Further Observations on the Catalytic Transformation of Benzoic Anhydrides into Fluorenones and Biphenyls

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The catalytic conversion of benzoic anhydrides into fluorenones and biphenyls by several rhodium compounds has been studied. Mixtures of aromatic anhydrides react generally as if they were mixed anhydrides, leading to the formation of asymmetrically substituted products. Equimolar amounts of the isolated phenyl–rhodium complex PhRhCl(PPh₃)₃ (7) and chlorocarbonylbis(triphenylphosphine)rhodium (2) react at 250° to give fluorenone and biphenyl. Both these compounds are assumed to be formed via the same rhodium intermediate.

In a previous publication[1] it has been shown that benzoic anhydride and some of its derivatives can be transformed catalytically by chlorotris(triphenylphosphine)rhodium(I), RhCl(PPh₃)₃ (1), and by chlorocarbonylbis(triphenylphosphine)rhodium(I), RhCl(CO)(PPh₃)₂ (2), into fluorenones, benzoic acids, carbon monoxide, small quantities of benzophenones, and, according to the experimental conditions, into varying amounts of biphenyls.

We have now extended this study, exploring the scope of the reaction and the possibility of using *mixtures* of anhydrides for the synthesis of fluorenones and biphenyls. In addition to 1 and 2, several other rhodium complexes, as well as anhydrous rhodium trichloride, proved to be effective catalysts for these reactions (Table I). Palladium dichloride, hydrated ru-

TABLE I
CONVERSION OF BENZOIC ANHYDRIDE TO FLUORENONE AND BIPHENYL BY VARIOUS CATALYSTS

	Reaction		Yield	
Catalyst[a]	Temp, °C	Time, hr	Fluorenone, mol %	Biphenyl, mol %
RhCl(CO)(PPh₃)₂[b]	240	4.5	35–52	2.2–3
RhCl(PPh₃)₃[b]	240	4.5	36–40	6–7
RhCl₃, anhydrous	290	6.5	26	3.6
Rh₂(CO)₄Cl₂	250	4	22	<1
RhCl₃(SbPh₃)₃	250	4	8	1
RhH(CO)(PPh₃)₃	250	3	6	<1
IrCl₃, 3H₂O	310	3.5	4.1	Traces
PdCl₂	350	4	4.0	Traces
RuCl₃, 3H₂O	290	6	1.3	Traces
RuCl₂(PPh₃)₃[c]	340	1	0.8	Traces

[a] Concentration 10⁻² mol per mol of anhydride. [b] *Cf.* ref 1. [c] 8 mol % of benzophenone was formed in this experiment.

thenium trichloride, and hydrated iridium trichloride possess low catalytic activity, while rhodium trichloride trihydrate and metallic rhodium have proved to be inactive under our conditions.

Mixtures of aromatic anhydrides, which often equilibrate with the (unstable) mixed anhydride,[2] could be decarbonylated by 1 to give the fluorenones expected from the *mixed* anhydrides (Table II). Thus a mixture of benzoic and *p*-chlorobenzoic anhydride gives, in addition to the unsubstituted fluorenone and 2,6-dichlorofluorenone,[1] also the "mixed" products, 2- and 3-monochlorofluorenone. A mixture of benzoic and *m*-chlorobenzoic anhydride yielded all four monochlorofluorenones, the 1 and 4 isomers in low yield. Equimolar amounts of *p*-chlorobenzoic and *p*-toluic anhy-

dride give both 2-chloro-6-methyl- and 6-chloro-2-methylfluorenone. The two ketones have been identified by their dipole moments: 4.6 and 2.7 D, respectively. These values are in agreement with the calculated figures of 4.35 and 2.58 D.[3] This decarbonylation seems, however, not to proceed well with some mixtures of benzoic anhydrides, possibly owing to the absence of sufficient quantities of the mixed anhydride in the equilibrium mixture. *E.g.*, a mixture of *p*-fluoro- and *p*-chlorobenzoic anhydride failed to yield significant amounts of the "mixed" chlorofluorofluorenones.

The formation of these "mixed" fluorenones can be explained by the pathway proposed in our previous paper.[1] This mechanism is further confirmed by the formation of 2,6-difluoro-,[4] 2,6-dibromo-,[5] and 1,3,5,7-tetramethylfluorenone from *p*-fluoro-, *p*-bromo-, and 3,5-dimethylbenzoic anhydride, respectively.

