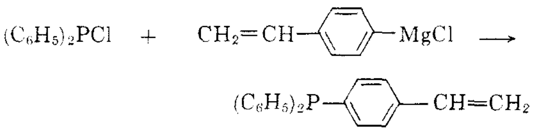
dure involves treating the Grignard reagent of the ketal from ethylene glycol and *p*-bromoacetophenone with diphenylchlorophosphine, followed by hydrolysis of the ketal, sodium borohydride reduction of the ketone to the alcohol, and finally dehydration to the desired product, I. An over-all yield of 22% based on diphenylchlorophosphine was reported.

We have investigated a simpler and more direct route to I, the reaction of *p*-styrylmagnesium chloride[2] with diphenylchlorophosphine.



(I)

Reactions of this Grignard reagent with triphenylgermanium bromide,[3] triphenyllead chloride,[3] triphenyltin chloride,[2,3] diphenyldibromogermane, and trimethylchlorosilane[4] are reported to give the corresponding substituted styrene. However, Senear, Valient, and Wirth[1] report that their attempts to prepare I from direct reaction of diphenylchlorophosphine with the Grignard led to immediate polymerization.

We wish to report that the direct reaction to prepare I can be carried out in good yield with only slight modification of the published procedures[2-4] for the synthesis of the tin, germanium, lead, and silicon substituted styrenes. These procedures involve adding the organometalloid halide compound to a solution of the Grignard[2] reagent maintained at 50–60°. We also, using these conditions, could not isolate any I. However, at 0–10° a 51% yield was obtained on a small scale and 31% on a larger scale. An even greater improvement was realized through the use of the inverse technique of addition. Under these conditions, small scale experiments at 50–60° gave 50% of I and a large scale experiment gave a 76% yield at 0–10°.

EXPERIMENTAL[5,6]

Reaction of p-styrylmagnesium chloride and diphenylchlorophosphine at 50° using inverse addition. The *p*-styrylmagnesium chloride was prepared by the method of Leebrick and Ramsden[2] using 9.7 g. of magnesium, 3 ml. of ethyl bromide, 27.6 g. (0.20 mole) of *p*-chlorostyrene, and 55 ml. of tetrahydrofuran, with the exception that the temperature was never allowed to exceed 60°. After adding an additional 50 ml. of tetrahydrofuran to the mixture on completion of the reaction, a 2-ml. sample was removed, hydrolyzed in water and the hydrolysate extracted with a few milliliters of carbon tetrachloride. Gas phase chromatography of the extract revealed mainly styrene plus a trace of *p*-chlorstyrene, indicating that the Grignard formation went to virtual completion. Dropping the extract into methanol revealed that some polymer was present.[7] The Grignard was slowly added to a solution of 31.5 g. (0.142 mole) of diphenylchlorophosphine in 150 ml. of tetrahydrofuran. The reaction was exothermic and the temperature was maintained between 50–60° using external cooling. The mixture was stirred for 10 min. after the addition was complete and was then poured nto 200 ml. of cold water containing 33 g. of ammonium chloride. This was extracted with tetrahydrofuran, 0.25 g. of *t*-butylcatechol added as an inhibitor, the extract was dried over sodium sulfate and reduced in volume to 75 ml. This was added to hexane resulting in the precipitation of 15 g. of polymer.[8] The tetrahydrofuran was removed from the filtrate leaving a mixture of solid and oil. The addition of 95% ethanol and subsequent filtration gave 20.25 g. (50%) of I, m.p. 65–75°. It was recrystallized from 95% ethanol, m.p. 77–8.°[9]

Anal. Calcd. for $C_{20}H_{17}P$: C, 83.31; H, 5.94; P, 10.74. Found: C, 82.63; H, 6.12; P, 11.06.

Reaction of p-styrylmagnesium chloride with diphenylchlorophosphine at 0–10° using inverse addition. The Grignard was prepared as before using 3.5 ml. of ethyl bromide, 29.1 g. of magnesium, 81.8 g. (0.59 mole) of *p*-chlorostyrene, and 165 ml. of tetrahydrofuran. After dilution with an additional 50 ml. of tetrahydrofuran this mixture was added to a solution of 111 g. (0.50 mole) of diphenylchlorophosphine in 400 ml. of tetrahydrofuran. The temperature was maintained at 0–10° during the addition and when complete it was allowed to warm to room temperature. It was worked up as before. The volume of the extract prior to addition into 1400 ml. of hexane was 400 ml. Only 7.0 g. of polymer was found. The filtrate, upon removal of solvent, revealed 109 g. of I, m.p. 65–75° which was readily purified by recrystallization from 95% ethanol.

