1.1 g. of the dienol ether derivative VIII which exhibited m.p.  $159-161^{\circ}$  after several crystallizations from acetone-methanol;  $[\alpha]_D - 109^{\circ}$ ;  $\lambda_{\max} 244 \text{ m}\mu (\log \epsilon 4.28)$ ;  $\nu_{\max} 1740$ , 1640, and 1600 cm.<sup>-1</sup>.

Anal. Calcd. for  $C_{21}H_{29}ClO_2$ : C, 72.27; H, 8.38; Cl, 10.16; O, 9.17. Found: C, 72.17; H, 8.39; Cl, 10.43; O, 9.26.

Catalytic Hydrogenation of 19-Chloro-3-ethoxyandrosta-3,5dien-17-one (VIII).—A solution of 1 g. of the foregoing dienol ether VIII in 150 ml. of ethyl acetate was hydrogenated with 0.5 g. of prereduced platinum oxide at atmospheric pressure.<sup>22</sup> The experiment was terminated after the absorption of 4.3 molar equiv. of hydrogen and processed in the usual manner to give a crystalline solid which was dissolved in hexane and adsorbed on 100 g. of silica gel. Elution with hexane-benzene (9:1) afforded 0.1 g. of 19-chloro-5 $\alpha$ -androstan-17-one (IIIh) which exhibited m.p. 118-120° after crystallization from acetone-methanol;  $[\alpha]D$  +75°;  $\nu_{max}$  1740 cm.<sup>-1</sup>; n.m.r. 18-methyl at 55 c.p.s. and 19-chloromethyl (2 protons) at 231 c.p.s.

Anal. Caled. for  $C_{19}H_{29}$ ClO: C, 73.85; H, 9.46; Cl, 11.47; O, 5.18. Found: C, 73.89; H, 9.37; Cl, 11.53; O, 5.23.

Continued elution with benzene-chloroform (1:1) afforded 0.03 g. of 19-chloro-3 $\beta$ -ethoxy-5 $\alpha$ -androstan-17-one (IIIi) with m.p. 93-95° after crystallization from acetone-methanol;  $[\alpha]_D + 80°$ ;  $\nu_{max}$  1740 cm.<sup>-1</sup>; n.m.r. 18-methyl at 55 c.p.s., methyl of 3 $\beta$ ethoxy group (3 protons) at 64, 72, and 79 c.p.s., methylene of 3 $\beta$ -ethoxy group (2 protons) at 201, 209, 215, and 222 c.p.s., and 19-chloromethyl (2 protons) at 228 c.p.s.

Anal. Calcd. for  $C_{21}H_{33}ClO_2$ : C, 71.45; H, 9.42; O, 9.07. Found: C, 71.33; H, 9.52; O, 9.12.

Continued elution with the same mixture provided 0.42 g. of 19-chloro- $5\alpha$ -androstan-3,17-dione (IIn), identical in all respects with an authentic sample.

# 1-Phenylcyclopenten-3-one Derivatives and Their Conversion into Bis- $\pi$ -(1-methyl-3-phenylcyclopentadienyl)titanium Dichlorides

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 $Bis-\pi-(1-methyl-3-phenylcyclopentadienyl)-$  and  $bis-\pi-(1-methyl-3-p-bromophenylcyclopentadienyl)titanium dichlorides were prepared from the lithium salts of the corresponding cyclopentadienes and titanium tetrachloride. The cyclopentadienyl compounds were obtained by the reaction of methylmagnesium bromide with 1-phenyl- or 1-p-bromophenylcyclopenten-3-ones. Attempts to prepare the related p-methoxy and p-methyl derivatives were unsuccessful.$ 

A series of substituted bis- $\pi$ -cyclopentadienyltitanium dichlorides was needed to determine how changing substituents in the cyclopentadienyl rings would affect the ability of these complexes, in combination with alkylaluminum halides, to polymerize ethylene.<sup>1,2</sup> To keep steric factors constant and also to keep the synthesis simple, we chose to prepare a series of bis- $\pi$ -(1methyl-3-phenylcyclopentadienyl)titanium dichlorides. The general method of preparation of these compounds from titanium tetrachloride and cyclopentadienide salts is well known<sup>3</sup> and the preparation of 1-methyl-3-phenylcyclopentadiene had already been described in the literature.<sup>4a</sup> It also appeared that *para*-substituted phenyl compounds could be used in this synthesis as well.

