Fragmentation of Some Trityl Compounds by Means of Hydride Transfer. A Reinvestigation of an Unusual Reaction Reported by Gomberg[1]

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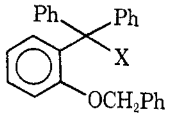
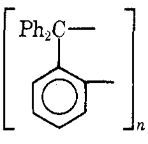
The thermal decomposition of trityl chloride **1a**, previously studied by Gomberg and Nishida, has now been reinterpreted with the aid of new experimental data. This reaction does not yield 1,1-diphenylbenzocyclopropene (**3a**) or products derived therefrom. At 70° in dry benzene-d_6, **1a** rearranges into an isomer **9** *via* a mechanism involving hydride transfer. The rearrangement is catalyzed by HCl, and it can be prevented by the addition of 2,6-lutidine. By-products of the rearrangement are benzaldehyde, phenol **7**, and acetal **10**; their formation involves adventitious moisture. In dry benzene-d_6 at room temperature, alcohol **1b** can be quantitatively converted into benzaldehyde and **7** by treatment with trifluoroacetic acid. The decompositions of **1a** and **1b** are shown to be similar mechanistically.

In 1923 Gomberg and Nishida[2] reported a remarkable reaction of the trityl chloride **1a**. Thermal decomposition of this substance was said to give benzaldehyde, HCl, and a "very interesting hydrocarbon..., unsaturated to the extent of two hydrogen atoms," which was capable of forming **2** by "instant polymerization."[2] The monomeric hydrocarbon was not actually isolated, and its structure received no further discussion. However, from these data[2] and more recent facts as well, it seemed to us that the monomer might have been either 1,1-diphenylbenzocyclopropene[3] (**3a**) or an isomeric diradical species **4a**. In agreement with this hypothesis, benzocyclopropenes containing radical-stabilizing substituents at C-1 (*e.g.*, **3b**) were known to experience facile thermal homolysis,[4] and the resulting diradicals (*e.g.*, **4b**) evidently could polymerize when other reaction paths were not favored.[4] Moreover, the formation of **3a** in a concerted manner (**5**, arrows) was recognizable as a [2 + 2 + 2] "cycloaddition" process, allowed by orbital symmetry.[5] Nevertheless, the proposed reaction[2] obviously lacked analogy, and an approximate thermochemical calculation suggested that it would require an activation energy, irrespective of mechanism, amounting to at least 46 kcal/mol (if **3a** were indeed a product).[6] Thus, it seemed that the process could not have occurred at the rates required by the existing data.[9]



1a, X = Cl
b, X = OH



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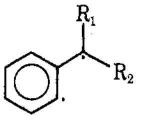
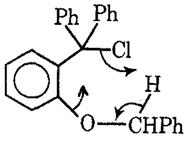
3a, $R_1 = R_2 =$ Ph
b, $R_1 =$ CN; $R_2 =$ Me



4a, $R_1 = R_2 =$ Ph
b, $R_1 =$ CN; $R_2 =$ Me



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The present paper reinterprets the unusual decomposition behavior of **1a** from the standpoint of new experimental information. An auxiliary investigation of a related reaction (the acid-catalyzed decomposition of alcohol **1b**) is also described herein.

Results and Discussion

Decomposition of Chloride 1a.—The chloride was prepared from diol **6** by a simple two-step sequence

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[1] Presented in part at the Combined Southeast-Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 2, 1970.

[2] M. Gomberg and D. Nishida, *J. Amer. Chem. Soc.*, **45**, 190 (1923).

[3] The first benzocyclopropene to be generally regarded as authentic was reported by R. Anet and F. A. L. Anet, *ibid.*, **86**, 525 (1964).

[4] (a) G. L. Closs, *Advan. Alicycl. Chem.*, **1**, 69 (1966); (b) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967).

[5] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 101–107.

[6] The overall process can be regarded as the sum of the following steps.

$$\mathbf{1a} \xrightarrow{\Delta H_1} (\dot{C}_6H_4)Ph_2CCl + PhCH_2O\cdot$$

$$PhCH_2O\cdot \xrightarrow{\Delta H_2} PhCHO + H\cdot$$

$$(\dot{C}_6H_4)Ph_2CCl \xrightarrow{\Delta H_3} \mathbf{4a} + Cl\cdot$$

$$H\cdot + Cl\cdot \xrightarrow{\Delta H_4} HCl$$

$$\mathbf{4a} \xrightarrow{\Delta H_5} \mathbf{3a}$$

A value of 102 kcal/mol is assigned to ΔH_1, since ΔH_1 should be closely approximated by *D* (Ph–OR) (where R = alkyl), and recent ΔH_{f° data[7] indicate that *D* (Ph–OMe) ≅ *D* (Ph–OEt) = 102 ± 1 kcal/mol. Literature values for ΔH_2 and ΔH_4 are 20 [estimated by P. Gray, P. Rathbone, and A. Williams, *J. Chem. Soc.*, 3932 (1960)] and −103 kcal/mol [S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965)], respectively. For ΔH_3, we use 48 kcal/mol, the reported value for *D* (Ph_3C–Cl).[8] To estimate ΔH_5, we first make the reasonable assumption that *D* (Ph_3C–Me) − *D* (Ph_3C–Cl) = *D* (*tert*-Bu-Me) − *D* (*tert*-Bu–Cl). From ΔH_{f° data,[7a] *D* (*tert*-Bu–Me) = 82 and *D* (*tert*-Bu–Cl) = 80 kcal/mol; hence, *D* (Ph_3C–Me) − 48 = 82 − 80, and *D* (Ph_3C–Me) = 50 kcal/mol. We next introduce ΔH_6 (**3b** → **4b**) and assume that $-\Delta H_5 - \Delta H_6 = D\ (Ph_3C\text{–}Me) - D\ [Ph(CN)(Me)C\text{–}Me]$. From work reported by Closs,[4a] ΔH_6 is "slightly lower" than 25 kcal/mol, and *D* [Ph(CN)-(Me)C–Me] has been assigned a value (perhaps rather questionable) of 54 kcal/mol [M. Hunt, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 5074 (1965)]. Therefore, $-\Delta H_5 - 25 = 50 - 54$; $\Delta H_5 = -21$ kcal/mol. Summing, we obtain ΔH (**1a** → HCl + PhCHO + **3a**) = $\Sigma\Delta H_{1-5}$ = 102 + 20 + 48 − 103 − 21 = 46 kcal/mol.

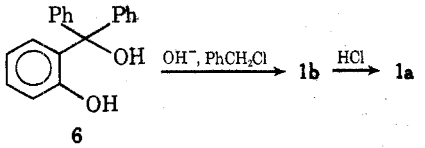
[7] (a) S. W. Benson and R. Shaw, *Advan. Chem. Ser.*, **75**, 288 (1968); D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969); S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *ibid.*, **69**, 279 (1969); (b) D. H. Fine and J. B. Westmore, *Chem. Commun.*, 273 (1969).

[8] A. H. Sehon and M. Szwarc, *Annu. Rev. Phys. Chem.*, **8**, 439 (1957).

[9] From yield data reported by Gomberg and Nishida,[2] half-lives can be calculated for their proposed decomposition of **1a**. Typical values obtained in this way (assuming first-order kinetics) are 39 hr (25°, xylene solution), 14 hr (100–120°, xylene solution), and 1.6 hr (140–150°, no solvent). In contrast, half-lives of *ca.* 10^{17}–10^7 hr are expected at 25–150° for a first-order reaction having an activation energy of 46 kcal/mol and a "normal" frequency factor of 10^{13} sec^{-1}. Ridiculously high frequency factors would have to be assumed to obtain agreement with experiment, and the experimental activation energy should certainly be higher than the overall ΔH for the reaction under discussion.

(Scheme I), using procedures similar to those already described.[2] Despite careful attempts at purification, our samples of **1a** contained 3–6 mol % of alcohol **1b**. However, a comparison of melting points and analytical data indicated that these samples were at least as pure as the product obtained by the earlier workers.[2]

SCHEME I



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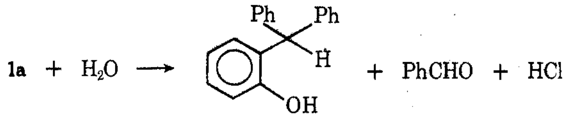
Gomberg and Nishida[2] studied the decomposition of neat **1a** at temperatures ranging from 60 to 130°. They also carried out decompositions of **1a** in xylene at 25–120°. Yields of HCl were determined in these experiments, but no organic products were isolated or identified. However, Gomberg and Nishida noted that the chloride acquired the odor of benzaldehyde on standing, and from a decomposition of the neat material at 140–150° they were able to isolate a considerable amount (73%) of benzaldehyde and a material thought to be **2** ($n = 4$), as well. With the expectation that decompositions in dilute solution would be much cleaner than those performed otherwise, we elected to begin our investigation of **1a** by observing its stability in benzene-d_6. This solvent was used rather than xylene[2] in order to permit direct monitoring of reactions by nmr spectrometry.

