[Contribution from the School of Chemistry of the University of Minnesota]

## THE PREPARATION OF SOME CHLOROMETHYLINDENES AND THE DETERMINATION OF THEIR REACTIVITIES TOWARDS SODIUM IODIDE<sup>1</sup>

C. F. KOELSCH AND R. V. WHITE

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The bimolecular rate constants for the reactions between sodium iodide and organic chlorides (1) depend in a largely unpredictable way on the structures of the latter substances. But even though a quantitative explanation for the rate constants is not available, still their values are qualitatively in agreement with our ideas of the reactivities of many types of organic chlorides (2). It was hoped that such rate constants could be used to determine if the indene nucleus substituted into methyl chloride has as great an influence on the reactivity of the halogen as does an aromatic ring similarly placed, and for this reason a study of the rates of reaction of some chloromethylindenes with sodium iodide was carried out.



The results obtained are listed in Table I. They indicate, as expected, that the reactivity of a substituted 2- or 3-chloromethylindene is greater than that of an alkyl chloride and lies in the range of reactivities of the substituted benzyl chlorides. But since the rate constants are so highly

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dependent on apparently insignificant structural features of the chloromethylindenes, it is not possible to make a precise summarizing statement.

Of more general interest than the reactivities are the syntheses of the compounds involved. To obtain 3-chloromethyl-2-phenyl-1-diphenyleneindene (VII),  $\alpha$ -methylstilbene was brominated, giving  $\alpha$ -bromo- $\alpha$ , $\beta$ -diphenylpropylene (I). The bromo compound was converted into a Grignard reagent, from which  $\alpha$ , $\beta$ -diphenylcrotonic acid (II) could be obtained in a yield of 30%, and this Grignard reagent with fluorenone yielded  $\alpha$ -diphenylene- $\beta$ , $\gamma$ -diphenylcrotyl alcohol (III). Under mild dehydrating conditions, the alcohol gave  $\alpha$ -diphenylene- $\beta$ , $\gamma$ -diphenyl-butadiene- $\alpha$ , $\gamma$  (IV), while under somewhat more vigorous conditions either

COMPOUND	$k(t_1)$	$k(t_2)$	Aª	k(50°)	Rb
3-Chloromethyl 2-phenyl-1-di- phenyleneindene (VII)	7.0 (0°)	13.02 (5°)	4091	(1461)¢	36,400
2-Chloromethyl-3-phenyl-1-di- phenyleneindene (XII)	0.525 (20°)	0.868 (25°)	3817	(8.51)°	212
2-Chloromethyl-1,1,3-tri- phenylindene (XVII)	0.874 (45°)	1.262 (50°)	3277	1.262	31
Chloroacetamide Benzyl chloride <sup>d</sup>	0.355 (25°) 0.786 (25°)	1.31 (30°)	4000	7.89	197
o-Bromobenzyl chloride <sup>d</sup> Chloroacetamide <sup>d</sup>	4.31 (-10°) 0.360 (25)	16.5 (0°) 0.603 (30°)	4200 4000	(3092)° 3.95	77,300 99

TABLE I Reactivities of Chloromethyl Compounds

$$a \log \frac{k(t_1)}{k(t_2)} = A\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

<sup>b</sup> R(butyl chloride, 50°) = 1.

• Calculated.

<sup>d</sup> From Conant, Kirner, and Hussey, Ref. 2.

the alcohol or the diene was converted into 3-methyl-2-phenyl-1-diphenyleneindene (V). This hydrocarbon, whose structure was substantiated by oxidation to benzoic acid and diphenylenephthalide, was brominated, and the bromo compound was converted *via* the acetate (VI) to 3-chloromethyl-2-phenyl-1-diphenyleneindene (VII).

The preparation of 3-chloromethyl-1,1,2-triphenylindene by an analogous series of reactions was abandoned after all attempts to crystallize  $\alpha, \alpha, \beta, \gamma$ -tetraphenylcrotyl alcohol (similar to III but prepared using benzophenone) or to obtain crystalline dehydration products from it had failed. A second attempt which might have led to 3-methyl-1,1,2-triphenylindene through the reaction between triphenylvinylmagnesium bromide and acetophenone, and a third through the reaction between methylmagnesium

iodide and 2,3,3-triphenylhydrindone were both unsuccessful. In each case the Grignard reagent enolized the ketone, and the latter was recovered after hydrolysis of the reaction mixture.