#### Results

1-Methyl-3-phenylcyclopentadiene was prepared by the procedure of Borsche and Menz.<sup>4a</sup> The position of the double bonds in the product has not been determined with certainty.



<sup>(1)</sup> D. S. Breslow and N. R. Newburg, J. Am. Chem. Soc., 81, 81 (1959).

The 1-methyl-3-phenylcyclopentadiene appeared to be quite unstable in air. The titanium complex was prepared from the freshly prepared diene by first making the lithium salt by reaction with 1 equiv. of *n*-butyllithium in ether solution and then adding 0.5 equiv. of titanium tetrachloride. The compound formed stable, red-purple prisms melting at  $224^{\circ}$ .<sup>4b</sup>



A similar series of reactions was carried out with pbromophenacyl bromide. Reactions were much slower with the p-bromo compound. The acetoacetic ester alkylation required refluxing overnight to go to completion rather than the 30 min. necessary for phenacyl bromide itself to react. The intermediate p-bromophenacylacetoacetic ester crystallized and was characterized. This product also reacted much more slowly with aqueous sodium hydroxide than the unsubstituted compound did. Under conditions where the unsubstituted compound cyclized completely, viz, boiling with 2% aqueous sodium hydroxide for 1 min., the pbromo derivative gave a mixture of products. The mixture was separated into two components by fractional crystallization. The more soluble compound,

<sup>(2)</sup> W. P. Long and D. S. Breslow, ibid., 82, 1953 (1960).

<sup>(3)</sup> G. Wilkinson and J. M. Birmingham, ibid., 76, 4281 (1954).

<sup>(4) (</sup>a) W. Borsche and W. Menz, Ber., 41, 190 (1908). (b) A referee has pointed out that this compound and the *p*-bromo analog described below should exist in *meso* and racemic forms. No attempt was made to separate isomers and consequently the products are probably mixtures of the two forms.

80% of the total, had two carbonyl bands in its infrared spectrum, 1730 and 1700 cm. $^{-1}$ , suggesting that it was 1-p-bromophenyl-1.4-pentanedione formed by decarboxylation of the *p*-bromophenacylacetoacetic ester. This structure was confirmed by carbon and hydrogen analysis and by the ultraviolet spectrum of the compound,  $\lambda_{\max} 255 \text{ m}\mu$  ( $\epsilon 14,000$ ). [The *p*-bromophenacylacetoacetic ester exhibited  $\lambda_{max}$  256 m $\mu$  ( $\epsilon$ (22,100).] The second compound in the mixture, 20%of the total, was the expected 1-p-bromophenylcyclopenten-3-one, judging by the single carbonyl band at 1725 cm.<sup>-1</sup> in its infrared spectrum, carbon-hydrogen analysis, and the ultraviolet spectrum,  $\lambda_{max}$  290 m $\mu$  ( $\epsilon$ 29,800). [The unsubstituted phenylcyclopentenone had  $\lambda_{\text{max}} 282 \text{ m}\mu \ (\epsilon \ 17,400).]$  Prolonged treatment of the 1-p-bromophenyl-1,4-pentanedione with hot aqueous base converted it completely into the less soluble product, the *p*-bromophenylcyclopentenone, as expected.



The *p*-bromophenylcyclopentenone reacted normally with methylmagnesium bromide, producing 1-methyl-3-*p*-bromophenylcyclopentadiene. This compound, too, appeared to be somewhat unstable. The diene was converted into the lithium salt with *n*-butyllithium and reacted with titanium tetrachloride to form bis- $\pi$ -(1-methyl-3-*p*-bromophenylcyclopentadienyl)titanium dichloride, obtained as stable purple crystals, m.p. 231°.

p-Methoxyphenacyl bromide reacted with sodioacetoacetic ester, apparently forming the expected pmethoxyphenacylacetoacetic ester. Treatment of this compound with boiling 2% aqueous sodium hydroxide for 5 min. led only to the formation of 1-p-anisyl-1,4pentanedione. Refluxing this compound for 8 hr. with 2% aqueous sodium hydroxide cyclized it to 1-p-anisylcyclopenten-3-one. All attempts to cause this ketone to react with methylmagnesium bromide or methyllithium were unsuccessful. Only recovered starting material could be isolated. The ketone probably formed mainly enol salts with the metal alkyls.