In the initial experiment, a solution of **1a** in dry benzene-d_6 was allowed to stand at room temperature under nitrogen. Slow formation of **1b** occurred despite the precautions taken to exclude moisture. After a few days, the solution also contained small amounts of benzaldehyde and a material later shown to be **7**. When the reaction was brought to completion by heating at 70°, quantitative yields of benzaldehyde and **7** were obtained. The adventitious incursion of 1 mol of water is required by this result, and the overall reaction therefore has the following stoichiometry.



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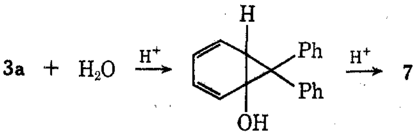
A mechanism involving acid-catalyzed hydration of benzocyclopropene **3a**, followed by an acid-catalyzed reorganization of the hydrate (Scheme II), was considered as a possible route to **7**. The hydration step did not seem entirely unreasonable, since iodine (an electrophilic reagent) had been reported to add to benzocyclopropene (unsubstituted) in a similar manner.[10] However, other mechanistic considerations suggested that the hydration of **3a** might well have given tritanol, a product which was not observed. Moreover, the absence of a cycloheptadienone also appeared to be significant, since such a product could have easily been formed from **8** *via* an alternative mode of cleavage.[10]

SCHEME II



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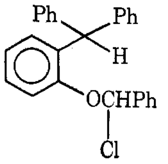
Further decomposition experiments provided definitive information about the detailed course and mechanism of the reaction. These runs were carried out in benzene-d_6 at 70° with no preliminary period of standing at room temperature. The extent of involvement of moisture was greatly reduced by this procedure, and in a typical case the products obtained (mol/mol of starting material) were the rearranged chloride **9** (0.85), acetal **10** (0.04), phenol **7** (0.08), and benzaldehyde (0.12). Compounds **9** and **10** were not actually isolated, but their presence was revealed by a variety of observations. Resonances due to the aliphatic protons of **9** and **10** were easily detected in the nmr spectra of the product mixtures, and the addition of pure **7** caused spectral changes which were consistent with the occurrence of an anticipated reaction:[11] **7** + **9** → **10** + HCl. Since the reaction involving moisture had already been shown to give equivalent amounts of benzaldehyde and **7**, the observed stoichiometry (**10** + **7** = benzaldehyde) was in accord with expectations. Slow hydrolysis of a product mixture with water-saturated benzene-d_6 indicated the presence of two species hydrolyzing at different rates, and treatment of other product mixtures with an excess of water containing 20% ^{18}O caused rapid and quantitative conversion of **9** and **10** into benzaldehyde and **7**. Mass spectral analysis showed that the **7** contained no ^{18}O (within the limits of experimental error), whereas the benzaldehyde contained 100 ± 5% of the theoretical maximum amount of the label. These results conclusively establish the presence of **9** and **10**, and they also rule out the mechanism of Scheme II, since that mechanism requires incorporation of ^{18}O into **7**.



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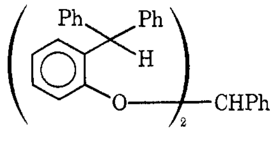

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The rearrangement of **1a** into **9** seemed to be the crucial decomposition step, and its mechanism was of obvious interest. Considering first the possibility of a rearrangement mechanism involving radicals, we note that *D* (C–Cl) in trityl chloride has been reported to be only 48 kcal/mol.[8] In the case of compound **1a**, *D* (C–Cl) should be lower by 1–3 kcal/mol.[12] Even so, the rate of the C–Cl homolysis of **1a** is undoubtedly very slow at 70°, and for this reason a *nonchain* radical

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(10) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965).

(11) H. Meerwein in "Methoden der Organischen Chemie (Houben-Weyl)," E. Müller, Ed., Vol. VI, part 3, Georg Thieme Verlag, Stuttgart, 1965, pp 237–239, and references cited therein.

(12) This range of values was estimated from equilibrium data for the homolytic dissociation of *o*-alkoxytrityl dimers and *o*-alkoxytrityl iodides. For the data used, see (a) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience, New York, N. Y., 1956, p 12; (b) S. T. Bowden, *J. Chem. Soc.*, 4235 (1957); (c) S. T. Bowden and D. T. Zalichi, *ibid.*, 4240 (1957).

rearrangement process seems extremely unlikely.[13] However, radical chain mechanisms initiated by C–Cl homolysis would appear to merit further consideration. Scheme III shows the propagation steps for two possible mechanisms of this type.

SCHEME III

Mechanism A

$$\mathrm{Ph_2\dot{C}(C_6H_4)OCH_2Ph \longrightarrow Ph_2CH(C_6H_4)O\dot{C}HPh}$$

$$\underset{\mathbf{11}}{\mathrm{Ph_2CH(C_6H_4)O\dot{C}HPh}} + \mathbf{1a} \longrightarrow \mathbf{9} + \mathrm{Ph_2\dot{C}(C_6H_4)OCH_2Ph}$$

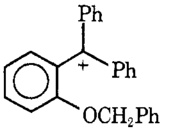
Mechanism B

$$\mathrm{Ph_2CCl(C_6H_4)O\dot{C}HPh \longrightarrow Ph_2\dot{C}(C_6H_4)OCHClPh}$$

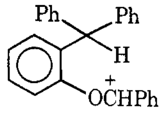
$$\mathrm{Ph_2\dot{C}(C_6H_4)OCHClPh} + \mathbf{1a} \longrightarrow \mathbf{9} + \mathrm{Ph_2CCl(C_6H_4)O\dot{C}HPh}$$

The resonance-stabilized radicals of Scheme III should resemble the polystyryl radical in their relative reactivity toward various substrates. Reactivity data for polystyryl radical are available in the form of chain transfer constants, which indicate that *p*-benzoquinone should be an extremely effective inhibitor for both mechanisms of Scheme III.[14] Experimental tests showed that *p*-benzoquinone did not significantly retard the rate of rearrangement of **1a**; thus we conclude that the rearrangement is not a homolytic process.

An alternative mechanistic possibility is an ionic path which, in its simplest variation, would involve hydride transfer to a carbonium ion intermediate. This hypothesis appears much more reasonable. In benzene solution, trityl chloride ionizes to a limited extent,[15] and the process is strongly catalyzed by potential proton donors.[15,16] Compound **1a** should behave similarly and, indeed, further experiments showed that its rearrangement was significantly accelerated by dry HCl and completely inhibited by 2,6-lutidine. These observations constitute very strong evidence for a heterolytic path, and they are considered further below. The carbonium ion[17] **12** derived from **1a** could be converted into **13** by an intramolecular 1,5-hydride shift.[18] Capture of **13** by chloride ion would give the rearranged chloride **9**, while reaction of **13** with moisture would give a protonated hemiacetal which should undergo rapid conversion into benzaldehyde and **7**. Reaction of **13** with **7** would give acetal **10**. Nucleophilic displacements on **9** could also give benzaldehyde, **7**, and **10**; such reactions were, in fact, demonstrated experimentally (see above).



12



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Mechanisms involving intermolecular hydride transfer can also be written for the decomposition of **1a**, but an intramolecular shift appears more likely. In the absence of overriding steric constraints, the intramolecular path seems highly favored for 1,5-hydride transfers to carbonium ions, in general, since this route is followed exclusively even in completely flexible acyclic systems.[19] Decomposition of **1a** *via* an intermolecular mechanism could have led to the buildup of metastable intermediates, but such products were never detected. It is true, of course, that the possible transition states for intermolecular hydride transfer should be stabilized by electron donation from two oxygen-containing substituents, whereas intramolecular transfer would be assisted by conjugative interaction involving only a single atom of oxygen. However, oxygen conjugation might be particularly helpful in the intramolecular case, since it would tend to impart quasi-aromatic character to the six-atom cyclic transition state required for intramolecular rearrangement of **12**. The apparent stability of the para isomer[20] of **1a** also argues against a mechanism involving intermolecular hydride transfer. Finally, it should be noted that intramolecular 1,5-hydride abstraction by a triaryl carbonium ion has been reported previously in at least one instance,[21] although the system studied was, admittedly, very favorably disposed toward an intramolecular path because of its spatial arrangement. These arguments are highly suggestive, but they cannot be regarded as conclusive. They do not rigorously exclude, for example, a mechanism for decomposition of **1a** involving anchimeric assistance by neighboring chlorine in an intermolecular hydride-transfer step.

