Catalytic Conversion of Benzoic Anhydrides into Fluorenones

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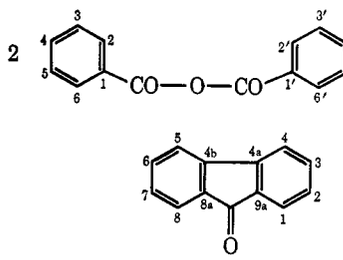
Received March 7, 1969

Chlorotris(triphenylphosphine)rhodium (1) has been shown to catalyze the transformation of benzoic anhydride to fluorenone and of substituted benzoic anhydrides to fluorenone derivatives. Benzoic anhydride and 1 react at 140° to give a divalent rhodium complex. A mechanism of the new catalytic reaction and a general pathway for the formation of the fluorenones is suggested.

Chlorotris(triphenylphosphine)rhodium (1), $RhCl(PPh_3)_3$, which has been shown to exhibit outstanding catalytic properties in numerous organic reactions,[1-12] catalyzes the conversion of benzoic anhydride into fluorenone in a novel reaction; if, for example, benzoic anhydride was heated with a catalytic quantity of the rhodium complex 1 at 240° for 4.5 hr, carbon monoxide was evolved. The resulting product consisted of 30% benzoic acid, 36% fluorenone, 6% biphenyl, 3% benzophenone, and *ca.* 25% unidentified tarry material. At 225°, the reaction is more selective, as benzoic acid and fluorenone are the primary products (eq 1). At higher temperatures than 240°, the formation of biphenyl increases, as shown in Table I. As this reaction appears to proceed *via* a different pathway, its study will be reported in a separate publication.

The behavior of substituted benzoic anhydrides, which is summarized in Table II, shows unequivocally



$$+ 2C_6H_5COOH + CO \quad (1)$$

that the reaction proceeds so that the carbon atoms 1 and 1′ in an *ortho*-substituted anhydride become atoms 4a and 8a in the fluorenone molecule, respectively, etc. The carbon atom 4b would then have to come from either the 2 or 6 position, and likewise the carbon atom 9a from the 2′ or 6′ position of the starting material. Thus the three *para*-substituted benzoic anhydrides studied (see Table II) gave only 2,6-disubstituted fluorenones on heating with 1. 2,6-Dimethylfluorenone was characterized by reduction (with red phosphorus and hydriodic acid) to the known 2,6-dimethylfluorene,[13] and 2,6-dichlorofluorenone by comparison with an authentic specimen.[14,15] The ketone obtained from *p*-deuteriobenzoic anhydride was assumed to be 2,6-dideuteriofluorenone on the strength of its nmr spectrum which resembles closely those of 2,6-dichloro- and 2,6-dimethylfluorenone (but not the spectrum of the unsubstituted parent compound). Although the mass spectrum indicated the presence of small quantities of nondeuterated and monodeuterated fluorenone in the preparation, these contaminants did not show up in the nmr spectrum.

By the above mechanism a *meta*-substituted benzoic anhydride would have been expected theoretically to yield a mixture of the 1,5-, 3,5-, 1,7-, and 2,6-disubstituted fluorenones. In fact, *m*-toluic anhydride gave only 1,7- and 2,6-dimethylfluorenone in the ratio 2:5. We shall refer to this fact in the further discussion.

The *ortho*-substituted benzoic anhydride studied, *o*-toluic anhydride, afforded the expected 1,5-dimethylfluorenone (identified by its oxidation to fluorenone-1,5-dicarboxylic acid),[16] but only in 5–10% yield.

In an attempt to obtain and identify the intermediates of this catalytic reaction, benzoic anhydride was treated with 1 in *o*-xylene at 140°. An insoluble yellow product resulted to which we assign the structure of chloro(phenyl)bis(triphenylphosphine)rhodium-(II) (5, Ar = C_6H_5) on the basis of the elementary

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TABLE I

TRANSFORMATION OF BENZOIC ANHYDRIDE BY 1 AT DIFFERENT TEMPERATURES

Expt	Temp, °C	Yield of neutral products, mol %: Fluorenone	Benzophenone	Biphenyl
1	225	42	Traces	Traces
2	240	36	3.5	5.7
3	270	27	2.8	10.4
4	350	4.8	3.1	36.0

$RhCl(PPh_3)_2(solvent)$ **2** $(ArCO)RhCl(PPh_3)_2$ **3** $ArRhCl(CO)(PPh_3)_2$ **4**