Reaction of p-styrylmagnesium chloride with diphenylchlorophine using direct addition at 0–10°. The Grignard was prepared as previously described from 9.7 g. of magnesium, 3 ml. of ethyl bromide, 27.6 g. (0.20 mole) of *p*-chlorostyrene, and 150 ml. of tetrahydrofuran. It was then cooled to 0° and 31.5 g. (0.142 mole) of diphenylchlorophosphine was slowly added while maintaining the temperature at 0–10°. The mixture was allowed to warm to room temperature and was then worked up as already described. Only 4.2 g. of polymer was obtained. From the precipitation filtrate, upon removal of the solvent, was isolated 20.9 g. (51%) of I.

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(2) J. R. Leebrick and H. E. Ramsden, *J. Org. Chem.*, **23**, 935 (1958).

(3) J. G. Noltes, H. A. Budding, and G. J. M. Van Der Kerk, *Recueil*, **79**, 408 (1960).

(4) A. E. Senear, J. Wirth, and R. Neville, *J. Org. Chem.*, **25**, 807 (1960).

(5) All melting points are uncorrected.

(6) The *p*-chlorostyrene was obtained from the Monomer-Polymer Laboratories of the Borden Co. and the diphenylchlorophosphine from Victor Chemicals. They were distilled prior to use.

(7) In every preparation of *p*-styrylmagnesium chloride, some polymer was noted at this stage.

(8) As polymer is always present, even at the Grignard stage, this technique of separating polymer from monomer is valuable in preparing the other known substituted styrenes—*i.e.*, Ge, Pb, Si, Sn, etc.—provided a medium can be found in which only the polymer is insoluble.

(9) Ref. 1 reports 74–76° for the crude product.

Thermal Decarboxylation of Diaryl Fumarates to Stilbenes

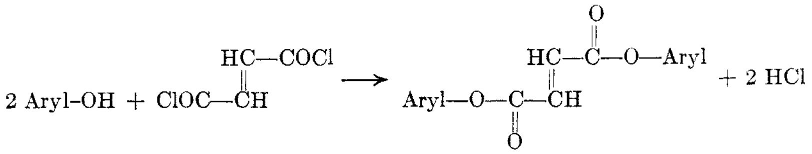
Sydney M. Spatz

Received March 23, 1961

Stilbene derivatives are useful in such varied fields as azo dyestuffs, optical brighteners, and

TABLE I

DIARYL FUMARATE DATA

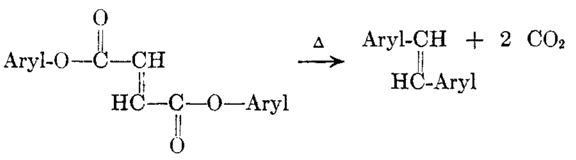


$$2\ \text{Aryl-OH} + \begin{array}{c}\text{HC—COCl}\\ \|\\ \text{ClOC—CH}\end{array} \longrightarrow \begin{array}{c}\text{O}\\ \|\\ \text{HC—C—O—Aryl}\\ \|\\ \text{Aryl—O—C—CH}\\ \|\\ \text{O}\end{array} + 2\ \text{HCl}$$

Aryl Radical	M.P.	Lit. M.P. (Ref.)	Yield, %	Halogen Calcd., %	Halogen Found, %
Phenyl	160–162[a]	161–162[b]	82,84		
2-Chlorophenyl	127.5–129.5[a]		50	21.1	20.3
4-Chlorophenyl	175–178[a]	170[c]	80,82	21.1	21.8
2,4-Dichlorophenyl	182–183[e]		70,80	35.0	33.8
2,4,6-Trichlorophenyl	172–174		57,60	44.8	44.8
2,4,6-Tribromophenyl	227–229		70,80	64.6	63.7
4-Methoxyphenyl	175–177[d]		88,96		
4-Ethoxyphenyl	135–138.5[d]		70		
β-Naphthyl	215–217[d]		27,31		
4-Nitrophenyl	225–226 dec.	219–221 dec.[c]	31,45		

