benzene–hexane afforded 0.25 g. of material, m.p. 279–281° (lit.,[20] m.p. 281–282°). The melting point was not depressed on admixture with an authentic sample of tetraphenylmethane. The infrared spectrum, potassium bromide pellet, was identical to that of an authentic sample of tetraphenylmethane.

Reaction of Triphenylmethyl with Hydrocinnamoyl Peroxide, 3,3,3-Triphenylpropanoyl Peroxide and *t*-Butyl Perbenzoate.[10]— The same general procedure as described for the reaction of cyclopropylformyl peroxide was followed except in the case of *t*-butyl perbenzoate where it was necessary to reflux the reaction mixture for 20 hr. to decompose the perester. Chromatography of the concentrated reaction mixtures on alumina gave in no case any indication for the formation of tetraphenylmethane.

(10) Detailed descriptions of these reactions can be found in H. Weiss, Ph.D. thesis, Rutgers, The State University, 1962.

The Chemistry of β-Bromopropionyl Isocyanate. III. Identification of Phenols and Anilines[1]

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The use of β-bromopropionyl isocyanate (I) in making solid derivatives of alcohols has been reported.[2] The use of I in making derivatives of phenols and aromatic amines is reported herein.

The reaction of I with phenols occurred readily in chloroform solution in the absence of a catalyst. The reaction did not appear to be subject to steric hindrance, since 2,6-diallylphenol, 2,6-diisopropylphenol, and 2,6-di-*tert*-butylphenol gave satisfactory derivatives under these conditions. Hydroquinone and resorcinol reacted satisfactorily, but phloroglucinol gave a mixture of two products whose structures have not been determined as yet.

The most serious limitation of the use of I with phenols occurred with the polynitrophenols. Mononitrophenols reacted readily, but no reaction was observed with 2,4-dinitrophenol or picric acid under the conditions specified. In this connection it is interesting that thiophenol reacted with I whereas hydrogen sulfide did not appear to do so.

Monofunctional aromatic amines reacted with I without difficulty. The products were easily isolated and purified. Diphenylamine formed a derivative without difficulty. The N-β-bromopropionyl-N′-arylureas formed from the reaction of I with aryl amines could be dehydrohalogenated to N-acrylyl-N′-arylureas with triethylamine.[3] Reaction of I with 2,4-dinitroaniline was unsuccessful.

Aromatic diamines gave products which were very insoluble in most solvents, and thus were very difficult to purify. This difficulty is sufficient to preclude recommendation of I as a reagent for preparing derivatives of diamino compounds.

Attempts were made to use I as a reagent for aliphatic amines. Considerable difficulty was noted, and I is not recommended for use in making derivatives of them. The amines reacted readily, but the β-bromopropionylureas thus formed are easily dehydrohalogenated by any excess of amine[4] to give an oily mixture of bromopropionyl- and acrylylureas. Certain of the aliphatic amines gave derivatives when low temperatures and