Attempts to produce 1-*p*-tolylcyclopenten-3-one by reaction of *p*-methylphenacyl bromide and sodioacetoacetic ester followed by reaction with base were completely unsuccessful. The alkylation step apparently went as expected to form *p*-methylphenacylacetoacetic ester, but the cyclization step took a different course. Analysis of the crystalline product, isolated from the reaction mixture in high yield, indicated the formula to be  $C_{15}H_{16}O_3$  rather than the expected  $C_{12}H_{12}O$ . It did not give a carbonyl test with 2,4dinitrophenylhydrazine in acidic ethanol, although it did have a carbonyl band in its infrared spectrum at 1725 cm.<sup>-1</sup>, and the ultraviolet spectrum was not as predicted. The ultraviolet spectrum had  $\lambda_{max}$  278 m $\mu$  ( $\epsilon$  18,000) while 1-phenylcyclopenten-3-one had  $\lambda_{max}$  282 m $\mu$  ( $\epsilon$ 17,400). The compound did not hydrogenate at atmospheric pressure at 25° with Adams catalyst. The n.m.r. spectrum indicated that the product contained a *p*-tolyl group, a vinyl hydrogen, two methyl groups, and an ethyl group.

The compound hydrolyzed on boiling with alcoholic potassium hydroxide to give a crystalline acid with an equivalent weight of 234 (calculated for  $C_{13}H_{12}O_3$ : 216). The acid could be distilled without decarboxylating. Reduction of the original ester with lithium aluminum hydride gave an alcohol of formula  $C_{13}H_{15}O_2$ . The reduced product still had strong ultraviolet absorption,  $\lambda_{max} 288 \text{ m}\mu$  ( $\epsilon 23,500$ ). Data indicate that the original ester is a furan derivative, I, formed by condensing two ketone carbonyls together and dehydrating. Accordingly, the lithium aluminum hydride reduction product should be the corresponding alcohol II. The structure of the alcohol was confirmed by its n.m.r. spectrum.



It is not clear why the *p*-methyl group in this system caused this completely different cyclization reaction to occur. The cyclization should not be base catalyzed and it may actually have taken place in the initial condensation reaction step rather than in the subsequent reaction with boiling 2% aqueous sodium hydroxide.

No further attempts were made to prepare p-methoxy- or p-methylphenylcyclopentadiene because bis- $\pi$ -(1-methyl-3-phenylcyclopentadienyl)- and bis- $\pi$ -(1methyl-3-p-bromophenyl)titanium dichlorides formed extremely poor polymerization catalysts under conditions where bis(cyclopentadienyl)titanium dichloride itself was quite a good catalyst.<sup>1</sup> The p-methoxy or p-methyl derivatives would, therefore, probably form poor catalysts also.

## Experimental

1-Phenylcyclopenten-3-one was prepared by the method of Borsche and Menz.<sup>4a</sup> From 25 g. of phenacyl bromide there was obtained 8 g. of crude solid ketone, b.p. 127-140° (2.5 mm.). The compound had  $\lambda_{max} 282 \text{ m}\mu \ (\epsilon \ 17,400)$  in methanol solution.

1-Methyl-3-phenylcyclopentadiene was also prepared by the procedure of Borsche and Menz.<sup>4a</sup> The crude product obtained from 21.4 g. of 1-phenylcyclopenten-3-one was distilled, b.p.  $80-135^{\circ}$  (3 min.), and recrystallized from hexane by cooling to  $-80^{\circ}$ . There was obtained 4.1 g. of colorless crystals of m.p.  $58.5-60^{\circ}$  (lit.<sup>4a</sup> m.p.  $62^{\circ}$ ). On standing in air, the compound polymerized. The infrared spectrum of the freshly prepared compound in carbon tetrachloride solution had olefin bands at 1605 (s) and 1635 (m) cm.<sup>-1</sup>. The ultraviolet spectrum in methanol solution had  $\lambda_{max}$  305 m $\mu$  ( $\epsilon$  8450).