[a] Identified also by conversion to the known, corresponding stilbene, listed in Table II. [b] Ref. 1. [c] Ref. 2. [d] Identified by conversion to the known, corresponding stilbene, listed in Table II. [e] After submission of this manuscript, P. G. Campbell, G. Sumrell, and C. H. Schramm, *J. Org. Chem.*, **26**, 697 (1961), reported the preparation of thus compound by a Schotten-Baumann reaction: yield 43%; m.p. 186–187°.

pharmaceuticals. Numerous syntheses of stilbene compounds are available but each synthesis has its limitations. The thermal decarboxylation of diaryl fumarate esters was first reported by Anschütz[1,2] but since then has not been exploited:



$$\begin{array}{c}\text{O}\\ \|\\ \text{Aryl-O—C—CH}\\ \|\\ \text{HC—C—O—Aryl}\\ \|\\ \text{O}\end{array} \xrightarrow{\Delta} \begin{array}{c}\text{Aryl-CH}\\ \|\\ \text{HC-Aryl}\end{array} + 2\ CO_2$$

Using a dry distillation technique, Anschütz prepared four stilbene compounds, as indicated in the above equation, where the aryl radical represents phenyl, 4-methylphenyl (or *p*-tolyl), 4-chlorophenyl, and 4-bromophenyl.

Recently, Miller and Teeter[3] reported the formation of 1-butene, 1-butanol, and carbon dioxide from the thermal decomposition of either dibutyl maleate or dibutyl fumarate. These workers were unable to detect insolable quantities of 5-decene, which product could be expected by analogy to the Anschütz reaction. It is therefore likely that the thermal decompositions of dialkyl and diaryl esters proceed by substantially different mechanisms.

Our interest in the chemistry of fumaryl chloride,[4] from which the intermediary diaryl fumarates (Table I) are readily prepared, led us to explore some further possibilities of the decarboxylation reaction first observed by Anschütz. Successful conversions to stilbene derivatives (Table II) were obtained when the aryl radical was 2-chlorophenyl, 4-chlorophenyl (confirming Anschütz), 2,4-dichlorophenyl, 2,4,6-trichlorophenyl, 2,4,6-tribromophenyl, 4-methoxyphenyl, 4-ethoxyphenyl, and 2-naphthyl. Only 4,4′-dinitrodiphenyl fumarate failed to yield the desired 4,4′-dinitrostilbene, confirming the early literature.[2] In this connection it was noted that of the ten diaryl fumarates examined, only the 4,4′-dinitrodiphenyl fumarate showed a "decomposition point" instead of the customary melting point. This difference in melting point behavior may be a limiting factor in the application of the Anschütz reaction.

Substitution of a solvent decarboxylation technique (Procedure B, Experimental) for the dry distillation method (Procedure A, Experimental) was useful in extending the scope of the reaction. For example, 4,4′-diethoxydiphenyl fumarate, 2,2′,-4,4′,6,6′-hexabromodiphenyl fumarate, and di-β-naphthyl fumarate afforded the corresponding stilbenes by application of the solvent method only.

The data in Table II show that the Anschütz reaction constitutes an additional useful tool in the growing list of stilbene syntheses.[5–13] As

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(1) R. Anschütz, *Ber.*, **18**, 1945 (1885); R. Anschütz and Q. Wirtz, *Ber.*, **18**, 1947 (1885); R. Anschütz, *J. Chem. Soc.*, **47**, 898 (1885); R. Anschütz and Q. Wirtz, *J. Chem. Soc.*, **47**, 899 (1885).

(2) R. Anschütz, *Ber.*, **60**, 1320 (1927).

(3) W. R. Miller and H. M. Teeter, *J. Org. Chem.*, **24**, 1816 (1959).

(4) S. M. Spatz (to Allied Chemical & Dye Corp.), U. S. Patent **2,653,168** (Sept. 22, 1953)

(5) F. C. Lorenz, *Ber.*, **7**, 1096 (1874).

(6) H. Wiechell, *Ann.*, **279**, 341 (1894).

(7) H. D. Law, *J. Chem. Soc.*, **91**, 759 (1907).

(8) A. G. Green, A. H. Davies, and R. S. Horsfall, *J Chem. Soc.*, **91**, 2078 (1907).

(9) E. Späth, *Monatsh.*, **35**, 473 (1914).

(10) J. H. Wood, J. A. Bacon, A. W. Meibohm, N. H. Throckmorton, and G. P. Turner, *J. Am. Chem. Soc.*, **63**, 1334 (1941).

