Isomerization of 4-Ethynylcyclopentene to 4-Vinylidenecyclopentene.—To a small glass tube was added sodium methoxide (34.1 mg., 0.632 mmole), dry diglyme (0.30 ml.), and III (0.0147 g., 0.160 mmole) which was purified by vapor phase chromatography and contained no detectable amount of IV. The tube was sealed and heated at 160° for 8 min. in a stirred oil bath. The tube was quickly cooled in an ice bath, opened, and the contents analyzed by vapor phase chromatography. The ratio of III to IV was found to be 83/17.

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Reaction of Triphenylmethyl with Several Peroxides

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Wieland and Meyer[1] discovered that triphenylmethyl reacts with benzoyl peroxide in benzene to give trityl benzoate, benzoic acid, and tetraphenylmethane. Work on various aspects of the mechanism of this reaction has been relatively extensive.[2] It seems well established that trityl benzoate is formed by attack of triphenylmethyl on benzoyl peroxide and by combination of triphenylmethyl with benzoyloxy radicals.[2d]

$$(C_6H_5)_3C\cdot + (C_6H_5CO_2)_2 \xrightarrow{C_6H_6} (C_6H_5)_4C + C_6H_5CO_2C(C_6H_5)_3 + C_6H_5CO_2H$$

Several workers have shown that formation of tetraarylmethanes occurs in aromatic solvents other than benzene.[2a,c] Several mechanisms have been suggested to account for the formation of tetraarylmethanes. The most recent has been suggested by Benkeser and Schroeder,[2c] who have postulated that tetraphenylmethane is formed by reaction of a π-complex of triphenylmethyl and benzene with benzoyl peroxide or a benzoyloxy radical.

Interestingly, apparently no one has demonstrated that the tetraarylmethane-forming reaction can be effected by any peroxide other than benzoyl. It was the purpose of this work to investigate this point. Triphenylmethyl was allowed to react with benzoyl peroxide, cyclopropylformyl peroxide, hydrocinnamoyl peroxide, 3,3,3-triphenylpropanoyl peroxide, and *t*-butyl perbenzoate. Triphenylmethyl induced the decomposition at room temperature of all of the diacyl peroxides. It was necessary to boil the benzene-*t*-butyl perbenzoate–triphenylmethyl reaction mixture to effect decomposition of the perester. Even so the total time required for decomposition was considerably less than that required for the decomposition of *t*-butyl perbenzoate in the absence of triphenylmethyl. Only with benzoyl peroxide and cyclopropylformyl peroxide could the formation of tetraphenylmethane be detected. With benzoyl peroxide a 14% yield was obtained,[3] while cyclopropylformyl peroxide yielded *ca.* 1% of tetraphenylmethane. It cannot be definitely stated that no tetraphenylmethane was formed with the other peroxides but if any was formed it must have been very little. For example, three separate decompositions of hydrocinnamoyl peroxide gave no evidence for tetraphenylmethane formation.

The results of these experiments show that the formation of tetraphenylmethane is dependent upon the nature of the peroxide used. Of greater significance is the correlation between the stability of the acyloxy radical derived from the peroxide and the formation of tetraphenylmethane. It seems well established, mainly on the basis of radical trapping experiments, that the benzoyloxy radical[4] is more stable towards decarboxylation than a cyclopropylcarboxy radical,[5] both of which are more stable than simple acyloxy radicals.[6]

The results obtained with the various peroxides indicate that the formation of tetraphenylmethane probably does not involve a direct reaction with the peroxide. If this were the case, it seems reasonable to suppose that all diacyl peroxides should be capable of participating in the reaction.[7] The results are in accord with a reaction path in which an acyloxy radical reacts with a π-complex of triphenylmethyl and solvent,[2c] although this is not the only possibility. For example, triphenylmethyl may react with a π-complex of the acyloxy radical with solvent.

It is interesting that other radicals, *i.e.*, various alkyl radicals which were undoubtedly present during the decompositions with the diacyl peroxides, did not promote the formation of tetraphenylmethane. Indeed the reaction seems limited to relatively stable acyloxy radicals. The true requirement may be that an electrophilic radical be present. This may well be due to a necessity for strong electron transfer contributions to the transition state which leads to tetraarylmethane.[8]

Experimental

Reaction of Cyclopropylformyl Peroxide and Triphenylmethyl.—A solution of triphenylmethyl was prepared by stirring 10 g. (0.08 mole) of triphenylmethyl chloride dissolved in 75 ml. of benzene with 35 g. (0.18 g.-atom) of mercury for 8 hr. under an atmosphere of nitrogen. To this solution was added 5.1 g. (0.03 mole) of cyclopropylformyl peroxide in 75 ml. of benzene. After stirring for 1 hr., the infrared spectrum of the mixture indicated that all of the peroxide had been decomposed. The mixture was filtered and concentrated to a volume of 35 ml. and then chromatographed on 60 g. of alumina. Elution with 20% benzene in petroleum ether (30–60°) afforded a white crystalline substance in the first 150 ml. of eluate.[9] Recrystallization from

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(1) H. Wieland and A. Meyer, *Ann.*, **532**, 179 (1937).

(2) (a) H. Wieland and A. Meyer, *ibid.*, **551**, 249 (1942); (b) G. S. Hammond, J. T. Rudesill, and F. J. Modic, *J. Am. Chem. Soc.*, **73**, 3929 (1951); (c) R. A. Benkeser and W. Schroeder, *ibid.*, **80**, 3314 (1958); (d) W. E. Doering, K. Okamoto, and H. Krouch, *ibid.*, **82**, 3579 (1960).

(3) Hammond and co-workers, ref. 2b, obtained yields of 20–30% of tetraphenylmethane depending on the reaction conditions.

(4) G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950)

(5) H. Hart and D. P. Wyman, *ibid.*, **81**, 4891 (1959).

(6) This order of stability is based upon the amount of parent acid formed during the decomposition of the peroxide in the presence of iodine and water. Using this technique, 96% benzoic acid,[4] 47% cyclopropane carboxylic acid,[5] and 10% hydrocinnamic acid have been obtained (H. Weiss, thesis, Rutgers, The State University, 1962).

(7) Such a reaction might have involved electron or hydrogen transfer from a π-complex to the peroxide.

(8) Many radical reactions are subject to this effect. See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 365–368, for a discussion of this matter.

(9) These conditions were determined as optimal from experiments with reaction mixtures obtained from the reaction of benzoyl peroxide and triphenylmethyl in benzene.

benzene–hexane afforded 0.25 g. of material, m.p. 279–281° (lit.,[2a] 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.

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(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.

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.

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

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(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).