Reactions of Derivatives of 1,2,3-Triphenylcyclopropene with Iron Salts[1-3]

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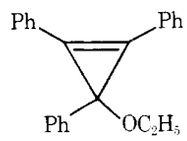
The reaction of 3-ethoxy-1,2,3-triphenylcyclopropene (1) with ferric chloride in refluxing ethanol gives 1,2,3-triphenylcyclopropene (3) and 2,3-diphenylindenone (4) as major products. It has been found that 1,2,3-triphenylcyclopropenylium bromide (5) reacts with ethanol or 2-propanol without iron(III) to give 3 and products associated with acid-catalyzed rearrangement of 3: 1,2-diphenylindene and ethers of 1,2,3-triphenylprop-2-en-1-ol. When 2-propanol was used, acetone was detected as a product. Thus, the formation of 3 in the reaction of 1 in the presence of ferric chloride is reduction of the triphenylcyclopropenylium cation (or the corresponding ether coordinated with an acid) by solvent. The pathway suggested for formation of 4 is equilibration to give 3-hydroxy-1,2,3-triphenylcyclopropene (11), followed by oxidation with iron(III) to give a ring-opened vinyl radical 12 which can be trapped with oxygen or by ligand transfer oxidation. The path to 4 involves cyclization either of 12 or the cation corresponding to it. Several other reaction pathways are ruled out on the basis of control experiments. In an attempt to generate 12 independently, treatment of 1,2,3-triphenylcyclopropenylium tetrafluoroborate (29) with potassium nitrite gives benzil, benzoic acid, 2-phenylisatogen, and benzonitrile in substantial amounts, but less than 1% of 4.

When 3-ethoxy-1,2,3-triphenylcyclopropene (**1**) is refluxed with ferric chloride in ethanol or 1,2,3-triphenylcyclopropenylium tetrachloroferrate (**2**) is treated with 1 equiv



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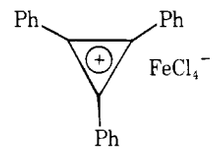

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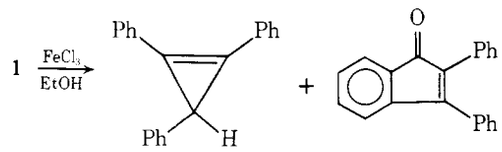
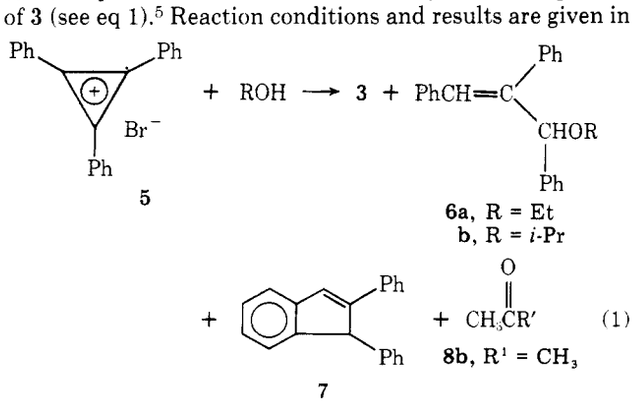
of base under the same conditions, the major products are 1,2,3-triphenylcyclopropene (**3**) (15%) and 2,3-diphenylindenone (**4**) (65%).[4] The reaction to give **3** does not require the



3 **4**

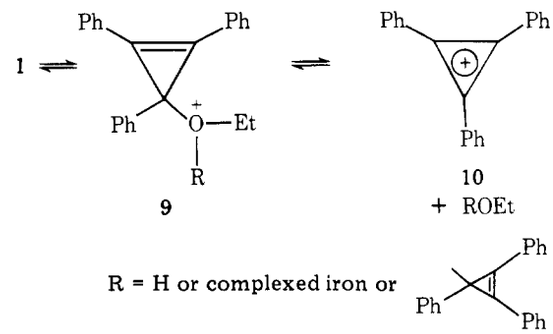
presence of iron, while the formation of **4** does. Thus, possible pathways to these products will be discussed separately. Our studies to elucidate the mechanism of formation of **4** illustrate the variety of reactions that free radicals can undergo in the presence of iron(III) which depend on the ligand on iron, the solvent, the temperature and the presence of oxygen.

Mechanism of Formation of 3. The evidence indicates that the presence of iron(III) or iron(II) is not necessary for the formation of **3** from **1**. For example, in both refluxing ethanol and 2-propanol, 1,2,3-triphenylcyclopropenylium bromide (**5**) alone will react to give **3** and/or products which can be explained on the basis of acid-catalyzed rearrangement of **3** (see eq 1).[5] Reaction conditions and results are given in Table I. Of note is that specially prepared "acid-free" **5** does not give acid-catalyzed rearrangement products of **3**. Compound **5**, prepared in the usual manner[6] and not carefully recrystallized, contains some hydrogen bromide as evidenced by the evolution of a gas acidic to litmus when **5** is heated in acetonitrile. Results with **2** parallel those from **5** (see Table II), although under these conditions indenone formation competes. Methanol and *tert*-butyl alcohol give at the most traces of **3**.



5 **6a**, R = Et; **b**, R = *i*-Pr **7** **8b**, $R^1 = CH_3$ (1)

There are other results which indicate that the reaction of **1** to give **3** is acid catalyzed. For example, **1** is stable in refluxing ethanol. Also, treatment of **2** in ethanol with 2 equiv of base leads to an 86% yield of **4** but no **3**. Thus, when **3** is formed from **1** in the presence of ferric chloride we favor the following mechanism. Acid present in the solution, either as a proton formed by solvolysis of ferric chloride (solutions are acidic to indicator paper and the response of a glass electrode indicates protons), some iron species, or **10**[7], facilitates the following equilibrium. In fact, there may be significant quantities of cation **10** present, because when **2** is treated with an equivalent of sodium hydroxide in methanol under nitrogen, conditions under which reduction does not take place and oxidation is limited, roughly 35% of a triphenylcyclopropenyl cation and no 3-methoxy-1,2,3-triphenylcyclopropene was isolated. Furthermore, we would expect more of **10** than **9** to be present at equilibrium, since the pK_as of ordinary aliphatic



9 **10** + ROEt

R = H or complexed iron or

ethers are −2 or less,[9] while the pK_R+ of **5** is 2.80.[6] Either **9** or **10** can react to give **3**: **9** by an intramolecular hydride transfer or **10** by an intermolecular hydride transfer from the solvent. Clearly, an intermediate protonated ether can be formed from either **5** or **2** as well as **1**. The isolation of acetone from the reaction of **5** in 2-propanol substantiates the hydride-transfer mechanism. The reason for lack of formation of **3** with **2** and *tert*-butyl alcohol is now obvious: there are no