To obtain 2-chloromethyl-3-phenyl-1-diphenyleneindene (XII),  $\alpha, \alpha$ diphenylpropylene was brominated, giving  $\beta$ -bromo- $\alpha, \alpha$ -diphenylpropylene (VIII). The bromide was converted into a Grignard reagent, and this with fluorenone yielded an oily carbinol (IX). Dehydration of this carbinol gave 2-methyl-3-phenyl-1-diphenyleneindene (X)<sup>2</sup> which was





<sup>2</sup> If it is considered that dehydration of IX proceeds through a positive organic ion, then the elimination of a proton from this ion resulting in cyclization can give 1,1-diphenyl-2-methyl-3,4-phenyleneindene. But such a structure is strained and will not be formed if a relatively unstrained product (X) is possible (3). This effect must likewise direct the ring closure of III to V, a case where the structure of the product was proved.

converted through its bromination product and the acetate (XI) into 2-chloromethyl-3-phenyl-1-diphenyleneindene (XII).

To obtain 2-chloromethyl-1,1,3-triphenylindene (XVII), the Grignard reagent from VIII was treated with benzophenone, yielding  $\beta$ -methyl- $\alpha, \alpha, \gamma, \gamma$ -tetraphenylallyl alcohol (XIII). This alcohol gave 2-methyl-1,1,3-triphenylindene (XIV) on dehydration, and the usual subsequent reactions through the bromo compound (XV) and the acetate (XVI) led to the desired chloromethyl compound (XVII). The structure assigned to XIV was confirmed by oxidation; with chromic acid, the indene gave *o*-benzoyltriphenylacetic acid and *o*-benzoyl- $\alpha, \alpha, \alpha$ -triphenylacetone.

Although no study of the reactivity of the product was made, *spiro*-2chloromethyl-3-phenylindene-1,9-xanthene (XX) was prepared by a series of reactions analogous to those just described. The starting materials were the Grignard reagent from VIII and xanthone, and the intermediates isolated were the spiran XVIII,<sup>3</sup> and the acetate XIX.



An attempt was made to obtain 1-bromomethyl-1,2,3-triphenylindene by brominating 1-methyl-1,2,3-triphenylindene (XXI). But since the product was found to contain an unreactive bromine atom, it is probable that substitution of an aromatic hydrogen took place. The 1-methyl-1,2,3-triphenylindene used was prepared by treating 1-bromo-1,2,3triphenylindene with methylmagnesium iodide. It melted at 96–98° and was obviously different from a compound melting at 118° described as 1-methyl-1,2,3-triphenylindene by Kohler and Nygaard (5). The synthesis used by these investigators, involving the dehydration of  $\alpha, \alpha, \beta, \gamma$ tetraphenylbutenol- $\gamma$  (XXII) with acetic anhydride, was repeated, and their 118° product was obtained. It was found that this substance was

<sup>3</sup> This structure is preferred to the one which would result by ring closure on the 4-position of the xanthene nucleus, since it is quite generally true that ring closures in a position meta to an ether oxygen are difficult (4).

converted into the 96–98° indene when it was treated with sulfuric acid in acetic acid. Furthermore, although oxidation of the 118° compound with chromic acid in acetic acid yielded o-( $\alpha$ -methyldesyl)benzophenone and o-dibenzoylbenzene as reported by Kohler and Nygaard, when the oxidation was carried out in the absence of acids with potassium permanganate in acetone there was obtained triphenylacrylophenone. These results indicate that the 118° compound is the diene (XXIII), and that the 96–98° substance is the indene XXI.