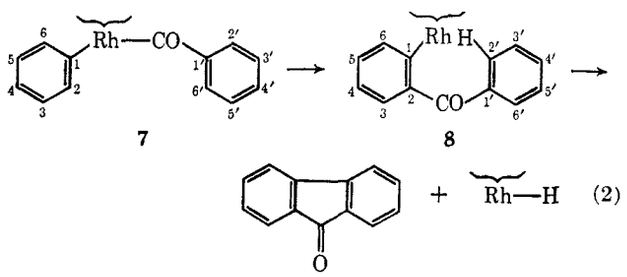
$ArRhCl(PPh_3)_2$ **5** $RhCl(CO)(PPh_3)_2$ **6**

analysis and the infrared spectrum. The presence of a phenyl–rhodium bond is made likely by the observation that the compound, heated above the melting point, gives an almost quantitative yield of biphenyl. Furthermore, by passing carbon monoxide through a suspension of the compound in methylene chloride, a complex mixture resulted that absorbed at 1680 cm^{-1} (ArCO–Rh).

The above formula **5** would indicate that the rhodium is present in the compound in the rare divalent state. Indeed, it has been shown by esr measurements that the compound **5** is paramagnetic even after repeated recrystallizations; it is thus unlikely that the effect is due to a spurious contaminant. The esr spectrum is composed of a large number of strong signals between $g = 2.85$ and 9.85, and their positions are shifted by rotation of the sample in the magnetic field. It should be mentioned that the starting material **1** did not show any resonance lines under the conditions of our measurements.[1a,17,18]

The well-known dissociation of **1** to **2** would open the way to a reaction of the latter with the benzoic anhydride to give a rhodium-containing carboxylate and benzoylchlorobis(triphenylphosphine)rhodium(II) (**3**, Ar = C_6H_5). Whilst such a compound has not been *isolated* in any of our experiments, we have found an indication of its existence by the appearance of a carbonyl absorption at 1685 cm^{-1} when *p*-chlorobenzoic anhydride was heated with **1** in boiling toluene. Compound **3** could isomerize, in a well-known manner, to the rhodium carbonyl derivative **4** which eventually would lose carbon monoxide and thus give **5**.

Whilst in boiling *o*-xylene (bp 140°) **5** is formed, chlorocarbonylbis(triphenylphosphine)rhodium(I) (**6**)[10b] is isolated when **1** and benzoic anhydride are heated in boiling mesitylene (bp 160°).[19] Although the catalytic transformation of benzoic anhydride to fluorenone takes place at even higher temperature at which we have not been able to isolate any defined rhodium complex, we assume that also **6** is a very active catalyst in our reaction.[20] Indeed, the isolated complex **6** is as active in the conversion of benzoic anhydrides into fluorenones as **1**. It could give, with the anhydride, a rhodium complex of type **7** having both an aryl and an aroyl ligand. A subsequent—probably electrophilic—attack of the aroyl group on either positions 2 or 6 of the aryl ligand would give a complex of type **8**,[21,22] which in turn would decompose to fluorenone by abstraction of the hydrogen atom at C-2 by the metal, the latter thus forming a rhodium–hydride complex (eq 2).



(2)

Indeed the formation of such a complex was proven by nmr: the crude reaction mixture (carefully freed from paramagnetic material insoluble in deuteriochloroform) showed a series of peaks centered at τ 27. This rhodium–hydride may be the source of the hydrogen required for the formation of the benzoic acid as the second product in our reaction. This would recall the transformation of phthalic anhydride to benzoic acid by dicobalt octacarbonyl.[23] The sequence of reactions assumed here and partly substantiated, would lead one to expect two steric effects: (a) a substituent located at position 3 of the aryl group in **7** should lower the rate of transformation of **7** to **8**, (b) both blocking of the hydrogen atom attached to C-2′ in compound **8** and the shielding of the Rh–C-1 bond in this complex should impede the eventual formation of a fluorenone. This is indeed in accordance with our observations.

para-Substituted anhydrides, in which the complex **8a** does not exhibit any steric hindrance, give relatively high yields of the 2,6-disubstituted fluorenones. The same applies to *one* of the intermediates, *viz.*, **8b** expected from *m*-toluic anhydride, whilst the formation of **8c** is obstructed by the methyl group at position 3. Thus it is reasonable that 1,7-dimethylfluorenone is formed in lower yield than the 2,6 isomer. In the other possible intermediates, **8d** and **8e**, the hydrogen atom to be abstracted is blocked by the methyl group at position 3′, preventing cyclization to the two possible

(17) D. R. Eaton and S. R. Suart, *J. Amer. Chem. Soc.*, **90**, 4170 (1968).