The hindered base, 2,6-lutidine, undoubtedly inhibits the decomposition by scavenging adventitious HCl. As was mentioned previously, all of our samples of **1a** contained small amounts of alcohol **1b**. In the absence of 2,6-lutidine, the nmr spectra of these

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[13] A half-life of 9 × 10^{11} hr is expected at 70° for a first-order reaction having a frequency factor of 10^{13} $\mathrm{sec^{-1}}$ and an activation energy of 45 kcal/mol. Our experimental half-life for decomposition of **1a** at 70° was never greater than 50 hr (see later discussion).

[14] At 70° *p*-benzoquinone is *ca.* 200 times as reactive as $\mathrm{CBr_4}$ toward polystyryl radical. *D* (C–Br) in $\mathrm{CBr_4}$ is *ca.* 49 ± 3 kcal/mol [A. H. Sehon and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **209**, 110 (1951); T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, England, 1958, p 205, and references cited therein], a value comparable to *D* (C–Cl) in compound **1a** (see above). However, polar effects might tend to cause radical **11** of mechanism A to be less reactive toward the C–Cl bond of **1a** than toward a C–Br bond of $\mathrm{CBr_4}$ (*cf.* C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 379–380), since **11** should be even more nucleophilic than the polystyryl radical, whose nucleophilicity is well established [Y. L. Spirin, *Russ. Chem. Rev.*, **38**, 529 (1969), and references cited therein]. In addition, the reactivity of **1a** toward halogen abstraction should be reduced, relative to that of $\mathrm{CBr_4}$, by steric factors and by a statistical factor of 4. Furthermore, a consideration of polar and steric effects suggests that **11** is likely to be more reactive than polystyryl radical toward *p*-benzoquinone, due to a predominating influence of polar factors. We therefore conclude that *p*-benzoquinone should be more than 800 times as reactive as the C–Cl bond of **1a**, toward radical **11** at 70°. Toward polystyryl radical at 68°, the relative reactivities of *p*-benzoquinone and benzyl methyl ether are *ca.* 4 × 10^2 and 6 × 10^{-4}, respectively, and toward this radical at 60°, *p*-benzoquinone is *ca.* 2 × 10^6 times as reactive as *p*-benzyloxyphenol-*O*-*d*. The quinone should therefore compete very effectively with **1a** in the intermolecular propagation step of mechanism B, and this competition should also be aided by polar and (probably) steric factors as well. These conclusions are based on chain-transfer constants tabulated by L. J. Young, G. Brandrup, and J. Brandrup in "Polymer Handbook," J. Brandrup and E. H. Immergut, Ed., Interscience, New York, N. Y., 1967, pp II 108–110 and II 113.

[15] C. G. Swain and M. M. Kreevoy, *J. Amer. Chem. Soc.*, **77**, 1122 (1955); E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai, and Y. Pocker, *J. Chem. Soc.*, 1265 (1957), and accompanying papers.

[16] (a) C. G. Swain and E. E. Pegues, *J. Amer. Chem. Soc.*, **80**, 812 (1958); (b) A. G. Evans, I. H. McEwan, and J. H. Thomas, *J. Chem. Soc.*, 4644 (1957).

[17] Throughout most of the discussion, the term "ion" is used for simplicity, although it is recognized that ions exist primarily as ion pairs or higher aggregates in benzene solution.

[18] For a recent review of intramolecular hydride transfers, see J. L. Fry and G. J. Karabatsos in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 14.

[19] R. K. Hill and R. M. Carlson, *J. Amer. Chem. Soc.*, **87**, 2772 (1965).

[20] M. Gomberg and C. C. Buchler, *ibid.*, **45**, 207 (1923).

[21] R. L. Letsinger and P. T. Lansbury, *ibid.*, **81**, 935 (1959).

samples failed to show the alcoholic proton peak. However, this peak appeared in its expected position when the lutidine was present. These results are consistent with the occurrence of a rapid exchange which is catalyzed by acid and suppressed by the hindered base. The presence of varying amounts of HCl thus accounts for the variability of the decomposition rates obtained with different samples of **1a** in the absence of any additives (see Experimental Section).

Ion **12** is presumably formed from **1a** in benzene-d_6, even in the absence of catalysts,[15] and the equilibrium constant for its quaternization reaction with 2,6-lutidine might prove to be rather large.[22] However, quaternization could not have caused a significant reduction in the decomposition rate, since it did not significantly reduce the concentration of **12**. This conclusion follows from the realization that **12** also equilibrates with un-ionized **1a**, whose concentration was not noticeably decreased by the base.[22]

Although **1a** failed to rearrange in the presence of 2,6-lutidine, it did undergo slow conversion to **1b**. This result was not expected. By analogy with conclusions reached by previous workers[15,16a] concerning nucleophilic displacements on trityl chloride, hydrolysis of **1a** should occur *via* ion **12** in benzene containing very small amounts of water. Furthermore, the work of Swain, *et al.*,[16a,22] on trityl chloride methanolysis suggests that 2,6-lutidine would not increase the hydrolysis rate of **1a** under our experimental conditions. If hydride transfer can indeed occur *via* **12**, it is therefore difficult to understand why **1a** did not rearrange to some extent when 2,6-lutidine was present. A possible explanation is that the spontaneous ionization of **1a** gives an intimate ion pair which is too stable to undergo hydride transfer, whereas HCl-catalyzed ionization produces (to some small degree) a more open ion pair (or, indeed, free **12**) whose reactivity is greater. However, several other rationalizations are also tenable at present, and no firm conclusions can be drawn in the absence of detailed kinetic studies.

Summarizing the results presented thus far, we conclude that the decomposition of **1a** in benzene-d_6 does not give **3a** and does not involve free radicals. It proceeds instead *via* an ionic path which involves hydride transfer and is extremely susceptible to acid catalysis. The exact nature of the hydride-transfer process remains an open question, and no evidence is available now with regard to the possible merger of discrete reaction steps into one or more concerted interactions.

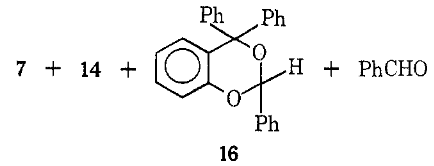
Several attempts were made to reproduce the results obtained by Gomberg and Nishida[2] in their decomposition of neat **1a** at 140–150° (see above). These experiments afforded complex product mixtures containing none of the starting chloride. Diphenylmethane and **7** were shown to be present, but the yields of benzaldehyde were very low (<4%), and no evidence could be obtained for the formation of **3a** or polymers derived therefrom. A similar reaction run at 180° gave 5–10% of benzaldehyde, as well as a number of impure solid fractions with molecular weights ranging from 869 to 2050. One of these fractions had properties (color, melting point, and molecular weight) which were similar to those reported[2] for **2** ($n = 4$). However, all of the fractions exhibited strong infrared absorption in the OH stretching region, and they were shown to contain 7–9% oxygen by elemental analysis. The reason for the discrepancy between these results and those reported by Gomberg and Nishida[2] is not apparent at present, but, in any event, it is clear that **1a** does not undergo high-temperature decomposition in the manner previously proposed.[2]

Decomposition of Alcohol 1b.—On the basis of the observations reported above, alcohol **1b** was expected to undergo facile acid-catalyzed fragmentation. Such behavior was indeed observed. At room temperature in benzene-d_6, the fragmentation was strongly catalyzed by trifluoroacetic acid (referred to hereafter as TFA), and it gave quantitative yields of benzaldehyde and **7** when it was carried out under these conditions. In a parallel experiment, TFA-*d* was used to catalyze the fragmentation of **1b**-*O*-*d*, and the resulting **7** was found to contain no methine deuterium. This observation supports the occurrence of hydride transfer[23] and rules out any route to **7** involving a benzocyclopropene intermediate (*cf.* Scheme II).

Under certain conditions, TFA had been reported to cleave aryl benzyl ethers into phenols and (presumably) benzyl trifluoroacetates.[24] This result suggested that the TFA-catalyzed fragmentation of **1b** might have occurred, at least in part, *via* a route involving ether cleavage followed by intermolecular hydride transfer. All steps after cleavage were required to be fast, since there was no evidence for the accumulation of stable intermediates (see Experimental Section). Mechanisms of this type are summarized in Scheme IV.