## EXPERIMENTAL

 $\alpha$ -Bromo- $\alpha$ , $\beta$ -diphenylpropylene (I).  $\alpha$ , $\beta$ -Diphenylpropanol was obtained in a yield of 88% by treating acetophenone with benzylmagnesium chloride. It boiled at 122-124°/2 mm. and melted at 49-51° (literature (6), m.p. 50-51°). The carbinol (182 g.) was boiled in acetic acid (250 ml.) containing sulfuric acid (0.8 ml.) for five hours; the resulting  $\alpha$ -methylstilbene (154 g.) melted at 79-81.5° (literature (7) 82-83°).

Bromine (126 g.) in acetic acid was added slowly and with stirring to a solution of  $\alpha$ -methylstilbene (147 g.) in acetic acid (400 ml.) at 60°. The mixture was then heated to boiling, and most of the acetic acid was distilled under reduced pressure. The product was washed, dried, and distilled through a Hickman still head, giving 159 g. (74%) of  $\alpha$ -bromo- $\alpha$ , $\beta$ -diphenylpropylene which boiled at 153-156° at 0.001 mm. The refractive index ( $n_{\rm D}$ ) was 1.6536 (15°), 1.6510 (20°), 1.6484 (25°), 1.6457 (30°).

Anal. Cale'd for  $C_{15}H_{13}Br: C, 65.9; H, 4.8.$ Found: C, 65.8; H, 5.4.

A Grignard reagent from  $\alpha$ -bromo- $\alpha,\beta$ -diphenylpropylene (10 g.), magnesium (1 g.), and ether (100 ml.) was carbonated by pouring onto solid carbon dioxide. The resulting  $\alpha,\beta$ -diphenylcrotonic acid (II), purified by solution in sodium carbonate, was obtained in yields of 30-35%. Recrystallized from ligroin it melted at 124-126°.

Anal. Calc'd for C16H14O2: C, 80.6; H, 5.9.

Found: C, 80.7; H, 6.0.

An attempt to cyclize  $\alpha,\beta$ -diphenylcrotonic acid (4.3 g.) to 2-phenyl-3-methylindone by heating it with phosphorus oxychloride (10 g.) in benzene gave  $\alpha$ -methylstilbene as the only crystalline product.

 $\alpha$ -Diphenylene- $\beta$ ,  $\gamma$ -diphenylbutadiene (IV). An ether solution of fluorenone (10.5 g.) was added to a Grignard reagent from  $\alpha$ -bromo- $\alpha$ ,  $\beta$ -diphenylpropylene (30 g.). The mixture, in which a yellow precipitate formed, was boiled for one hour and then decomposed with iced hydrochloric acid. The ether was removed and the oily residue was dissolved in acetic acid (50 ml.) containing three drops of sulfuric acid. The solution was heated to boiling and then cooled, giving  $\alpha$ -diphenylpene- $\beta$ ,  $\gamma$ -diphenylbutadiene which melted at 185–190°; yield, 21–28%. Recrystallized from acetic acid, the diene formed yellow platelets that melted at 197–198°.

Anal. Calc'd for C<sub>28</sub>H<sub>20</sub>: C, 94.3; H, 5.7.

Found: C, 93.5; H, 6.2.

3-Methyl-2-phenyl-1-diphenyleneindene (V). The indene was obtained when the boiling with acetic acid-sulfuric acid described in the preceding paragraph was prolonged to thirty minutes. But since the indene was more soluble than the diene, it could be isolated in better over-all yield if the diene was isolated first. One gram of the diene boiled for one hour with 30 ml. of acetic acid containing a few drops of sulfuric acid gave 0.75 g. of pure 3-methyl-2-phenyl-1-diphenyleneindene. This substance formed white plates that melted at 152.5-153.5°.

Anal. Calc'd for C<sub>28</sub>H<sub>20</sub>: C, 94.3; H, 5.7.

Found: C, 94.3; H, 5.5.

The indene (1 g.) in acetic acid (40 ml.) containing chromic anhydride (1.3 g.) was allowed to stand at room temperature for twenty-four hours. The mixture was then worked up in the usual way giving benzoic acid and diphenylenephthalide. The latter melted at  $220-222^{\circ}$  (literature (8),  $219-220^{\circ}$ ).

Anal. Calc'd for C<sub>20</sub>H<sub>12</sub>O<sub>2</sub>: C, 84.5; H, 4.2.