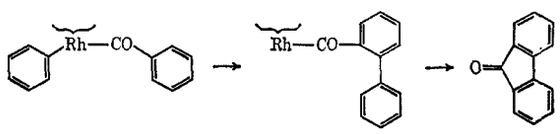
(18) A referee has suggested that the complex **5** may be derived from *ter*valent, not from *di*valent rhodium. As rhodium is low spin in its complexes, it does not seem to us that tervalent rhodium would show paramagnetism. In any event, the proposed mechanism would not appear to be affected by this point. Another referee questioned whether the complex **5** is monomolecular. This, indeed could not be proven, as the compound is not sufficiently soluble in any solvent. It can, however, be recrystallized from a very large amount of xylene.

(19) It is a moot question whether under the conditions of fluorenone formation (230°) **6** decarbonylates to **2** or not. Wilkinson, *et al.*,[10c] claim that the decarbonylation of **6** takes place above 200°, while according to Ohno and Tsuji[10d] the complex is stable at least up to 260°.

(20) It is, of course, difficult to ascribe whether any of the various complexes identified, and, if so, which, is the "true" catalyst in this sequence of reactions.

(21) Obviously, two different rhodium compounds may be formed from **6** and the anhydride, one having an aryl group and one having an aroyl group as ligand; they could react *inter*molecularly to form complex **8**.

(22) One referee suggested an alternative mechanism which assumes that the biphenyl system is formed first, and not from the aroyl–aryl–rhodium complex, as we assume. This possibility cannot be excluded on the basis of



the evidence at hand; however, the steric considerations outlined in the text are the same in both schemes.

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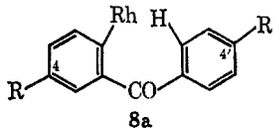
TABLE II
CONVERSION OF BENZOIC ANHYDRIDES INTO FLUORENONES BY 1

Anhydride (g/g of catalyst)	Reaction Temp, °C	Reaction Time, hr	Fluorenone formed	Yield,[a] %
Benzoic (4.0/0.2)	240	4.5	Unsubstituted	72
o-Toluic (5.1/0.2)	235	3	1,5-Dimethyl-	5–10
m-Toluic (5.0/0.2)	240	2.5	2,6-Dimethyl-	34
			1,7-Dimethyl-	14
p-Toluic (3.5/0.18)	240	3.5	2,6-Dimethyl-	72
p-Chlorobenzoic (10/0.2)	240	4	2,6-Dichloro-	50
p-Deuteriobenzoic (5.0/0.2)	245	3	2,6-Dideuterio[b]	91

[a] Calculations are based on 2 mol of anhydride leading to 1 mol of fluorenone. [b] Contaminated with some mono- and undeuterated fluorenone.



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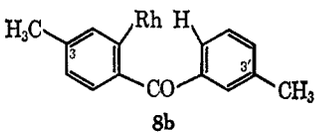

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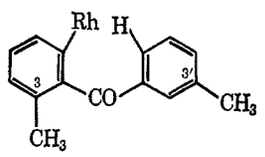

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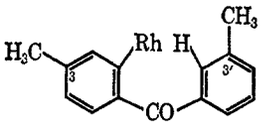
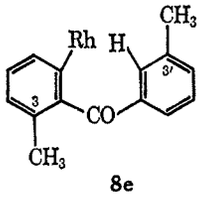


8d



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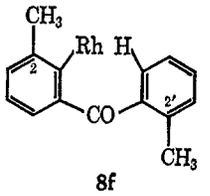
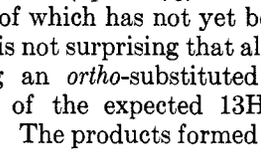


8f

dimethylfluorenones other than the 2,6 and the 1,7 isomer.

In the complex **8f**, from *o*-toluic anhydride, the Rh–C bond is strongly shielded by the neighboring methyl group; thus the formation of 1,5-dimethylfluorenone in very low yield is not unexpected. The main reaction (34%/mol of anhydride) is the formation of 2,3′-ditolyl ketone, which is accompanied by varying quantities (up to 7%) of a lactone, $C_{16}H_{14}O_2$, the structure of which has not yet been elucidated.

It is not surprising that also α-naphthoic anhydride—being an *ortho*-substituted benzoic anhydride—gives none of the expected 13H-dibenzo[*a*,*g*]fluoren-13-one (**10**). The products formed were α,β-dinaphthyl ketone



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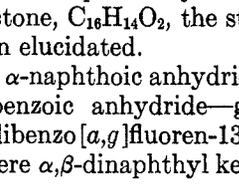

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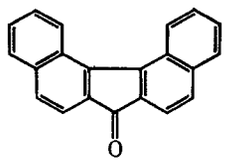

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(**9**, 14%), small quantities of a lactone, $C_{22}H_{14}O_2$, and surprisingly, a 32% yield of 13H-dibenzo[*a*,*i*]fluoren-13-one (**11**). This would indicate that the cyclization reaction is accompanied (or preceded) by an isomerization to a rhodium derivative of naphthalene in the β position.

It is noteworthy that benzoic *acids* are partially converted into fluorenones when heated with **1**; benzoic acid gives 5.6% fluorenone (for each 2 mol of acid) when heated at 235° for 2 hr with **1** and 28% at 250° for 2 hr. We assume that under these conditions part of the acid, which is not decarboxylated, is first dehydrated to the corresponding anhydride.

Also nonaromatic anhydrides react with **1** (or **6**), although the products are of different nature. One mole of hydrocinnamic anhydride, when treated with 0.01 mol of **1** at 300° for 3 hr, gives 0.15 mol of diphenethyl ketone, 0.35 mol of hydrocinnamic acid, and 0.5 mol of styrene. The formation of styrene is at least formally equivalent to the hydrogen abstraction occurring in **8**.

Experimental Section

The general procedure used for the conversion of aromatic acid anhydrides into derivatives of fluorenone is illustrated by the following example.

Fluorenone from Benzoic Anhydride.—A mixture of 4.0 g of benzoic anhydride and 0.2 g of chlorotris(triphenylphosphine)-rhodium (**1**) was placed in a flask preheated at 250° and connected to a distilling apparatus and a gas collector. After a few minutes, carbon *monoxide* began to be evolved. The bath temperature was lowered by 10° and the heating was continued for 4.5 hr (until the evolution of the gas, which consisted at that time mainly of carbon *dioxide*,[24] had practically ceased). The reaction mixture was cooled and digested with 10% aqueous sodium hydroxide, and the neutral material was taken up in warm benzene or methylene chloride. The *aqueous* layer was acidified and the precipitate was filtered and recrystallized from water to yield 1.3 g (60%)[25] of benzoic acid. The *organic* solution was washed with water, dried, and concentrated and the residue was purified either by column chromatography (on alumina) or by preparative vapor phase chromatography on a 5-ft-long column packed with 10% SE-30 on Chromosorb W at 200°. Thus, 0.155 g (5.7%) of biphenyl, 0.097 g (3%) of benzophenone, and 1.15 g (0.36 mol/mol of anhydride or 72% of the theoretical yield) of fluorenone were obtained. The products were identified by comparison with authentic samples.

When the above experiment was carried out with 0.1 g of *trans*-chlorocarbonylbis(triphenylphosphine)rhodium (**6**) and 2.7 g of benzoic anhydride at 240°, similar results were obtained. In one experiment, in which 2.2% biphenyl and 1.7% benzophenone were formed, the yield of fluorenone exceeded the theoretical value by 4%. Obviously, part of the benzoic acid formed has also been converted into fluorenone under these conditions.

Transformation of Benzoic Acid into Fluorenone.—A mixture of 4.0 g of benzoic acid and 0.2 g of **1**, heated for 4 hr at 230°, as

(24) The catalyst causes decarboxylation of free aromatic acids, though slowly, as we have indicated in previous studies (*cf.* ref 10a).

(25) The yield of acid from the anhydride was calculated, in accordance with eq 1, on the basis of 1 mol of acid from 1 mol of anhydride charged.

described above, yielded 0.3% biphenyl, 5.2% fluorenone (based on 1 mol of ketone from 2 mol of acid), and no benzophenone.

On repetition of the experiment applying direct heating to allow the benzoic acid to reflux vigorously (at 249°) for 2 hr, the yields of biphenyl, benzophenone, and fluorenone rose to 0.9, 0.2, and 28%, respectively. In this process, the rhodium compound was partially reduced to the free metal which precipitated as a mirror.

2,6-Dimethylfluorenone was obtained from *p*-toluic anhydride and 1 or, together with 1,7-dimethylfluorenone, from *m*-toluic anhydride (Table II). A suitable separation column was 7 ft long, packed with 17.5% diethylene glycol succinate and 2.5% Carbowax 20M on acid-washed Chromosorb P. The 2,6-dimethylfluorenone, recrystallized from ethanol at −70°, formed yellow prisms: mp 82°; $\bar{\nu}_{max}^{KBr}$ (C=O) 1700 cm^{-1}; nmr ($CDCl_3$) τ 2.4–3.0 (m, 6 H), 7.65 (s, 3 H), 7.68 (s, 3 H).

Anal. Calcd for $C_{15}H_{12}O$: C, 86.5; H, 5.8. Found: C, 86.3; H, 5.8.

2,6-Dimethylfluorene.—A mixture of 34 mg of the foregoing ketone, 94 mg of 55% hydriodic acid (analytical grade), 48 mg of red phosphorus, and 2 ml of acetic acid was refluxed for 20 hr. The excess phosphorus was filtered off and washed with acetic acid, and the filtrate was treated with aqueous sodium bisulfite and neutralized with 5% potassium hydroxide. The fluorene derivative was extracted with benzene; thus 25 mg (79%) of 2,6-dimethylfluorene, mp 66–67° (from ethanol) (lit.[13] mp 67°), was obtained.

1,7-Dimethylfluorenone was obtained by chromatographic separation from its mixture with the 2,6-dimethyl isomer (see above): yellow crystals; mp 75–76° (from ligroin) (lit.[26] mp 76°); nmr ($CDCl_3$) τ 2.6–3.1 (m, 6 H), 7.44 (s, 3 H of C-1 CH_3), 7.69 (s, 3 H of C-7 CH_3).

1,7-Dimethylfluorene resulted in 78% yield when 55 mg of the foregoing ketone was reduced with red phosphorus and hydriodic acid in acetic acid, essentially in the manner described for the preparation of 2,6-dimethylfluorene: mp 107° (lit.[10] mp 107°); λ_{max}^{EtOH}, mμ (log ϵ), 269 (4.44), 275 (4.33), 293 (3.95), 297 (3.90), 304 (3.95) [lit.[26] 269 (4.31), 275 (4.22), 293 (3.82), 297 (3.72), 304 (3.92)].

The **1,3,5-trinitrobenzene derivative** melted at 96° (lit.[26] mp 98°).

2,3′-Bitolyl, 2,3′-Ditolyl Ketone, and 1,5-Dimethylfluorenone from *o*-Toluic Anhydride.—*o*-Toluic anhydride (5.1 g) was heated at 235° for 3 hr in the presence of 0.12 g of **1**. The neutral fraction was separated from 2.2 g (80%) of *o*-toluic acid and was shown by vapor phase chromatography (using either a 5-ft-long 10% SE-30 or a 5% Apiezon L column) to be composed of 1% **2,3′-bitolyl**, 34% **2,3′-ditolyl ketone**, 5% (10% of the theoretical value) **1,5-dimethylfluorenone**, and 7% colorless lactone $C_{16}H_{14}O_2$, mp 95°, with a retention time similar to that of 1,5-dimethylfluorenone [$\bar{\nu}_{max}^{KBr}$ 1780 cm^{-1}; nmr ($CDCl_3$) τ 2.48–3.06 (m, 7 H), 3.42 (s, 1 H), 7.25 (s, 3 H), 7.52 (s, 3 H), mol wt 238].

Both 2,3′-bitolyl and 2,3′-ditolyl ketone [$\bar{\nu}_{max}^{KBr}$ 1650 cm^{-1}; nmr ($CDCl_3$) τ 7.65 (s, 3 H), 7.70 (s, 3 H)] were identified by comparison with authentic samples.

The dimethylfluorenone was obtained as a yellow oil that crystallized from petroleum ether (bp 40–60°) and was separated from some pale yellow needles of mp 193–195° by recrystallization from the same solvent. It melted at 35–40°. The nmr spectrum (in $CDCl_3$) shows in addition to the expected signals at τ 7.38 (C-1 CH_3) and 7.61 (C-5 CH_3] the presence of some peaks possibly due to traces of another dimethylfluorenone (perhaps the 1,7-dimethyl isomer).