TABLE OF DERIVATIVES

Parent compound	M.p. of derivative, °C.	Solvent[a]	% C Calcd.	% C Found	% H Calcd.	% H Found
Phenol	106–107	C	44.1	44.3	3.70	3.50
p-Chlorophenol	138–139	M	39.2	39.3	2.96	2.90
p-Nitrophenol	146–147	I	37.9	38.0	2.86	2.74
p-Methoxyphenol	93–94	C	43.7	44.0	4.00	4.10
p-*tert*-Butylphenol	146–147	M	51.2	51.0	5.49	5.65
p-Phenylphenol	170–171	T	55.2	55.1	4.05	4.12
o-Chlorophenol	127–127.5	E	39.2	39.1	2.96	2.67
o-Nitrophenol	129–130	M	37.9	37.6	2.86	2.78
o-Allylphenol	91–92	C	50.0	50.1	4.52	4.49
o-Isopropylphenol	99–100	E	49.7	49.5	5.13	5.21
1-Naphthol	133–133.5	C	52.2	52.1	3.76	3.60
2-Naphthol	143–144	M	52.2	52.0	3.76	3.77
3,4-Dimethylphenol	105–106	M	48.0	47.7	4.70	4.60
2,6-Dimethylphenol	158–159	M	48.0	47.8	4.70	4.63
3,5-Dimethylphenol	155–156	M	48.0	47.9	4.70	4.55
2,5-Dimethylphenol	126–127	M	48.0	47.9	4.70	4.49
2,6-Diallylphenol	123–124	E	54.6	54.2	4.58	4.30
2,6-Diisopropylphenol	111–112	E	53.9	54.0	6.22	6.00
2,6-Di-*tert*-butylphenol	107–109	E	56.2	56.3	6.82	6.95
p-Cresol	148–149	I	46.2	46.3	4.23	4.40
Eugenol	80–81	C	49.1	49.4	4.71	4.64
Isoeugenol	141–142	M	49.1	49.3	4.71	4.70
Hydroquinone	209–210	T	36.1	36.3	3.03	3.32
Resorcinol	165–166	I	36.1	36.3	3.03	3.12
Ammonia	181–182	M	24.6	24.9	3.62	3.51
Benzylamine	165–166	M	46.3	46.1	4.60	4.87
Aniline	183–184	M	Previously reported			
N-Methylaniline	92–93	M	46.3	46.1	4.56	4.40
o-Toluidine	162–163	E	46.3	46.5	4.56	4.69
m-Toluidine	151.5–152.5	C	46.3	46.3	4.56	4.64
p-Toluidine	196.5–197.5	E	46.3	46.0	4.56	4.42
o-Phenetidine	224–225	E	45.7	45.8	4.76	4.90
m-Chloroaniline	181–182	E	39.2	39.5	3.27	3.18
o-Nitroaniline	192–193	M	38.0	38.1	3.16	3.05
p-Nitroaniline	222–223	M	38.0	38.2	3.16	3.00
p-Bromoaniline	209–210	M	34.3	34.6	2.86	2.86
2-Aminopyridine	170.5–172	M	39.7	40.0	3.68	3.76
2,5-Dimethoxyaniline	236.5–237.5	E	43.5	43.8	4.53	4.34
2,5-Dichloroaniline	183–184	M	35.3	35.5	2.65	2.46
o-Phenylenediamine[b]	222–225 (dec.)		36.2	37.3	3.45	3.64
m-Aminophenol	186–187	M	36.1	36.4	3.23	3.23
β-Phenylethylamine	153–152	M	48.2	48.5	5.02	4.89
Diphenylamine	129–130	M	55.4	55.2	4.32	4.45
Bis(*p*-aminophenyl)methane[b]	250–260		(None attempted)			

[a] Crystallization solvents: E, ethanol; I, isopropyl alcohol; M, methanol; T, tetrahydrofuran. [b] Too insoluble for crystallization in common solvents.

(1) Support from National Science Foundation grants G-7850 (Undergraduate Research Participation Program) and G-9914 is gratefully acknowledged.

(2) H. W. Johnson, Jr., H. A. Kreyssler, and H. L. Needles, *J. Org. Chem.*, **25**, 279 (1960).

(3) H. W. Johnson, Jr., R. E. Lovins, and M. Reintjes, *ibid.*, **24**, 1391 (1959); N. W. Gabel and S. B. Binkley, *ibid.*, **23**, 643 (1958).

(4) H. W. Johnson, Jr., and M. Schweizer, *ibid.*, **26**, 3666 (1961).

dilute solutions were used, and ammonia gave a product which was insoluble in chloroform (and thus unable to react further).

The derivatives prepared from amines and phenols appeared to be stable to ordinary laboratory storage conditions when reasonably pure.

In general, our experience with the use of I as a reagent for preparing derivatives may be summarized a follows: for aliphatic alcohols—good in most cases, particularly useful with fairly unreactive alcohols; for aliphatic amines—not recommended; for phenols—good, except for very acidic phenols; for aromatic amines—good for monoamino compounds. The principal advantage of I is that reaction with water yields β-bromopropionamide which can be removed from the product by crystallization in most cases; aryl isocyanates yield diarylureas which are more difficult to remove from the product. The increase in molecular weight of an alcohol or amine upon reaction with I is 178, which compares favorably with 119 for phenyl isocyanate and 169 for naphthyl isocyanate.

Experimental

The phenols and amines used in this work were obtained from commercial sources. Melting points were determined with a Koffler block. Analyses were performed by Dr. Weiler and Dr. Strauss, Oxford.

The method of preparation of I has been reported previously.[2]

Preparation of Derivatives.—A suspension of 1.0 g. (0.0056 mole) of N-bromosuccinimide, 10 ml. of chloroform (dried over calcium chloride), 0.5 ml. of allyl chloride, and a small amount (*ca.* 10 mg.) of benzoyl peroxide was refluxed for 30 min. The now-clear solution was allowed to cool to room temperature, and an approximately equimolar amount of the phenol or aniline dissolved in a few milliliters of chloroform was added. If the amine or phenol was insoluble in chloroform, it was dissolved in a few milliliters of tetrahydrofuran. A vigorous reaction ensued in most instances. The solution was cooled in an ice bath, and in many instances the product crystallized from the reaction mixture. The solid was filtered and crystallized from the solvent indicated in the table. If no solid precipitated, low boiling petroleum ether was added to precipitate the product. The solid was then crystallized from the solvent indicated in the table.