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Table I. Reaction of 5 with Various Alcohols[a]

mmol of 5	Solvent (mL)	Product in % yield 1	3	5	6a or b[b]	7	O ‖ CH_3CCH_3
0.43	EtOH (100)		17		44		
0.43	EtOH (110)			15	26[e]	29[e]	
0.43[f]	EtOH (100)	18	65				
0.45	*i*-PrOH (50)		59		14		
5.81	*i*-PrOH (100)[g]				40	32	6[i]
0.30	MeOH (20)			100[j]			

[a] All reactions were run in air, bath temperature 120-130 °C, 20-24 h. [b] Authentic samples of **6a** and **b** were prepared from (*E*)-1,2,3-triphenylprop-2-en-1-ol,[c] acid, and ethanol and 2-propanol, respectively. Spectroscopic and analytical data appear under Experimental Section. These syntheses parallel the synthesis of the corresponding methyl ether.[c] Although the assignment of the stereochemistry (*E*) is based on weak evidence,[c] formation of the *E* isomer can be rationalized on the basis that other acid-catalyzed ring-opening reactions of 1,2-diphenylcyclopropenes have given exclusively the allyl isomer in which the two phenyls are cis.[d] [c] R. E. Lutz and E. H. Rinker, Jr., *J. Am. Chem. Soc.*, 77, 368 (1955). [d] G. A. Kudryautseva and O. A. Nesmeyanova, *Izv. Akad. Nauk Kaz. SSSR, Ser. Khim.*, 2357 (1974); J. A. Pincock, R. Morchat, and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 7536 (1973). [e] Based on recovered starting material. [f] Acid-free cation was prepared by refluxing the material in acetonitrile containing Linde molecular sieve 4-A for 0.5 h after HBr evolution ceased (as detected by wet pH paper), decanting the solution, and collecting the product in the usual manner. Presumably, the first two entries in the table differ because of differing amounts of acid in different samples of the cation which are not treated in this manner. [g] Roughly 5% of a product was isolated which was tentatively identified as (*Z*)-1,2,3-triphenylpropene. It had an infrared spectrum very similar to the infrared (kindly supplied by Professor G. Griffin) of an authentic specimen and UV similar to that reported: λ_{max} (EtOH) 259 (lit.[h] 260 nm). [h] G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965). [i] Isolated as 2,4-DNP derivative prepared from first 20 mL of distillate from the reaction mixture. Isopropyl alcohol is not oxidized in a detectable amount by air under the reaction conditions. [j] Since recovered starting material melted 230-250 °C (dec), small amounts of impurities could have been present. Infrared was identical to that of starting material.

hydrogens appropriately situated to give hydride transfer. It may seem anomalous that the reduction does not occur in methanol. However, it has been found that, although the reduction of triphenylcarbinol to triphenylmethane in acid proceeded well with ethanol and 2-propanol, suitable conditions could not be found for the same reduction in methanol.[10]

Mechanism of Indenone Formation. An outline of our conclusions concerning the mechanism of the formation of **4** appears in Scheme I. The important features of this scheme are formation of 3-hydroxy-1,2,3-triphenylcyclopropene (**11**) which is oxidized to give a ring-opened radical **12**. The pathways to **4** from **12** can involve reversible cyclization to radical **13** which is subsequently oxidized and/or oxidation to **14** followed by cyclization to cation **15** which loses a proton to give **4**.[11]

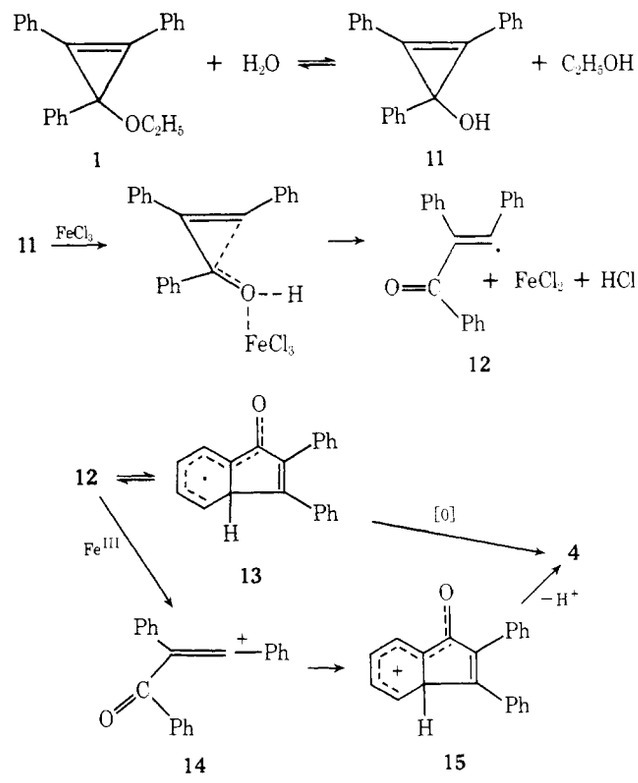
Evidence for a Cyclopropenol Intermediate. Particularly suggestive is the fact that when **2** is treated with an equivalent of base in refluxing water the two major products are **4** (48%) and 1,2,3-triphenylprop-2-en-1-one (**16**) (35%). The latter has typically been presented as the product of base-catalyzed ring opening of **11**.[12] Also, because of the acid catalysis necessary for the formation of **3**, it is highly probable that both **1** and **11** are present in the reaction mixture with **10** as an intermediate between them (see above). Finally, the formation of vinyl radical **12**, which we have unequivocally

Table II. Reaction of 2 in Various Alcohols

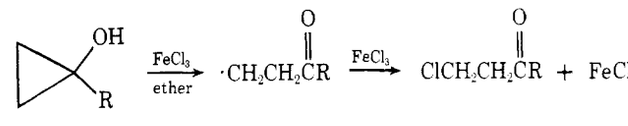
Solvent 2 + $^-$OH	% yield 3	4
MeOH[a]	0	85
EtOH[a]	15	65
EtOH[b]	0	86
i-PrOH[a]	24[c]	56[c]
t-BuOH[a]	Trace ?	65

[a] 0.152 g (0.33 mol) of **2**, 0.35 mmol of NaOH in 20 mL of solvent, 0.34 mL of H_2O, reflux 20 h. [b] 1.029 g (2.22 mmol) of **2**, 4.36 mmol of NaOH in 45 mL of solvent, reflux 20 h. [c] Average of two runs.