Anal. Calcd for $C_{15}H_{12}O$: C, 86.5; H, 5.8. Found: C, 86.7; H, 5.8.

1,5-Dicarboxyfluorenone.—The above dimethylfluorenone (50 mg), 0.25 g of potassium permanganate, and 30 ml of 10% aqueous sodium carbonate were refluxed for 6 hr with stirring. The mixture was acidified with dilute sulfuric acid and the manganese dioxide formed reduced by addition of sodium sulfite. The orange precipitate was filtered and recrystallized from glacial acetic acid, affording 5 mg of fluffy orange needles of the dicarboxylic acid, mp 290–295° (lit.[16] mp 295–299°).

2,6-Dichlorofluorenone was obtained (25 mol %/mol of anhydride, 50% yield) when 4.6 g of *p*-chlorobenzoic anhydride was heated with 0.2 g of **1** at 240° for 4 hr. The yield could not be improved by heating the reaction mixture for an additional 6-hr period, though during this time 60% of the chlorobenzoic acid, formed initially, was decarboxylated to chlorobenzene. The purification of the fluorenone derivative was achieved by gas chromatography using a 3-ft-long column packed with 10% SE-30 on Chromosorb W, at 210°; it was identified by comparison with an authentic sample:[14] mp and mmp 200°. Both samples also had identical ir, uv, and nmr spectra.

p-Deuteriobenzoic Acid.—*p*-Bromodeuteriobenzene was best prepared by addition of 156 g of *p*-dibromobenzene in 400 ml of ether to a refluxing mixture of 80 g of the same dibromide, 28 g of magnesium, and 200 ml of ether in an atmosphere of nitrogen and at a rate so as to keep the mixture refluxing gently. After 2 hr at 34° and cooling to 0°, 30 ml of deuterium oxide was added and the mixture was worked up in the usual manner, giving after two successive fractional distillations 57 g (37%) of *p*-bromodeuteriobenzene:[27] bp 153°; nmr (AB spectrum) τ 2.48, 2.82 (J = 8 cps).

A Grignard solution prepared from 61 g of the foregoing compound and 8 g of magnesium in 240 ml of dry ether was added to a stirred slurry of 500 g of Dry Ice and 300 ml of ether. The mixture was allowed to warm to room temperature, hydrochloric acid was added, and the organic acid was extracted with 10% ammonia solution. The free deuterated acid was recrystallized once from water and once from heptane, affording 33 g (77%) of colorless crystals: mp 121°; nmr ($CDCl_3$) (AB spectrum) τ 1.78, 2.45 [J = 9 cps, 0.07 (COOH)].

Anal. Calcd for $C_7H_5DO_2$:[28] C, 68.3; H, 4.9. Found: C, 67.9; H, 4.8.

***p*-Deuteriobenzoic anhydride** was prepared in 56% yield by heating the foregoing acid with a twofold excess of acetic anhydride, followed by distillation of the acetic acid formed and the excess reagent. On trituration and two successive recrystallizations from petroleum ether (bp 40–60°), colorless crystals of mp 43° resulted: nmr ($CDCl_3$) (AB spectrum) τ 1.84, 2.50 (J = 8 cps).

Anal. Calcd for $C_{14}H_8D_2O_3$:[28] C, 73.7; H, 4.4. Found: C, 73.9; H, 4.5.

2,6-Dideuteriofluorenone was obtained in 91% yield (1 mol from 2 mol of anhydride) from 5.5 g of the foregoing anhydride and 0.2 g of **1** at 250° (3 hr). Purification was carried out by vapor phase chromatography on a 3-ft-long 10% SE-30 on Chromosorb W column, followed by recrystallization from benzene and hexane: yellow prisms, mp 83°.

Anal. Calcd for $C_{13}H_6D_2O$:[28] C, 85.7; H, 4.4. Found: C, 85.9; H, 4.7.

The mass spectrum indicates some contamination with mono- and undeuterated fluorenone.

