Acknowledgment. We wish to thank the National Science Foundation for a generous grant which supported this work. We also wish to thank Dr. Eric Nordlander for helpful discussions, and to acknowledge technical assistance from H. Mains who carried out some preliminary studies.

Carbonium Ions with Multiple Neighboring Groups. I. Synthesis[1a]

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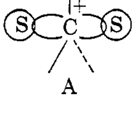
Abstract: Carbonium ions with more than one neighboring group available for interaction with the cation center are an unexplored class of considerable potential interest. Among the phenomena expected are fluctuating coordinated structures, intramolecular solvation, and possibly pentacoordination of carbon. This paper describes the synthesis of 26 substituted triphenylcarbinols, and the related carbonium ions, as well as five benzophenone derivatives. The subsequent paper details studies on the interaction between the neighboring groups and carbonium ion (and ketone) centers.

The chemistry of neighboring group interactions has played a dominant role in the study of carbonium ions.[2] In a sense the coordination of an oxygen or sulfur or halogen atom from a neighboring group with a carbon cation center is a form of internal solvation of such a center. In contrast to typical solvent molecules, however, the atom in the neighboring group is readily identified chemically and spectroscopically because of its additional attachment to the carbonium ion. Furthermore, in cases where internal solvation is sterically possible it generally has great entropy advantages over the analogous interaction with a similar solvent molecule from the external environment. Remarkably, no study has apparently yet been undertaken of carbonium ions with more than one neighboring group available for participation. We felt that such species might have a number of interesting properties.

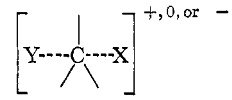
1. **Fluctuating Structures.** If one after the other of the neighboring nucleophilic groups becomes coordinated with the carbon cation, one should have species which are perpetually undergoing nucleophilic substitution reactions. These would be at the least chemical curiosities, and they might also be useful in adding to our general understanding of such reactions.

2. **Doubly Solvated Ions.** According to the Doering–Zeiss hypothesis[3] two solvent molecules may interact with a carbonium ion by coordination on the two faces (A). Despite some efforts to detect this phenomenon by kinetic means[4] there is not yet good evidence for the type of pentacoordinate carbon represented in A. Extensive work has been done on two other types of pentacoordinate carbon: the carbons in molecules with delocalized π electrons have three σ bonds and two partial π bonds, while carbons in nonclassical carbonium ions, and in hexamethyldialuminum,[5] have pentacoordinate carbons in which a single lobe of a hybrid orbital is involved in three-center bonding. Pentacoordination of the trigonal-bipyramid type, as in A, is, of course, well known for silicon and other elements below the first row, and is presumably found in CH_5^+, detectable in the mass spectrometer.[6] If a structure such as A represents an important mode of solvation of carbonium ions, this might be detected in at least some molecules with two neighboring groups able to take up positions on the two carbon faces.



A

3. **The SN2 Intermediate.** Pentacoordinate species related to A represent real reaction intermediates in substitution reactions at elements below the first row, such as silicon.[7] For the SN2 reaction at carbon, considerable interest has centered around the question of whether the trigonal bipyramid (B) is an intermediate (at the bottom of some kind of energy well) or simply an unstable atomic configuration along the reaction path. There is no solid evidence yet available



B

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[1] (a) Partial support by the Hoffman-La Roche Research Foundation is gratefully acknowledged; (b) NSF Postdoctoral Fellow, 1964–1965; (c) NIH Predoctoral Fellow, 1966–1967.

[2] For a partial review, *cf.* A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[3] W. von E. Doering and H. H. Zeiss, *J. Am. Chem. Soc.*, **75**, 4733 (1953).

[4] C. G. Swain and E. E. Pegues, *ibid.*, **80**, 812 (1958), and earlier papers.

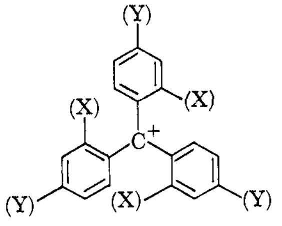
[5] For review, *cf.* K. Ziegler in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 5.

[6] Reference to studies on this long-known species can be found in F. H. Field and M. S. Munson, *J. Am. Chem. Soc.*, **87**, 3289 (1965).

[7] C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, pp 103–113; *cf.* J. Y. Carey and R. West, *J. Am. Chem. Soc.*, **85**, 4035 (1963), for an isolated pentacoordinate siliconium ion.

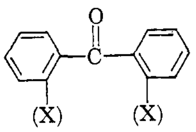
on this point. Since the difference between A and B is chiefly a matter of charge distribution, a species like B might be observable for carbonium ions in which two neighboring groups coordinate strongly enough to remove most of the charge from the carbons.

In order to investigate these questions we have synthesized a number of *ortho*-substituted triphenylmethyl cations (C). Substituents X are various possible neighboring groups, while substituents Y are various conjugating groups. The advantages of this particular choice are several. First, cations of type C are easily synthesized. Second, this type of carbonium ion is stable in a variety of media, and olefin formation by loss of a proton is not possible. Against this is the disadvantage that the positive charge in C will be in general appreciably delocalized, so that solvation at a particular carbon atom may be less likely here. The geometry of C is good, since models show that the X groups we use are essentially forced to lie on the faces of the central carbon atom. On the other hand, various effects which may result from increased twisting of the phenyl groups in C must be corrected for. The visible–ultraviolet spectra of C can be used to study structures with particular X and Y groups, and the extent of interaction of X with the carbonium ion can be modified by varying both the carbon basicity of X and, by changing Y, the electrophilicity of the central carbon. It is also of interest that the important kinetic work which has been done[4] to study the molecularity of carbonium ion solvation was concerned with triphenylmethyl cation.



C

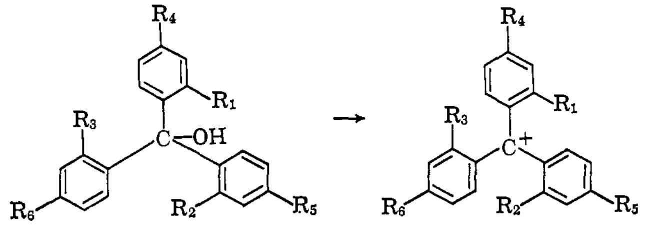
In the course of this work methods also become available for the synthesis of substituted benzophenones (D) in which, again, the X groups are potential internal solvent molecules. Solvation effects on the ultraviolet spectra of ketones are well known.[8] With our compounds D we have tried to investigate the number of solvent molecules with which the ketone actually interacts.



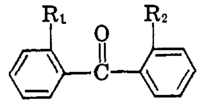
D

In this paper we describe the synthesis of the relevant compounds: the carbinols (I), cations (II), and ketones (III) given in Chart I; all substituents are H unless otherwise specified. The subsequent paper is concerned with the investigation, by physical methods, of their precise structures and properties.

Chart I

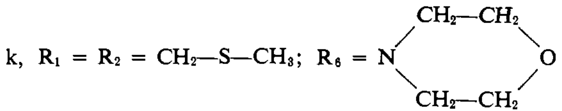


I II



III

a, $R_1 = CH_2{-}S{-}CH_3$
b, $R_1 = R_2 = CH_2{-}S{-}CH_3$
c, $R_1 = R_2 = R_3 = CH_2{-}S{-}CH_3$
d, $R_1 = CH_2{-}S{-}CH_3$; $R_5 = OCH_3$
e, $R_1 = R_2 = CH_2{-}S{-}CH_3$; $R_6 = OCH_3$
f, $R_1 = R_2 = CH_2{-}S{-}CH_3$; $R_4 = R_5 = R_6 = OCH_3$
g, $R_4 = N(CH_3)_2$
h, $R_1 = CH_2{-}S{-}CH_3$; $R_5 = N(CH_3)_2$
i, $R_1 = R_2 = CH_2{-}S{-}CH_3$; $R_6 = N(CH_3)_2$
j, $R_1 = R_2 = CH_2CH_2CH_3$; $R_6 = N(CH_3)_2$

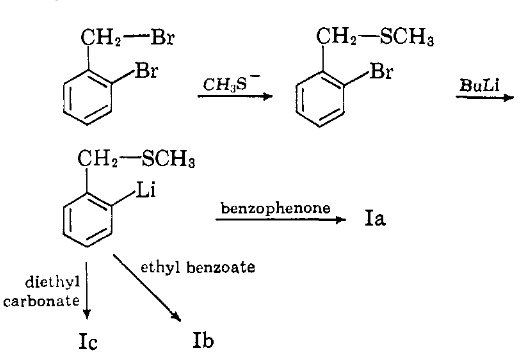


k, $R_1 = R_2 = CH_2{-}S{-}CH_3$; $R_6 = N(CH_2{-}CH_2)_2O$

l, $R_1 = CH_2{-}SO_2{-}CH_3$
m, $R_1 = R_2 = CH_2{-}SO_2{-}CH_3$
n, $R_1 = R_2 = R_3 = CH_2{-}SO_2{-}CH_3$
o, $R_1 = CH_2{-}O{-}CH_3$
p, $R_1 = R_2 = CH_2{-}O{-}CH_3$
q, $R_1 = R_2 = R_3 = CH_2{-}O{-}CH_3$
r, $R_1 = CH_2{-}CH_2{-}CH_3$
s, $R_1 = R_2 = CH_2{-}CH_2{-}CH_3$
t, $R_1 = R_2 = R_3 = CH_2{-}CH_2{-}CH_3$
u, $R_1 = CH_2{-}CH_2{-}CH_2{-}CH_3$
v, $R_1 = R_2 = CH_2{-}O{-}CH_3$; $R_6 = N(CH_3)_2$
w, $R_1 = SCH_3$
x, $R_1 = R_2 = SCH_3$
y, $R_4 = SCH_3$
z, $R_4 = R_5 = SCH_3$

Results

The synthetic scheme is straightforward. *o*-Bromobenzyl bromide was converted into the ether or thioether and this was treated with *n*-butyllithium. The resulting *o*-lithiobenzyl derivative was added to benzophenone, ethyl benzoate, or diethyl carbonate to produce, respectively, the mono-, bis-, or tris-substituted triphenylcarbinol.



By use of appropriate modifications of this scheme carbinols Ia–Iz were prepared. These were converted into isolated characterized carbonium ion salts (or cyclized isomers) in several cases, but generally the cations were prepared in solution and characterized spectroscopically, as is described in the accompanying

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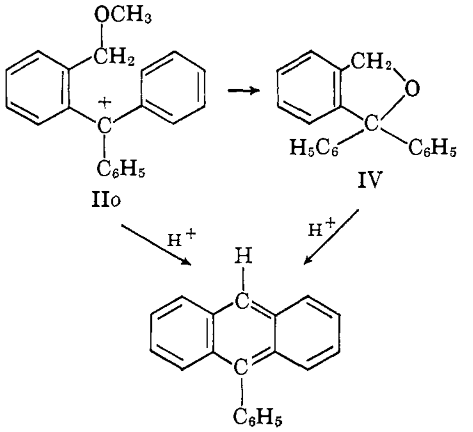
(8) *Cf.* H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962.

paper. In every case the cations or cation solutions were quenched to the starting carbinols in good yield by addition of base; in a few cases this quenching was very slow, as the next paper describes.

Some of the cation solutions decomposed with time, and for these the physical measurements were done immediately. In the case of *o*-(methoxymethyl)triphenylmethyl cation (IIo) it was found that the decomposition in solution leads to α,α-diphenyldihydroisobenzofuran (IV), and that this is further converted by the acid medium into 9-phenylanthracene. The other decompositions were not investigated in detail, but kinetic instability of such species as the *o*-bis-*n*-propyl (IIs) and tris-*n*-propyl (IIt) cations in acid solution is surprising and deserves further study.



The ketones IIIa, IIIb, IIIl, IIIm, and IIIs were prepared from our intermediates. Thus, reaction of *o*-lithiobenzyl methyl sulfide with benzonitrile, and acid hydrolysis of the product imine, affords IIIa. IIIb was prepared conveniently, but in low yield, by the addition of carbon dioxide to the above organolithium, while IIIl and IIIm, the sulfones, were obtained by oxidation of IIIa and IIIb. Finally, the di-*n*-propyl ketone IIIs was obtained by reaction of *o*-lithio-*n*-propylbenzene with ethyl formate and oxidation of the resulting benzhydrol.

Experimental Section[9]

o-**Bromobenzyl Methyl Sulfide.** To a solution of sodium ethoxide (2.6 g of sodium in 48 ml of ethanol) at 0° was added 7.1 ml of methanethiol, followed by addition of 30 g of *o*-bromobenzyl bromide over a period of 15 min. The resulting heterogeneous mixture was refluxed for 35 min after which 44 ml of ethanol was distilled off through a 6-in. Vigreaux column. Extraction with ether and distillation afforded 23.1 g (88%) of *o*-bromo-(α-thiomethoxy)toluene, bp 104–107° (5.2 mm). *Anal.* Calcd for C_8H_9BrS: C, 44.25; H, 4.15. Found: C, 44.35, 44.34; H, 4.31, 4.07.

The nmr spectrum (neat) consisted of complex absorption at δ 7.8–6.8 and singlets at δ 3.68 and 1.91; the areas were in the ratio 4.2:2.0:3.0.

m-**Bromomethyl-***p***-bromoanisole.** A mixture of 45 ml of carbon tetrachloride, 15 g of *p*-bromo-*m*-methylanisole,[10] 13.3 g of N-bromosuccinimide, and 0.6 g of benzoyl peroxide was heated from room temperature to reflux over a period of 25 min. Soon after the start of the reflux period the solution turned orange. After 10 min the spontaneous heating had stopped and almost immediately thereafter the solution became colorless. The mixture was filtered and evaporation of the filtrate yielded 13.2 g (63%) of crude product, mp 83–88°. Recrystallization of this material from low-boiling petroleum ether (bp 30–60°) yielded material melting at 91.0–91.7°, whose nmr spectrum ($CDCl_3$) consisted of complex absorption at δ 7.5–6.6 and singlets at δ 4.52 and 3.74. *Anal.* Calcd for $C_8H_8Br_2O$: C, 34.32; H, 2.88; Br, 57.08. Found: C, 34.24; H, 2.97; Br, 57.65.

2-Bromo-5-methoxy-α-thiomethoxytoluene. The above bromomethylanisole was converted into 2-bromo-5-methoxy-α-thiomethoxytoluene as described for *o*-bromobenzyl methyl sulfide. Distillation of the reaction product afforded a 79% yield of material, bp 120–122° (2.7 mm), which solidified after distillation, mp 33–35°. The nmr spectrum (neat) consisted of complex aromatic absorption, a slightly split singlet at δ 3.78–3.80, and a singlet at δ 1.95 with relative areas of 3.0:5.0:3.0. The analytical sample was recrystallized from hexane. *Anal.* Calcd for $C_9H_{11}BrOS$: C, 43.74; H, 4.49. Found: C, 43.61; 43.81; H, 4.38, 4.47.

o-**Bromo-***n***-propylbenzene** was prepared from *o*-bromobenzaldehyde by reaction with ethylmagnesium bromide, dehydration, and hydrogenation using the procedure which has been reported[11] for the *meta* isomer. The compound, bp 42–44° (2 mm) (lit.[12] bp 217° (760 mm)), has the expected nmr spectrum with typical propyl multiplets and a pattern in the aromatic region characteristic of *ortho* substitution. The compound could also be prepared as described[12] by direct bromination of *n*-propylbenzene. We found the isolation in a pure state required preparative vpc, and the procedure was less convenient synthetically.

Ethyl *p***-(4-Morpholinyl)benzoate.** A mixture of 50 g (0.3 mol) of ethyl *p*-aminobenzoate and 16 g (0.11 mol) of β,β'-dichlorodiethyl ether was heated at 200° for 2 hr, then cooled. The resulting yellow solid was extracted with ether for several hours in a Soxhlet apparatus; removal of ether afforded 15 g of crude product. Recrystallization from ether yielded 6.2 g (28%), mp 81.5–82.5°. *Anal.* Calcd for $C_{13}H_{17}O_3N$: C, 66.36; H, 7.28. Found: C, 66.63, 66.46; H, 7.32, 7.54. The nmr spectrum was as expected, with typical ethyl, morpholinyl, and *para*-disubstituted benzene multiplets.

o-**Bromothioanisole.**[13,14] A mixture of 105 ml of quinoline, 35 ml of pyridine, 25 g of *o*-dibromobenzene, and 12.8 g of cuprous methyl mercaptide was heated for 3 hr at 160–180° with stirring under reflux. The standard work-up, followed by rough vacuum distillation and preparative vpc (5-ft Carbowax, 230°), afforded 5.3 g (25%) of pure product, along with 3.0 g of *o*-dibromobenzene and 1.0 g of *o*-bis(thiomethoxy)benzene. The nmr spectrum showed a four-proton multiplet at δ 7.4–6.58 characteristic of *ortho*-disubstituted benzene, and a three-proton singlet at δ 2.28.

p-**Bromothioanisole.** Applying the above procedure to *p*-dibromobenzene, with isolation by extraction and alumina chromatography, afforded a 17% yield of the product, mp 38.5–40° (lit.[14] mp 37°), along with 12% of *p*-bis(thiomethoxy)benzene, mp 77–80° (lit.[15] mp 85°). The monosulfide has an nmr spectrum with four aromatic protons as an AB quartet centered at δ 7.28, and three protons at δ 2.36.

Substituted Triphenylcarbinols. Nmr spectra of these compounds are presented in the accompanying paper.

o,o'-**Bis(thiomethoxymethyl)triphenylcarbinol (Ib).** To 12 ml of a 21.8% (by weight) solution of *n*-butyllithium in hexane (0.024 mol) in a 100-ml three-necked flask under N_2 at 0° was added a solution of 5.3 g (0.024 mol) of *o*-bromobenzyl methyl sulfide in 10 ml of anhydrous ether over 10 min. After stirring for 1 hr, 1.9 g (0.012 mol) of ethyl benzoate in 10 ml of anhydrous ether was added over 10 min. After 1 additional hr of stirring, 10 ml of H_2O was added and the resulting precipitate was collected and recrystallized from hexane: 1.95 g (62%), mp 107–108°, raised to 108–108.5° on a second recrystallization. *Anal.* Calcd for $C_{23}H_{24}OS_2$: C, 72.59; H, 6.34; S, 16.83. Found: C, 72.75; H, 6.49; S, 16.82.

In a similar manner, the following triarylcarbinols were prepared.

o-**(Methoxymethyl)triphenylcarbinol (Io)** was obtained in 71% yield from *o*-bromobenzyl methyl ether[16] (1 equiv) and benzophenone (1 equiv), mp 113–115°. *Anal.* Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 83.24; H, 6.55.

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[9] Nmr spectra are referred to an internal tetramethylsilane standard; melting points are determined with a calibrated thermometer.

[10] R. A. B. Bannard and L. C. Leith, *Can. J. Chem.*, **34**, 1464 (1956).

[11] C. S. Marvel and D. G. Botteron, *J. Am. Chem. Soc.*, **63**, 1482 (1941).

[12] J. H. Lamneck, Jr., *ibid.*, **76**, 1106 (1954).

[13] Our procedure is adapted from that of *Org. Syn.*, **42**, 22 (1962), for the preparation of *o*-phenylene bisthiomethyl ether.

[14] T. van Hove, *Bull. Soc. Chim Belges*, [5] **12**, 930 (1927).

[15] Th. Zincke and W. