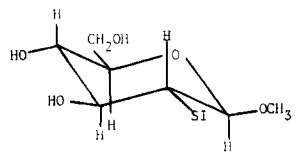
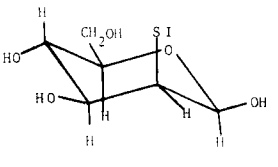
in the configuration at C-2, show strong, negative and positive CEs, respectively, is in agreement with the conclusion that any contribution from ring bonds for an equatorial 1-, 2-, or 4-SI group need not be considered.

The mutual cancellation of the vicinal bond contributions in **7–9** necessitates the consideration of homovicinal bonds. These bonds are coplanar with the equatorial 2- or 3-SI group attachment bond and the chiralities that they have with the SI group transition moments are deduced by using the perferred conformation of the SI group about its attachment bond in which the methine hydrogen atom of the salicylidenimino group eclipses the hydrogen atom at the chiral center to which the nitrogen atom is attached.[13] On this basis, methyl 2-(salicylidenimino)-2-deoxy-β-D-glucopyranoside (**7**) is correctly predicted to



7

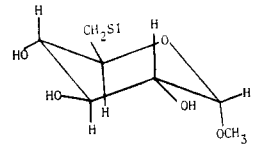


8-12

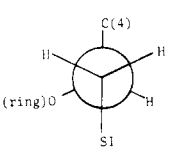
show positive Cotton effects. For **8** and **9** substantial cancellation of the homovicinal bond contributions occurs, but since the contribution by the C(5)–C(6) bond is greater than that by the C(1)–O bond, the CEs are predicted to be weakly negative and weakly positive, respectively. In agreement with this analysis, the CEs for **8** are weakly negative, and none is observed for **9**.

For **10–12** the presence of α and β anomers must be considered. Both anomers of **10** and **11** are predicted to show positive CEs, and the overall prediction for **10** and **11** is unambiguously positive. The SI group in **12** is preferably in an axial conformation (β-**12**), and the vicinal ring bond contribution must be taken into account. Since the sign of the observed CEs is the algebraic sum of a number of mutually cancelling vicinal C–C and C–O bond contributions present in both anomers, an unambiguous prediction as to the sign of the observed Cotton effects is not possible. That no CE for **12** was observed confirms this assessment.

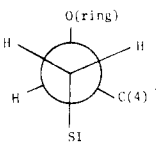
The SI group in methyl 6-(salicylidenimino)-6-deoxy-α-D-glucopyranoside (**13**) is not attached to the tetra-



13



22a



22b

hydropyran ring, and two rotamers of the SI group about the C(6)–C(5) bond, **22a** and **22b** with positive and negative contributions, respectively, must be considered. The experimentally observed weak, positive CEs suggest the greater importance of conformer **22a**. In **14–16**, each with an SI group at C-3 and C-6, the contribution to the CEs of both SI groups must be considered. The equatorial conformation and large separation of the 3-SI and 5-(SImethyl) groups in **14** and **15** is such that coupling between the SI groups[8] should be unimportant, and the contribution from each chromophore can be assessed separately. The contribution from the 3-SI group in **14** is strongly negative (cf. **6**) and is stronger than the weak, positive 6-SI contribution. The CEs for **14** are then unambiguously predicted to be negative. The 3-SI contribution in **15** is weakly negative (cf. **8**), but the weak, positive contribution from the 6-SI group does not allow a prediction of the sign of the CEs. The preferred chair conformation of **16** requires that either the 3-SI group or the 5-(SImethyl) group be in an axial conformation with the possibility of dynamic coupling[8] between the two SI groups. The couplet centered at 259 nm in the spectrum of **16** confirms dynamic coupling, and no prediction as to the chirality of this coupling and hence the sign of the observed Cotton effects is made. The same appears to be true for the *N*-salicylidene derivatives of the amino oligosaccharide antibiotics.[5] The relatively strong CEs in the spectra of these derivatives indicate dynamic coupling among the three or more SI groups, and the conformational mobility of these systems prevents prediction as to the sign of the observed CEs.