Reinvestigation of the decarbonylation of *m*-toluic anhydride by 1 (and also by anhydrous rhodium trichloride) showed that in addition to the previously isolated 1,7- and 2,6-dimethylfluorenone, traces of 1,5- and 3,5-dimethylfluorenone are also formed; these isomers had been predicted by our theory but had not been isolated before. 3,5-Dimethylfluorenone was identified by reduction to the known 3,5-dimethylfluorene[6] and by its nmr spectrum (*vide infra*).

It has been shown that the transformation of substituted benzoic anhydrides to fluorenone is subject to steric effects.[1] Particularly pronounced is the impediment to cyclization of the intermediate 4 (or 6) caused by the shielding of the hydrogen atom to be extruded. In order to find out whether this steric effect is associated with the large size of the triphenylphosphine ligands, we treated *m*-toluic anhydride with rhodium trichloride at 290°. The results (Table II, footnote *d*) proved, however, that this phosphine-free catalyst behaves in the same manner as 1. On the other hand it should be borne in mind that, in the rhodium trichloride catalyzed reaction, the ratio of 2,6- plus 3,5-dimethylfluorenone to 1,5- plus 1,7-dimethylfluorenone is close to unity, while, in the reaction catalyzed by 1, it is 2.6. Though this comparison has only a qualitative meaning (because of the difference in temperature at which the catalyses with 1 and with RhCl₃ could be carried out), it may suggest that the step 3 → 4 in Scheme I, in which an acylation takes place at an *ortho* position to the

(1) J. Blum and Z. Lipshes, *J. Org. Chem.*, **34**, 3076 (1969).

(2) *Cf.* J. M. Zeavin and A. M. Fisher, *J. Amer. Chem. Soc.*, **54**, 3738 (1932).

(3) The calculations as based on the structure of fluorenone proposed by E. D. Hughes, C. G. Le Fèvre, and R. J. W. Le Fèvre, *J. Chem. Soc.*, 202 (1937).

(4) J. L. Fletcher, M. J. Namkung, W. H. Wetzel, and H. L. Pan, *J. Org. Chem.*, **25**, 1342 (1960).

(5) N. Campbell, W. Anderson, and J. Gilmore, *J. Chem. Soc.*, 446 (1940).

(6) B. Longo, *Atti. Accad. Sci. Torino, Classe Sci. Fis. Mat. Nat.*, **73**, 440 (1938); *Chem. Abstr.*, **33**, 6286⁸ (1939).

TABLE II
CONVERSION OF SUBSTITUTED BENZOIC ANHYDRIDE BY 1 TO FLUORENONES

Anhydride	Registry no.	Temp, °C	Time, hr	Fluorenone formed	Yield, %[a]
		Reaction			
Benzoic + p-toluic	25569–87–3	250	5	Unsubstituted[b]	18
				2-Methyl-[b]	24
				3-Methyl-[b]	20
				2,6-Dimethyl-[b]	15
Benzoic + p-chlorobenzoic	21961–55–7	240	4	Unsubstituted[b]	12
				2-Chloro-[b]	8
				3-Chloro-[b]	12
				2,6-Dichloro-[b]	3
Benzoic + m-chlorobenzoic	25569–89–5	240	4	Unsubstituted[b]	8
				1-Chloro-[b]	3
				2-Chloro-[b]	8
				3-Chloro-[b]	10
				4-Chloro-[b]	3
				2,6-Dichloro-[b]	4
				Unidentified dichloro-	<1
p-Chlorobenzoic + p-toluic	25569–90–8	250	4	2,6-Dichloro-[b]	24
				2,6-Dimethyl-[b]	16
				2-Chloro-6-methyl-	14
				6-Chloro-2-methyl-	13
p-Fluorobenzoic + p-chlorobenzoic	25569–91–9	250	4	2,6-Difluoro-[c]	18
				2,6-Dichloro-[b]	26
				Unidentified chlorofluoro-	<1
m-Toluic[d]		235	3	1,5-Dimethyl-[b]	1
				1,7-Dimethyl-[b]	12
				2,6-Dimethyl-[b]	30
				3,5-Dimethyl-	4
3,5-Dimethylbenzoic		300	1	1,3,5,7-Tetramethyl-	14
p-Fluorobenzoic		250	3	2,6-Difluoro-[c]	40
p-Bromobenzoic		240	4	2,6-Dibromo-[e]	44