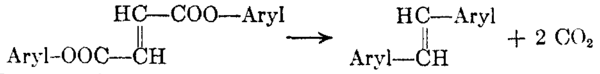
(11) R. L. Shriner and A. Berger, *Org. Syntheses*, **23**, 86 (1943).

(12) F. Bergmann and D. Schapiro, *J. Org. Chem.*, **12**, 57 (1947).

(13) R. A. Barnes, *J. Am. Chem. Soc.*, **70**, 145 (1948)

TABLE II

STILBENES FROM DIARYL FUMARATES



$$\text{Aryl-OOC—CH}{=}\text{HC—COO—Aryl} \longrightarrow \text{Aryl—CH}{=}\text{HC—Aryl} + 2\ CO_2$$

Aryl Radical	M.P.	Lit. M.P. (Ref.)	Procedure A Yield, %	Procedure B Yield, %	Halogen Calcd., %	Halogen Found, %
Phenyl	122.5–123.8	124[a]	29.9	19.1		
2-Chlorophenyl	96–97.2	97[b]	32.5	10.8, 19.1	28.5	26.2
4-Chlorophenyl	174–175	170[c]; 177[d]	16.8, 21.0	32.6, 35.1	28.5	28.5
2,4-Dichlorophenyl	157–159	—	—	29.6, 30.8	44.7	43.0
2,4,6-Trichlorophenyl	216–217	—	—	30.4, 63.9	55.0	53.5
2,4,6-Tribromophenyl	243.5–245.5	—	0	11.4, 12.2	73.4	71.5
4-Methoxyphenyl	211–212	211[e]; 212[f]; 213–214[g]	—	56.4, 65.6		
4-Ethoxyphenyl	203–205	207[f]	0	38.0		
β-Naphthyl	250–251.2	254–255[h,i]	0	29.5		
4-Nitrophenyl	—		—	0		

[a] Ref. 14. [b] Ref. 15. [c] Ref. 2. [d] Ref. 9. [e] Ref. 16. [f] Ref. 8. [g] Ref. 7. [h] Ref. 17. [i] Ref. 18.

now developed, the reaction is limited to the preparation of symmetrically substituted stilbenes.

The fumarates reported in Table I were identified by one or more of the following methods: comparison of observed melting points with literature values, elementary analyses, or conversion to a known stilbene. Similarly, the stilbenes of Table II were identified by melting point comparison with literature values, analytical data and/or conversion from a known fumarate. Six of the nine stilbenes obtained had been reported previously. In these cases, our melting points corresponded to the values reported for the *trans* structure. Consequently, the *trans* configuration is assigned to the hitherto unreported 2,2′-,4,4′-tetrachloro-, 2,2′-,4,4′-,6,6′-hexachloro-, and the 2,2′-,4,4′-,6,6′-hexabromostilbenes.

EXPERIMENTAL

General procedure for the diaryl fumarate esters. The preparation of 4,4′-dimethoxydiphenyl fumarate exemplifies the general procedure used in the syntheses of the intermediary esters. A variety of solvents, benzene, toluene, chlorobenzene, and solvent naphtha, may be used. The reaction proceeds also without a solvent, but the subsequent processing becomes cumbersome.

4,4′-Dimethoxydiphenyl fumarate. A 500-ml. round-bottom flask, equipped with an agitator, a thermometer, and a reflux condenser protected by a calcium chloride tube, was charged with 100 ml. of dry solvent naphtha and 55.8 g. (0.45 mole) of *p*-methoxyphenol. The agitated mixture was warmed until solution was effected; then 30.6 g. (0.2 mole) of fumaryl chloride was added in one portion. The agitated solution was refluxed for 5 hr., cooled to 20°, and filtered. The dried product was recrystallized from 1100 ml. of hot benzene. The yield of recrystallized 4,4′-dimethoxydiphenyl fumarate, m.p. 175–177°, was 63 g. (96%).

General procedures for the decarboxylation of diaryl fumarate. The broad range in yields from 0 to 68% (Table II) suggests that optimum conditions, when ascertained, will not be uniform. A development study to maximize yields to theoretical was not carried out. Of the two decarboxylation procedures examined, one was frequently superior to the other for a specific decarboxylation. *Procedure A*, a modification of the Anschütz distillation technique, entailed an initial 5–6 hr. of heating at 280–290°, followed by atmospheric distillation at 340–350°. *Procedure B* involved refluxing of a suspension-solution of the ester in Dowtherm for 36–50 hr., followed by cooling to room temperature, filtration, and recrystallization or trituration with a suitable solvent. A satisfactory preparation of hexachlorostilbene required 103 hr. of reflux.