Scheme IV was tested in several ways, but no evidence was obtained for its operation. When excess TFA (10 mol equiv) was added to a benzene-d_6 solution of **14** (1.2 mol equiv) and **6** (1.0 mol equiv), phenol **7** was formed in a slow reaction. However, none of the starting ester was consumed, and neither benzaldehyde nor **16** (see below) could be detected among the products. No attempts were made to elucidate the detailed course of this reaction, although the TFA-induced formation of **7** from **6** alone was verified by a separate experiment.

A benzene-d_6 solution of **6** (1.0 mol equiv) and benzyl alcohol (1.3 mol equiv) was treated with TFA (15 mol equiv). The ensuing reaction was rapid initially, but its rate decreased markedly before **6** was consumed. At a conversion level of 83%, the products (mol/mol of starting **6**) were **7** (0.50), **14** (0.78), **16** (0.33), and benzaldehyde (0.17). Benzaldehyde and **7** must have resulted from the reduction of ion **15** with benzyl alcohol, while formation of **14** by direct esterification of TFA was independently shown to be feasible. The structure of **16** and its mode of formation were estab-



16

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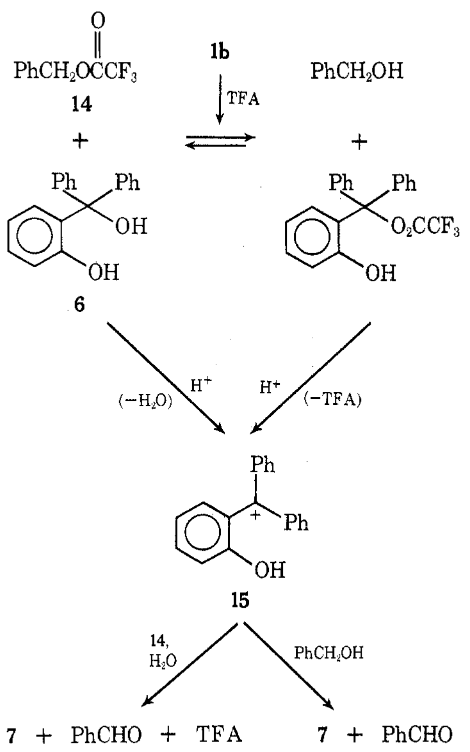
[22] *Cf.* C. G. Swain and Y. Okamoto, *J. Amer. Chem. Soc.*, **92**, 3409 (1970), and references cited therein.

[23] *Cf.* P. D. Bartlett and J. D. McCollum, *ibid.*, **78**, 1441 (1956).

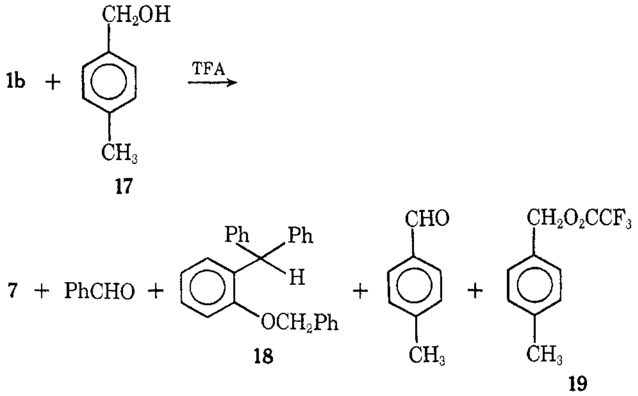
[24] J. P. Marsh, Jr., and L. Goodman, *J. Org. Chem.*, **30**, 2491 (1965).

SCHEME IV



lished by a separate synthesis of the substance from benzaldehyde and **6**, using TFA as the catalyst. Since **14** and **16** were not produced in the TFA-catalyzed decomposition of **1b**, their formation from benzyl alcohol and **6** was regarded as further evidence against the mechanisms of Scheme IV. However, Scheme IV was already known to require very rapid formation of benzaldehyde and **7** following the initial cleavage, and this could have accounted for the different product distributions observed in the two different systems.

A reaction of **1b** (1.0 mol equiv) with alcohol **17** (2.9 mol equiv) and TFA (6.0 mol equiv) was carried out under the usual conditions. When all of **1b** had reacted, 0.11 mol equiv of **17** remained, and the products (mol/mol of **1b**) were **7** (0.84), benzaldehyde (0.84), **18** (0.16, identified by comparison with a reference sample prepared by benzylation of **7**), *p*-tolualdehyde (0.16), and **19** (2.60).



The aldehydes, phenol **7**, and ether **18** were undoubtedly formed *via* hydride transfers, while **19** evidently resulted from a direct esterification. Alcohol **17** was present in relatively high concentration (greater than the concentration of **1b**) throughout the course of the reaction, and its intrinsic hydride-donating ability was predicted to be greater than that of benzyl alcohol or ester **14** under these experimental conditions.[25] Therefore, if the mechanism(s) of Scheme IV had been operative, fragmentation of **1b** in the presence of **17** should have given considerable amounts of **14** and/or benzyl alcohol, which would have been largely converted to **14** *in situ*. Moreover, the following stoichiometric relationships should then have been observed for the products: benzaldehyde < **7**, *p*-tolualdehyde > **18**. Since these inequalities did not obtain and no **14** was detected, we conclude that *none* of the fragmentation occurred *via* Scheme IV. It should also be noted that this experiment gave the "normal" cleavage products (benzaldehyde and **7**) in relatively high yields, a result constituting permissive evidence for hydride transfer by a rapid intramolecular route.

The behavior of **1b** toward formic acid was also a matter of interest. Formic acid is ordinarily an excellent reagent for the reduction of tritanols to triarylmethanes.[12c,26] However, its reaction with **1b** gave no **18**, and the major products were shown to be benzaldehyde and **7**. By analogy with behavior reported for similar molecules,[27] **1b** would be expected to undergo very rapid and extensive (perhaps essentially quantitative) ionization (to form **12**) upon dissolution in formic acid. Intermolecular hydride transfer between two positively charged species is not a favored process; thus the fragmentation of **1b** observed in formic acid would seem to be best rationalized in terms of an intramolecular transfer path.

From the foregoing observations we conclude that the acid-catalyzed decomposition of **1b** proceeds by a mechanism which closely resembles, in all probability, the one proposed for **1a**.

Related Reactions.—Although *o*-alkoxytrityl cations have been generated previously in many chemical and physicochemical studies,[28] their self-induced decomposition due to hydride transfer has apparently not been noticed before. Unlike **1a**, *o*-methoxy-[2,28a,29] and *o*-ethoxytrityl chloride[12c] seem to have no tendency to undergo spontaneous fragmentation. (*o*-Methoxyphenyl)diphenylmethanol does not decompose in hot acid solution under nonreducing conditions,[28a] and both it[26a,c,d] and the corresponding *o*-ethoxy alcohol[12c] give triarylmethanes when they are treated with formic acid. Solutions of the *o*-methoxytrityl cation have

[25] Extensive protonation of the potential hydride-donating species might have altered their relative reactivities,[23] but this effect should have been insignificant under the conditions employed here.

[26] For representative examples, see (a) H. Kauffmann and P. Pannwitz, *Ber.*, **45**, 766 (1912); (b) A. Kovache, *Ann. Chim.* (*Paris*), **10**, 184 (1918) [*Chem. Abstr.*, **13**, 441 (1919)]; (c) D. I. Roberts and S. T. Bowden, *Recl. Trav. Chim. Pays-Bas*, **49**, 665 (1930); (d) S. T. Bowden, D. L. Clarke, and W. E. Harris, *J. Chem. Soc.*, 874 (1940); (e) S. T. Bowden and K. I. Beynon, *ibid.*, 4244, 4253 (1957); (f) R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, **60**, 889 (1964).

[27] W. R. B. Arthur, A. G. Evans, and E. Whittle, *J. Chem. Soc.*, 1940 (1959); R. Stewart and T. Mathews, *Can. J. Chem.*, **38**, 602 (1960).

