Attempted preparation of 1,2,3,4-tetrahydro-3-phenanthrone. Used in the 2-tetralone method with benzene as a solvent, ethylene, aluminum chloride, and 1-naphthylacetyl chloride gave 20 g. of ethylbenzene, b.p. 134–135°, n_D^{25} 1.4931, and a small amount of di- and triethylbenzenes, b.p. 95–115° (25–30 mm.). Treatment of the residue with ethyl alcohol yielded 7 g. of acenaphthenone, m.p. 115–117°. Recrystallization from ethyl alcohol or petroleum ether (b.p. 60–68°) m.p. to 121°. A mixed melting point with a known sample showed no depression. Also isolated was 3 g. of a white, crystalline solid which could not be identified.

LAWRENCE, KAN.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Participation of Carbon Disulfide in the Friedel-Crafts Reaction

PHILIP D. GEORGE

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Carbon disulfide participated to a major extent when used as a solvent for the reaction of chloromethyltrimethylsilane with benzene in the presence of an equimolar amount of aluminum chloride. Bright red trimethylsilylmethyl dithiobenzoate, $C_6H_5CS_2CH_2Si(CH_3)_3$, was formed in about 50% yield. Under the same conditions *n*-amyl chloride behaved normally with formation of amyl-substituted benzenes and no sulfur-containing products. Extensive participation of carbon disulfide was also qualitatively observed in the reaction of chloromethyltrimethylsilane with chlorobenzene, octene-1, isooctane, and *n*-octane and also in the reaction of (chloromethyl)methyldichlorosilane with benzene, all in the presence of an equimolar amount of aluminum chloride.

Carbon disulfide is ordinarily regarded as an excellent solvent for Friedel-Crafts reactions because it is generally believed not to participate in such reactions.[1] However, we have found instances in which participation of carbon disulfide becomes the main reaction, apparently with formation of dithio esters as the major product.

Thus refluxing equimolar quantities of chloromethyltrimethylsilane, benzene and aluminum chloride in excess carbon disulfide resulted in gradual consumption of the aluminum chloride. There was no evolution of hydrogen chloride, but a bright red lower layer formed which reached a constant volume in four hours. Separating, hydrolyzing, washing, drying, and distilling this material gave a bright red liquid product.

This substance appeared to be trimethylsilylmethyl dithiobenzoate formed according to the following equation:

$$C_6H_6 + CS_2 + ClCH_2Si(CH_3)_3 \xrightarrow[AlCl_3]{} C_6H_5CS_2CH_2Si(CH_3)_3$$

Quantitative analysis for carbon, hydrogen, sulfur, silicon, chlorine, and molecular weight substantiated this supposition, although exact agreement with theoretical values was not achieved. The infrared spectrum of the product was consistent with the structure proposed[2] and also suggested that one of the contaminants was a thiol ester, $C_6H_5COSCH_2Si(CH_3)_3$, arising from hydrolysis or oxidation of the dithio ester or the intermediate reaction complex.

The identity of the product was further supported by experiments aimed at ascertaining its progenitor. Ethyldimethylchlorosilane, which might have arisen from chloromethyltrimethylsilane by rearrangement,[3] gave no red oil on being refluxed with benzene, carbon disulfide, and aluminum chloride. Neither did trimethylchlorosilane nor diethyldichlorosilane. When carbon disulfide was omitted from the reaction mixture—*i.e.* when chloromethyltrimethylsilane, benzene and aluminum chloride were refluxed—the major products were methylethylpolysiloxanes and toluene. The former apparently arose from rearrangement of the starting material.[3] The toluene probably arose from hydrogen chloride cleavage of benzyltrimethylsilane initially formed by coupling.

The preparation of trimethylsilylmethyl dithiobenzoate was carried out under various conditions. A yield of 43% was obtained upon refluxing equimolar amounts of chloromethyltrimethylsilane, benzene, and aluminum chloride in excess carbon disulfide for four hours; the bright red lower liquid layer was hydrolyzed on ice, washed, dried, and distilled. A product obtained from a similar run by steam distillation seemed to contain more thiol ester. In another run satisfactory results were obtained when the amount of carbon disulfide was reduced to theoretical and excess benzene was used as the solvent. When only a catalytic amount

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[1] (1) Actually a few instances of such participation have been reported. The first such instance was with pyrazolones —E. Benary and A. Schmidt, *Ber.*, **57**, 517 (1924). Other instances were later demonstrated with phenol, phenol ethers and even benzene itself, but the yields were vanishingly small—H. Jorg, *Ber.*, **60B**, 1466 (1927).