The importance of suitable reaction conditions is illustrated by the failure of 4,4′-diethoxydiphenyl fumarate to yield 4,4′-diethoxystilbene, after direct heating at 260–290° for 5.33 hr., followed by atmospheric distillation to 390°. On the other hand, this stilbene was isolated in 38% yield by heating the ester in boiling Dowtherm for 48 hr.

The attempted decarboxylation of 2,2′-,4,4′-,6,6′-hexabromodiphenyl fumarate by Procedure A yielded nothing but tarry material and hydrogen bromide fumes. The same reaction, effected in Dowtherm, gave an 11.4% yield of the hexabromostilbene.

The direct heating and distillation of di-β-naphthyl fumarate also yielded a black, tarry mass which resisted purification to the *sym*-di-β-naphthylethylene. By heating the ester in boiling Dowtherm for 50 hr., a 29% yield of the ethylenic product was realized.

It is not to be inferred from the preceding examples that Procedure B is always the one of choice. The direct distillation of 2,2′-dichlorodiphenyl fumarate gave a 32% yield of 2,2′-dichlorostilbene in contrast to the 11–19% yields obtained by Procedure B. On the whole, however, the majority of the fumarates was decarboxylated more conveniently by Procedure B, that is, by heating in a high-boiling solvent, such as Dowtherm, than by Procedure A, *i.e.*, in the absence of solvent. A final comparison points up the 17–21% yield of 4,4′-dichlorostilbene from 4,4′-dichlorodiphenyl fumarate by Procedure A *versus* a 33–35% yield by Procedure B.

2,2′-Dichlorostilbene. Procedure A. Twenty-five grams of 2,2′-dichlorodiphenyl fumarate was charged to a 150-ml. distilling flask, fitted with a thermometer extended close to bottom of flask. The ester was heated slowly to 285° (internal liquid temperature) and kept on 285–290° for 5.75 hr. The fraction which distilled at 340–350° (liquid temperature) weighed 10 g. and was the crude 2,2′-dichlorostilbene. The solidified distillate was recrystallized from 15 ml. of 2B anhydrous ethanol to yield 6 g. (32.5%) of the stilbene, m.p. 91.5–95.5°. A second recrystallization raised the melting point to 95–97° and reduced the yield to 28.9%.

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(14) A. Michaelis and H. Lange, *Ber.*, **8**, 1314 (1875).

(15) A. H. Gill, *Ber.*, **26**, 651 (1893).

(16) K. Kopp, *Ber.*, **25**, 603 (1892).

(17) W. Wislicenus and H. Wren, *Ber.*, **38**, 510 (1905).

(18) W. Friedman, *Ber.*, **49**, 1352 (1916).

4,4′-Dimethoxystilbene. Procedure B. A round-bottom flask, equipped with an air condenser, was charged with 25 g. (0.076 mole) of 4,4′-dimethoxydiphenyl fumarate and 125 g. of Dowtherm. The mixture, becoming homogeneous on warming, was refluxed for 36 hr. The contents were cooled to 20°, filtered on a Büchner funnel, and either funnel-washed or slurry-washed twice with 25-ml. portions of cold ethanol. The yield of almost white to pale tan, nacreous crystals of 4,4′-dimethoxystilbene, melting at 211–212°, was 12 g. (65.6%).

Halogen analyses. The halogenated compounds of Tables I and II were decomposed for analyses by the Parr bomb technique instead of by the Carius method. In all cases but one, the found halogens were equal to or less than the theoretical. The data suggest a condition which may not be so much a reflection of the purity of the compounds as it is a limitation on the Parr decomposition, especially for compounds high in halogen. As a control, a sample of tetrabromophthalic anhydride, characterized by a theoretical bromine content of 69.1%, showed a 67.8% content by Parr combustion *versus* a 69.3, 69.4% content by Carius combustion.

Acknowledgment. The author is indebted to Audrey K. Lord and Emily A. Bundy for their assistance with this work.