Conformation analysis for the preferred conformation of the 5-SI group about the C(4)–C(5) bond in **17**, similar to that for the 6-SI group in **13**, can also be made. On the basis of a preferred conformation similar to **22a**, weak, positive CEs are predicted for **17**.

For the remaining compounds in Table I (**18–20**), the CEs arise by a similar mechanism. Predictions as to signs of the observed CEs are not possible by the summation of bond contributions because of the conformational varients present. It is to be noted, however, that **18** and **19** with epimeric 5-SI groups show essentially enantiomeric CD curves with a positive CE near 315 nm for **18** and a negative CE for **19**.[4]

Acknowledgment. We thank the National Science Foundation for a grant (CHE77-24293) supporting this work.

Registry No. **3**, 19124-27-7; **4**, 19124-28-8; **5**, 19124-32-4; **6**, 19124-36-8; **7**, 19124-33-5; **8**, 19124-34-6; **9**, 19124-35-7; β-**10**, 51471-41-1; α-**10**, 75684-29-6; β-**11**, 75684-30-9; α-**11**, 75684-31-0; β-**12**, 75684-32-1; α-**12**, 75684-33-2; **13**, 19124-37-9; **14** (C-6) derivative, 75626-76-5; **14** (C-3) derivative, 75626-77-6; **15** (C-6) derivative, 75626-78-7; **15** (C-3) derivative, 75626-79-8; **17**, 19124-38-0.

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Bromination of Tetraphenylethane and Triphenylethane

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Received August 14, 1980

Recently, the photochemical bromination of pentaphenylethane was shown to lead to triphenylmethyl bromide and diphenylmethyl dibromide.[1] These products were proposed to arise by the prior formation of the pentaphenylethyl radical and the corresponding ethyl bromide. The latter then dissociates to triphenylmethyl and bromodiphenylmethyl which account for the final products.

Strangely, there are no literature reports on the bromination of either tetraphenylethane or 1,1,2-triphenylethane. Since either of these could lead to a combination of six bromines and/or phenyls grouped about the central ethane, it seemed of some interest that these reactions be examined. The products could reflect on the operational balance between the steric factors, resonance stabilization, and bond strengths which appear to be of importance in

(1) W. B. Smith and M. C. Harris, *J. Org. Chem.*, **45**, 355 (1980).

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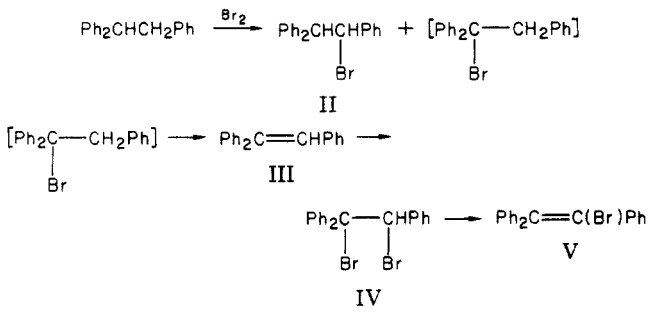
Scheme I



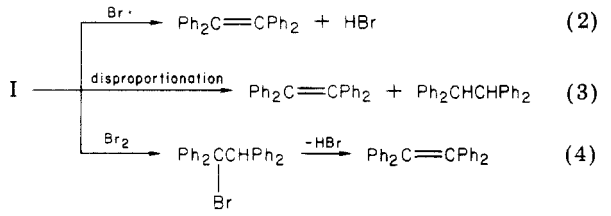
the chemistry of systems such as hexaphenylethane and pentaphenylethane.

The photobromination of tetraphenylethane in carbon tetrachloride with 1 equiv of bromine gave only tetraphenylethylene and hydrogen bromide. With 2 equiv of bromine the products were the same, the balance of the bromine remaining unreacted. It is well-known that bromine does not add to the ethylene double bond and that excess bromine must be present before the formation of tetrakis(*p*-bromophenyl)ethylene occurs.[2] Even when the reaction is carried out in an ice bath with calcium carbonate present, only the ethylene is produced. There seems to be no report in the literature of the existence of 1-bromo-1,1,2,2-tetraphenylethane.