[a] Calculations are based on 2 mol of anhydride leading to 1 mol of fluorenone. [b] Compared with authentic sample. [c] Mp 176–178° (cf. ref 4). [d] With anhydrous RhCl₃ at 290° and 7 hr, the yields of 1,5-, 1,7-, 2,6-, 2,7-, and 3,5-dimethylfluorenone were 2.8, 15.4, 16.5, 0.4, and 2.2%, respectively. [e] Mp 200–201° (cf. ref 5).

SCHEME I
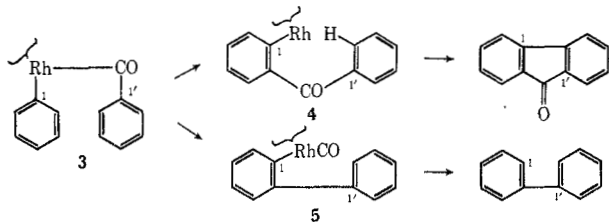
rhodium-bearing carbon, is hindered by the voluminous triphenylphosphine ligands. It appears that these factors play a part in determining the details of the reaction paths, but that they are not the only factors involved.

Some further clarification of the reaction mechanism has been made possible by a study of the reaction between chloro(phenyl)bis(triphenylphosphine)rhodium-(II), PhRhCl(PPh₃)₂ (7), and the rhodium–carbonyl complex 2 (both formed in the reaction of benzoic anhydride and 1[1]) at 250°. In addition to benzene and triphenylphosphine, the formation of 11.1% biphenyl and 15.6% fluorenone has been observed. While at least part of the biphenyl may have been formed by the pyrolysis of 7, the fluorenone can only result from carbonylation of 7 by 2 (or phenylation of 2 by 7) to give an aroyl–rhodium complex that would undergo further phenylation to a compound of type 3. It is clear that the above mechanism accounts also for the observations made in the experiments with mixed anhydrides.

As mentioned before[1] biaryls are formed when benzoic anhydrides are treated with 1 at higher temperatures than those required for the formation of fluorenones. We have now studied this additional reaction, using substituted and "mixed" benzoic anhydrides. p-Toluic and o-toluic anhydride yield each a single bitolyl, 3,4'- and 2,3'-bitolyl, respectively. m-Toluic anhydride is transformed into a mixture of 2,3'- and 3,4'-bitolyl (see Table III). Bitolyls carrying methyl groups at the ortho positions are formed in lower yields, probably because of steric interference. A mixture of benzoic and p-toluic anhydride gives, in addition to biphenyl and 3,4'-bitolyl, also 3- and 4-methylbiphenyl.

This method of biphenyl formation is obviously different from the known oxidative coupling of aromatic hydrocarbons by palladium complexes[7,8] by which all the possible structural isomers are obtained. The selectivity in our system is rationalized with the aid of a metal–ion promoted mechanism, in which the same intermediate 3 in involved, which is the key intermediate in the formation of the fluorenones. Schemes I and II represent possible pathways (cf. footnote 22 of ref 1).

This mechanism can, however, explain only part of the results. Both p-bromo- and p-chlorobenzoic anhydride give mixtures of halogenated biphenyls, albeit in low yields, in which the 4,4'-dihalo derivatives predominate (see Table III). In these cases either

(7) I. Moritani, Y. Fujiwara, S. Teranishi, H. Itatani, and M. Matsuda, Amer. Chem. Soc., Div. Petrol. Chem. Prepr., **14**, B 172 (1969).
(8) Cf. M. O. Unger and R. A. Fouty, J. Org. Chem., **34**, 18 (1969), and references therein.