**Bis**(1-methyl-3-phenylcyclopentadienyl)titanium Dichloride.— In a heavy-walled Pyrex bottle was placed 4.0 g. of 1-methyl-3-phenylcyclopentadiene. The bottle was closed with a selfsealing butyl rubber lined metal cap with two holes in the metal for hypodermic injections. The bottle was flushed with nitrogen by means of a 20-gauge needle inserted through the rubber-lined cap. Then 20 ml. of dry ether was added. The solution was cooled to  $0^{\circ}$  and 16.5 ml. of 1.55 M n-butyllithium in hexane was added. After being mixed well, 1.5 ml. of titanium tetrachloride was added; the mixture was vigorously shaken for ca. 10 min. The solution and red-purple solid were allowed to stand overnight and then the bottle was opened and the solid was scraped out and filtered from the solution with the help of 50 ml. of pentane. The solid was dissolved in methylene chloride and filtered from the insoluble salts. The filtrate was concentrated to about 15 ml. and 50 ml. of pentane was added. After being cooled to about  $-20^{\circ}$ , the solution yielded red-purple crystals. These were filtered and recrystallized the same way twice more to give a good yield of red-purple prisms, m.p. 224-225°. The ultraviolet spectrum in methylene chloride solution had  $\lambda_{max}$  246 m $\mu$ (e 27,200), 288 (19,900), 316 (16,700), 462 (1720), and 550 (945).

Anal. Caled. for C<sub>24</sub>H<sub>22</sub>Cl<sub>2</sub>Ti: C, 67.15; H, 5.17; Cl, 16.52. Found: C, 66.62; H, 5.21; Cl, 17.2.

3-Carboethoxy-5-*p*-bromophenyl-2,5-pentanedione.—To a solution of 9.0 g. of sodium metal dissolved in 600 ml. of dry ethanol was added, at room temperature, 54 g. of ethyl acetoacetate followed by a slurry of 105 g. of *p*-bromophenacyl bromide in 150 ml. of warm dry ethanol. The reaction mixture was refluxed for 24 hr. and then about half of the alcohol was distilled off. The residue was cooled and mixed with water. The oil, which solidified, was taken up in ether, washed well with water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the crude product. A small sample, after two recrystallizations from hexane, formed colorless plates which melted at 75–77°. The ultraviolet spectrum in methanol solution had  $\lambda_{max}$  256 m $\mu$  ( $\epsilon$  22,100). The infrared spectrum in chloroform solution had three carbonyl bands: 1750, 1730, and 1700 cm.<sup>-1</sup>.

Anal. Caled. for  $C_{14}H_{15}BrO_4$ : C, 51.39; H, 4.62. Found: C, 51.27, 51.24; H, 4.83, 4.72.

1-p-Bromophenyl-1,4-pentanedione.-The crude ester from the above reaction was added to 3 l. of boiling 2% aqueous sodium hydroxide and after boiling for 90 sec. the flask was cooled in ice-water. After cooling for 2 hr., the solid was filtered off and air dried. The product was a mixture containing about 80% of the 1,4-diketone and about 20% of 1-p-bromophenylcyclopenten-3-one as determined by its ultraviolet spectrum. The less soluble cyclopentenone derivative was separated by dissolving the mixture in hexane and filtering off the less soluble material. Then cooling of the hexane solution gave colorless needles of the diketone. Two more crystallizations from hexane gave 7.36 g. of colorless needles of the pure diketone, m.p. 74-75°. The infrared spectrum of the product in carbon tetrachloride solution had carbonyl bands at 1730 and 1700 cm.<sup>-1</sup>. The ultraviolet spectrum in methanol solution had  $\lambda_{max} 255 \text{ m}\mu$  ( $\epsilon 14,000$ ) with a shoulder at 286 m $\mu$ .

Anal. Caled. for  $C_{11}H_{11}BrO_2$ : C, 51.78; H, 4.35. Found: C, 52.08; H, 4.17.

1-p-Bromophenylcyclopenten-3-one.—The crude ketone mixture obtained from the mother liquors of the above recrystallizations (10-15 g.) was refluxed with 200 ml. of 2% sodium hydroxide dissolved in ethanol for 5 min. On cooling the product crystallized from the solution. It was filtered off and recrystallized from ethanol to give 5.5 g. of colorless crystals, m.p. 127-128°. The infrared spectrum in carbon tetrachloride solution had a single carbonyl band at 1725 cm.<sup>-1</sup>. The ultraviolet spectrum in methanol solution had  $\lambda_{max}$  290 mµ ( $\epsilon$  29,800).

*Anal.* Caled. for  $C_{11}H_{3}BrO$ : C, 55.72; H, 3.83. Found: C, 55.85; H. 3.89.