[28] See, *inter alia*, ref 2, 12c, 26a,c,d and (a) A. Baeyer, *Justus Liebigs Ann. Chem.*, **354**, 152 (1907); (b) K. Ziegler and H. Wollschitt, *ibid.*, **479**, 90 (1930); (c) K. Brand, *J. Prakt. Chem.*, [2], **109**, 1 (1925); (d) H. Lund, *J. Amer. Chem. Soc.*, **49**, 1346 (1927); (e) J. C. Martin and R. G. Smith, *ibid.*, **86**, 2252 (1964); (f) M. J. Sabacky, C. S. Johnson, Jr., R. G. Smith, H. S. Gutowsky, and J. C. Martin, *ibid.*, **89**, 2054 (1967); (g) I. Lifschitz, *Recl. Trav. Chim. Pays-Bas*, **53**, 191 (1934); (h) H. Kauffmann and I. Fritz, *Ber.*, **41**, 4423 (1908); (i) H. Kauffmann and F. Kieser, *ibid.*, **45**, 2333 (1912); (j) H. Kauffmann and F. Kieser, *ibid.*, **46**, 3788 (1913); (k) G. Wittig and G. Fuhrmann, *ibid.*, **73**, 1197 (1940); (l) G. Wittig and G. Harborth, *ibid.*, **77**, 306 (1944).

[29] C. S. Marvel, J. Whitson, and H. W. Johnston, *J. Amer. Chem. Soc.*, **66**, 415 (1944).

been studied spectrally[28c] and by conductometry[2,28b] with apparently no evidence of decomposition. Facile rearrangement of mono-*o*-alkoxytrityl cations thus seems to require a substituent which is more reactive than methoxy or ethoxy, although it is possible that trityl cations containing these and other simple *o*-alkoxy substituents might be found to rearrange if the reaction were looked for carefully under favorable conditions.

Hydride transfer from the benzyloxy group gives a very stable carbonium ion and is obviously a favored process, but clear-cut evidence for the rearrangement of an *o*-benzyloxytrityl cation has not been forthcoming until now. However, Gomberg and McGill[30] found that (3-benzyloxy-2-naphthyl)diphenylchloromethane acquired the odor of benzaldehyde on standing, and this observation presumably signifies the occurrence of another reaction which is analogous to those described herein.

Experimental Section[31]

Materials.—Reagent grade benzene and benzene-d_6 were dried over sodium. The redried ether used for operations with **1a** (see below) was prepared by treating commercial anhydrous ether with calcium chloride and sodium, in succession (sodium reacted vigorously when the predrying step was omitted). Petroleum ether was the fraction boiling at 30–60°. Oxygen-18-enriched water (Diaprep Inc.) had a nominal ^{18}O content of 20 atom % and was stated by the supplier to contain less than 10 atom % of deuterium. A mass spectral analysis of this material indicated an ^{18}O content of 20.7 atom %. Trifluoroacetic acid-*d* (Diaprep Inc.) was shown to contain 99.1 ± 0.1 atom % deuterium by nmr analysis *vs.* an internal standard (anhydrous toluene). Gaseous HCl was dried by passage through sulfuric acid. *p*-Benzoquinone was purified by sublimation; 2,6-lutidine (Aldrich) was dried over potassium hydroxide. The other chemicals used were either commercial materials of high quality or substances prepared by standard literature procedures. Purities were established by spectrometric methods, vpc analysis, and the determination of appropriate physical constants.

Instrumental Analysis.—Infrared, 100-MHz nmr, and high-resolution mass spectra were obtained with Perkin-Elmer Model 21, Varian Model HA-100, and AEI MS-9 spectrometers, respectively. Unless noted otherwise, nmr measurements were made at ambient temperature on dilute solutions containing TMS. Quantitative nmr analyses of benzene-d_6 solutions were corrected for slight solvent absorptions. Nmr peak multiplicities are designated as s (singlet) or m (complex multiplet). Exact measurements of m/e are referred to $C = 12$ amu. Oxygen-18 analyses were performed directly on total product mixtures, using high-resolution mass spectrometry. The analytical peaks were parent m/e's; their elemental compositions were established by exact mass measurements. Sensitivity factors for peaks differing only in isotopic composition were assumed to be identical. Benzaldehyde peak intensities were corrected for contributions due to fragments derived from **7**; these contributions were determined from the mass spectrum of pure **7** and found to be quite small. Programmed temperature vpc analyses were performed with an F & M instrument (Model 500) equipped with a 15 ft. × 0.25 in. (o.d.) stainless steel column containing SE-30 (2%) on acid-washed, DMCS-treated Chromosorb W (40–60 mesh). The carrier gas was helium; column temperature was increased from 100 to 350° at the rate of 8°/min.

(*o*-Benzyloxyphenyl)diphenylmethanol (1b).—Gomberg and Nishida's description[2] of the preparation of **1b** omits several useful details. The following method may be regarded as an amplification of their procedure.

A nitrogen-blanketed suspension of (*o*-hydroxyphenyl)diphenylmethanol[2,28a] (**6**, 14.00 g, 0.0507 mol) in 1 *N* aqueous sodium hydroxide (60 ml) was stirred rapidly at 85° until complete dissolution of the diol occurred. Benzyl chloride (9.0 g, 0.071 mol) was then added, and after an additional 30 min of warming (85 ± 1°) and stirring under nitrogen, the hot mixture was filtered with suction. The recovered solid was washed several times with water and then with cold (−78°) methanol; it weighed 15.19 g (82% yield; larger scale runs occasionally gave crude yields as high as 96%) and melted at 176.5–178°. A single recrystallization of the product from benzene, followed by thorough washing of the recovered crystals with dry ether, gave 14.37 g of pure **1b** as white clusters: mp 177–177.5° (lit.[2] mp 172°); ir (CS_2) 3505 cm^{-1} (medium, sharp, hindered OH), no C=O; nmr (CCl_4, 60°) δ 6.4–7.3 (m, 19, aromatic H), 4.83 (s, 2, CH_2), and 4.72 ppm (s, 1, OH).

Samples of **1b** containing no impurities detectable by nmr occasionally melted over very wide ranges of temperature (beginning as low as 70°) and acquired the odor of benzaldehyde on melting. These samples usually exhibited the correct melting point for pure **1b** after rigorous drying *in vacuo* at 60°, or after thorough washing with anhydrous ether.

Benzyl α-Chloro-α,α-diphenyl-*o*-tolyl Ether (1a).—In our hands, attempts to obtain **1a** by the published method[2] invariably gave impure products that failed to melt sharply and usually gave evidence of decomposition (benzaldehyde odor, brown melt) on melting. High sensitivity of **1a** toward moisture and/or incomplete conversion of **1b** were apparently the principal sources of difficulty, since the impure chloride was always found to contain a considerable amount of the starting alcohol. Repeated trials eventually led to development of the following modified procedure, which consistently afforded **1a** in a satisfactory state of purity.

A well-stirred mixture of alcohol **1b** (10.00 g, 27.3 mmol), anhydrous calcium chloride (10 g), and benzene (110 ml) was bubbled with a rapid stream of dry HCl for 20 min. No undissolved **1b** could be detected visually at the end of this time. An additional 20 g of the drying agent was added, and the mixture was stoppered tightly under an atmosphere of dry HCl and allowed to stand for 6 hr in the dark with occasional shaking. The drying agent was then removed by suction filtration and washed with several fresh portions of dry benzene. Concentration *in vacuo* of the combined filtrate and washings to a volume of *ca.* 35 ml, followed by refrigeration under argon, suction filtration, and rapid washing of the recovered solid with cold (5°) redried ether (see "Materials," above), gave 7.20 g of the crude chloride, mp 148–156° with slight decomposition. Dissolution of the product in hot redried ether (*ca.* 35 ml/g), followed by chilling to 5°, afforded 4.17 g (40%) of purified **1a** as small snow-white needles: mp 150–153° (lit.[2] mp 146°); ir (CS_2) 3520 cm^{-1} (very weak, OH of residual **1b**); nmr (CCl_4) δ 6.7–7.4 (m, 19, aromatic H) and 4.84 ppm (s, 2, CH_2). In C_6D_6 the CH_2 protons of **1a** and **1b** appear at δ 4.56 and 4.36 ppm, respectively. Quantitative nmr analyses of C_6D_6 solutions showed that our best samples of **1a** contained *ca.* 3 mol % of the alcohol.

Anal.[32] Calcd for $C_{26}H_{21}ClO$: Cl, 9.21. Found: Cl, 9.39.

In agreement with earlier observations,[2] **1a** was found to decompose slowly on storage. However, purified samples were reasonably stable when stored with proper precautions. One sample of the purified material was kept for 8 weeks over Drierite in a darkened, continuously evacuated vessel (pressure ≦ 10 mm). The sample had then acquired a pink color and was found to contain 6 mol % of **1b**; no other impurities were detected.