Scheme I



trapped as an intermediate (see below), from the cyclopropenol and iron(III) has precedence in the redox chemistry of cyclopropanols studied by Th. Deboer, Depuy, and their coworkers.[13] In particular, ferric chloride produces β-ketoalkyl radicals which undergo ligand transfer oxidation to the corresponding chloro ketones.[13a] Only ring-opened radicals can be detected by ESR even though stereochemical studies suggest attack at the O–H bond rather than at a C–C bond.[13b]



Thus, if cyclopropoxy radicals are formed, they have a very short lifetime. Because the strain energy of cyclopropenes is so much higher than that of cyclopropanes, it is highly likely that a cyclopropenoxy radical would not be a discrete intermediate and that **11** would ring open directly to **12** in the presence of iron(III).

Our results leave little doubt about **11** as an intermediate to the formation of **4**.[14] Unfortunately, more direct evidence for the intermediacy of **11** has not been possible, since despite many attempts we and others have been unable to synthesize it.[15]

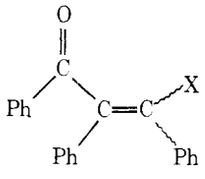
Evidence for a Vinyl Radical. In order to obtain infor-

Table III. Reaction of 1 with FeX_3 at Room Temperature

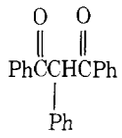
1 →	4	17a or + b	+ 18	+ PhC(=O)—C(=O)Ph	+ $PhCO_2H$[a]
$CH_3CN/FeCl_3$	18%	9	14		22
$CH_3CN/FeCl_3$[b] degassed	26	5	None		None
$EtOH/FeCl_3$	2	33	c	19	56
$CH_3CN/FeBr_3$	Trace?	50	6		70

[a] Yield based on possible 1 mol of benzoic acid produced/mol of 1. [b] 46% of 1 was recovered. [c] A small quantity might have been present in the reaction mixture.

mation about any intermediates between **11** and **4**, the course of the reaction was observed in aqueous ethanol and aqueous acetonitrile at ambient temperatures (Table III). The use of acetonitrile as solvent precludes the reduction leading to **3**. We were particularly hopeful, in light of Depuy's work (see above), that products of ligand transfer oxidation of radical **12** might be obtained. We were therefore most pleased to find significant amounts of 3-halo-1,2,3-triphenylprop-2-en-1-ones (**17**; analytical data and alternate syntheses are given in the



17a, X = Cl
b, X = Br



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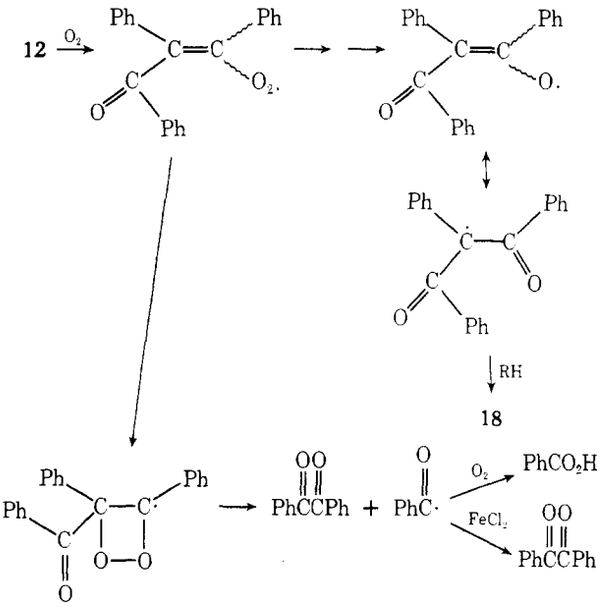
Experimental Section) as products, particularly when ferric bromide was the oxidant.[16] That these reactions represent ligand transfer oxidation and not halogenation due to disproportionation of the ferric halides in solution[17] is shown by several control experiments. Both **3** and 3-hydroxymethyl-1,2-diphenylcyclopropene are stable to ferric halides under these reaction conditions.[18] The fact that the reaction of **1** with ferric bromide in acetonitrile does not give significant amounts of indenone while ferric chloride does can be explained by the fact that ferric bromide is a better ligand transfer agent than ferric chloride.[19]

In addition to the halovinyl ketones **17**, dibenzoylphenylmethane (**18**),[16] benzil, and benzoic acid were isolated from the reactions run at room temperature.[20] All three are the result of radical **12** reacting with molecular oxygen as evidenced by their diminished yield at reflux temperatures[21] and absence when the reaction is run in degassed solvent.[22] The simplest mechanism for the formation of these products is shown in Scheme II (of course, others are possible). Several groups of workers have demonstrated that radicals like **19** cleave readily in the manner shown.[23] The oxidation of acyl radicals to carboxylic acids is a well-known process, and it has been shown that iron(II) may facilitate the coupling of benzoyl radicals to form benzil.[24]

Cationic vs. Radical Cyclization to Form 4. While none of our experiments have unequivocally demonstrated whether the cyclization leading to **4** is a reversible homolytic process or an electrophilic process,[25] at this time we favor the electrophilic mechanism (see Scheme I) as the major pathway at room temperature. The critical experiment which led us to consider these alternatives was the drastic solvent effect on the reaction pathway when ferric chloride was used as the oxidant. That is, in aqueous acetonitrile at room temperature the major product is **4**, while in aqueous ethanol the major products are the isomeric chloro ketones **17a** (see Table III). Recently, Nonhebel has convincingly shown that phenyl radical addition to aromatics is a reversible process.[27b] However, complete equilibration does not take place at temperatures below 100 °C, and the reversibility of the process is reduced when Cu(II) is added to oxidize the intermediate radical. Both of these observations lead us to believe that if a reversible radical addition were taking place in our system substantial amounts of radical **13** should be oxidized in the presence of ferric chloride even in aqueous ethanol. The solvent effect is best rationalized by assuming that the oxidation potential of ferric chloride in acetonitrile is higher than it is in ethanol[28] and thus the oxidation of **12** to **14** takes place only in acetonitrile. The minor amounts of indenone **4** produced in ethanol may be the result of a radical cyclization. Either pathway is possible at elevated temperature.