The compound was more conveniently prepared directly from the crude 3-carboethoxy-5-*p*-bromophenyl-2,5-pentanedione prepared from 105 g. of *p*-bromophenacyl bromide as described above by refluxing it with 3 l. of 2% aqueous sodium hydroxide for 2.5 hr. The brown solid obtained on cooling was separated, dried, and vacuum distilled, b.p. 150-175° (3 mm.). Recrystallization from methanol gave 26.4 g. of the pure ketone, m.p. 126.4-128°.

Bis(1-p-bromophenyl-3-methylcyclopentadienyl)titanium Dichloride.—In a 500-ml., three-necked, round-bottomed flask equipped with a stirrer, a dropping funnel, and a condenser which was connected to a nitrogen inlet and mercury-trap outlet, was placed 18.8 g. of 1-bromophenylcyclopenten-3-one and 150 ml. of dry ether. The mixture was stirred and 60 ml. of 3 *M* methylmagnesium bromide in ether was added dropwise. A large insoluble lump formed initially, but it redissolved by the time the addition was complete. The mixture was refluxed under nitrogen for 3 hr. and allowed to stand overnight. Cold dilute sulfuric acid was then added and the ether layer was separated. The acid layer was extracted again with ether, and the combined extracts were washed with water and with aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. A vacuum distillation of the ether solution gave 11.0 g. of the crude diene, b.p. 120-135° (33 mm.), m.p. 105-110°. The ultraviolet spectrum in methanol solution had  $\lambda_{max}$  317 m $\mu$  ( $\epsilon$ 16,400) and 226 m $\mu$  ( $\epsilon$  11,700).

In a centrifuge bottle was placed 10.5 g. of the crude diene and the bottle was capped and flushed with nitrogen as described for the preparation of bis(1-phenyl-3-methylcyclopentadienyl)titanium dichloride above. After the injection of 100 ml. of dry ether, the solution was cooled to  $-80^{\circ}$  (crystals of the diene separated) and 25 ml. of 1.94 M n-butyllithium in n-hexane was added. The solution was shaken and allowed to come to about -20° and 2.5 ml. (4.3 g.) of titanium tetrachloride was added. The solution soon became purple-brown and solid separated. The reaction mixture was allowed to warm and stand at room temperature overnight. Then the solvent was evaporated in vacuo and the product was extracted from the solid residue with methylene chloride by putting the solid in a Soxhlet extractor and extracting overnight under a nitrogen atmosphere. The dark red extract was diluted with about five times as much pentane. After standing several hours, the purple-brown solid was filtered off and recrystallized again from methylene chloridepentane. There was obtained 3.0 g. of product, m.p. 234-237°.

Anal. Calcd. for  $C_{24}H_{20}Br_2Cl_2Ti$ ; C, 49.10; H, 3.43. Found: C, 48.89; H, 3.79.

Another gram of product was isolated by concentrating the mother liquors, m.p. 231-232°.

1-p-Anisyl-1,4-pentanedione.—To a solution of 2.7 g. of sodium metal dissolved in 200 ml. of dry ethanol was added 20 g. of ethyl acetoacetate followed by a solution of 27 g. of p-methoxyphenacyl bromide in 150 ml. of dry ethanol. The reaction mixture was refluxed for about 20 hr. and then about half of the solvent was distilled off. The residue was diluted with water, the oil was extracted with ether, and the extracts were washed with water and dried over magnesium sulfate. The ether was evaporated on the steam bath and the oil left was added to 1 l. of boiling 2%aqueous sodium hydroxide. After boiling for 5 min. the mixture was cooled in ice-water and the product was extracted with ether. The extracts were washed with water and dried over anhydrous magnesium sulfate. Distillation of the ether solution gave the crude diketone as a fraction of b.p. 120-160° (4 mm.). Two recrystallizations from ether-hexane gave 6.5 g. of colorless needles, m.p. 43.5-47.0°. Two more recrystallizations of the product from methanol solution by cooling in Dry Ice gave material of m.p. 46-48°. The infrared spectrum in carbon tetrachloride solution had carbonyl bands at 1690 and 1715 cm.<sup>-1</sup>. The ultraviolet spectrum in methanol solution had  $\lambda_{max}$  264 m $\mu$ (e 23,300).

Anal. Calcd. for  $C_{12}H_{14}O_3$ : C, 69.88; H, 6.84. Found: C, 69.91, 70.13; H, 6.94, 7.00.