A small portion of **1a** (0.20 g, 0.52 mmol) was stirred overnight with 1 *N* aqueous sodium hydroxide (20 ml) and dioxane (10 ml). The suspended solid was then removed by suction filtration and washed well with water; from its melting point (172.5–176.5°) it was judged to be mostly **1b** (0.19 g, 100% crude yield). Recrystallization of the solid from benzene–petroleum ether gave 0.09 g of white microcrystals which were shown to be pure **1b** by melting point, mixture melting point, and ir spectral comparisons.

Decompositions of Chloride 1a. A. In Benzene-d_6 Solution.—These reactions were carried out in nmr tubes under nitrogen, using chloride samples that contained 3–6 mol % of **1b**. Product compositions are reported as (moles of compound)/(moles of starting **1a** + moles of starting **1b**); they were calculated from

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[30] M. Gomberg and W. J. McGill, *J. Amer Chem. Soc.*, **47**, 2392 (1925).

[31] Boiling points and melting points are uncorrected. The melting points were determined with a Fisher-Johns apparatus. Unless noted otherwise, elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The drying agent was usually Drierite; all exceptions are noted appropriately. Evaporations were carried out on rotary evaporators at room temperature under *ca.* 10 mm of pressure.

[32] Analysis by neutron activation was performed in this laboratory under the direction of Mr. J. O. Beauxis.

nmr spectra with an accuracy estimated to be within ±5% of the values given.

A solution of the chloride (18 mg, 0.044 mmol of **1a**, 0.003 mmol of **1b**) in dry benzene-d_6 (0.45 ml) was allowed to stand at room temperature. Slow formation of additional **1b** was the only reaction detected initially. Small amounts of benzaldehyde and **7** were present after a few days, and after 1 week of standing the mixture had the following composition: **1a**, 0.67; **1b**, 0.17; benzaldehyde, 0.16; **7**, 0.16 mol/mol. The solution was then heated at 70 ± 1° for 3 days, allowed to stand at room temperature for an additional 5 days, and reanalyzed. The only detectable constituents were benzaldehyde and **7**; their identifications were confirmed by comparisons of chemical shifts and vpc retention times, using authentic materials as references.

Several decompositions of **1a** were carried out in dry benzene-d_6 at 70 ± 1° without a preliminary period of standing at room temperature. In a typical experiment, the starting material (35 mg, 0.086 mmol of **1a**, 0.005 mmol of **1b**) was dissolved in 0.39 ml of solvent. Complete decomposition had occurred after 42 hr of heating, and the product composition was then shown to be: **7**, 0.08; **9**, 0.85; **10**, 0.04; benzaldehyde, 0.12 mol/mol. Compound **9** gave sharp singlets at δ 6.73 [(ArO)CHClPh] and 6.06 ppm (Ph_2ArCH). These peaks appeared to be equal in intensity, although accurate integration of the downfield peak was prevented by aromatic end absorption. Compound **10** produced singlets at δ 6.54 [1, $(ArO)_2CHPh$] and 6.09 ppm (2, Ph_2ArCH). Addition of one drop of water caused the very rapid destruction of both **9** and **10**, and after a few minutes the spectrum indicated the formation of benzaldehyde and **7** in essentially quantitative yields. These substances were identified by the usual comparisons, and the absence of other products was confirmed by vpc analysis. In a separate experiment, the product mixture was hydrolyzed more slowly by adding water-saturated benzene-d_6 instead of pure water. In this case the singlets assigned to **10** disappeared faster than those assigned to **9**, a result verifying the presence of two hydrolyzable constituents. A further experiment involved the addition of a large amount of **7** to an unhydrolyzed product mixture (in benzene-d_6). This addition caused immediate formation of more **10** and decreased the **9**:**10** ratio. Several product mixtures were hydrolyzed with $H_2{}^{18}O$ and then quickly subjected to mass spectral analysis following rapid concentration under nitrogen. Maximum theoretical ^{18}O contents were calculated on the assumption that the benzaldehyde and **7** already formed by adventitious hydrolysis would not undergo isotopic exchange with the labeled water. The experimentally determined ^{18}O contents follow: for benzaldehyde, 95–105; for **7**, 0–3% (of the theoretical maximum values).

Product analyses at intermediate conversion levels provided data which were used to calculate half-lives for the rearrangement of **1a** in benzene-d_6 at 70 ± 1°, assuming first-order kinetics. These one-point kinetic runs gave half-lives ranging from *ca.* 6 to 50 hr for different samples of the chloride. However, aliquots taken from the same batch of chloride over a period of 1–3 days showed half-lives that were reproducible to within ±25%. Table I presents typical data for a series of runs made with some aliquots of this type. No new products were formed in the runs with *p*-benzoquinone and HCl, and the quinone caused no significant changes in product distribution. Compound **10** could not be detected in runs using HCl, but the product distributions obtained in these runs were not significantly altered otherwise. The half-life given for the lutidine experiment was calculated by assuming 1% rearrangement at 89.1 hr. No rearrangement was actually detected, although the **1b** content had risen to 16 mol % at the end of this time.

TABLE I

HALF-LIVES FOR THE REARRANGEMENT OF **1a** (0.2 *M*) IN BENZENE-d_6 AT 70°

Additive (mol equiv)[a]	Half-life, hr
	8.1 ± 2.0[b]
p-Benzoquinone (1.2)	11.4
HCl (g)[c]	4.2 ± 0.1[b]
2,6-Lutidine (1.1)	>6 × 10^3 [d]

[a] Mol/mol of (**1a** + **1b**). All **1a** samples contained *ca.* 5 mol % of **1b**. [b] Average of two runs. [c] Saturated solution. [d] See text.

B. Without Solvent.—These decompositions were carried out in a small thermostated distilling flask equipped with a gas inlet tube (wide-bore capillary) extending nearly to the surface of the vessel's contents. The side arm of the flask led to a chilled U-tube receiver. Before application of heat, the assembled apparatus (containing **1a**) was purged with inert gas, which was dry CO_2 unless noted otherwise. A rapid inert gas sweep was maintained throughout the heating period.

In an attempt to repeat the experiment described by Gomberg and Nishida,[2] 3.00 g of purified **1a** was heated for 3.0 hr at 145–146° while the temperature of the cold trap was kept at *ca.* −15°. Slow evolution of benzaldehyde (detected by odor) and HCl (detected with pH paper) occurred throughout the reaction period, but no condensate was collected in the cold trap, and the pot residue (a reddish brown glass when cool) had decreased in weight by only 0.14 g. [In the experiment of Gomberg and Nishida,[2] 0.6 g (73%) of benzaldehyde was said to have been collected in the distillation receiver.] Analysis of the residue by vpc, nmr, and mass spectrometry indicated that it was a complex mixture containing appreciable amounts of **7** and diphenylmethane (identified by appropriate comparisons with authentic specimens), as well as several unidentified substances. Benzaldehyde and **1a** were shown to be absent, and no evidence could be obtained for the presence of polymers derived from **3a**. In accordance with the reported work-up procedure,[2] one-half of the residue was crystallized from ethanol–ether. Chilling to −10° was necessary to induce precipitation. The recovered material (0.10 g) was a pale yellow powder that melted at 85–95° and was shown by nmr and mass spectral analysis to be a mixture of **7** and other materials. The nmr spectrum showed several unidentified peaks in the aliphatic region, and the mass spectrum again provided no evidence for the presence of polymerized **3a**. Further concentration and chilling of the ethanol–ether solution yielded a yellow gum that could not be induced to crystallize.

In a second experiment, 1.93 g of **1a** was heated under argon for 3.2 hr while the pressure of the system was kept at 240–250 mm by means of a vacuum line equipped with a manostat. The pot residue weighed 1.82 g, and the cold trap contained only 0.02 g of impure benzaldehyde (yield, *ca.* 4%).

The first experiment was repeated using a cold trap temperature of −40°. Only 0.02 g of material (mostly water by nmr analysis) was collected in the trap, and the pot residue weighed 2.93 g. Crystallization of the residue from ethanol–ether gave 0.24 g of cream-colored powder: mp 85–95° (*cf.* above); ir (CS_2) 3505 (medium, OH) and 3320 cm^{-1} (medium, OH), no C=O.

Anal. Found: C, 83.64; H, 5.59; Cl, 0.28; mol wt (benzene), 702.

