-Acetoxy-7-oxo-1,4,5,6-tetrahydro-1,2,3,4-tetraphenyl-1,4-methanobenzene (I) was obtained by heating 10 g. of tetracyclone in 50 ml. of vinyl acetate in a pressure bottle at 95–100° for 72 hr. The excess ester was removed under pressure. The residue was recrystallized from butanol, followed by acetic acid the yield was 80%. The substance melted at 200°.

Anal. Calcd. for $C_{33}H_{26}O_3$: C, 84.4; H, 5.5. Found: C, 84.3; H, 5.5.

The 1,4-dimethyl analog (II) was similarly obtained by heating 4 g. of the dissociating dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone[9] with vinyl acetate for 24 hr. It was recrystallized twice from ligroin; yield, 3.8 g. (77%), m.p., 100°.

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.4; H, 6.1. Found: C, 76.3; H, 6.3.

Isomerizations: 1,2,3,4-Tetraphenylbenzene to its 1,2,4,5-isomer. Six grams of the 1,2,3,4-isomer and 1 g. of anhydrous aluminum chloride in 80 ml. of dry benzene was refluxed for 5 hr. and treated by appropriate manipulation. After evaporation of the benzene layer from the aqueous acid decomposition, the solid residue was triturated with methanol and crystallized from a large volume of butanol, benzene–methanol, and benzene–*t*-pentyl alcohol in order. The yield of the 1,2,4,5-isomer, m.p. 266°, which was identical with an authentic specimen,[14] was 1.9 g. (31%). 2,3-Diphenyl-*p*-xylene, m.p. 108°, was similarly rearranged after 4.5 hr. and recrystallization from butanol; yield was 2 g. (32%). m.p. 170°.

Anal. Calcd. for $C_{20}H_{18}$: C, 93.0; H, 7.0; mol. wt., 258. Found: C, 92.8; H, 7.2; mol. wt. in boiling benzene, 269. 2,3,5-Triphenylxylene was also rearranged to an isomer, m.p. 205°.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.4; H, 6.6. Found: C, 93.4; H, 6.5.

Acknowledgment. We are pleased to have had the invaluable help of Mr. Glenn Happ for the mass spectra and that of Miss Thelma Davis for the infrared spectra measurements.

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