1-p-Anisylcyclopenten-3-one.-The acetoacetic ester alkylation with p-methoxyphenacyl bromide was carried out as described above but with 52 g. of ethyl acetoacetate and 74 g. of *p*-methoxyphenylacyl bromide. The crude product obtained after evaporation of the ether solution was refluxed for 8 hr. with 2400 ml. of 2% aqueous sodium hydroxide. After cooling, the solid formed was filtered off and air dried. Two recrystallizations from benzene-hexane gave 13 g. of ketone, m.p. 136-137°. Two further recrystallizations from methanol with cooling in Dry Ice followed by sublimation in vacuo gave nearly colorless crystals of m.p. 142.5-144°. The infrared spectrum in chloroform solution had a carbonyl band at 1690 cm.<sup>-1</sup>. The ultraviolet spectrum in methanol solution had  $\lambda_{max}$  311 m $\mu$  ( $\epsilon$  27,600) and 230 m $\mu$  ( $\epsilon$  13,800). The n.m.r. spectrum at 60 Mc. of the compound in deuteriochloroform solution had bands at -159a multiplet with area 2 (methylene group next to the double bond in the cyclopentenone ring), at -191 a multiplet with area 2 (methylene next to the carbonyl group), at -246 a singlet with area 3 (methoxyl methyl), at -412 a triplet of area 1 (vinyl hydrogen), and at -444 to -487 c.p.s. a distorted AB quartet with area 4 (aromatic protons) with reference to tetramethylsilane as an internal standard.

Anal. Caled. for  $C_{12}H_{12}O_2$ : C, 76.57; H, 6.43. Found: C, 76.21; H, 6.84.

All attempts to treat the ketone with methylmagnesium bromide in ether or with methyllithium in ether led only to the isolation of starting compound in moderate yield.

3-Carboethoxy-2-methyl-5-p-tolyifuran.—To a solution of 8.7 g. of sodium metal dissolved in 700 ml. of dry ethanol was added 50 g. of ethyl acetoacetate followed by a solution of 80 g. of p-methylphenacyl bromide in 200 ml. of warm ethanol. The reaction mixture was refluxed overnight. Most of the solvent was then distilled off and the residue was diluted with water. The product was extracted with several portions of ether; the extracts were washed with water and dried over anhydrous magnesium sulfate. The oil obtained after evaporating the solvent was refluxed for 30 min. with a solution of 40 g. of sodium hydroxide dissolved in 21. of water. After cooling, the product was extracted from the solution with several portions of ether. After washing the extracts with water and drying over anhydrous magnesium sulfate, the solution was distilled under reduced pressure. The product, 16 g. of b.p. 135-145° (2.5 mm.), was a greenish yellow liquid which soon solidified. Several recrystallizations from methanol gave 8 g. of pale yellow prisms, m.p. 82-83°. The ultraviolet spectrum in methanol solution had  $\lambda_{max}$  278 m $\mu$ ( $\epsilon$  18,000). The infrared spectrum contained a carbonyl band at 1725 cm.<sup>-1</sup>. The n.m.r. spectrum in deuteriochloroform solution at 60 Mc. had six types of protons: at  $-78.5^{\circ}$  a triplet with area 3 (methyl in ester group), at -136 a singlet with area 3 (p-tolyl methyl), at -154 a singlet with area 3 (methyl on the furan ring), at -254 a quartet with area 2 (methylene of the ester group), at -405 a singlet of area 1 (hydrogen on the furan ring), and at -426 to -448 c.p.s. an AB quartet of area 4 (aromatic protons) with reference to tetramethylsilane as an internal standard.

Anal. Calcd. for C15H16O3: C, 73.75; H, 6.60. Found: C, 73.69; H, 6.73.

A 1.0-g. sample of the compound was hydrolyzed by refluxing it with 10 ml. of 1.0 M potassium hydroxide in ethanol and

2 ml. of water for 5 hr. The addition of water and dilute hydrochloric acid precipitated the product. After filtering and drying overnight in air, it was recrystallized from chloroform. Pale yellow crystals of m.p. 234-235° were obtained. The ultraviolet spectrum in methylene chloride solution had  $\lambda_{max}$  280 m $\mu$  ( $\epsilon$ 23.100).

Anal. Calcd. for C<sub>13</sub>H<sub>21</sub>O<sub>3</sub>: C, 72.21; H, 5.60; equiv. wt., 216. Found: C, 72.37; H, 5.79; equiv. wt., 234.