TABLE III

CONVERSION OF AROMATIC ANHYDRIDES BY 1 INTO BIARYLS

Anhydride	Reaction Temp, °C	Reaction Time, hr	Biaryl formed	Yield, %[a]
o-Toluic	285	3	2,3'-Bitolyl[b]	1.0
m-Toluic	285	2.5	2,3'-Bitolyl[b]	3.7
			3,4'-Bitolyl[b]	9.3
p-Toluic	285	2	3,4'-Bitolyl[b]	17
3,5-Dimethylbenzoic	300	0.75	2,3',4,5'-Tetramethylbiphenyl	4.0
			3,3',5,5'-Tetramethylbiphenyl	1.0
p-Fluorobenzoic	290	1.5	3,4'-Difluorobiphenyl[b,c]	3.7
p-Chlorobenzoic	285	2.5	4,4'-Dichlorobiphenyl[b,d]	3.0
p-Bromobenzoic	285	3	4,4'-Dibromobiphenyl[b,d]	0.35
			Other dibromobiphenyls	0.18
2-Thenoic	285	0.25	2,2'-Bithienyl[e]	8.0
			2,3'-Bithienyl[f]	3.9
Benzoic + p-toluic	290	3	Biphenyl[b]	0.9
			3-Methylbiphenyl[b]	2.5
			4-Methylbiphenyl[b]	2.5
			3,4'-Bitolyl[b]	2.7

[a] Calculations are based on 1 mol of anhydride leading to 1 mol of biaryl. [b] Compared with an authentic sample. [c] Colorless oil. *Anal.* Calcd for $C_{12}H_8F_2$: C, 75.8; H, 4.2. Found: C, 75.8; H, 4.2. Nmr spectrum showed an unsymmetric multiplet centered at δ 7.3 ppm. [d] When the catalyst was replaced by a mixture of 19.6 mg of 2,5-di-t-butylhydroquinone and 327 mg of 1, less than 0.01% of halobiphenyl was obtained. [e] Separated from 2,3'-bithienyl on a 2.6 m × 6.4 mm column, packed with 10% Apiezon L on Chromosorb W at 190°. Analysis and melting point confirm the structure; *cf.* W. Sternkopf and J. Roch, *Justus Liebigs Ann. Chem.*, 482, 260 (1930). [f] The melting point is identical with that reported by J. Teste and N. Lozach, *Bull. Soc. Chim. Fr.*, 492 (1954).

TABLE IV

NMR SPECTRA OF SOME METHYLATED FLUORENONES

Position of methyl groups	Chemical shifts of CH_3 hydrogen atoms, δ (ppm) C-1, C-8	C-2, C-7	C-3, C-6	C-4, C-5	Ref
1,5-Di-Me	2.75			2.48	a
1,7-Di-Me	2.56	2.31			b
2,6-Di-Me		2.32	2.35		a
3,5-Di-Me[c]			2.34	2.47	This work
2,4,5-Tri-Me		2.32		2.44, 2.49	b
1,3,5,7-Tetra-Me[c]	2.58	2.32	2.36	2.52	This work

[a] See ref 1. [b] J. Goodfroid, *Bull. Soc. Chim. Fr.*, 2962 (1964). [c] In CCl_4.

SCHEME II
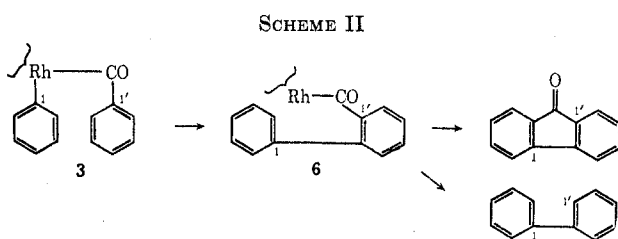
oxidative coupling of the halobenzenes (formed by decarboxylation of the halobenzoic *acids*) or homolytic fission of the anhydrides used, may be invoked. In support of this hypothesis, we have shown that relatively small amounts (19.6 mg per 327 mg of 1) of free-radical scavengers, such as 2,5-di-t-butylhydroquinone, interfere strongly with the formation of the halobiphenyls, but are without effect on the transformation of benzoic and p-toluic anhydride to the corresponding biaryls.

Some anhydrides are converted to biaryls by both pathways, the metal–ion promoted and the free-radical mechanism. 3,5-Dimethylbenzoic anhydride, *e.g.*, gives, in addition to 4% asymmetric 2,3',4,5'-tetramethylbiphenyl, 1% 3,3',5,5'-tetramethylbiphenyl, and 0.1% a third tetramethyl derivative. The yield of these latter compounds could be further reduced by 2,5-di-t-butylhydroquinone.