Found: C, 84.7; H, 4.2.

3-Chloromethyl-2-phenyl-1-diphenyleneindene (VII). A solution of bromine (2.12 g.) in chloroform (10 ml.) was added to 3-methyl-2-phenyl-1-diphenyleneindene (4.3 g.) in 20 ml. of the same solvent. The mixture was exposed to direct sunlight, causing the bromine to disappear rapidly, and the chloroform was evaporated. The resulting bromo compound, crystallized from ligroin but not analyzed, was boiled for ten minutes with potassium acetate (4 g.) in acetic acid (60 ml.). The potassium bromide was filtered and the filtrate was concentrated and cooled, giving the acetate VI (4.8 g.). Recrystallized from acetic acid, 3-acetoxymethyl-2-phenyl-1-diphenyl-eneindene formed colorless prisms that melted at 172-173°.

Anal. Calc'd for C<sub>30</sub>H<sub>22</sub>O<sub>2</sub>: C, 86.9; H, 5.4.

Found: C, 86.9; H, 5.8.

The acetoxy compound was recovered unchanged after treatment in boiling acetic acid with hydrogen chloride, but the desired chloro derivative was obtained when the acetoxy compound (3.85 g.) was heated at  $150^{\circ}$  for four and one-half hours in a sealed tube with 20 ml. of a mixture of equal volumes of acetic acid and conc'd hydrochloric acid. Recrystallized from acetic acid, 3-chloromethyl-2-phenyl-1-diphenyleneindene (VII) formed colorless prisms (2.7 g.) that melted at 145.5–146.5°.

Anal. Calc'd for C<sub>28</sub>H<sub>19</sub>Cl: C, 86.0; H, 4.9.

Found: C, 85.9; H, 5.2.

 $\beta$ -Bromo- $\alpha$ ,  $\alpha$ -diphenylpropylene (VIII).  $\alpha$ ,  $\alpha$ -Diphenylpropylene (7) was obtained in a yield of 74% by treating ethyl propionate with phenylmagnesium bromide and dehydrating the resulting carbinol by heating it at 215°. The propylene (143 g.) in acetic acid (200 ml.) was treated with bromine (38 ml.) and the dibromide was decomposed by heating the mixture on a steam-bath. The solution was poured into water and the oil was distilled, giving 166 g. (82%) of  $\beta$ -bromo- $\alpha$ ,  $\alpha$ -diphenylpropylene which boiled at 169-173° at 13 mm. (literature (9), 169-170°/12).

2-Methyl-3-phenyl-1-diphenyleneindene (X).  $\beta$ -Bromo- $\alpha$ ,  $\alpha$ -diphenylpropylene (40 g.), magnesium (3.7 g.), and a crystal of iodine in ether (500 ml.) usually started to react after five to ten minutes; in some cases it was necessary to add a drop of ethyl bromide. The reaction proceeded briskly for twenty minutes, and the mixture was then boiled for two hours. To such a Grignard reagent was added an ether solution of fluorenone (26.4 g.); the mixture was boiled for thirty minutes and then decomposed with iced hydrochloric acid. The carbinol formed could not be crystallized; it was accordingly dissolved in acetic acid containing a little sulfuric acid; the solution was boiled for ten minutes and then cooled. The 2-methyl-3-phenyl-1-diphenyl-eneindene so obtained crystallized from acetic acid in the form of fine white plates (23.5 g., 45%) that melted at 173–174.5°.

Anal. Calc'd for C<sub>28</sub>H<sub>20</sub>: C, 94.3; H, 5.7. Found: C, 94.1; H, 5.7. 2-Chloromethyl-3-phenyl-1-diphenyleneindene (XII). 2-Methyl-3-phenyl-1-diphenyleneindene (16 g.) was brominated and the bromo compound was treated with potassium acetate in the same way as described for the 3-methyl-2-phenyl isomer. There was obtained 14.5 g. of 2-acetoxymethyl-3-phenyl-1-diphenyleneindene (XI) which melted at 148.5-150° after crystallization from acetic acid.

Anal. Calc'd for C<sub>30</sub>H<sub>22</sub>O<sub>2</sub>: C, 86.9; H, 5.4.

Found: C, 86.7; H, 5.5.

A solution of the acetoxy compound (12 g.) in hot acetic acid (60 ml.) was saturated with hydrogen chloride; 2-chloromethyl-3-phenyl-1-diphenyleneindene precipitated before the solution cooled. Recrystallized from acetic acid containing hydrogen chloride, it formed white needles (9.5 g.) that melted at  $134-136^{\circ}$ .

Anal. Calc'd for C<sub>28</sub>H<sub>19</sub>Cl: C, 86.0; H, 4.9.

Found: C, 85.6; H, 4.9.

2-Methyl-1,1,3-triphenylindene (XIV). Benzophenone (26.7 g.) in ether was added to a Grignard reagent prepared from 40 g. of  $\beta$ -bromo- $\alpha$ ,  $\alpha$ -diphenylpropylene. The oily carbinol obtained by working up the reaction mixture in the usual way was boiled with acetic acid-sulfuric acid, and the product was recrystallized from acetic acid. There was obtained 21.5 g. of 2-methyl-1,1,3-triphenylindene which formed white prisms that melted at 157-159.5°.

Anal. Calc'd for C<sub>28</sub>H<sub>22</sub>: C, 93.8; H, 6.2.

Found: C, 93.6; H, 6.2.

2-Methyl-1, 1, 3-triphenylindene (4 g.) in 200 ml. of hot acetic acid was treated with 5 g. of chromic anhydride. After five minutes the reaction was complete. The solution was poured into water, the products were filtered, washed, and taken up in ether. This solution was shaken with 10% sodium carbonate, and the insoluble sodium o-benzoyltriphenylacetate formed was filtered and crystallized from methanolether. It melted and decomposed at 129° (literature (10), 130°). The neutral compound left in the ether by the sodium carbonate treatment was o-benzoyl- $\alpha, \alpha, \alpha$ -triphenylacetone; from acetic acid it formed colorless prisms (0.7 g.) that melted at 172–173.5°.

Anal. Calc'd for C28H22O2: C, 86.1; H, 5.7.

Found: C, 85.8; H, 5.9.

2-Chloromethyl-1,1,3-triphenylindene (XVII). Bromine (3.7 g.) in 30 ml. of chloroform was added slowly to a stirred boiling solution of 2-methyl-1,1,3-triphenylindene (24 g.) in 100 ml. of chloroform. The reaction proceeded smoothly in direct sunlight, and when the bromine had disappeared the chloroform was distilled. The product was crystallized from ethyl acetate, giving 20 g. of 2-bromomethyl-1,1,3triphenylindene which formed large white prisms that melted at 154-156°.

Anal. Calc'd for C<sub>28</sub>H<sub>21</sub>Br: C, 76.9; H, 4.8.

Found: C, 76.8; H, 4.9.

The bromo compound (20 g.), boiled for ten minutes in acetic acid with potassium acetate (6 g.), yielded 2-acetoxymethyl-1,1,3-triphenylindene (XVI). The product, recrystallized from acetic acid, formed colorless prisms (13 g.) that melted at 178.5-180°.

Anal. Calc'd for  $C_{30}H_{24}O_2$ : C, 86.5; H, 5.8. Found: C, 86.3; H, 5.8.

To a concentrated solution of 2-acetoxymethyl-1,1,3-triphenylindene (13 g.) in hot acetic acid was added 10 ml. of acetic acid which had been saturated with hydrogen chloride. After the mixture had been allowed to cool it deposited 2-chloromethyl-1,1,3-triphenylindene; recrystallized from ethyl acetate the compound formed colorless prisms (10.5 g.) that melted at  $154-155.5^{\circ}$ .

Anal. Calc'd for C<sub>28</sub>H<sub>21</sub>Cl: C, 85.6; H, 5.4. Found: C, 85.3; H, 5.4.

Spiro-2-methyl-3-phenylindene-1,9-xanthene (XVIII) was obtained in a yield of 18% using xanthone and the Grignard reagent from  $\beta$ -bromo- $\alpha$ ,  $\alpha$ -diphenylpropylene. From acetic acid it formed colorless prisms that melted at 153.5-155°.

Anal. Calc'd for C<sub>28</sub>H<sub>20</sub>O: C, 90.3; H, 5.4.

Found: C, 90.4; H, 5.6.

Spiro-2-acetoxymethyl-3-phenylindene-1,9-xanthene (XIX) was obtained from the above spiran (2.5 g.) by bromination and then treatment with potassium acetate. From acetic acid it formed small white prisms (1.4 g.) that melted at 203.5-205°.

Anal. Calc'd for C<sub>30</sub>H<sub>22</sub>O<sub>3</sub>: C, 83.7; H, 5.1.

Found: C, 83.6; H, 5.4.

Spiro-2-chloromethyl-3-phenylindene-1,9-xanthene (XX) was obtained by warming the acetoxy spiran (1 g.) with acetic acid which had been saturated with hydrogen chloride. It formed colorless prisms (0.4 g.) that melted at 144-145°.

Anal. Calc'd for C<sub>28</sub>H<sub>19</sub>ClO: C, 82.6; H, 4.7.

Found: C, 82.5; H, 4.9.

1-Methyl-1, 2, 3-triphenylindene. 2,3-Diphenylindone was obtained in a yield of 52% from 2-phenylindandione-1,3 and phenylmagnesium bromide. It was converted into 1,2,3-triphenylindenol-1 by treatment with phenylmagnesium bromide. This difficultly crystallizable carbinol was isolated in the form of its methyl ether, prepared by dissolving the carbinol in methanol containing a few drops of sulfuric acid (yield 80%). The resulting 1-methoxy-1,2,3-triphenylindene (30 g.) was warmed with 20 ml. of acetic acid which had been saturated with hydrogen bromide. On cooling, the solution deposited 1-bromo-1,2,3-triphenylindene (30 g.) which melted at  $125-127^{\circ}$  (literature (10),  $129^{\circ}$ ).

To a solution of methylmagnesium iodide containing 5 g. of magnesium was added 30 g. of 1-bromo-1,2,3-triphenylindene in benzene (150 ml.). The mixture was boiled for three hours and then worked up in the usual way giving 1-methyl-1,2,3-triphenylindene, which formed small white prisms (13 g.) that melted at 96-98° after crystallization from acetic acid.

Anal. Calc'd for C<sub>28</sub>H<sub>22</sub>: C, 93.8; H, 6.2. Found: C, 94.1; H, 5.9.

Several brominations of 1-methyl-1,2,3-triphenylindene under varied conditions gave products melting unsharply in the range 140–165°. Bromination with one equivalent of bromine in acetic acid gave a product which sintered at 162° and melted at 170–171°. None of the products reacted with boiling alcoholic silver nitrate; the 170–171° compound was analyzed.

Anal. Calc'd for C<sub>28</sub>H<sub>21</sub>Br: C, 76.9; H, 4.8.

Found: C, 76.9; H, 5.1.

 $\alpha, \alpha, \beta, \gamma$ -Tetraphenylbutadiene- $\alpha, \gamma$  (XXIII). Triphenylacrylophenone was prepared in yields of 30-40% by the action of benzoyl chloride on triphenylvinylmagnesium bromide (11). Treated with methylmagnesium iodide according to the procedure of Kohler and Nygaard, triphenylacrylophenone (22 g.) yielded  $\alpha, \alpha, \beta, \gamma$ tetraphenylbutenol- $\gamma$  (11 g.) which melted at 96-98° (literature (5), 96-97°).

Tetraphenylbutenol (3 g.), boiled for five hours with sodium acetate (1 g.) in acetic anhydride (15 ml.), gave 2.2 g. of  $\alpha, \alpha, \beta, \gamma$ -tetraphenylbutadiene which melted at 118.5-120°. A solution of the diene (1.62 g.) in acetone (80 ml.) was boiled while powdered potassium permanganate was added in portions as long as its color was discharged; a total of 6.16 g. of the oxidizing agent was consumed. The solution was

filtered and evaporated, and the residue was crystallized from ethanol. There was obtained 0.95 g. of triphenylacrylophenone, which melted at 146–147° alone and at 147.5–148.5° when mixed with an authentic sample. For further identification, the triphenylacrylophenone was reduced with zinc dust in acetic acid to  $\alpha, \beta, \beta$ -triphenyl-propiophenone, which melted at 180–181° (literature (12), 181°) alone or mixed with an authentic sample.

Boiled for five minutes in acetic acid containing a drop of sulfuric acid,  $\alpha, \alpha, \beta, \gamma$ -tetraphenylbutadiene- $\alpha, \gamma$  was converted into 1-methyl-1,2,3-triphenylindene, and similar treatment of  $\alpha, \alpha, \beta, \gamma$ -tetraphenylbutenol- $\gamma$  gave the same product. In each case the reaction proceeded quantitatively and the identity of the product was confirmed by direct comparison with 1-methyl-1,2,3-triphenylindene obtained from 1-bromo-1,2,3-triphenylindene.

Rate studies. The procedures of Conant (2) were followed closely. The concentration of sodium iodide was 0.04 N and that of organic chloride 0.2 molar. As a check on technique, the reaction constant for chloroacetamide at  $25^{\circ}$  was determined and found to be 0.348 (1 hour) and 0.362 (2 hours); Conant reports the value 0.360 for this halide under the same conditions.

AT 0°			AT 5°		
Time, hours	Percentage reacted	k	Time, hours	Percentage reacted	k
0.167	22.89	6.97	0.167	38.25	13.19
.25	31.93	6.95	.25	50.30	12.95
.333	39.16	6.80	.333	59.04	12.91
.417	48.19	7.51			
.5	51.81	6.77			
Av		7.00			13.02

2-chloromethyl-3-phenyl-1-diphenyleneindene						
AT 20°		AT 25°				
0.5	5.52	0.491	0.5	9.64	0.876	
1.0	12.10	.561	1.0	18.39	.878	
1.5	15.97	.507	1.5	25.44	.874	
2.0	19.77	.539	2.0	31.95	.855	
Av		0.525			0.868	

2-CHLUROMETHIL-1, 1, 3-TRIPHENILIND	IDENE
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AT 45°		AT 50°			
0.5	9.68	0.873	0.5	14.37	1.337
1.0	18.47	.884	1.0	25.51	1.285
1.5	26.09	.881	1.5	34.31	1.236
2.0	31.97	.847	2.0	41.41	1.189
Av		0.874			1.262

## SUMMARY

The preparations of three indenes chloromethylated in the five-membered ring are described, and measurements of the reactivities of these substances towards sodium iodide in acetone are reported.

It is shown that a compound previously formulated as 1-methyl-1,2,3triphenylindene is in reality  $\alpha, \alpha, \beta, \gamma$ -tetraphenylbutadiene- $\alpha, \gamma$ .

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## REFERENCES

- (1) CONANT AND KIRNER, J. Am. Chem. Soc., 46, 232 (1924).
- (2) CONANT AND HUSSEY, J. Am. Chem. Soc., 47, 476 (1925); CONANT, KIRNER AND HUSSEY, J. Am. Chem. Soc., 47, 488 (1925).
- (3) KOELSCH, J. Am. Chem. Soc., 54, 3384 (1932).
- (4) JACOBSON AND ADAMS, J. Am. Chem. Soc., 46, 1312 (1924); FIESER AND BRAD-SHER, J. Am. Chem. Soc., 58, 1738 (1936); CHATTERJEE AND BARPUJARI, J. Indian Chem. Soc., 17, 292 (1940).
- (5) KOHLER AND NYGAARD, J. Am. Chem. Soc., 52, 4136 (1930).
- (6) HELL, Ber., 37, 453 (1904).
- (7) KLAGES, Ber., 35, 2646 (1902).
- (8) KOELSCH, J. Am. Chem. Soc., 55, 3398 (1933).
- (9) HELL AND BAUER, Ber., 37, 230 (1904).
- (10) KOHLER, Am. Chem. J., 40, 217 (1908).
- (11) KOELSCH, J. Am. Chem. Soc., 54, 2045 (1932).
- (12) KOHLER AND HERITAGE, Am. Chem. J., 34, 571 (1905).