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

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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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(1) C. F. Koelsch, *J. Am. Chem. Soc.*, **55**, 3394 (1933).

(2) C. F. Koelsch and P. R. Johnson, *J. Am. Chem. Soc.*, **65**, 567 (1943).

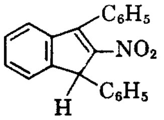
(3) F. A. Howell and D. A. H. Taylor, *J. Chem. Soc.*, 3011 (1957).

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

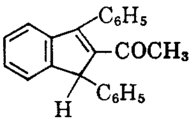
(5) C. F. Koelsch, *J. Org. Chem.*, **25**, 2088 (1960).

at C-2. Similarly 1,1,3-trimethylindene reacts at C-2 with cumyl carbonium ion.[6]

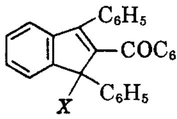
In the present work, 1,3-diphenylindene was found to be attacked readily by nitric acid in acetic acid, but this reagent formed much resinous material and only a little 1,3-diphenyl-2-nitroindene (I). Use of copper nitrate in place of nitric acid gave less resin and a 45% yield of I. This yellow product dissolved in aqueous alcoholic potassium hydroxide forming a deep green solution, stable in air, which gave back I on acidification. Vigorous oxidation of I with chromic acid gave *o*-dibenzoylbenzene. Benzyl chloride and alcoholic potassium hydroxide converted I into 1-benzyl-1,3-diphenyl-2-nitroindene, also obtained by nitration of 1-benzyl-1,3-diphenylindene. With acrylonitrile, I gave an oil which could be hydrolyzed to 1,3-diphenyl-2-nitro-1-indenepropionic acid.



I



II



III

Friedel-Crafts acylations of 1,3-diphenylindene proceeded better in benzene than in nitrobenzene. In benzene, diphenylindene formed a difficultly soluble red aluminum chloride complex which dissolved when an acylating agent was added. Acetyl chloride gave a 72% yield of 2-acetyl-1,3-diphenylindene (II). This colorless ketone formed a deep red solution in aqueous alcoholic potassium hydroxide, rapidly bleached by air. Oxidation of II with chromic acid gave *o*-dibenzoylbenzene.

Benzoyl chloride gave a 75% yield of 2-benzoyl-1,3-diphenylindene (III. $X = H$). This ketone formed a deep purple solution in aqueous alcoholic potassium hydroxide, rapidly decolorized by air with formation of 2-benzoyl-1,3-diphenyl-1-indenol (III, $X = OH$). The autoxidation required one atom of oxygen and no peroxide was isolated, although low temperature studies[7] were not made. 2-Benzoyl-1,3-diphenylindene reacted with phenylmagnesium bromide to form a deep green solution, decolorized by air with formation of III ($X = OH$). With acetyl chloride the indenol gave 2-benzoyl-1-chloro-1,3-diphenylindene (III. $X = Cl$) converted by methanol into 2-benzoyl-1,3-diphenyl-1-methoxyindene (III. $X = OCH_3$). 2-Benzoyl-1,3-diphenylindene reacted with bromine furnishing 2-benzoyl-1-bromo-1,3-diphenylindene (III. $X = Br$) which yielded the methoxy derivative with methanol. With methyl sulfate and sodium isopropoxide, 2-benzoyl-1,3-diphenylindene gave 2-benzoyl-1,3-diphenyl-1-methylindene (III. $X = CH_3$), also obtained by Friedel-Crafts benzoylation of 1,3-diphenyl-1-methylindene. Hydroxymethylation of III ($X = H$) resulted when it was treated with formalin and base.

Phthalic anhydride and 1,3-diphenylindene in benzene yielded 43% of 2-*o*-carboxylbenzoyl-1,3-diphenylindene; 40% of the diphenylindene was recovered, and 22% of *o*-benzoylbenzoic acid was isolated. Similarly, *o*-bromobenzoyl chloride gave 62% of 2-*o*-bromobenzoyl-1,3-diphenylindene. Like the sample benzoyl derivative, both of these indenes gave colored solutions in alcoholic base, bleached by air with formation of the corresponding indenols.

EXPERIMENTAL

1,3-Diphenyl-2-nitroindene (I). A solution of 10 g. of diphenylindene in 15 ml. of acetic acid was mixed with 5 g. of copper nitrate in 15 ml. of acetic acid and heated to 100° for 10 min. Cooling then gave a crystalline mixture of copper acetate and nitro compound which was removed, washed with a little methanol and much water. Crystallization from methanol gave 4.6 g. of pure product, yellow prisms, m.p. 105–106°.

Anal. Calcd. for $C_{21}H_{15}NO_2$: C, 80.5; H, 4.83. Found: C, 80.3; H, 5.07.

The nitro compound was recovered unchanged after it had been treated with 10% chromic acid in acetic acid for 1 hr. at 30°, but at 90° it was oxidized to *o*-dibenzoylbenzene, yield 76%.