[2] (2) C. S. Marvel, P. de Radzitzky, and J. J. Brader, *J. Am. Chem. Soc.*, **77**, 5997 (1955), tentatively assigned the 8.5 μ infrared absorption band to the C=S group in dithio esters as a result of their studies of simple aliphatic dithio esters.

[3] (3) F. C. Whitmore, L. H. Sommer, and J. R. Gould, *J. Am. Chem. Soc.*, **69**, 1976 (1947).

of aluminum chloride was used, no dithio ester was formed.

The behavior of chloromethyltrimethylsilane in this reaction was in marked contrast to that of *n*-amyl chloride. The alkyl halide gave the normally expected amyl-sybstituted benzenes and no sulfur-containing derivatives even in the residue.

Reactions qualitatively similar to the above dithio ester formation occurred with other combinations of reactants. Thus like benzene, chlorobenzene gave a red oil upon being refluxed with chloromethyltrimethylsilane and aluminum chloride in carbon disulfide. The product probably contained trimethylsilylmethyl dithiochlorobenzoate, $ClC_6H_4CS_2CH_2Si(CH_3)_3$, as the major constituent.

Another combination of reactants that gave a red liquid product was (chloromethyl)methyldichlorosilane, benzene, and aluminum chloride in carbon disulfide. In this case, however, the reaction required about six days for completion. Hydrolysis of the product gave a polymer that probably contained the $[—SiCH_3(C_6H_5CS_2CH_2)O—]$ group as the major constituent.

The reactions of octene-1, 2,4,4-trimethylpentane and *n*-octane, respectively, with chloromethyltrimethylsilane and carbon disulfide in the presence of aluminum chloride were also qualitatively investigated. The olefin produced a brown lower layer from which were isolated materials containing substantial amounts of silicon and sulfur. The branched paraffin gave a bright red lower layer in the reaction mixture, and the starting materials were consumed. The *n*-octane gave a bright red lower layer from which was isolated a substantial amount of product containing thiocarbonyl, thiol ester and silicon-methyl groups.

This report of our investigation includes our qualitative findings because we do not presently expect to do any further work in this area and because these findings may be important to others in view of the widespread use of carbon disulfide as a solvent for Friedel-Crafts reactions.

EXPERIMENTAL

Starting materials. The chloromethyl silicon compounds used were purified materials made under the supervision of Dr. J. R. Ladd. Other reagents such as benzene, carbon disulfide, and anhydrous aluminum chloride were C.P. materials. The various alkylchlorosilanes were redistilled before use.

Reaction of chloromethyltrimethylsilane, carbon disulfide, benzene, and aluminum chloride. In a round-bottom flask fitted with a reflux condenser protected by a drying tube were placed 136 g., 1.0 mole, of anhydrous aluminum chloride, 300 ml. of carbon disulfide, 122 g., 1.0 mole, of chloromethyltrimethylsilane and 78 g., 1.0 mole, of benzene. Refluxing the reaction mixture resulted in gradual solution of the aluminum chloride with formation of a red lower layer whose volume did not increase after about 4 hr. No hydrogen chloride evolution was observed, and the weight loss was only 6 g. The reaction mixture was poured on cracked ice, and the deep red lower layer was separated with the aid of ether. Fractional distillation of the product after it was dried with anhydrous sodium sulfate gave 360 ml. of ether, 25 ml. of inter-cut, 280 ml. of carbon disulfide, 10.6 g. of inter-cut, and 17.9 g. of benzene. At this point decomposition seemed to be setting in, so the residue was simple-distilled at less than 1 mm.