The same procedure has been used to prepare derivatives on a 50-g. scale.

To prepare the derivatives of aliphatic amines, *e.g.*, benzylamine, it was necessary to add an equimolar amount of the amine very slowly, with stirring, keeping the solution temperature below 5°. The preparation of β-bromopropionylurea (from I and ammonia) was accomplished by bubbling gaseous ammonia into the chloroform solution, from which the derivative precipitated immediately.

The Monoaddition of Phenylsilane to Cyclic Polyolefins[1]

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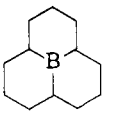
Recently several workers have reported the addition of diborane or triethylamineborane to 1,5,9-cyclododecatriene to give perhydro-9b-borphenalene (I).[2,3] It seemed possible that an analogous reaction might take place with silicon in place of boron. We have attempted to add phenylsilane to the same triolefin using benzoyl peroxide and chloroplatinic acid as catalysts. In neither case is any of the desired tricyclic silicon analog of I obtained. Chloroplatinic acid catalysis led only to polymeric material, but with benzoyl peroxide a



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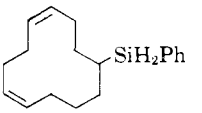

II

16% yield of 9-phenylsilyl-1,5-cyclododecadiene (II) was obtained. The monoaddition product is completely unreactive toward further addition, being recovered unchanged after seven days of heating with benzoyl peroxide catalyst. Similar results were obtained in the addition of phenylsilane to 1,5-cyclooctadiene, which led only to the monoadduct, 5-phenylsilylcycloöctene.

The reluctance of silicon to add to form the perhydrosilaphenalene ring may result in part from the large radius of the silicon atom, which would prevent the molecule from assuming a strainless configuration. However, unsuccessful attempts to cyclize 5-pentenyldichlorosilane by intramolecular Si–H addition suggest that the mechanism of silane addition may require a geometry which makes the formation of a six-membered ring unfavorable. With either chloroplatinic acid or benzoyl peroxide, 5-pentenyldichlorosilane gave none of the desired 1,1-dichlorosilacyclohexane, even though the latter compound can assume a strainless chair-like configuration.[4]

Experimental

9-Phenylsilyl-1,5-cyclododecadiene.—Fifteen milliliters (0.12 mole) of phenylsilane and 22 ml. (0.12 mole) of 1,5,9-cyclododecatriene in 150 ml. of dry heptane were refluxed for 3 days during which time a total of 2.5 g. of benzoyl peroxide was added in 250 mg. increments at 6–10-hr. intervals. After cooling, the mixture was shaken with an aqueous solution 1 *N* each in ammonia and ammonium chloride in order to remove benzoic acid formed in decomposition of the peroxide. The organic layer was separated, dried, and fractionally distilled. After removal of heptane and unreacted starting materials, the only volatile product, a colorless liquid, was distilled at 114–127° (0.15 mm.); yield 5.0 g., 16%. A large residue of polymeric material was left in the flask. The product had $n^{25}D$ 1.5449, d^{26}_4 1.0197.

Anal. Calcd. for $C_{18}H_{26}Si$: C, 79.92; H, 9.69; Si, 10.38. Found: C, 80.15; H, 9.57; Si, 10.29.

The infrared spectrum of the product showed a very strong band at 2120 cm.$^{-1}$ (Si—H) as well as a weak doublet at 1600 cm.$^{-1}$ (C=C). The proton magnetic resonance spectrum showed a cluster of lines near τ = 2.8, a sharp line at τ = 5.83, and a broad unresolved band from τ = 8.0 to 9.4. These resonances are assigned to phenyl, silane, and a mixture of methylene and vinylic protons, respectively; the relative integrated intensities were 5.0:1.8:20. A semiquantitative base-catalyzed hydrolysis of the substance in aqueous tetrahydrofuran yielded 1.7 moles of hydrogen per mole of compound.

Attempted Addition Using Chloroplatinic Acid Catalyst.—A 5.8-ml. sample (0.046 mole) of phenylsilane and 8.4 ml. (0.046 mole) of 1,5,9-cyclododecatriene and a small amount of chloroplatinic acid in isopropyl alcohol were dissolved in 50 ml. of dry heptane, and the solution was refluxed for 24 hr. The heptane

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract no. AF49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

(2) R. Köster, *Angew. Chem.*, **69**, 684 (1957); G. Rotermund and R. Köster, *ibid.*, **74**, 329 (1962).

(3) N. N. Greenwood and J. H. Morris, *J. Chem. Soc.*, 2922 (1960).

(4) R. West, *J. Am. Chem. Soc.*, **76**, 6015 (1954).