A solution of 0.5 g. of I and 0.5 g. of benzyl chloride in 5 ml. of alcohol was treated dropwise at the boiling point with 10% aqueous potassium hydroxide until further addition of base gave no deep green color. Volatile materials were then removed with steam, and the residue was crystallized from acetic acid giving 0.7 g. of *1-benzyl-1,3-diphenyl-2-nitroindene*, yellow prisms, m.p. 177–179°.

Anal. Calcd. for $C_{28}H_{21}NO_2$: C, 83.3; H, 5.25. Found, C, 83.3; H, 5.42.

The same nitro compound was obtained in 57% yield from 1-benzyl-1,3,-diphenylindene[8] by nitration with copper nitrate in acetic acid.

When a solution of 0.5 g. of I and 0.4 g. of acrylonitrile in 5 ml. of *tert*-butyl alcohol was treated with 1 drop of 30% potassium hydroxide in methanol a deep green solution resulted. The color faded in 1 min., and was not restored by addition of more base. The product was a yellow oil that could not be obtained crystalline, but when it was boiled with a mixture of equal volumes of water, acetic acid and sulfuric acid for 2 hr., it gave *1,3-diphenyl-2-nitroindene-1-propionic acid*, yellow needles from acetic acid, m.p. 188–190°.

Anal. Calcd. for $C_{24}H_{19}NO_4$: C, 74.8; H, 4.97. Found: C, 74.8; H, 5.06.

The *methyl ester*, from the acid and 5% sulfuric acid in methanol by boiling for 30 min., formed yellow prisms from methanol, m.p. 103–104°.

Anal. Calcd. for $C_{25}H_{21}NO_4$: C, 75.2; H, 5.30. Found: C, 74.9; H, 5.31.

The same acid was obtained in nearly quantitative yield by nitration of 1,3-diphenylindene-1-propionic acid using copper nitrate in acetic acid.

2-Acetyl-1,3-diphenylindene (II). A solution of 5 g. of 1,3-diphenylindene in 25 ml. of benzene was treated with 4 g. of powdered aluminum chloride, giving a red-brown oily precipitate, and then with 2 ml. of acetyl chloride, whereupon the mixture became homogeneous. It was heated to 60° for 5 min., then decomposed with iced hydrochloric acid. Removal of volatile material with steam left an oil which crystallized after it had been kept for 3 days under ether-ligroin. Re-

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(6) R. A. Barnes and B. D. Beitchman, *J. Am. Chem. Soc.*, **76**, 5430 (1954); L. M. Adams, R. J. Lee, and F. T. Wadsworth, *J. Org. Chem.*, **24**, 1186 (1959).

(7) *Cf.* Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 5449 (1958).

(8) C. F. Koelsch, *J. Am. Chem. Soc.*, **56**, 1605 (1934).

crystallization from methanol gave 4.2 g. of faintly yellow coarse needles, m.p. 96–97°, b.p. 255° at 15 mm.

Anal. Calcd. for $C_{23}H_{18}O$: C, 89.0; H, 5.85. Found: C, 88.8; H, 5.72.

2-Benzoyl-1,3-diphenylindene (III. X = H). A solution of 27 g. of 1,3-diphenylindene in 100 ml. of benzene, treated with 20 g. of powdered aluminum chloride and then with 20 g. of benzoyl chloride, was warmed under reflux for 10 min. and then decomposed with iced hydrochloric acid. Removal of volatile materials with steam left a crystalline residue. Recrystallization from acetic acid gave 28.3 g. of colorless prisms, m.p. 145–146°. The ketone gave a deep orange-yellow color with concentrated sulfuric acid.

Anal. Calcd. for $C_{28}H_{20}O$: C, 90.3; H, 5.41. Found: C, 90.6; H, 5.68.

2-o-Bromobenzoyl-1,3-diphenylindene formed faintly yellow prisms from benzene-ligroin, m.p. 170–172°. It gave an orange-yellow color with concentrated sulfuric acid. Its purple solution in alcoholic sodium ethoxide did not eliminate sodium bromide when it was boiled for 1 hr.

Anal. Calcd. for $C_{28}H_{19}BrO$: C, 74.4; H, 4.23. Found: C, 73.9; H, 4.11.

2-o-Carboxybenzoyl-1,3-diphenylindene, prepared in similar fashion using phthalic anhydride was separated from unchanged diphenylindene by extraction with aqueous sodium carbonate, and *o*-benzoyl benzoic acid was removed from it by extraction with hot benzene. It formed pale yellow prisms from acetic acid, m.p. 202–203°, that gave an orange-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{29}H_{20}O_3$: C, 83.6; H, 4.84. Found: C, 83.4; H, 5.10.