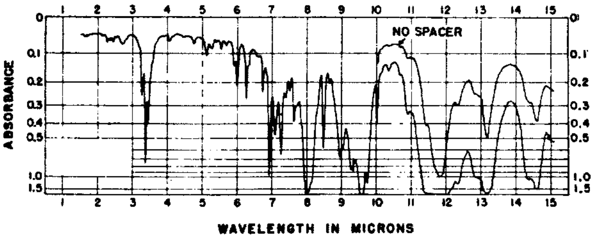

Fig. 1. $C_6H_5CS_2CH_2SiMe_3$

Cut	B.P.	n_D^{20}	Wt., G.
4	37–107		6.2
5	103	1.5973	34.6
6	104	1.6013	46.7
7	107	1.6030	22.1
8	109	1.6019	6.8
9	136	1.6032	10.4
10	Residue		19.0
11	Trap		22.1
12	Loss		16.6

Sodium light was used for the refractive indexes because the bright red color of the product vitiated the refractometer dispersion setting. The infrared spectra of fractions 5–7 indicated the presence of trimethylsilyl and phenyl groups. A sharp band at 6.0 μ, probably due to the carbonyl of a thiol ester, gradually decreased in intensity as the distillation progressed; however, the band at 8.48 μ, probably due to thiocarbonyl, remained essentially constant in intensity. The infrared spectrum of fraction 7 is shown in Figure 1. Redistillation of part of cut 6 showed that most of it boiled at 95° at 0.1 min. and had n_D^{20} 1.5941–1.6033. Fractions 5–7 represented 103 g., 0.43 mole, 43% crude yield of the trimethylsilylmethyl dithiobenzoate.

Anal. Calcd. for $C_{11}H_{16}S_2Si$: C, 54.94; H, 6.71; S, 26.67; Si, 11.68; mol. wt., 240.5. Found for cut 6: C, 52.3; H, 7.4; S, 26.1; Si, 13.6; Cl, <0.1; mol. wt., 224. Found for cut 7: C, 51.8; H, 6.8; S, 25.1; Si, 13.1.

Other runs were also carried out. In a run like the above except that the red oil was steam-distilled, the main product was a bright red liquid, b.p. 110–120° at 0.1 mm., n_D^{20} 1.593, which contained 16.6% sulfur and 11.9% silicon, and whose infrared spectrum was similar to that of the preceding product except for a very strong thiol ester band at 6.0 μ.

In a run in which excess benzene was used, similar results were obtained. A red oil formed when 0.2-mole quantities of chloromethyltrimethylsilane, anhydrous aluminum chloride and carbon disulfide were refluxed for 6 hr. in 60 ml. of benzene. After being poured on cracked ice and washed successively with water, aqueous potassium hydroxide and water again, the product was dried with Drierite and distilled. There was obtained 5.9 g., 0.025 mole, 13% yield of trimethylsilylmethyl dithiobenzoate, b.p. 97–117° at <1 mm., n_D^{20} 1.6021–1.6042.

Similar results were obtained in a run in which the benzene was added after the other ingredients had been refluxed together. When 0.2-mole quantities of chloromethylsilane and anhydrous aluminum chloride were refluxed in 60 ml. of carbon disulfide for 0.5 hr., the reaction mixture became mushy. Addition of 0.2 mole of benzene followed by several hours refluxing gave a red lower layer. The crude product upon being worked up in the usual way gave 21 g., 43% yield of trimethylsilymethyl dithiobenzoate, b.p. 99–103° at <1 mm., n_D^{20} 1.6030–1.6110.

In a run like the preceding ones above except that (a) the red oil was poured on 200 ml. of concd. hydrochloric acid mixed with a couple of liters of cracked ice and (b) the alkali wash was omitted, the main product was 139 g., 0.58 mole, 58% yield, of clear red-brown liquid trimethylsilymethyl dithiobenzoate b.p. 125° at 0.2 mm. The infrared spectra of the distillation fractions were very similar to those of the first product obtained, and there was present the sharp band at 6.0 μ which decreased in intensity as the distillation progressed.

The foregoing variations on working up the product were made in an effort to avoid the formation of the thiol ester contaminant which had been presumed to arise through hydrolysis. As they were unsuccessful, it appeared desirable to check air oxidation of the product as a possible source of the contaminant. Bubbling air through the product at room temperature in fine bubbles at the rate of about 1 l. per min. for 36 hr. gave no change in weight and infrared spectrum.

No red oil formed in a run in which only a catalytic amount of aluminum chloride was used. The recovery of unchanged benzene and chloromethylsilane was substantially complete.