2-Thenoic anhydride gives two biphenyl-type compounds. In this case the symmetric 2,2'-bithienyl is formed in preference to 2,3'-bithienyl. p-Phenylbenzoic anhydride is transformed under our standard conditions only into traces of a quaterphenyl, the second product being di-p-biphenylyl ketone; none of the expected 2,6-diphenylfluorenone is formed.

The previous study of hydrocinnamic anhydride[1] has been supplemented by an investigation of lauric anhydride. Catalytic amounts of 1 at 275° (for 4.5 hr) give a mixture of 20% 1-undecene, 2% isomeric undecenes, 30% laurone (12-tricosanone), and 41% lauric acid. The low degree of the isomerization of 1-undecene is surprising, as the catalytic decarbonylation of lauroyl chloride by 1 at 250° is coupled with isomerization of the resulting undecene to an extent of 56%.

Some of the decarbonylation products obtained in this study have been identified by nmr spectroscopy. The nmr data for some representative methylated fluorenones and biphenyls are summarized in Tables IV and V. They indicate that distinct chemical shifts may be assigned to the methyl hydrogen atoms at the various positions of the fluorenone and biphenyl molecules. This enabled us to elucidate the structures of the unknown 3,5-dimethyl- and 1,3,5,7-tetramethyl-fluorenone, as well as those of 2,3',4,5'- and 3,3',5,5'-tetramethylbiphenyl.

TABLE V

NMR SPECTRA OF SOME METHYLATED BIPHENYLS

Position of methyl groups	Chemical shifts of CH₃ hydrogen atoms, δ (ppm)			Ref
	o	*m*	*p*	
2,4'-Di-Me[a]	2.225		2.375	This work
3,3'-Di-Me[a]		2.36		This work
3,4'-Di-Me[a]		2.35	2.37	This work
4,4'-Di-Me[a]			2.375	This work
2,2',4,4'-Tetra-Me	2.03		2.37	b
2,3',4,5'-Tetra-Me[a]	2.23	2.345	2.36	This work
3,3',5,5'-Tetra-Me[a]		2.34		This work

[a] In CCl₄. [b] High Resolution Nmr Spectra, Varian Associates, Palo Alto, Calif., The National Press, U. S. A., 1963, Spectrum No. 659.

Experimental Section

The catalysts RhCl(PPh₃)₃,[9] RhCl(CO)(PPh₃)₂,[10] RhH(CO)(PPh₃)₃,[11] RhCl₃(SbPh₃)₃,[10] and RuCl₂(PPh₃)₃[12] have been prepared essentially as described in the literature.

p-Fluorobenzoic anhydride was obtained in 21% yield when a mixture of 10 g of *p*-fluorobenzoic acid and 70 g of acetic anhydride was refluxed for 24 hr. The crude anhydride was flash distilled at 2 mm and recrystallized from hexane: mp 108–110°; ir (KBr) 1720 and 1780 cm⁻¹.

Anal. Calcd for C₁₄H₈F₂O₃: C, 64.1; H, 3.1; F, 14.5. Found: C, 64.2; H, 3.4; F, 14.2.

p-Phenylbenzoic anhydride was formed in 82% yield upon refluxing 10 g of *p*-phenylbenzoic acid with 70 g of acetic anhydride for 48 hr: mp 141–142° (from hexane); ir (KBr) 1720 and 1763 cm⁻¹. The analytical sample was further purified from a small contamination by the free acid by heating it at 130° and 2 mm for 5 hr; the free acid sublimed off.

Anal. Calcd for C₂₆H₁₈O₃: C, 82.5; H, 4.8. Found: C, 82.5; H, 4.7.

3,5-Dimethylbenzoic Anhydride.—A mixture of 9.5 g of 3,5-dimethylbenzoyl chloride and 26.5 g of dry pyridine was refluxed for 5 min, cooled, and poured onto 60 g of crushed ice and 28 ml of concentrated hydrochloric acid. The crystalline anhydride was washed with 10 ml of cold methanol and 10 ml of dry benzene to yield 8 g (90%) of the colorless anhydrides: mp 127° (from benzene); ir (KBr) 1715 and 1785 cm⁻¹; nmr (CCl₄) 2.35 (s, 12), 7.22 (s, 2), 7.71 (s, 4).

Anal. Calcd for C₁₈H₁₈O₃: C, 76.6; H, 6.4. Found: C, 76.7; H, 6.5.