Reactions of III (X = H). (*a*) *Autoxidation*. When a suspension of 1.1 g. of the ketone in 25 ml. of 2% methanolic potassium hydroxide was shaken in absence of air, a small amount dissolved to form a deep purple solution. This was rapidly decolorized when oxygen was admitted; shaking in absence of oxygen caused reappearance of the purple color. The process was repeated until all the solid had dissolved. The nearly colorless solution soon deposited 1.0 g. of *2-benzoyl-1,3-diphenyl-1-indenol* (III. X = OH), m.p. 182–184°. An additional 0.1 g. was obtained from the mother liquor. Recrystallization from ethyl acetate-ligroin gave prisms, m.p. 183–184°, that gave a deep purple color with concentrated sulfuric acid.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.6; H, 5.19. Found: C, 86.7; H, 5.09.

When 1 g. of the indenol was boiled for 15 min. with 4 ml. of acetyl chloride, it formed a deep yellow solution. Evaporation under reduced pressure at 100° left a yellow glass that became crystalline on keeping under ether. Recrystallization from ethyl acetate gave 0.5 g. of 2-benzoyl-1-chloro-1,3-diphenylindene, colorless needles, m.p. 190–192°.

Anal. Calcd. for $C_{28}H_{19}ClO$: C, 82.8; H, 4.68. Found: C, 83.2; H, 4.81.

When the chloro compound was boiled for 15 min. with methanol, it gave *2-benzoyl-1,3-diphenyl-1-methoxyindene*, which crystallized from ether-ligroin very slowly; m.p. 93–95°.

Anal. Calcd. for $C_{29}H_{22}O_2$: C, 86.5; H, 5.51. Found: C, 86.2; H. 5.66.

(*b*) *Bromination*. A solution of 1 g. of 2-benzoyl-1,3-diphenylindene and 0.5 g. of bromine in 5 ml. of acetic acid became nearly colorless after it had been boiled for 15 min. Cooling gave 1.1 g. of yellow nodules, which were recrystallized from benzene-ligroin and ethyl acetate–ligroin. The resulting 2-benzoyl-1-bromo-1,3-diphenylindene formed pale yellow plates, m.p. 190–193°.

The same product was obtained in more easily crystallized form by using carbon tetrachloride instead of acetic acid, but the bromination then required 4 hr. Analysis indicated the presence of a considerable amount of more highly brominated material.

Anal. Calcd. for $C_{28}H_{19}BrO$: C, 74.5; H, 4.22. Found: C, 72.8; H, 4.31.

With methanol, the bromo compound gave a methoxy derivative identical with the one obtained from the chloro compound.

(*c*) *Methylation*. The deep purple mixture obtained by adding 1 g. of 2-benzoyl-1,3-diphenylindene to a solution of 0.25 g. of sodium in 10 ml. of isopropyl alcohol became yellow when it was treated with 1.5 g. of methyl sulfate and then boiled for 10 min. There was obtained 0.9 g. of *2-benzoyl-1,3-diphenyl-1-methylindene*, pale yellow prisms from acetic acid, m.p. 143–145°. A mixture with an equal weight of starting material (m.p. 145–146°) had a m.p. of 127–131°, and unlike the starting material it gave no color with alcoholic potassium hydroxide.

Benzoylation of 1,3-diphenyl-1-methylindene, using benzoyl chloride and aluminum chloride in benzene gave the same compound (III. X = CH_3), identified by mixed melting point and infrared spectrum.

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.1; H, 5.74. Found: C, 90.2; H, 5.90.

(*d*) *Hydroxymethylation*. A mixture of 0.9 g. of 2-benzoyl-1,3-diphenylindene, 3 ml. of methanol, and 0.5 ml. of 20% methanolic potassium hydroxide was treated with 2 ml. of 40% formalin and warmed to 50°. An oil soon precipitated which became solid during 5 min. Recrystallization from ethyl acetate–ligroin gave a nearly quantitative yield of 2-benzoyl-1,3-diphenyl-1-hydroxymethylindene (III. X = CH_2OH), colorless cubes, m.p. 137–138°.

Anal. Calcd. for $C_{29}H_{22}O_2$: C, 86.5; H, 5.51. Found: C, 85.9; H. 5.46.

With piperdine and formalin, 2-benzoyl-1,3-diphenylindene gave a base whose hydrochloride was insoluble in water but easily soluble in alcohol; the salt darkened at 160°; m.p. 171°. It was not analyzed.

2-o-Carboxybenzoyl-1,3-diphenyl-1-indenol, obtained by aerating the red-purple solution of 2-*o*-carboxybenzoyl-1,3-diphenylindene in methanolic potassium hydroxide, formed faintly yellow prisms from ethyl acetate–ligroin, m.p. 220–221° with gas evolution. It gave a red-purple solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{29}H_{20}O_4$: C, 80.5; H, 4.66. Found: C, 80.0; H, 4.89.

2-o-Bromobenzoyl-1,3-diphenylindenol, obtained similarly from 2-*o*-bromobenzoyl-1,3-diphenylindene, had a m.p. of 148–150° and gave a deep purple solution in sulfuric acid.

Anal. Calcd. for $C_{28}H_{19}BrO_2$: C, 71.9; H, 4.08. Found: C, 71.9; H, 4.38.

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MINNEAPOLIS, MINN.