Attempted chromatographic purification. In an effort to purify the product, 50 g. was chromatographed on a column of alumina wet with hexamethyldisiloxane. The column was then eluted with hexamethylsililoxane until the eluate came through colorless. Three distinct bands were obtained—purple, yellow, and rust-colored going from top to bottom. The column was sectioned, and extracted with ether, and the extracts were evaporated leaving a few tenths gram each of materials whose infrared spectra were suggestive of C_6H_5-$SOCO_2H$, $(C_6H_5COS—)_2$, and $C_6H_5COSCH_2Si(CH_3)_3$. Evaporation of the hexamethyldisiloxane left a bright red liquid product whose infrared spectrum was the same as the starting material except for estimated reductions of 50%, 30%, 90%, 90%, 50%, 100% and 50% respectively in the intensities of the bands at 6.02 μ 8.48 μ, 8.97 μ, 9.75 μ, 10.03 μ, 12.80 μ, and 14.35 μ.

Anal. Calcd. for $C_{11}H_{16}S_2Si$: C, 54.9; H, 6.7; S, 26.7; mol. wt., 241. Found: C, 49.6; H, 7.9; S, 24.5; mol. wt., 237.

Precursor of the red oil. The following experiments were carried out to learn whether the red oil was formed from chloromethyltrimethylsilane or from compounds, such as ethyldimethylchlorosilane or trimethylchlorosilane, which might be formed from it during the reaction.

No red oil formation or other evidence of reaction was observed on refluxing for 24 hr. a reaction mixture consisting of 0.2 mole quantities of diethyldichlorosilane and aluminum chloride in 60 ml. of carbon disulfide. Addition of 1 ml. of chloromethylsilane followed by 24 hr. of refluxing also resulted in no evidence of reaction. When 0.2 mole of chloromethyltrimethylsilane was added and the reaction mixture was refluxed for several hours, the usual amount of red oil formed.

No evidence of reaction was observed when 1-mole amounts of trimethylchlorosilane, benzene, and aluminum chloride were refluxed for 5 hr. in carbon disulfide. Most of the starting material was recovered; the hydrolysate of the reaction mixture contained less than 11.2 g. boiling above 100°, of which less than 1 g. boiled above 170°.

No red oil formation or other evidence of reaction was observed on refluxing for 3 days a reaction mixture consisting of 0.2-mole quantities of diethyldichlorosilane, benzene, and aluminum chloride in 60 ml. of carbon disulfide.

Omission of carbon disulfide. Practically no hydrogen chloride evolution occurred when 60 ml., 0.43 mole, of chloromethyltrimethylsilane in 215 ml. of benzene was refluxed for 1.5 hr. with 17 g., 0.13 mole, of anhydrous aluminum chloride. At the outset the reaction was very vigorous and had to be controlled with an ice bath. The reaction mixture was washed with water, dried with Drierite and fractionally distilled. The product was a complex mixture which contained little or no benzyltrimethylsilane, the expected coupling product. Found in substantial amounts were components tentatively identified as methylethylpolysiloxanes and toluene. The former probably arose from rearrangement of the starting material. The latter probably arose from hydrochloric acid cleavage of the benzyltrimethylsilane that was probably formed.

Substitution of myl de for chlororachliomethyltrimethylsilane. Into a round bottom flask fitted with a reflux condenser protected by a drying tube were placed 26.5 g. (0.2 mole) of anhydrous aluminum chloride, 60 ml. of carbon disulfide, 15.5 g. (0.2 mole) of benzene, and 21.3 g. (0.2 mole) of *n*-amyl chloride. Refluxing the reaction mixture resulted in hydrogen chloride evolution, which stopped after 6 hr. A very small red lower layer formed, and not all the aluminum chloride was consumed.

After being poured on cracked ice and washed with water the crude product was dried with Drierite and fractionally distilled. There was obtained: 4.8 g., 31% recovery, of unchanged benzene, b.p. 78–80°. n_D^{20} 1.5013; 4.3 g., 0.029 mole, 21% yield of amylbenzenes, b.p. 39–55° at 2–5 mm., n_D^{20} 1.4890–1.4901; 3.0 g. of a product, b.p. 95–107° at <1 mm., n_D^{20} 1.5270– 1.5532; and 2 ml. of viscous residue. The infrared spectra of the products were consistent for amylbenzenes. Quantitative analysis of the higher boiling fractions and the residue showed the presence of less than 0.1% sulfur.

Reaction of chloromethyltrimethylsilane, carbon disulfide, chlorobenzene, and aluminum chloride. The reaction of 366 g. (3.0 moles) of chloromethyltrimethylsilane, 388 g. (3.0 moles) of chlorobenzene, 400 g. (3.0 moles) of anhydrous aluminum chloride, and 900 ml. of carbon disulfide was carried out in the manner previously described for benzene. Substantially, the same behavior was observed during the 4-hr. reflux period except that upon first being warmed the reaction mixture appeared to be getting out of control and was therefore cooled briefly with an ice bath.