In another experiment, 2.90 g of **1a** was heated at 180° for 3.0 hr while the cold trap was cooled to −40°. The distillate weighed 0.08 g, and its major constituent was shown to be benzaldehyde (yield, 5–10%) by nmr analysis. Programmed temperature vpc analysis showed that the residue contained only traces of volatile constituents. No evidence for **3a** (either monomeric or polymerized) was forthcoming from the residue's mass spectrum, and the nmr spectrum showed that benzaldehyde and **1a** were absent. Crystallization of the residue from ethanol–ether gave the following fractions (fraction number, weight, melting point, molecular weight in benzene): 1, 0.48 g, 155–165°, 2050;[33] 2, 0.50 g, 149–160°, 1120; 3, 0.36 g, 139–147°, 1370;[33] 4, 0.58 g, 125–133°, 990; 5, 0.20 g, 107–117°, 869. All fractions were pale orange powders. Fraction 4 was of particular interest because of its apparent similarity to the supposed tetrameric **3a** (lit.[2] mp 126–129°, lit.[2] mol wt 860–869) of Gomberg and Nishida. However, fraction 4 was conclusively shown not to have this type of structure by a variety of observations: ir (CS_2) 3540 cm^{-1} (strong, OH), no C=O; nmr (CCl_4) δ 6.1–7.4 (poorly resolved m, relative area *ca.* 17, aromatic H), 5.4–5.7 (poorly resolved m, relative area 1.0, Ar_3CH? and Ar_2CHO?), and 4.2–5.3 ppm (several broad, weak, and poorly resolved peaks, some of which disappeared on acidification).

Anal. Found: C, 86.53; H, 5.71; Cl, 0.12.

The other fractions had similar elemental compositions (ranges of found values: C, 85.7–87.0; H, 5.4–5.8; Cl, 0.1–0.4), and their nmr and ir spectra were similar to those of fraction 4.

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(33) Osmometric molecular weight determination was performed in this laboratory under the direction of Dr. L. Westerman.

α,α-Diphenyl-*o*-cresol (7).—The following method of synthesis was employed by Baeyer,[28a] who did not include procedural details in his published account of the experiment.

A mixture of diol **6** (5.00 g, 18.1 mmol), zinc dust (7.5 g), and glacial acetic acid (25 ml) was stirred vigorously and heated under reflux for 2 hr. The hot mixture was filtered with suction, and the filter cake was washed with several portions of fresh solvent. Water was added in increments, with stirring, to the combined filtrate and washings until precipitation appeared complete. The crude product was then recovered by suction filtration and washed well with water; it weighed 4.65 g (yield, 99%) and was actually quite pure [mp 126–126.5° (lit.[28a] mp 124°)]. Recrystallization from benzene–petroleum ether gave **7** as white clumps: mp 127–127.5°; ir (CS_2) 3560 cm^{-1} (medium and rather broad, phenolic OH); nmr (CCl_4) δ 6.5–7.4 (m, 14, aromatic H), 5.62 (s, 1, aliphatic H), and 4.39 ppm (s, 1, disappears on acidification, OH); mass spectrum (70 eV) *m/e* 260.1199 (strong; calcd for $C_{19}H_{16}O$, 260.1201).

Decompositions of Alcohol 1b.—The reactions described in parts A–C were carried out in nmr tubes. All reactions were run under nitrogen.

A. With Trifluoroacetic Acid.—Trifluoroacetic acid (25 mg, 0.22 mmol) was added to a solution of **1b** (12 mg, 0.033 mmol) in dry C_6D_6 (0.48 ml), and the nmr spectrum of the dark mixture was recorded at frequent intervals until all of the alcohol had been consumed. The only detectable products were benzaldehyde and **7**; they were formed quantitatively within 0.6 hr. Product identifications were based on chemical shifts, vpc retention times, and spectral analyses of trapped vpc fractions, using pure reference compounds for comparison.

B. With Trifluoroacetic Acid-*d* Using 1b-*O-d*.—Alcohol **1b** underwent partial conversion to **1b**-*O-d* when it was kept for several days in warm (50°) benzene–CH_3OD solution. Continued repetition of the exchange procedure eventually gave **1b**-*O-d* containing 84 ± 1 atom % deuterium (according to nmr analysis). A solution of this material (24 mg, 0.065 mmol) in dry C_6D_6 (0.45 ml) was added under nitrogen to 89 mg (0.78 mmol) of CF_3CO_2D (see "Materials," above), and the progress of the reaction was followed by nmr. Quantitative formation of benzaldehyde and **7** occurred within 12 min, and careful expanded-scale integration showed that the PhCHO and Ph_2ArCH signals were of equal intensity (within the probable limits of experimental error, which were ±5–10%). Calculations based on these signals yielded the correct (measured) value for the total aromatic area.

C. With Trifluoroacetic Acid in the Presence of Alcohol 17.—Trifluoroacetic acid (35 mg, 0.31 mmol) was added to a solution of **1b** (19 mg, 0.052 mmol) and **17** (18 mg, 0.15 mmol) in dry C_6D_6 (0.46 ml), and the mixture was allowed to stand at room temperature with occasional analysis by nmr. No metastable intermediates were detected spectrally during the course of the reaction. After 8 hr the conversions of **1b** and **17** were *ca.* 91 and 79%, respectively, but further conversion of **1b** was quite slow. No **1b** remained after 8 days of reaction, and nmr analysis then gave the following result (yields are given in moles/moles of **1b**): **7**, 0.84 ± 0.02; benzaldehyde, 0.84 ± 0.02; **18**, 0.16 ± 0.02; *p*-tolualdehyde, 0.16 ± 0.02; **19**, 2.60 ± 0.07; **17**, 0.11 ± 0.01. All of the aliphatic proton resonances were resolved to a degree sufficient to allow their separate integration and identification by means of spectral reruns following the addition of authentic samples. The CHO protons originally had identical chemical shifts, but this degeneracy was easily removed by dropwise addition of triethylamine, and the downfield CHO peak was then shown to be that due to *p*-tolualdehyde by using the pure material for comparison. A similar comparison established the absence of **14**, and the presence of **7** and **18** was verified by comparing their vpc retention times and the ir and nmr spectra of trapped vpc fractions *vs.* those of authentic specimens.

D. With Formic Acid.—In close conformity with the procedure employed by Kauffmann and Pannwitz for reduction of (*o*-methoxyphenyl)diphenylmethanol,[26a] a solution of **1b** (1.00 g, 2.73 mmol) in formic acid (8.15 ml of "98–100%" material, *ca.* 215 mmol) was heated under reflux, with stirring, until the original dark red color had disappeared. After 30 min the pale rose-colored solution was evaporated *in vacuo*, and the residue was examined by nmr and vpc. A complete quantitative analysis was not attempted; however, comparisons with pure reference compounds showed that **1b** and **18** were absent and that benzaldehyde and **7** were the major products of the reaction (yields were roughly equivalent and were estimated to be at least 70–80%).

Benzyl α,α-Diphenyl-*o*-tolyl Ether (18).—This preparation was carried out under nitrogen. Phenol **7** (4.40 g, 16.9 mmol) was dissolved in 1 *N* aqueous sodium hydroxide (40 ml) by stirring and heating to 100°. Benzyl chloride (3.00 g, 23.7 mmol) was added to the hot solution, and after 40 min of heating (93–100°) and stirring, more of the benzyl halide (2.00 g, 15.8 mmol) was introduced. Stirring was continued for an additional 65 min at 92–93°; then the mixture was cooled to room temperature and extracted with benzene (100 ml in three portions). Evaporation of the dried extracts gave a semisolid residue, which was crystallized twice from methanol. The second crystallization afforded 2.22 g (38%) of **18** as small snow-white needles: mp 168.5–169.5°; ir (CS_2) no OH or C=O; nmr (CCl_4) δ 6.7–7.3 (m, 19, aromatic H), 5.86 (s, 1, methine H), and 4.88 ppm (s, 2, CH_2); mass spectrum (70 eV) *m/e* 350.1659 (medium; calcd for $C_{26}H_{22}O$, 350.1671).

Anal. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.33. Found: C, 89.15; H, 6.45.

Reactions of (*o*-Hydroxyphenyl)diphenylmethanol (6) with Ester 14 and Benzyl Alcohol in the Presence of Trifluoroacetic Acid.—Trifluoroacetic acid (36 mg, 0.32 mmol) was added to an nmr tube containing a solution of **6** (8.9 mg, 0.032 mmol) and **14** (7.5 mg, 0.037 mmol) in dry C_6D_6 (0.48 ml). The reaction mixture was allowed to stand at room temperature under nitrogen with occasional analysis by nmr. After 68 hr, none of **14** had reacted, and neither **16** nor benzaldehyde had been formed. However, **7** was present (0.37 ± 0.02 mol/mol of starting **6**), and several unidentified peaks were detected in the aromatic region of the spectrum. Compound **7** was identified by chemical shift comparisons made *vs.* authentic material in two different solvent media (C_6D_6 and CCl_4). In a parallel experiment, **14** was omitted, and similar results were obtained.