Scheme II



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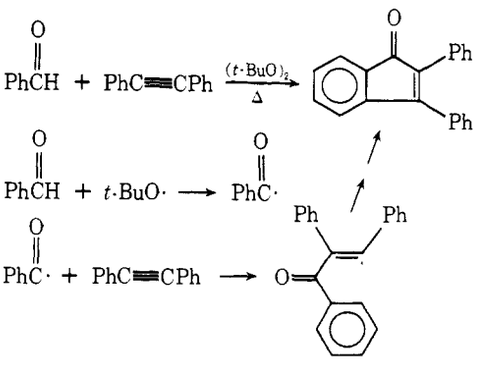
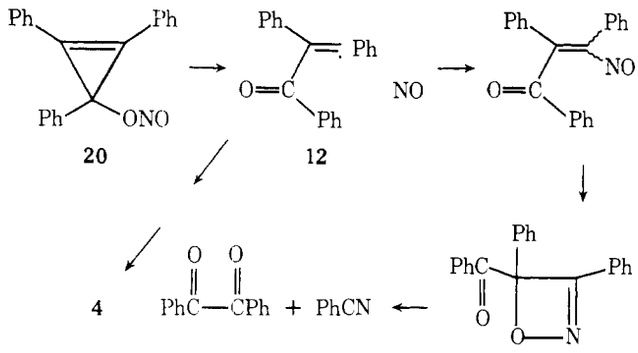
That the radical **12** can cyclize is illustrated by the formation of **4** in 11% yield when benzaldehyde, diphenylacetylene, and *tert*-butyl peroxide are refluxed in bromobenzene (see Scheme III).[29]

Another approach to the investigation of the reactivity of radical **12** would be through thermolysis of 1,2,3-triphenylcyclopropenyl nitrite (**20**). Although Jones and Kobzina synthesized a compound which was either a nitro or nitrite derivative of 1,2-diphenylcyclopropene,[30] work with cyclopropyl nitrites[31] led us to believe that a cyclopropenyl nitrite would not be stable at ordinary temperatures. In order to generate nitrite **20**, we simply mixed 1,2,3-triphenylcyclopropenyl tetrafluoroborate with an excess of potassium nitrite in aqueous acetonitrile at room temperature. The following products were obtained: **4** (<1%), benzil (22%), benzoic acid (10%), 2-phenylisatogen (11%),[4] and benzonitrile (substantial

Scheme III



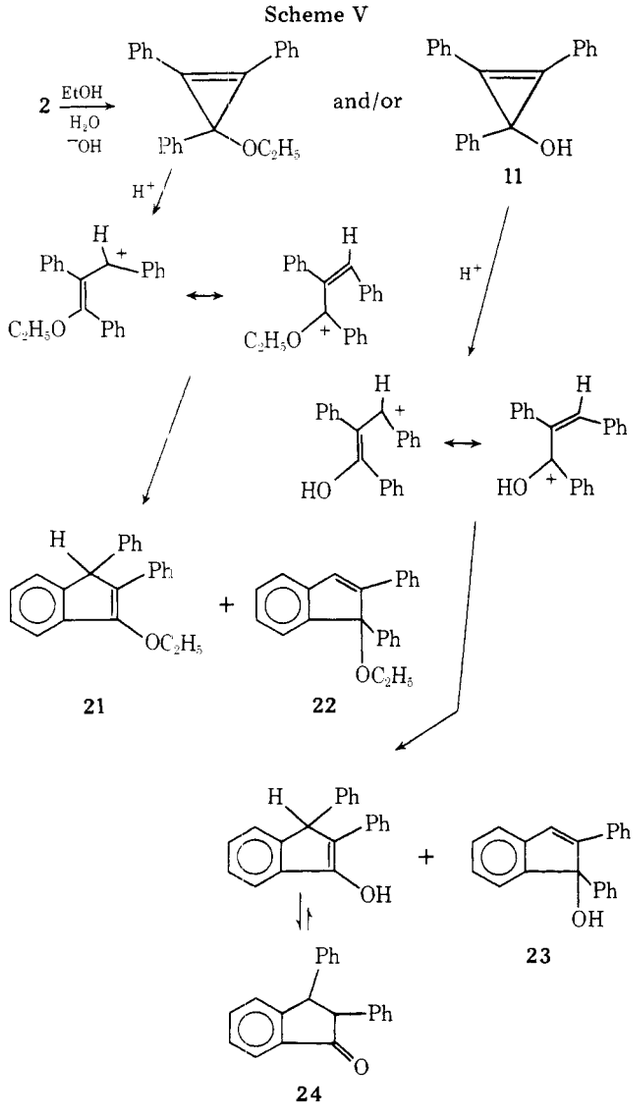
Scheme IV



amounts). Under degassed conditions about the same amount of indenone and benzil were produced, starting with 1,2,3-triphenylcyclopropenylium bromide and sodium nitrite in ether–water. The other products might have been present, but were not looked for.

The most reasonable explanation for formation of **4**, benzil, and benzonitrile is shown in Scheme IV. The initially formed nitrite **20** loses nitric oxide to give **12**. This radical can cyclize to give **4** or it can react with nitric oxide to give a vinylnitroso compound. This can rearrange to give benzil and benzonitrile, a process with ample precedent in the literature.[32] Because capture of the radical **12** by nitric oxide is such a favorable process, these experiments do not say anything about the mechanistic pathway to **4** in our experiments with **1** and iron salts.

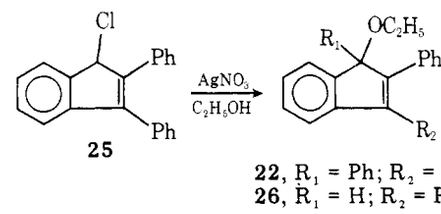
Scheme V



Several other possible mechanisms for indenone formation which we have considered and ruled out are discussed in the next two sections.

Possible Friedel–Crafts Reaction. Formation of 2,3-diphenylindenone might be the result of two successive reactions: Friedel–Crafts cyclization of an intermediate formed from **1** or 3-hydroxy-1,2,3-triphenylcyclopropene (**11**) (see Scheme V) followed by oxidation to **4**. Precedent for the cyclization is the previously cited rearrangement of **3** to 1,2-diphenylindene catalyzed by acetic acid–sulfuric acid.[5b] The reaction is also catalyzed by $[(C_2H_4)PtCl_2]_2$.[33] Thus, we first investigated the reaction of 1,2,3-triphenylprop-2-en-1-one (**16**), the product of ring-opening of **11**,[11] with ferric chloride under the reaction conditions. It did not undergo cyclization; in fact, it was recovered almost quantitatively. Thus, the Friedel–Crafts pathway became doubtful, since it was unlikely that the carbonium ions formed on ring opening of **1** or **11** would retain excess energy from the relief of strain long enough to undergo cyclization before this energy was dissipated to the solvent. However, to have an unequivocal answer, we decided to test for **21–24** as intermediates by ascertaining whether or not they were oxidized to **4** under the reaction conditions.

Compound **21** was available from the reaction of **1** with cuprous bromide (see Experimental Section). Compound **22** was prepared by the solvolysis of 1-chloro-2,3-diphenylindene (**25**)[34] in ethanolic silver nitrate. In fact, **25** gave two products, **22** and **26**; **22** being the minor product of the reaction. Although **23** was known,[35] its synthesis was most easily effected by the solvolysis of **25** in acetone–water–silver nitrate. Again,



the desired compound was the minor product. Compound **24** was synthesized by a method in the literature.[36] The results of treatment of **21–24** with 1 and 2 mol of ferric chloride under the usual reaction conditions are given in Table IV. Although minor amounts of **21–24** or their degradation products with ferric chloride might have been missed in the workup of the reaction of **1** with ferric chloride, none of these compounds was present in significant amount. Since **21–24** are not oxidized to **4** to any large extent, none of them is considered to be an important intermediate in the formation of the indenone.

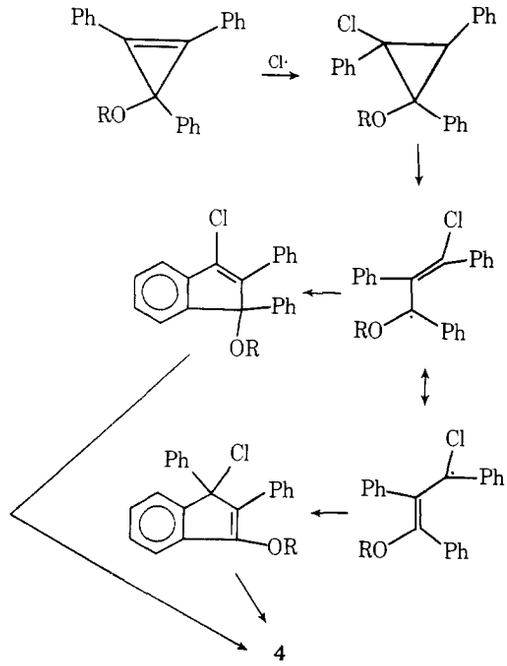
Possible Reaction of Chlorine Radical. Another mechanism which has been ruled out is one in which the ligand on iron is the essential reactant. Such a reaction with a chlorine atom is indicated in Scheme VI.[37] However, we have checked the reaction of **1** with two other iron compounds, ferric nitrate nonahydrate and ferric perchlorate hexahydrate in ethanol under the usual reaction conditions. The nitrate and **1** gives 74% of **4**, while the perchlorate gives 54% of **4** and 20% of **7** or **3**. Although nitrate radicals do sometimes add to olefins in oxidation reactions,[38] we have not found a precedent for this kind of reaction with perchlorate salts.

Experimental Section

All melting points were uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 137 spectrophotometer. Ultraviolet spectra were recorded with a Cary Model 14 spectrophotometer. Nuclear magnetic resonance spectra were taken with a Varian A-60 NMR spectrometer.

Gas chromatography was performed with a Varian 70 Aerograph

Scheme VI



Model 90-P gas chromatograph on a 10-ft, 20% SE-30 on Anakron A (60–80 mesh) column at 160 °C. TLC layers were prepared according to Stahl with silica gel GF. The size of the thick-layer plates (1 mm in thickness) was 20 × 20 cm. Eluants were reagent grade. Microanalyses were performed by Baron Consulting Co., Orange, Conn.

Preparation of 1,2,3-Triphenylcyclopropenylium Tetrachloroferrate (2). In a 150-mL beaker, 0.650 g (2.1 mmol) of 3-ethoxy-1,2,3-triphenylcyclopropene (1)[39] was dissolved in 50 mL of anhydrous ether to which 0.324 g (2.0 mmol) of ferric chloride in 30 mL of anhydrous ether was slowly added with stirring. A yellow powder precipitated, yield 0.870 g (125%), mp 240–245 °C. Recrystallization (CH_3CN) gave fine yellow crystals, mp 251 °C [lit.[40] mp 253–254 °C]. The IR spectrum was identical to that of 1,2,3-triphenylcyclopropenylium bromide.

Anal. Calcd for $C_{21}H_{15}Cl_4Fe$: C, 54.19; H, 3.23; Cl, 30.45; Fe, 12.0. Found: C, 54.37; H, 3.25; Cl, 30.76; Fe, 10.6.

Characterization of 6a and 6b. Compound **6a** is white needles (EtOH in the cold): mp 67–68 °C; IR (KBr) 6.25, 6.7, 9.0, 14.3 μm; UV (EtOH) λ_{max} 260 nm (log ε 4.20); NMR ($CDCl_3$) δ 1.2 (3 H, t, J = 7 Hz, Me), 3.6 (2 H, q of d, J = 7, 3 Hz, CH_2), 5.0 (1 H, br s, >CHO–), 6.2–7.4 ppm (16 H, m, vinylic + Ph).

Anal. Calcd for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 88.14; H, 7.29.

An authentic sample was prepared in a manner completely analogous to that reported for the preparation of 1-methoxy-1,2,3-triphenylprop-2-ene[41] and was identical (IR, mixture mp) to the samples isolated from the reaction of **5** with ethanol.

Compound **6b** is white needles (*i*-PrOH): mp 82.5–83.5 °C; IR (KBr) 6.25, 6.7, 9.15, 14.3 μm; UV (EtOH) λ_{max} 260 nm (log ε 4.21); NMR ($CDCl_3$) δ 1.2 [6 H, d, J = 6 Hz, $(CH_3)_2C$], 3.9 (1 H, m, J = 6 Hz, >CHO–), 5.2 (1 H, br s, CHPh), 6.8–7.6 (16 H, m, vinylic + Ph).

Anal. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.37. Found: C, 87.64; H, 7.32.

An authentic sample was prepared by refluxing for 20 h 0.1 g (0.35 mmol) of (*E*)-1,2,3-triphenylprop-2-en-1-ol[41] in 50 mL of isopropyl alcohol containing 0.010 g of *p*-toluenesulfonic acid. The solution was cooled, poured into water, and extracted with ether which was dried ($MgSO_4$) and removed in vacuo to give a white solid, mp 81.5–83.5 °C. This sample and samples isolated from the reaction of **5** with isopropyl alcohol were identical (IR, mixture mp).

Preparation of Lower Melting 3-Chloro-1,2,3-triphenylprop-2-en-1-one (17a). To phenylmagnesium bromide in 150 mL of ether prepared from 15.7 g (0.1 mol) of bromobenzene and 2.43 g (0.1 g atom) of Mg was added 20 g (0.08 mol) of 3-chloro-2,3-diphenylpropenal[42] dissolved in 300 mL of benzene. After all the benzene had been added, the mixture was refluxed for 2 h, allowed to cool to room temperature, poured into saturated ammonium chloride, and worked up in the usual manner to give a yellow oil. This was crystallized with difficulty from ethyl acetate–petroleum ether to give 20 g (75%) of yellow needles of 3-chloro-1,2,3-triphenylprop-2-en-1-ol (**30**), mp 45–55 °C, mp 93–100 °C after drying in vacuo. An analytical sample (white needles, ether–hexane) gave mp 110–111 °C; IR (KBr) 2.8 (O–H), 9.6, 14.3 μm; UV (EtOH) sh 245 nm (log ε 3.98); NMR ($CDCl_3$) δ 2.2 (1 H, br s, OH), 5.8 (1 H, br s, >CH), 6.9–7.8 ppm (15 H, m, Ph).

Anal. Calcd for $C_{21}H_{17}ClO$: C, 78.62; H, 5.34; Cl, 11.05. Found: C, 78.42; H, 5.28; Cl, 11.43.

Oxidation of 3.20 g (0.01 mol) of **30** by the method of Ratcliffe and Rodehorst[43] gave 2.8 g (88%) of **17a**, mp 98–100 °C. A sample prepared for analysis (EtOH) had mp 99.5–100.5 °C, IR (KBr) 6.0, 6.1, 7.9, 13.0, 14.4 μm; UV (EtOH) λ_{max} 256 nm (log ε 4.33); NMR ($CDCl_3$) δ 6.8–8.1 ppm (m), actually two contiguous multiplets ca. 6.8–7.8 ppm (13 H) and 7.7–8.1 ppm (2 H, ortho H on benzoyl). The IR of this compound was nearly identical to that of higher melting **17b**.

Anal. Calcd for $C_{21}H_{15}ClO$: C, 79.12; H, 4.74; Cl, 11.12. Found: C, 79.11; H, 4.84; Cl, 11.49.

Preparation of Higher Melting 3-Chloro-1,2,3-triphenylprop-2-en-1-one (17a). To 1 g (3.2 mmol) of 1 in 60 mL of acetonitrile was added 1.105 g of $CuCl_2 \cdot 2H_2O$ dissolved in 2.5 mL of water and 5 mL of acetonitrile.[44] The solution was stirred for 1 h, poured into water, and extracted twice with ether which was washed, dried ($MgSO_4$), filtered, and removed under reduced pressure to give an oil. This was chromatographed on alumina. Elution with petroleum ether gave an oil which, upon scratching in ethanol at dry ice temperatures, crystallized. Fractional crystallization (EtOH) gave 0.142 g (14%) of lower melting **17a**, mp 94–97 °C, and 0.050 g (5%) of higher melting **17a**, mp 105–106 °C: IR (KBr) 6.0, 14.4 μm; UV (EtOH) λ_{max} 257 (log ε 3.97), sh 280 nm (log ε 3.72); NMR ($CDCl_3$) δ 7.9–8.3 (1.5 H, m, H ortho on benzoyl), 6.7–7.7 ppm (13.5 H, m, all other phenyl hydrogens); mass spectrum, calcd for $C_{21}H_{15}ClO$: mol wt 318.0811; found: 318.0803. IR and mixture melting point showed higher melting **17a** to be identical to the crystalline chloro ketone obtained from $FeCl_3$ and 1 in CH_3CN–H_2O at room temperature (see Table V). The IR of this compound was very similar to the IR of the lower melting **17b**.

Preparation of Higher Melting 3-Bromo-1,2,3-triphenylprop-2-en-1-one (17b). The 3-bromo-2,3-diphenylpropenal was synthesized by the method of Arnold and Holy[45] in 32% yield: mp 157–161 °C [lit.[45] mp 165 °C]. To phenylmagnesium bromide in ether, prepared from 7.2 g (0.046 mol) of bromobenzene and 1.1 g (0.045 g-atom) of Mg was added 11 g (0.038 mol) of 3-bromo-2,3-diphenylpropenal, mp 161–164 °C, partially dissolved in 100 mL of dry benzene. The cloudy reaction mixture was refluxed for 2 h, allowed to cool to room temperature, and poured into ammonium chloride–water. The water layer was extracted two times with ether which was washed with water, dried ($MgSO_4$), and removed in vacuo to give an oily solid. Recrystallization (benzene–hexane) gave 9.5 g, mp 128–131 °C, and 1.85 g, mp 121–125 °C, yield 11.35 g (81%). An analytical sample (ethyl acetate–hexane) gave mp 133–134 °C: IR (KBr) 2.94, 9.7, 14.4 μm; UV (EtOH) sh 261 (log ε 3.82), 230 nm (log ε 4.27); NMR ($CDCl_3$) δ 2.4 (1 H, br s, OH), 5.7 (1 H, s, >CH), 6.7–7.9 ppm (15 H, m, Ph).

Anal. Calcd for $C_{21}H_{17}BrO$: C, 69.05; H, 4.69. Found: C, 69.35; H, 4.84.

Oxidation of 3.65 g (0.01 mol) of the above alcohol by the method of Ratcliffe and Rodehorst[43] gave 2.6 g (71%) of higher melting **17b**, mp 106–108 °C. A sample prepared for analysis (benzene–hexane) had mp 107–108 °C: IR (KBr) 6.0, 6.1, 7.9, 13.0, 14.4 μm; UV (EtOH) λ_{max} 252 (log ε 4.38) nm; NMR ($CDCl_3$) δ 7.7–7.9 (2 H, m, H ortho on benzoyl), 6.9–7.6 ppm (13 H, m, all other phenyl hydrogens).

Anal. Calcd for $C_{21}H_{15}BrO$: C, 69.43; H, 4.16; Br, 22.00. Found: C, 69.75; H, 4.20; Br, 22.29.

Synthesis of Lower Melting 3-bromo-1,2,3-triphenylprop-2-en-1-one (17b). A mixture of 0.502 g (1.6 mmol) of 1 and 0.284 g (1.6 mmol) of *N*-bromosuccinimide (purified by the method of Dauben and McCoy)[46] in 25 mL of CCl_4 was refluxed for 22 h. After 5 h almost all of the solid had dissolved and the solution was colorless. Almost all of the solvent was removed in vacuo to give a thick oil to which was added 5 mL of anhydrous acetonitrile. After standing in the freezer, 0.413 g (53%) of colorless crystals, of what is probably 1-bromo-3-ethoxy-3-succinimido-1,2,3-triphenylpropene (**27**), mp 167–168.5 °C, was collected. A sample prepared for analysis (benzene–hexane) had mp 184–185 °C: IR (KBr) 5.8, 7.6, 8.6, 13.3, 14.3 μm; UV (CH_3CN) sh 266 nm (log ε 3.69); NMR ($CDCl_3$) δ 1.0 (3 H, t, J =

Table IV. Extent of Oxidation of Possible Intermediates

	21	22	23	24
1 mol of $FeCl_3$				
% indenone	9	None	Trace	6
2 mol of $FeCl_3$				
% indenone	20	None	Trace	9

7 Hz, CH_3), 2.9 (4 H, s, CH_2CH_2), 3.5 (2 H, q, J = 7 Hz, CH_2), 7.1–8.0 ppm (m, 15 H, Ph); mass spectrum, parent peaks m/e 489, 491.

Anal. Calcd for $C_{27}H_{24}BrNO_3$: C, 66.01; H, 4.90; N, 2.86; Br, 16.34. Found: C, 65.75; H, 4.81, N, 2.60; Br, 16.72.

After several months in a stoppered flask, the residue was treated with ether, giving 0.035 g of fluffy solid, mp 197–200 °C. A sample recrystallized for analysis (EtOH) gave white fluffy needles, mp 205–206.5 °C, probably 1,2,3-triphenyl-3-succinimidoprop-2-en-1-one (**28**): IR (KBr) 5.9 (succinimide C=O), 6.05 (PhC=O), 7.3, 8.6, 13.4, 14.3 μm; UV (EtOH) λ_{max} 258 nm (log ε 4.28); NMR ($CDCl_3$) δ 2.5 (br s, 4 H, $-CH_2CH_2-$), 6.7–8.2 ppm (m, 15 H, Ph).

Anal. Calcd for $C_{25}H_{19}NO_3$: C, 78.73; H, 5.02; N, 3.68. Found: C, 78.74; H, 5.09; N, 3.57.

Further treatment of the residue by refluxing in 6:1 acetonitrile–water for 30 min left an oil from which was isolated, by treatment with ether, 0.013 g of **28**. Thick-layer chromatography gave 0.120 g of a mixture of the higher and lower melting isomers of **17b**, NMR analysis showing the higher melting isomer predominating 2:1. Also, about 0.010 g of dibenzoylphenylmethane (**18**) was isolated from the thick-layer plate.

Hydrolysis of 0.186 g of **27** was effected by refluxing in 6 mL of water/acetonitrile (1:5) for 30 min. The mixture was poured into a beaker and the solvent allowed to evaporate. The white powder was thick-layer chromatographed to give 0.150 g (100%) of lower melting **17b**, mp 98–100 °C. A sample prepared for analysis (EtOH) had mp 101.5–102 °C: IR (KBr) 6.0, 14.4 μm; UV (EtOH) λ_{max} 256 nm (log ε 4.37); NMR ($CDCl_3$) δ 7.9–8.3 (2 H, m, H ortho on PhC=O) 6.9–7.7 ppm (13 H, m, all other Ph); mass spectrum, parent peaks m/e 362, 364.

Anal. Calcd for $C_{21}H_{15}BrO$: C, 69.42; H, 4.13; Br, 22.03. Found: C, 69.30; H, 4.29; Br, 21.69.

Succinimide was also obtained from the TLC: 0.0260 g (64%), mp 123–125 °C [lit.[47] mp 125–126 °C]; IR identical to Sadtler Infrared No. 482.[48]

Isolation of Chlorovinyl Ketones 17a. Reactions in which the isomeric **17a** were found used 0.150 g of **1** and an equivalent of ferric chloride in acetonitrile–water at room temperature for 0.5 h. The workup by thick-layer chromatography gave a chlorovinyl ketone band (average yield, 0.015 g) practically contiguous with the indenone band even after several elutions; fractions from several runs were mixed. After standing in benzene–hexane for several months in the freezer, the crude chlorovinyl ketone mixture crystallized and one pure isomer, the higher melting isomer, could be obtained. It was identical to the higher melting isomer obtained from chlorination of **1** with $CuCl_2$ in acetonitrile. The presence of the other isomer could be detected by NMR in the region for the ortho hydrogens of the benzoyl group.

Preparation of 3-Ethoxy-1,2-diphenylindene (21). A mixture of 0.118 g (0.375 mmol) of **1**, 0.056 g (0.375 mmol) of CuBr, and 15 mL of absolute EtOH was refluxed for 12 h, yielding a very pale green clear solution with a trace of cream-colored solid. Thick-layer chromatography gave five fractions (plus a non-benzene-soluble component); the major fraction was a white solid (0.100 g, 85%): white feathers (EtOH); mp 130.5–132 °C; IR (KBr) 6.25, 7.45, 9.35, 9.8 μm; UV (EtOH) λ_{max} 313 (log ε 4.35), sh 302 (log ε 4.34), 242 (log ε 4.10), 235 nm (log ε 4.15); NMR ($CDCl_3$) δ 1.4 (3 H, t, J = 7 Hz, Me), 4.2 (2 H, q, J = 7 Hz, CH_2), 4.9 (1 H, s, >CH–), 7.1–7.8 ppm (14 H, m, Ph).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.68; H, 6.65.

Further evidence for the structure of **21** is that refluxing in EtOH–$AgNO_3$ for 20 h gives 39% 2,3-diphenylindanone[4] (hydrolysis product) as well as 58% recovered starting material.

Preparation of 1-Ethoxy-2,3-diphenylindene (26) and 1-Ethoxy-1,2-diphenylindene (22). To a stirred solution of 0.150 g (0.5 mmol) of 1-chloro-2,3-diphenylindene[34] in 25 mL of EtOH was added 0.255 g (0.5 mmol) of $AgNO_3$. All the $AgNO_3$ finally dissolved after heating for 15 min on a steam bath, and a whitish precipitate formed, which was collected and not analyzed. Evaporation of the filtrate in vacuo left an orange-green oil which was thick-layer chromatographed. Two distinct fractions were collected, the first exhibiting weak blue fluorescing and the second pronounced blue fluorescing under short-wavelength UV.

Fraction 1 (0.020 g 13%) was identified as **22:** white needles (EtOH–H_2O); mp 93–96 °C; IR (KBr) 9.0, 9.25, 9.3, 13.0, 13.35, 14.25 μm; UV (EtOH) λ_{max} 314 (log ε 4.31), 327 (log ε 4.32), 342 (log ε 4.10), sh 243 (log ε 4.38), 251 mm (log ε 4.35); NMR ($CDCl_3$) δ 1.1 (3 H, t, J = 7 Hz, Me), 3.2 (2 H, m, CH_2), 7.25 ppm (15 H, m, vinylic + Ph).