The reaction mixture was poured on 2 kg. of cracked ice, the organic layer was separated, and it was stirred with 200 ml. of 5% sodium bicarbonate solution for 1 hr. The product was then washed with two 100-ml. portions of water and dried over 100 g. of anhydrous sodium sulfate.

Volatile material was stripped at reduced pressure and room temperature, and then 157 g. of material, b.p. 38–148° at 0.1 to 4 mm., was distilled and discarded. Further distillation of the remaining 357 g. gave 267 g. of bright red product, b.p. 140–180° at 4 mm., n_D^{20} 1.59, and 70 g. of solid back tar as residue. As the fractions were collected a small amount of solid appeared, and though the last 25 g. of distillate solidified completely, it was not 4,4′-dichlorobiphenyl because it dissolved readily in hexane. The combined distillate fractions solidified on standing in a refrigerator, but melted on warming to room temperature except for a few percent which remained solid.

The main product obtained had an infrared spectrum, shown in Fig. 2, consistent for trimethylsilymethyl dithiochlorobenzoate (containing some thiol ester) and hence represented 0.97 mole, 32% crude yield of this compound which evidently contained other products.

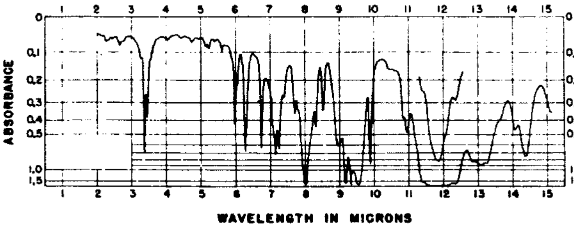

Fig. 2. Product from C_6H_5Cl, CS_2, and $ClCH_2SiMe_3$

Anal. Calcd. for $C_{11}H_{15}ClS_2Si$: C, 48.1; H, 5.5; Cl, 12.9; S, 23.3; Si, 10.2. Found: C, 46.0; H, 6.9; Cl, 8.3; S, 26.2; Si, 13.6.

An earlier run had been made on a 0.2-mole scale in the same way except that the product was washed with aqueous potassium hydroxide and then with water until neutral. The dried product was distilled whereupon there was obtained 9.0 g., 40% recovery, of chlorobenzene, b.p. 128–130°, and 8.4 g. of a light red oil, b.p. 115–141° at 0.1 mm, n_D^{20} 1.5521–1.5613, from which there crystallized on standing a few tenths of a gram of 4,4′-dichlorobiphenyl, m.p. 146–147°, negative Si, positive Cl. The main product had an infrared spectrum very similar to that of the product above; the absorbances indicated about twice the thiol ester carbonyl content, about the same thiocarbonyl content and about half the aromatic content.

Anal. Calcd. for $C_{11}H_{15}ClS_2Si$: C, 48.1; H, 5.5; Cl, 12.9; S, 23.3; Si, 10.2; mol. wt., 274. Found: C, 43.6, 43.3, 42.8, 42.9; H, 7.3, 7.5, 7.0, 7.1; Cl, 5.8, 6.5; S, 24.2, 23.5; Si, 16.6, 15.3; mol. wt., 269.

Reaction of (chloromethyl)methyldichlorosilane, carbon disulfide, benzene, and aluminum chloride. When 0.2-mole quantities of (chloromethyl)methyldichlorosilane, benzene, and aluminum chloride were refluxed in 60 ml. of carbon disulfide, separation of a red oil occurred very slowly for 6 days. The product was poured on cracked ice, washed successively with water, potassium hydroxide and water, and then it was dried with Drierite and distilled. After carbon disulfide was removed at 45–47° there remained 26.1 g. of a black, malodorous, benzene-insoluble, cheesy gum. This product contained [—$Si(CH_3)(C_6H_5CS_2CH_2)O$—] groups as the major constituent.

Anal. Calcd. for $C_9H_{10}OS_2Si$: C, 47.8; H, 4.5; S, 28.3; Si, 12.4. Found: C, 43.9; H, 4.9; S, 14.8; Si, 16.6.

Reaction of chloromethyltrimethylsilane, carbon disulfide, octene-1, and aluminum chloride. Into a round bottom flask fitted with a reflux condenser protected by a drying tube were placed 122 g., 1.0 mole, of chloromethyltrimethylsilane, 137 g., 1.0 mole, of anhydrous aluminum chloride, 59 g., 0.53 mole, of octene-1, and 370 ml. of carbon disulfide. Refluxing the reaction mixture for 4 hr. resulted in the separation of a large lower layer. Evaporation of the 280 ml. upper layer on the steam bath left a 101 g. residue whose hydrolysate contained 9.0% Si, 7.2% S, and 10% chloromethyltrimethylsilane (by infrared analysis).

The 450-ml. lower layer from the original reaction mixture was poured on cracked ice, and the product was then freed of solvent on the steam bath. After being dried the black viscous residue weighed 110 g. It contained 14.3% Si and 17.4% S. Fractional distillation at <1 mm. gave: 27 g., b.p. <35°; 22.7 g., b.p. 110–157° (Found: 42% C, 9.0% H, 18.9% S, 18.7% Si); and 53.6 g. of black viscous residue (Found: 17.0% S, 7.0% Si).

Reaction of chloromethyltrimethylsilane, carbon disulfide, isooctane, and aluminum chloride. When 0.2-mole quantities of chloromethyltrimethylsilane, 2,4,4-trimethylpentane, and aluminum chloride in 100 ml. of carbon disulfide were refluxed for 16 hr., the aluminum chloride was consumed and approximately 50 ml. of bright red lower layer formed. Distillation of the carbon disulfide layer showed that it contained little isooctane or chloromethyltrimethylsilane and only about 5–10 g. of material that was probably chloromethyldimethylchlorosilane.

Reaction of chloromethyltrimethylsilane, carbon disulfide, n-octane, and aluminum chloride. When 0.2-mole quantities of chloromethyltrimethylsilane, *n*-octane, and anhydrous aluminum chloride in 100 ml. of carbon disulfide were refluxed for 16 hr., the aluminum chloride was consumed and a bright red lower layer formed without hydrogen chloride evolution. The reaction mixture was poured on 500 ml. of cracked ice and 40 ml. of concd. hydrochloric acid with vigorous stirring, and the organic layer was washed repeatedly with water and then dried. Evaporation to constant weight by heating on the steam bath with a stream of nitrogen and finally under vacuum overnight left a 17-g. residue whose infrared spectrum showed the presence of a thiol ester carbonyl, thiocarbonyl, and silicon-methyl. The infrared absorption bands and their intensities at 0.025 inch film thicknesses were as follows: 3.37 μ (1.15), 5.95 μ(0.57), 6.85 μ (0.45), 71.0 μ (0.46), 7.25 μ (0.56), 8.00 μ (>1.5), 8.49 μ (0.26), 8.95 μ (0.66), 9.4 μ (>1.5), 10.45 μ (0.31), 11.8 μ (>1.5), and 14.4 μ (0.76).

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SCHENECTADY, N.Y.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Electrophilic Substitution in 1,3-Diphenylindene

C. F. KOELSCH

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1,3-Diphenylindene undergoes nitration and acylation at C-2. The resulting substances are acidic, forming salts which can be alkylated. 2-Benzoyl-1,3-diphenylindene reacts rapidly with oxygen in presence of alkali forming 2-benzoyl-1,3-diphenyl-1-indenol.

To obtain precursors of 2-substituted 1-indyl free-radicals, nitration and acylation of 1,3-diphenylindene have been studied. A few examples of electrophilic substitution in indenes have been reported previously. Bromination and nitration of 1-diphenylene-3-phenylindene yield 2-bromo- and 2-nitro derivatives[1]; nitration of 1,1-dimethyl-3-phenylindene yields the 2-nitro derivative.[2] Indene itself polymerizes under Friedel-Crafts conditions but ethyl 3-indenepropionate, ethyl 3-indenebutyrate, and the nitriles corresponding to these esters react with acetyl chloride and aluminum chloride to form 2-acetyl derivatives, and indene-3-butyric acid undergoes intramolecular acylation at C-2 (cyclization) with phosphorus pentachloride.[3] 1,3-Diphenylindene is brominated[4] and carboxylated[5]

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(4) C. F. Koelsch, *J. Org. Chem.*, **25**, 130 (1960).

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