2,3'- and 3,4'-Dichlorobiphenyl.—A solution of *m*-chlorobenzenediazonium chloride (prepared from 80 g of *m*-chloroaniline) was added during 30 min to a stirred mixture of 254 g of chlorobenzene and 140 ml of 5 N aqueous sodium hydroxide. The stirring was continued for 12 hr at room temperature, and the organic layer was steam distilled. The distillate was fractionated at 2 mm and the material of bp 150–180° was collected to yield 19 g (13%) of a mixture of the two biaryls. The separation of 2,3'- and 3,4'-dichlorobiphenyl was carried out on a 2 m × 6.4 mm vpc column, packed with 10% diethylene glycol succinate on Chromosorb W, at 170°. The 2,3'-dichlorobiphenyl (retention time, 23 min) was treated with excess butyllithium and carbon dioxide to yield 27% biphenyl-2,3'-dicarboxylic acid of mp 213–214° (lit.[13] 215–216°). The second peak (retention time, 39 min) consisted of 3,4'-dichlorobiphenyl. The ratio of 2,3'-:3,4'-dichlorobiphenyl was 5:8.

Anal. Calcd for C₁₂H₈Cl₂: C, 64.6; H, 3.6; Cl, 31.8. Found (2,3' isomer): C, 64.3; H, 3.9; Cl, 32.1. Found (3,4' isomer): C, 64.7; H, 3.6; Cl, 31.8.

The catalytic transformation reactions of the various anhydrides listed in Tables I, II and III are illustrated by the following examples.

Reaction of 3,5-Dimethylbenzoic Anhydride and 1.—A mixture of 3 g of 3,5-dimethylbenzoic anhydride and 150 mg of chlorotris-

(triphenylphosphine)rhodium (1) was placed in a Claisen flask connected with a receiver and a gas collector, and heated at 300° for 4.5 hr, during which time 0.41 g (18%) of *m*-xylene distilled over. The cooled reaction mixture was digested with 10% aqueous sodium hydroxide, and the neutral material was taken up into warm benzene. The aqueous layer yielded upon acidification 1.6 g (50%) of 3,5-dimethylbenzoic acid. The organic layer was washed with water, dried, and concentrated, and the residue chromatographed on alumina. The first fraction of hydrocarbons was further separated on a 2 m × 6.4 mm vpc column, packed with 10% SE-30 on Chromosorb W at 170°. The first peak (retention time, 19 min) consisted of 2,3',4,5'-tetramethylbiphenyl (4 mol %), which forms a viscous oil (nmr spectrum, see Table V).

Anal. Calcd for C₁₆H₁₈: C, 91.4; H, 8.6. Found: C, 91.4; H, 9.0.

The second hydrocarbon (1 mol %), having a retention time of 29 min, corresponded to 3,3',5,5'-tetramethylbiphenyl: mp 44° (lit.[14] 43–45°); nmr spectrum δ 2.34 (s, 12), 6.96 (s, 2), 7.18 (s, 4). A third tetramethylbiphenyl (retention time, 13 min) was formed in a very low yield (0.1 mol %).

The yellow carbonyl-containing fraction obtained from the column chromatography was further purified by preparative vpc on a 2 m × 6.4 mm column, packed with 2% XE-60 on Chromosorb W at 200°, to yield 7 mol % (14% yield) of 1,3,5,7-tetramethylfluorenone: mp 117°; ir (KBr) 1710 cm⁻¹ (for nmr spectrum, see Table IV).

Anal. Calcd for C₁₇H₁₆O: C, 86.4; H, 6.8. Found: C, 86.1; H, 6.8.