α,β-Dinaphthyl Ketone (9) and Dibenzo[*a*,*i*]fluorenone (11) from α-Naphthoic Anhydride.—A mixture of 8.1 g of α-naphthoic anhydride and 0.27 g of **1** was heated at 240° for 4 hr. The resulting neutral fraction was separated by three successive chromatographies on alumina and fractional recrystallization from ethyl acetate, methanol, and nitromethane to yield 1.34 g (21%) of naphthalene, 1.0 g (14%) of **α,β-dinaphthyl ketone (9)**, and 1.13 g (32% of the theoretical yield) of **dibenzo[*a*,*i*]fluorenone (11)**. The naphthalene and the dinaphthyl ketone (mp 135°[29]) were compared with authentic samples. The red fluorenone derivative was found to be contaminated with traces of a colorless lactone from which it could be freed by heating with nitromethane (the lactone crystallizes from this solvent), and proved to have the properties reported in the literature: plates of mp 265°[29] (from ligroin); $\bar{\nu}_{max}^{KBr}$ (C=O) 1690 cm^{-1}; λ_{max}^{EtOH}, mμ (log ϵ), 236 (4.51), 262 (4.38), 299 (4.82), 376 (3.54), 396 (3.62), 460 (2.60);[30] mol wt (mass spectrograph) 280.

The colorless lactone was recrystallized from ligroin: mp 166–167°; its analysis corresponded to $C_{22}H_{14}O_2$; mol wt 310; $\bar{\nu}_{max}^{KBr}$ (C=O) 1763 cm^{-1}; λ_{max}^{EtOH}, mμ (log ϵ), 247 (4.34), 287 (4.11).

Styrene and Diphenethyl Ketone from Hydrocinnamic Anhydride.—The decomposition of 18 g of this anhydride by **1** was carried out at 300° (at a lower temperature the reaction proceeded extremely slowly). During a period of 3 hr 6.6 g of styrene (quantitative yield, assuming 1 mol of styrene/mol of anhydride) distilled off, characterized by comparison with an authentic sample. The residue was separated into 6.7 g (70%) of hydro-

(26) T.P. C. Mulholland and G. Ward, *J. Chem. Soc.*, 4676 (1954).

(27) L. H. P. Weldon and C. L. Wilson, *ibid.*, 235 (1946).

(28) The total hydrogen content is calculated as ^1H in accordance with the analytical methods.

(29) R. H. Martin, *ibid.*, 679 (1941).

(30) DMS UV Atlas, Vol. 2, Verlag Chemie, Weinheim and Butterworths, London, 1966, spectrum E7/T3.

cinnamic acid and 2.2 g (15%) of diphenethyl ketone. The latter compound was compared with a sample prepared by dry distillation of barium hydrocinnamate at 340–350°. Both absorbed at $\bar{\nu}_{max}^{KBr}$ (C=O) 1700 cm^{-1}; nmr ($CDCl_3$) τ 2.83 (br s, 10 H), 7.19, 73.7, 7.58 [J = 5, 7, and 5 cps (sextet 4 H)].

The red **2,4-dinitrophenylhydrazone** melted at 115°[31] (from ethanol).

Reaction of Benzoic Anhydride with 1 in Aromatic Hydrocarbons as Solvents.—To a stirred solution of 0.41 g of 1 in 10 ml of *o*-xylene at 140°, there was added 0.1 g of benzoic anhydride. A yellow precipitate started to separate immediately. After heating for 30 min at 140°, the mixture was filtered, while still hot. On cooling of the filtrate to 0°, a second complex precipitated. It was found to be pure chlorocarbonylbis(triphenylphosphine)rhodium (6): mp 203–205°, $\bar{\nu}_{max}^{Nujol}$ 1965 cm^{-1}.

Anal. Calcd for $C_{37}H_{30}ClOP_2Rh$: C, 64.3; H, 4.3; Cl, 5.1. Found: C, 64.0; H, 4.4; Cl, 5.4.[10b]

The first *insoluble* precipitate was heated either with benzene or better with methylene chloride to remove the still adhering compound 6 and dried at room temperature at 0.5 mm. Thus was obtained 0.104 g of yellow crystals, mp 232–233°, of **chloro(phenyl)bis(triphenylphosphine)rhodium(II)** (**5**, Ar = C_6H_5).

Anal. Calcd for $C_{42}H_{35}ClP_2Rh$: C, 68.2; H, 4.7; Cl, 4.8. Found: C, 68.0, 68.2; H, 4.9, 4.3; Cl, 4.8, 4.7.

The complex does not show any carbonyl absorption in the infrared spectrum and is too insoluble for nmr measurements. The esr spectrum, in which strong lines between g = 2.85 and 9.85 are observed, indicated the paramagnetic character of the compound.