3-Hydroxymethyl-2-methyl-5-p-tolylfuran.-To a slurry of 1.0 g. of lithium aluminum hydride in 100 ml. of dry ether was added dropwise under nitrogen a solution of 4.8 g. of the above ester in 50 ml. of ether. After the addition, the solution was refluxed for 2 hr. and cooled. Then, 5 ml. of ethyl acetate was added followed by cold dilute hydrochloric acid. The aqueous layer was separated and then extracted again with ether. The combined extracts were washed once with water and then with aqueous sodium bicarbonate. After the solution was dried over anhydrous magnesium sulfate, the solvent was evaporated on a steam bath and the residue was recrystallized several times from ether-pentane solution at 0°. There was obtained from 1 g. of colorless crystals, m.p. 98-99°. The ultraviolet spectrum in methanol solution had  $\lambda_{max}$  288 mµ ( $\epsilon$  23,500). The n.m.r. spectrum at 60 Mc. in deuteriochloroform had the following peaks: at -114 a singlet with area 1 (hydroxy proton), at -139 a singlet with area 6 (both methyl groups), at -265 a singlet with area 2 (methylene group), at -388 a singlet with area 1 (proton on the furan ring), and at -424 to -448 c.p.s. an AB quartet of area 4 (aromatic protons) with reference to tetramethylsilane as an internal standard

Anal. Caled. for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>: C, 76.81; H, 7.41. Found: C, 77.09; H, 7.07.

Acknowledgment.-The n.m.r. spectra were measured by Dr. M. M. Anderson of these laboratories.

# Bromomethylenecycloalkanes

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Methods for the preparation of bromomethylenecycloalkanes are described. The application of the Wittig reaction is shown to involve appreciable abstraction of bromine as well as hydrogen from bromomethyltriphenylphosphonium bromide to produce ultimately a mixture of methylenecycloalkane and bromomethylenecycloalkane. The decarboxylative debromination of  $\alpha$ -bromo-1-bromocycloalkylacetic acids is shown to give high yields of pure bromomethylenecycloalkanes. Alternatively, pure vinyl bromides can be obtained by the addition of bromine to methylenecycloalkanes in the presence of a small amount of pyridine, followed by dehydrobromination of the resulting dibromide with potassium t-butoxide in t-butyl alcohol.

The need for a convenient general method of preparing bromomethylenecycloalkanes<sup>2</sup> prompted a study of the various synthetic routes available for these compounds. As the most direct route to exocyclic vinyl bromides the Wittig reaction<sup>3</sup> is the most likely choice. However, attempts to adapt the Wittig procedure to the synthesis of bromomethylenecycloalkanes by employing bromomethyltriphenylphosphonium bromide invariably led to the recovery of large quantities of cycloalkanone, even when an excess of organolithium reagent was employed, and to the production of methylenecycloalkanes together with a low yield (5-30%) of the desired vinyl bromide. Similar results have been reported by Seyferth.<sup>4</sup>

When phenyllithium was employed to generate the ylide, not only was benzene recovered, but a large amount of bromobenzene was produced. With either

*p*-tolyllithium or *p*-chlorophenyllithium appreciable quantities of p-bromotoluene and p-bromochlorobenzene, respectively, were obtained and little, if any, benzene and bromobenzene were detected. These observations demonstrate that initial bromine abstraction by the base competes favorably with proton abstraction to give a mixture of methylene- and bromomethylenephosphoranes. The fact that additional side reactions take place was indicated by the failure

$$\begin{array}{rcl} [\mathrm{Ph}_{3}\mathrm{P}-\mathrm{CH}_{2}\mathrm{Br}]\mathrm{Br}^{-} + \mathrm{Ar}\mathrm{Li} \longrightarrow \\ & & & & & \\ \mathrm{Ar}\mathrm{H} + \mathrm{Ar}\mathrm{Br} + \mathrm{Ph}_{3}\mathrm{P}=\mathrm{CH}_{2} + \mathrm{Ph}_{3}\mathrm{P}=\mathrm{CH}\mathrm{Br} \end{array}$$

$$(CH_2)_n C = 0 \rightarrow (CH_2)_n C = CH_2 + (CH_2)_n C = CHBr$$

of the phosphonium salt to react completely with the organolithium compounds and by the formation of small amounts of bromobenzene and benzene when methyllithium and butyllithium were used to generate the ylide. The latter observation suggests that the

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