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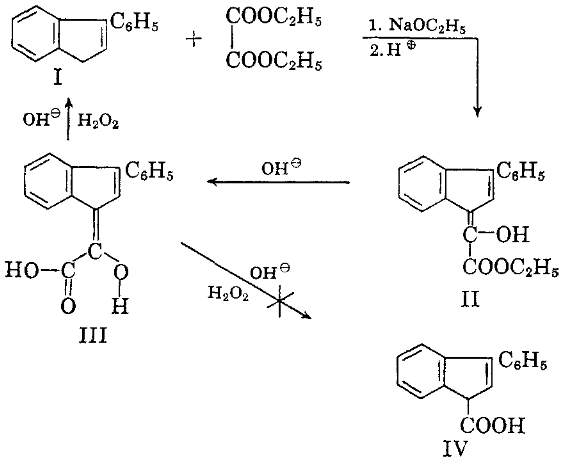
Condensation and Addition Reactions of 3-Phenylindene

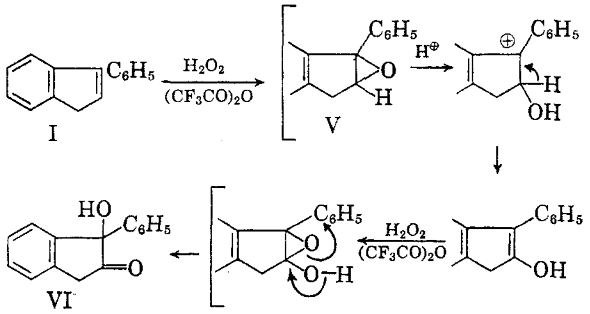
BORIS WEINSTEIN[1]

Received March 23, 1961

Some time ago we had occasion to study the condensation of 3-phenylindene (I) with diethyl oxalate in the presence of sodium ethoxide. The product of the reaction, ethyl 3-phenylindenylglyoxylate (II), exhibited an intense hydroxyl absorption at 2.91 μ and a single carbonyl band at 5.91 μ. Therefore, it probably existed in the enol form in the solid state. On hydrolysis with cold aqueous alkali, the ester afforded 3-phenylindenylglyoxylic acid (III). The free acid possessed a weak hydroxyl peak at 2.86 μ, which could be due to a hydrogen bonding effect, as well as a carbonyl absorption at 5.97 μ. An attempted decarbonylation of III with hot alkali and hydrogen peroxide gave the parent compound I instead of the expected 3-phenylindenecarboxylic acid (IV).



In addition 3-phenylindene was treated with hydrogen peroxide and trifluoroacetic anhydride[2] in the expectation of obtaining 3-phenylindene-2,3-epoxide (V). However, a compound believed to be 3-phenyl-3-hydroxylindan-2-one (VI) was isolated from the reaction. The infrared spectrum showed a hydroxyl absorption at 2.85 μ as well as a cyclopentanone band at 5.70 μ. The structure assigned to VI was supported by its lack of reactivity to the Sarett reagent (chromium trioxide–pyridine). A suggested mechanism for the conversion of I to VI is as follows:



Finally I was hypobrominated to produce 1-phenyl-2-bromoindan-1-ol (VII). This compound was synthesized previously by treatment of I with *N*-bromosuccinimide in aqueous acetone to yield a mixture of stereoisomeric bromohydrins.[3] The sharp melting point of our VII indicated that it may be a single *dl*-isomer pair. A *trans* relationship between the bromo- and hydroxyl-groups is probable on the basis of the analogous hypobromination of indene.[4] Compound VII exhibited at 2.95 μ the expected hydroxyl absorption.

EXPERIMENTAL[5]

3-Phenylindene (I). To a 1-l. three-neck flask equipped with addition funnel, stirrer, and condenser capped with a calcium chloride drying tube were added magnesium turnings (7.3 g., 0.30 g.-atom), an iodine crystal, bromobenzene (3.0 g.), and dry ether (150 ml.). As soon as the reaction began, the remainder of the bromobenzene (34.5 g., 0.22 mole) in ether (150 ml.) was added over a half-hour period

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[1] Present address: Stanford Research Institute, Menlo Park, Calif.

(2) W. D. Emmons, A. S. Pagano, and J. P. Freeman, *J. Am. Chem. Soc.*, **76**, 3472 (1954).

(3) A. S. Kende, *Chemistry & Industry*, 1053 (1956).

(4) C. M. Suter and H. B. Milne, *J. Am. Chem. Soc.*, **62**, 3473 (1940).

(5) Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected. Infrared spectra were determined as potassium bromide disks using the Baird Model B spectrophotometer.