(31) H. A. Weidlich and M. M. Delius, *Ber.*, **74**, 1195 (1941).

p-Toluic anhydride gave in the analogous experiment only chlorocarbonylbis(triphenylphosphine)rhodium (6); the same was the case for benzoic anhydride and 1 in boiling mesitylene, whilst in boiling benzene or toluene benzoic anhydride did not react with the rhodium complex 1 at all.

When a mixture of 0.59 g of *p*-chlorobenzoic anhydride, 0.185 g of 1, and 2 ml of toluene was refluxed for 1 hr, the orange-yellow crystals that separated proved to be a mixture of a rhodium–aroyl complex and 6, having strong absorption bands at 1685 and 1965 cm^{-1} (relative intensities of 1.4:1). When the experiment was repeated in 3 ml of *o*-xylene, the mixture showed the same absorption peaks, but the ratio of intensities was 1:2.5. Heating either of the two mixtures in boiling mesitylene for 30 min caused the aroyl carbonyl peak at 1685 cm^{-1} to disappear.

Registry No.—1, 14694-95-2; **5** (Ar = C_6H_5), 21537-43-9; 6, 13938-94-8; benzoic anhydride, 93-97-0; *o*-toluic anhydride, 607-86-3; *m*-toluic anhyride, 21436-44-2; *p*-toluic anhydride, 13222-85-0; *p*-chlorobenzoic anhydride, 790-41-0; *p*-deuteriobenzoic anhydride, 21494-28-0; 1,5-dimethylfluorenone, 21436-47-5; 2,6-dimethylfluorenone, 21436-48-6; 2,6-dideuteriofluorenone, 21436-49-7; *p*-deuteriobenzoic acid, 4551-62-6.

Acknowledgment.—The authors wish to thank Professor Ernst D. Bergmann for his advice.

The Synthesis, Spectral Properties, and Chemical Ring Opening of Tricyclo[3.3.0.0^{2,8}]octan-3-one, a Rigid Model for Unsymmetrical Cyclopropyl Ketone Participation

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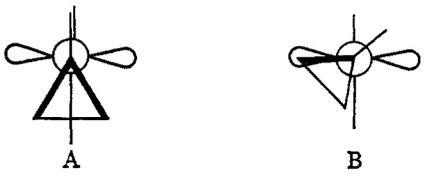
Received January 20, 1969

Stereomodels reveal that the skeletal framework of tricyclo[3.3.0.0^{2,8}]octan-3-one (4) constitutes a rigid model for cyclopropyl ketone participation in an unsymmetrical conformation. Ketone 4 and three specifically deuterated derivatives (C_2-*d*, C_4-d_2, and C_8-*d*) were synthesized. These compounds were used, in conjunction with spin decoupling experiments, to interpret the nmr spectrum of ketone 4. Unambiguous chemical shift assignments for the C_1, C_2, C_4, C_5, and C_8 protons were made. The major fragmentation pathway of this tricyclic ketone in the mass spectrum involves the loss of ketene to give a base peak at *m/e* 80. Reductive cleavage of ketone 4 with lithium in liquid ammonia yielded as products 95% *cis*-bicyclo[3.3.0]octan-3-one (12) and 5% bicyclo[3.2.1]-octan-3-one (13). Treatment of ketone 4 with hydrogen bromide in methylene chloride gave, after reductive removal of the bromine atom, a mixture of 80% 12 and 20% 13. Interpretation of these results in terms of ground-state cyclopropyl ketone delocalization in an unsymmetrical conformation is discussed. The stereoselectivity of the dissolving metal cleavage is consistent with the known stereoelectronic requirements for reductive elimination of α-substituted ketones. The product mixture from the acid-catalyzed opening appears to reflect (in part) thermodynamic control. It is concluded that an evaluation of product composition data from either of these general chemical probes is not a valid method to assess ground-state cyclopropyl ketone delocalization.

It has been firmly established that freely rotating systems containing a cyclopropane ring adjacent to an electron-deficient center (carbonyl group[4] or carbonium ion[5]) adopt the symmetrical, bisected conformation A in preference to the unsymmetrical geometry B. Collectively, these data have been advanced in support of the theoretical prediction[6] that maximum delocalization should occur in the bisected conformation A. A more rigorous test of this hypothesis, however, requires a



A B

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(2) Partial financial support from the University of Texas Research Institute is gratefully acknowledged.

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