One may postulate several radical pathways to ethylene production during the photobromination reactions of tetraphenylethane. Presumably the postulation of the formation of tetraphenylethyl (I) may serve as a common first step (eq 1). The ethylene may be formed from I by

$$Ph_2CH_2CH_2Ph_2 + Br\cdot \rightarrow \underset{\mathbf{I}}{Ph_2\dot{C}-CHPh_2} + HBr \quad (1)$$

any of three pathways (eq 2–4). Paths 2 and 3 are sta-



tistically unlikely second-order radical processes in dilute solution. Path 4 is consistent with the previous observations on pentaphenylethane[1] and, as will be seen, with the results for triphenylethane below. Available hydrogen bromide or bromine may serve as a Lewis acid to account for the ionic elimination of hydrogen bromide.

The products formed during the bromination of 1,1,2-triphenylethane are shown in Scheme I. Depending on the ratios of reactants, concentrations, and temperatures more or less of each of the products II–V has been found. Thus, when a 0.05 M solution of the ethane was photobrominated with 1 equiv of bromine in carbon tetrachloride, carbon and proton NMR showed the reaction mixture to contain 14% unreacted starting material, 14% II, 62% III, and 10% IV. At 0 °C, a 0.5 M solution with 1 equiv of bromine showed 42% starting material, 11% II, and 47% IV. Compound IV is quite unstable in solution, readily losing hydrogen bromide on standing at room temperature to form V.

The postulation of 1-bromo-1,1,2-triphenylethane as an unstable intermediate in the formation of the ethylene III is, of course, consistent with the mechanistic proposal for the tetraphenylethane above. However, III could potentially arise from the dehydrobromination of II. It was observed though that II was stable under the reaction conditions. The preparation of a comparison sample was carried out with phosphorus tribromide (reported) and the corresponding alcohol and by the reaction of hydrogen bromide on the same alcohol (unreported). The course of these reactions was followed by proton NMR and failed to show any elimination to the ethylene at room temperature. It, therefore, appears that the ethylene III must arise from the tertiary bromide as proposed.

Experimental Section

Tetraphenylethane was kindly provided by Professor P. D. Bartlett. 1,1,2-Triphenylethane was prepared by the method of Hauser and Hamrick.[3] Comparison samples of triphenyl- and tetraphenylethylene were from Aldrich. Samples of 1,2-dibromo-1,1,2-triphenylethane and 1-bromo-1,2,2-triphenylethylene were prepared by the procedures of Meisenheimer and Schlichenmaier.[4]

1-Bromo-1,2,2-triphenylethane. A sample (1 g) of 1,2,2-triphenylethanol (mp 87–88 °C, prepared by the conventional Grigard reaction of phenylmagnesium bromide with diphenylacetaldehyde) in 10 mL of chloroform was treated with 2 mL of phosphorus tribromide at room temperature overnight. The mixture was poured into water and extracted with methylene chloride. The extract was recovered by rotary evaporation under vacuum. Crystallization of the residue from hexane gave 250 mg of 1-bromo-1,2,2-triphenylethane, mp 116–118 °C (see NMR parameters below). Anal. Calcd for $C_{20}H_{17}Br_2$: C, 71.22; H, 5.08. Found: C, 71.40; H, 5.20.

Proton NMR Data. Proton NMR spectra were determined in deuteriochloroform on a Varian EM 390. The aromatic region of proton chemical shifts for these compounds is sufficiently complex as to preclude a detailed analysis. However, prominent peaks could often be used to confirm or deny the presence of a given compound suggested by other NMR evidence. A brief summary of pertinent proton NMR data follows: 1,1,2-triphenylethane, AB_2 system, δ_A 4.18, δ_B 3.30, J = 7.8 Hz; tetraphenylethane, δ 4.96 (1 H); triphenylethylene, δ 6.80 (1 H); 1,2,2-triphenylethanol, AB system, δ_A 4.18, δ_B 5.30, J = 8 Hz; 1-bromo-1,2,2-triphenylethane, AB system, δ_A 4.65, δ_B 5.57, J = 11.4 Hz; 1,2-dibromo-1,1,2-triphenylethane, δ 6.10 (1 H).

Carbon-13 NMR Data. Carbon-13 spectra were determined in deuteriochloroform at 15 MHz on a JEOL FX-60 using an 8K transform. The chemical shifts for 1,1,2-triphenylethane, tetraphenylethane, 1,1,2-triphenylethylene, and tetraphenylethylene have been given before.[5] The aromatic regions for the molecules of interest frequently badly overlapped. Consequently, only those assignments of interest in this study are given here: 1-bromo-1,2,2-triphenylethane, C-1, 57.4, C-2, 60.3; 1,2,2-triphenylethanol, C-1, 76.8, C-2, 60.3; 1,2-dibromo-1,1,2-triphenylethane, C-1, 59.4, C-2, 77.3; 1-bromo-1,2,2-triphenylethylene, C-1, 122.1, C-2, 141.0 (assignment uncertain).

Brominations. All photobrominations were carried out by using 0.5 mmol of 1,1,2-triphenylethane or 1,1,2,2-tetraphenylethane (167 mg) in the appropriate amount of carbon tetrachloride (either 1 mL for 0.5 M reagents or 10 mL for 0.05 M reagents) with either 1 or 2 equiv of bromine. Reactions were conducted under nitrogen by using a standard fluorescent light for illumination. Upon completion of the reaction the solutions were evaporated under reduced pressure and taken up in deuteriochloroform, and the proton and carbon NMR spectra were determined. Product yields were estimated by integration of the proton NMR peaks or, where that was not feasible, by a comparison of peak heights.

Acknowledgment. The generous support of The Robert A. Welch Foundation is hereby gratefully acknowledged.

(2) W. B. Smith, *J. Magn. Reson.*, **23**, 365 (1976).

(3) C. R. Hauser and P. J. Hamrick, *J. Am. Chem. Soc.*, **79**, 3142 (1957).

(4) J. Meisenheimer and W. Schlichemaier, *Justus Liebigs Ann. Chem.*, **456**, 144 and 146 (1927).

(5) T. W. Proulx and W. B. Smith, *J. Magn. Reson.*, **23**, 477 (1976).

Registry No. II, 18495-77-7; III, 58-72-0; IV, 74064-34-9; 1,1,2,2-tetraphenylethane, 632-50-8; 1,1,2,2-tetraphenylethylene, 632-51-9; 1,1,2-triphenylethane, 1520-42-9; bromine, 7726-95-6; 1,2,2-triphenylethanol, 2294-93-1; 1-bromo-1,2,2-triphenylethylene, 1607-57-4.

Exclusive Ortho α-Chloroacetylation of Phenols

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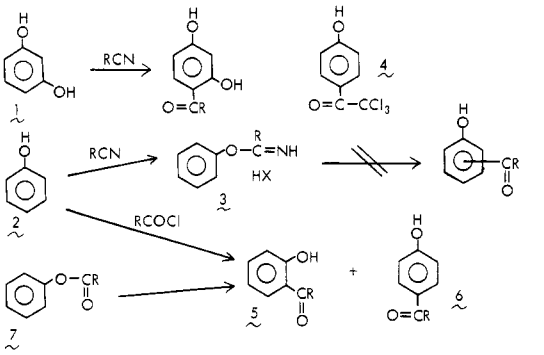
Received June 19, 1980

Resorcinol (1) can be easily acylated on the aromatic ring by treatment with nitriles in the presence or absence of Lewis acids such as zinc chloride or aluminum chloride in acidic medium (Houben–Hoesch reaction), while in contrast, phenol (2) itself can not be ring-acylated by a similar treatment, giving only a salt of iminomethyl phenyl ether (3) (Scheme I). Moreover, an attempt at thermal rearrangement of 3 gives no ring-acylated product by treatment with or without acidic catalyst. The only exception is that 2 reacts with trichloroacetonitrile, giving directly 4-(trichloroacetyl)phenol (4).[1a] On the other hand, Friedel–Crafts reaction of 2 or anisole with acyl chloride in the presence of various acidic catalyst gives 2- and 4-ring-acylated products (5 and 6), with a predominant amount of the latter in all cases.[1b] Further, Fries rearrangement of phenol esters (7) always gives a mixture of 5 and 6.[1c] Thus, no regioselective ortho-acylation reaction of 2 has been known to date.