Reaction of *m*-Toluic Anhydride and Anhydrous Rhodium Trichloride.—*m*-Toluic anhydride (4 g) was heated in the presence of 33 mg of anhydrous rhodium trichloride at 290° for 7 hr. The neutral fraction obtained was analyzed on a 5.2 m × 6.4 mm vpc column, packed with 10% stabilized diethylene glycol succinate on Chromosorb W. The biaryls were separated at 170° into 2,3'- (0.5 mol %) and 3,4'-bitolyl (4 mol %). (Authentic samples were prepared from *m*-toluenediazonium chloride and toluene in a similar way as the analogous chlorobiphenyls described above.) The dimethylfluorenones were separated at 235° into five peaks, corresponding to 1,7-, 1,5-, 2,6-, 2,7-, and 3,5-dimethylfluorenone. The yields were 2.8, 15.4, 16.5, 0.4, and 2.2%, respectively. 1,5-, 1,7-, and 2,6-dimethylfluorenone were compared with authentic samples.[1] The structure of 2,7-dimethylfluorenone was proven by its nmr spectrum [(CCl₄) 2.34 (s, 6), Table IV, footnote b] and melting point of 156° (lit.[15] 157°). The material corresponding to the last peak on the vpc chromatogram showed an nmr spectrum indicating the structure of 3,5-dimethylfluorenone (see Table IV), mp 102–104°.

Anal. Calcd for C₁₅H₁₂O: C, 86.5; H, 5.8. Found: C, 86.8; H, 6.1.

A quantity of 10 mg of this fluorenone was reduced with 28 mg of 55% hydrochloric acid (analytical grade), 14 mg of red phosphorus, and 0.6 ml of acetic acid (reflux for 20 hr), to yield a few crystals of 3,5-dimethylfluorene, mp 81–82° (from ethanol) (lit.[6] 81–82°).

Reaction of a Mixture of *p*-Chlorobenzoic and *p*-Toluic Anhydride with 1.—A mixture of 2.1 g of *p*-chlorobenzoic anhydride, 1.9 g of *p*-toluic anhydride, and 0.2 g of 1 was heated at 250° for 5 hr. The reaction mixture was extracted with chloroform, freed from the carboxylic acids, and separated by preparative tlc on silica gel, using carbon tetrachloride and benzene (3:7) as eluent. The fluorenones formed three yellow bands: the two extreme ones consisted of 2,6-dimethyl-[1] and of 2,6-dichlorofluorenone.[1] The middle broad band proved to be a mixture of two fluorenone derivatives that were separated on a 2.2 m × 6.4 mm vpc column, packed with 10% XE-60 on Chromosorb W at 220°. The first fraction was 6-chloro-2-methylfluorenone according to its dipole moment (2.7 ± 0.1 D), mp 150°, ir (Nujol) 1725 cm⁻¹. The second fraction proved to be 2-chloro-6-methylfluorenone: μ 4.6 ± 0.2 D; mp 208°; ir (Nujol) 1725 cm⁻¹. The yields of 2,6-dimethyl-, 2,6-dichloro-, 2-chloro-6-methyl-, and 6-chloro-2-methylfluorenone were 16, 24, 14, and 13%, respectively.

Anal. Calcd for C₁₄H₉ClO: C, 73.5; H, 3.9. Found (2-chloro-6-methylfluorenone): C, 73.5; H, 4.2. Found (6-chloro-2-methylfluorenone): C, 73.5; H, 4.2.

Reaction of Lauric Anhydride with 1.—Lauric anhydride (4 g) and 0.2 g of 1 were heated for 4.5 hr at 275°. Extraction of the

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(11) D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 2660 (1968).

(12) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 28, 945 (1966).

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reaction mixture with 10% aqueous sodium hydroxide afforded on acidification 1.7 g (41%) of lauric acid. The neutral residue was analyzed on the following vpc columns: (a) 10% SE-30, (b) 10% diethylene glycol succinate, (c) 5% Apiezon M, and (d) 5% β,β'-oxydipropionitrile on Chromosorb W. There were isolated 20% 1-undecene, 2% other undecenes (mainly *trans*-2-undecene), and 30% 12-tricosanone of mp 68°.[16]

Registry No.—*p*-Fluorobenzoic anhydride, 25569-77-1; *p*-phenylbenzoic anhydride, 25327-57-5; 3,5-dimethylbenzoic anhydride, 25569-79-3; 2,3'-dichlorobiphenyl, 25569-80-6; 3,4'-dichlorobiphenyl, 2974-90-5; 2,3',4,5'-tetramethylbiphenyl, 25569-82-8; 1,3,-

5,7-tetramethylfluorenone, 25569-83-9; 3,5-dimethylfluorenone, 25569-84-0; 6-chloro-2-methylfluorenone, 25569-85-1; 2-chloro-6-methylfluorenone, 25569-86-2; *o*-toluic anhydride, 607-86-3; *m*-toluic anhydride, 21436-44-2; *p*-toluic anhydride, 13222-85-0; *p*-chlorobenzoic anhydride, 790-41-0; *p*-bromobenzoic anhydride, 1633-33-6; 2-thenoic anhydride, 25569-97-5; 2,4'-dimethylbiphenyl, 611-61-0; 3,3'-dimethylbiphenyl, 612-75-9; 3,4'-dimethylbiphenyl, 7383-90-6; 4,4'-dimethylbiphenyl, 613-33-2; 3,3',5,5'-tetramethylbiphenyl, 25570-02-9.