Fraction 2 (0.052 g, 33%) was identified as **26:** white tiny needles (EtOH–H_2O); mp 101–102.5 °C; IR (KBr) 8.95, 9.05, 9.25, 12.85, 13.1, 13.3, 14.1, 14.3 μm; UV (EtOH) λ_{max} 315 (log ε 4.11), 242 (log ε 4.45) nm; NMR ($CDCl_3$) δ 1.0 (3 H, t, J = 7 Hz, Me), 3.3 (2 H, q, J = 7 Hz, CH_2), 5.7 (1 H, s, –CHO–), 7.4 ppm (14 H, m, Ph).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found for **22:** C, 88.65; H, 6.69. Found for **26:** C, 88.55; H, 6.60.

Preparation of 1-Hydroxy-1,2-diphenylindene (23). To a solution of 0.151 g (0.5 mmol) of 1-chloro-2,3-diphenylindene[34] in 6 mL of acetone was added 0.234 g of $AgNO_3$ dissolved in 3.5 mL of water. The cloudy mixture was refluxed on a steam bath for 2 h, then poured into water, and extracted three times with ether which was washed, dried ($MgSO_4$), and removed in vacuo to give an orange oil which was thick-layer chromatographed. Isolation of the first fraction gave 0.026 g (18%) of **23,** mp 132–135 °C. Recrystallization (benzene–hexane) gave mp 135–137 °C (lit.[35] mp 138.7–139.5 °C), NMR ($CDCl_3$) δ 2.1 (1 H, s, OH), 7.0–7.7 ppm (15 H, m, vinylic + Ph). The second fraction gave 0.075 g (53%) of 1-hydroxy-2,3-diphenylindene, mp 114–117 °C, after recrystallization (benzene–hexane). If heated very slowly this material softens at 118 °C and melts 134.5–135 °C [lit.[34] mp 132–135 °C). The infrared spectrum of this compound was identical to the infrared of the product of reduction of 2,3-diphenylindenone with sodium borohydride.

Reaction of 29 with Potassium Nitrite. A 500-mL flask was charged with 2.024 g (5.7 mmol) of 1,2,3-triphenylcyclopropenyl tetrafluoroborate–hydroxyfluoroborate[11] (**29**) and 115 mL of dry CH_3CN. The mixture was magnetically stirred at room temperature for 10 min to dissolve the salt. A solution of 5.21 g (57 mmol) of KNO_2 in 7.5 mL of distilled water was then added in one portion with good stirring followed by an additional 90 mL of CH_3CN. The bright orange mixture was stirred for 3.5 h. Dry benzene (45 mL) was then added, the mixture was filtered, and the solvent was evaporated in vacuo. The residue had a strong odor of bitter almonds. Gas chromatography of an ethereal wash of the residue confirmed the presence of benzonitrile as indicated by an identical retention time with an authentic sample. A collected sample had mass spectrum, calcd for C_7H_5N: mol wt 103.0422; found: 103.0420; IR identical to that of an authentic sample except for a weak extraneous peak at 1724 cm^{-1}.

In a separate experiment, the material after evaporation of the benzene was partitioned between ether and water, and the aqueous layer (pH 6) was extracted with five 75-mL portions of ether. The organic extracts were washed with five 25-mL portions of fresh ether. The alkaline solution was saturated with NaCl, acidified to pH 2 with 6 N HCl, and extracted with ether. After drying ($MgSO_4$), the solvent was removed in vacuo to give 68 mg (10%) of benzoic acid, mp 117–119 °C, identical (IR, mixture mp) with an authentic sample.

The ethereal solution of nonacidic material was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residual red oil was chromatographed on 200 g of Woelm silica gel. Five fractions were collected. Fraction one was eluted with 250 mL of hexane and consisted of 2 mg of an unidentified yellow solid. Fraction two, a red-orange band, eluted with 250 mL of 1% ether–hexane and 375 mL of 3% ether–hexane, contained in addition to benzonitrile 260 mg (22%) of benzil, mp 93–95 °C (mixture mp 93.5–94 °C) and <1% 2,3-diphenylindenone (IR).

Fraction three, eluted with 250 mL of 3% ether–hexane and 250 mL of 5% ether–hexane, gave only small amounts of intractable oils after preparative thick-layer chromatography.

Fraction four, a red-orange band, was eluted with 350 mL of 5% ether–hexane. The red solid, purified by preparative layer chromatography and recrystallization (ether), was 2-phenylisatogen (70 mg, 11%), mp 189–191 °C [lit.[49] mp 185–186 °C]; mass spectrum, calcd for $C_{14}H_{19}NO_2$: mol wt 223.0634. Found: 223.0635; IR (nujol) identical to lit.[48]

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 75.37; H, 4.08; N, 6.28. Found: C, 75.02; H, 4.38; N, 6.25.

Fraction five was eluted with 600 mL of ether. TLC showed the presence of at least four compounds. Preparative thick-layer chromatography produced only intractable glasses.

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Registry No.—**1,** 13668-0306; **2,** 64163-62-8; **3,** 16510-49-9; **4,** 1801-42-9; **15,** 4919-51-1; **6a,** 64163-17-3; **6b,** 64163-18-4; *cis*-**16,** 7512-67-6; *trans*-**16,** 7474-65-9; *cis*-**17a,** 64163-19-5; *trans*-**17a,** 64163-20-8; *cis*-**17b,** 64163-21-9; *trans*-**17b,** 64163-22-0; **18,** 4888-39-5; **21,** 27331-18-6; **22,** 64163-23-1; **23,** 64163-24-2; **24,** 7474-64-8; **26,** 64163-25-3; **27,** 64163-26-4; **28,** 64163-27-5; **29,** 741-16-2; **30,** 38395-

70-9; ferric chloride, 7705-08-0; EtOH, 64-17-5; *i*-PrOH, 67-63-0; (*E*)-1,2,3-triphenylprop-2-en-1-ol, 57015-16-4; phenyl bromide, 108-86-1; 3-chloro-2,3-diphenylpropenal, 14063-81-1; 3-bromo-2,3-diphenylpropenal, 36998-45-5; *N*-bromosuccinimide, 128-08-5; 1-chloro-2,3-diphenylindene, 4023-85-2; 1-hydroxy-2,3-diphenylindene, 53347-50-5; benzil, 134-81-6; 2-phenylisatogen, 1969-74-0; MeOH, 67-56-1; *t*-BuOH, 75-65-0; $FeBr_3$, 10031-26-2; 3-bromo-2,3-diphenylpropanol, 64163-28-6.

Supplementary Material Available: Table V entitled "Reactions of 1 and 2 and Control Experiments" (7 pages). Ordering information is given on any current masthead page.

References and Notes

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