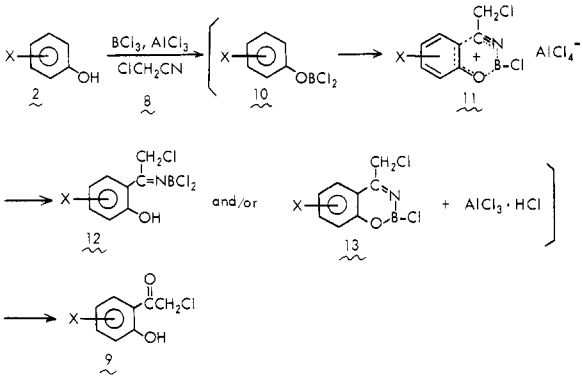
By continuing studies of our previously reported specific ortho-substitution reaction of aniline,[2] we found that using a combination of boron trichloride and aluminum trichloride could solve this problem. Namely, the reaction of 2 and chloroacetonitrile (8) in the presence of boron trichloride and aluminum trichloride in dichloromethane, dichloroethane, or benzene at room temperature or under reflux gave, after acidic workup, 2-hydroxy-α-chloroacetophenone (9) exclusively. The desired product could also be obtained by using phenyldichloroborane[3] instead of boron trichloride (Table I, run 4). The presence of from 0.1 to 1 mol equiv of aluminum trichloride was indispensable, because the reaction did not proceed with boron trichloride or phenyldichloroborane alone. Therefore, we assumed that aluminum trichloride might stabilize very unstable phenoxydichloroborane 10[4] (Scheme II) initially formed, which otherwise would have easily decomposed into triphenoxyborane and boron trichloride under disproportionation, in order to generate a stabilized intermediate such as tetrachloroaluminate (11).[5] From 11, (2-hydroxyphenyl ketimino)chloroborane (12 and/or 13) may be formed and aluminum trichloride regenerated.

The clear difference between our method and the conventional "Houben–Hoesche" reaction[1a] could be seen in

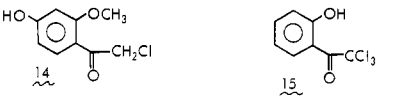
Scheme I



Scheme II



runs 11 and 14. Namely, the product in run 11 was **9g** whereas the conventional method gave the isomer **14**, in which the introduced carbon chain was situated para to the hydroxy group. In run 14, our method gave only 2-(trichloroacetyl)phenol (**15**), while in contrast, the conventional one afforded the 4-isomer (**4**) exclusively.



We tested the addition of other Lewis acids instead of aluminum trichloride and found that zinc or stannic chloride or titanium tetrachloride gave **9** only in 5–8% yield and ferric chloride gave, at best, only a 20% yield.

The compound **9** series gave reasonable analytical[10] and spectral data, namely, broad bands at about 3000 to 3100 cm^{-1} (strongly hydrogen-bonded OH) and peaks at about 1650 cm^{-1} (C=O) in the IR spectra and reasonable absorption bands in the NMR spectra (see Table I).

The limitation of this reaction was that the phenols having an electron-withdrawing group gave the desired product only in poor to modest yields. For example, chlorophenols gave the corresponding products in the yields shown in runs 6–8, indicating the effect of ortho,para orientation with deactivation due to the chloro substituent, and a similar reaction of 2- and 4-nitrophenols gave only the starting materials. As a further limitation, acetonitrile or benzonitrile did not react with 2 under these conditions. But our method is very convenient for obtaining compounds **9**, which are useful starting materials for preparing 2*H*-benzofuranones, intermediate compounds for the synthesis of natural and biologically interesting substances.[11]

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