(16) An authentic sample was prepared as described by J. C. Sauer, "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 560.

The Mechanism of the Reaction of 2'-Iodo-2-bromomethylbiphenyl with Methyllithium to Yield Fluorene

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The mechanism of the cyclization of 2'-iodo-2-bromomethylbiphenyl to fluorene using methyllithium was investigated. Evidence that this conversion proceeds by the direct displacement of the benzylic bromine by an aromatic anion is presented.

We have been interested in the synthesis of the strained hydrocarbon **1** as a likely precursor to dibenzo-[*cd,gh*]pentalene (**2**). Compound **2** can be visualized as a perturbed [12]annulene. The recent synthesis[1] of hydrocarbon **1**, as well as the dianion of **2**, prompts us to report our results at this time.

1   **2**   **3**
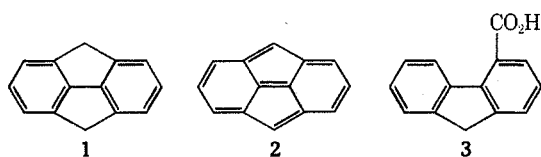
Friedel–Crafts cyclization of the readily available fluorene-4-carboxylic acid (**3**) cannot be expected to serve as a synthetic method for the preparation of **1**. This acylation would proceed through an acylium ion which must attack the aromatic ring along the π orbital,[2] an impossibility for the rigid, planar acid **3**. We therefore sought a method that would circumvent this difficulty and turned to an investigation of methods potentially capable of converting 5-iodo-4-bromomethylfluorene (**4**) to **1**. We chose to study the cycliza-

4   **5**
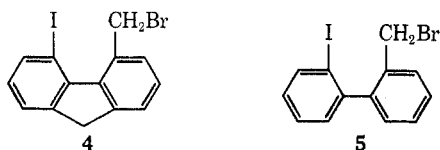
tion of 2'-iodo-2-bromomethylbiphenyl (**5**) as an easily prepared model for this cyclization. Our investigations were limited to those reactions, such as a back-side displacement of the benzylic bromine by an aromatic

anion, which would cyclize **5** in a manner that would not require large changes in geometry. Several reactions were investigated, including those with Zn, Zn–Cu couple, Mg, Ni(CO)₄,[3] and methyllithium. Methyllithium proved to be the most satisfactory reagent, affording fluorene in yields of 69–71%. In order to determine whether the cyclization of **5** with methyllithium was indeed proceeding through the desired back-side displacement of the benzylic bromine, a study of the mechanism of this reaction was undertaken and our results are reported below.

A search of the literature provides little information about the relative rates of halogen–lithium exchange for iodobenzene and benzyl bromide, except that the order of reactivity of the halides is I > Br > Cl.[4] We therefore chose to work with methyllithium, the least reactive of the alkyllithiums,[5] in order to enhance any differences in the halogen–lithium exchange rates.

An ethereal solution of **5** at 0° was treated with 2 equiv of methyllithium, allowed to come to room temperature, and worked up with ammonium chloride solution to afford fluorene in isolated yields of 69–71%. The remaining material had no iodine as shown by a lack of absorption at lower field than δ 7.80 (aromatic protons ortho to iodine) in the nmr spectrum.

A priori there are four possible mechanisms for this conversion (Scheme I). Recent work[6,7] indicates that the halogen–lithium exchange reaction proceeds by a one-electron transfer to give a caged radical pair. These radicals may complete the halogen–metal exchange by transferring a second electron or they may

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(3) The yields of fluorene obtained from Zn or Zn–Cu couple were 1–6%, those from Mg were 30%, and those from Ni(CO)₄ were 2–46%, depending upon the solvent used. A paper on the cyclization of **5** with Ni(CO)₄ will appear at a later date.
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