A solution of **6** (7.5 mg, 0.027 mmol) and benzyl alcohol (3.7 mg, 0.034 mmol) in dry C_6D_6 (0.79 ml) was prepared in an nmr tube. Trifluoroacetic acid (46 mg, 0.40 mmol) was added, and the resulting dark mixture was allowed to stand at room temperature under nitrogen. Analysis by nmr showed that the initial reaction was quite rapid. However, the rate soon decreased, and an nmr spectrum taken after 16.7 hr indicated the following composition (moles/moles of starting **6**): **7**, 0.50 ± 0.03; **14**, 0.78 ± 0.04; **16**, 0.33 ± 0.02; benzaldehyde, 0.17 ± 0.01; **6**, 0.17 ± 0.01. The value for **6** could be in error, since it was calculated by difference using the total aromatic area. All other constituents were identified by comparisons of chemical shifts. These were made with solutions of the product mixture in C_6D_6 or CCl_4, following the addition of authentic specimens.

A similar experiment was performed using 55 mg (0.20 mmol) of **6**, 22 mg (0.20 mmol) of benzyl alcohol, 0.79 ml of dry C_6D_6, and 41 mg (0.36 mmol) of trifluoroacetic acid. In this case the rate of disappearance of **6** was slow even at the outset, and diol conversions were estimated to be only *ca.* 34 ± 3 and 65 ± 3% after reaction times of 10 and 34 days, respectively. The following compounds (moles/moles of starting **6**) were also present after 34 days: **7**, 0.34 ± 0.02; **14**, 0.58 ± 0.03; **16**, 0.31 ± 0.02; benzaldehyde, 0.03 ± 0.01; benzyl alcohol, 0.05 ± 0.01.

The preceding experiment was repeated on a larger (tenfold) scale, using ordinary dry benzene as solvent. After 14 days of standing, the mixture was shaken with 1 *N* aqueous sodium hydroxide and filtered with suction. The precipitate was washed several times with fresh benzene, and after the washings had been combined with the original filtrate, the benzene layer was removed and washed with two additional 15-ml portions of the caustic solution. Clarification of the combined aqueous layers was achieved by extraction with two 25-ml portions of ether. The extracts and the benzene solution were then combined, washed several times with water, dried, and evaporated. Extraction of the residue with 20 ml of warm (50°) 1 *N* sodium hydroxide, followed by two recrystallizations of the insoluble material from petroleum ether, gave 40 mg (6%) of **16**, mp 167–168°. The identity of the product was confirmed by a mixture melting point determination and an ir spectral comparison.

2,4,4-Triphenyl-1,3-benzodioxane (16).—Trifluoroacetic acid (0.69 g, 6.1 mmol) was added dropwise during 0.2 hr to a stirred solution of diol **6** (0.55 g, 2.0 mmol) and benzaldehyde (0.21 g, 2.0 mmol) in dry benzene (20 ml). After 1.8 hr of standing under nitrogen, the solution was evaporated to give an off-white solid residue which, in view of its melting point (166–168°), was presumed to be an essentially pure material. Recrystallization of the solid from petroleum ether afforded silky snow-white needles (0.51 g, 71%) of **16**: mp 168–169°; ir (CS_2) no OH or C=O; nmr (CCl_4) δ 6.7–7.6 (m, 19, aromatic H) and 5.87 ppm (s, 1, aliphatic H).

Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53; mol wt, 364. Found: C, 85.85; H, 5.51; mol wt (benzene), 377.

Registry No.—**1a**, 30316-41-7; **1b**, 30316-42-8; **7**, 4970-23-4; **9**, 30309-97-8; **10**, 30309-98-9; **16**, 30309-99-0; **18**, 30310-00-0.

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Chemical Syntheses with Bergmann–Schlenk Adducts. VII.[1] Benzil Dianil

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The reduction of benzil dianil (**1**) with sodium in tetrahydrofuran produced the *N,N'*-disodio-*N,N'*-diphenyl-α,α'-stilbenediamine (**2**). Chemical reactions of this compound with ethyl chloroformate, diethyl oxalate, methyl iodide, allyl bromide, 1,3-dihalopropanes, and water were examined. A cis configuration is suggested for **2**.

In continuing our study[1] of the synthetic utility of Bergmann–Schlenk adducts of conjugated bisimines, a compound in which the azomethine groups were united through the carbon atoms rather than the nitrogens was selected. The natural choice was benzil dianil (**1**) but the preparation of this venerable compound offered some difficulties. Julian's procedure,[2] utilizing benzil as starting material, proved adequate but required careful control of the reaction conditions. The seemingly more convenient procedure[3] for the preparation of **1** using *N*-benzylideneaniline as starting material was, in our hands, only sporadically successful. However, as Becker has recently shown,[4] this reaction depends on the initial formation of α,α'-dianilinostilbene and its subsequent oxidation to benzil dianil (**1**). By slightly modifying Becker's procedure, a convenient synthesis of **1** was obtained.

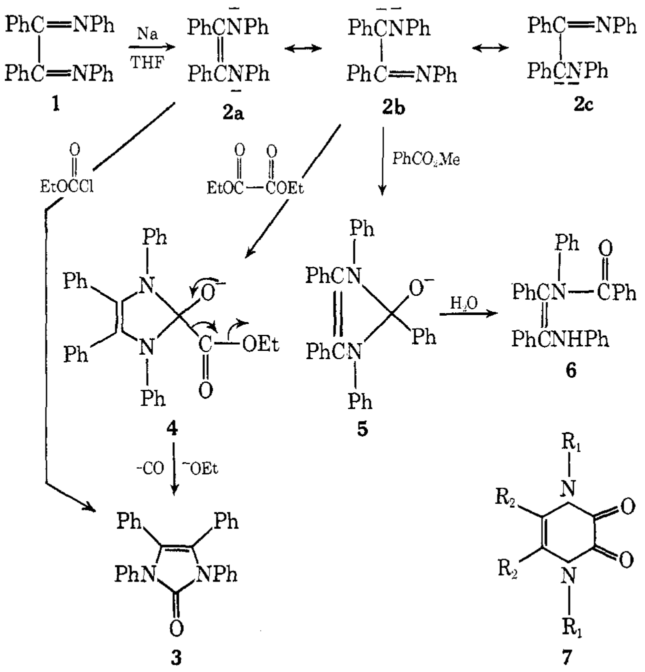
With tetrahydrofuran as solvent and sodium metal as reducing agent, benzil dianil (**1**) was rapidly converted to an adduct **2**, containing 2 g-atoms of sodium per mole of dianil. The initially formed radical anion provided an opaque red-brown solution which changed to a transparent red as the formation of the dianion **2** neared completion.

As observed earlier,[1] the reaction of only one of the two azomethine groups would appear to reflect stabilization of the dianion by the remaining azomethine group participating in the delocalization of the added electrons. Resonance structures involving an azaallylic[5] anion (**2a–c**) can be formulated.

Acylation.—Several reactions were used to characterize the dianion **2** and those employing esters are summarized in Scheme I. With either 1 or 2 mol of ethyl chloroformate, an excellent yield of the known compound 1,3,4,5-tetraphenyl-1,3-imidazolin-2-one (**3**) was isolated. Surprisingly, this same product was isolated when diethyl oxalate was used. Since the expected amount of carbon monoxide was evolved, the initially formed product **4** readily decarbonylates to provide **3**. The unstable intermediate has been formulated as **4** rather than the alternative **7** ($R_1 = R_2 = Ph$, which might conceivably be formed and suffer a base-catalyzed benzil–benzilic acid rearrangement to **4**) since the known compounds[6,7] **7** ($R_1 = Ph$, $R_2 = H$ and $R_1 = Me$, $R_2 = H$) appear quite stable.

Scheme I

Acylation of the Benzil Dianil Disodium Adduct



Diethyl dimethylmalonate failed to react with the dianion **2**.

With methyl benzoate the dianion **2** provided *N*-benzoyl-α,α'-dianilinostilbene (**6**) identical with an authentic sample.[8,9] Formation of only a monobenzoyl derivative is reminiscent of the behavior of the diastereomeric *N,N'*-disodio-*N,N'*-1,2-tetraphenylethylenediamines.[9] The explanation offered there applies equally

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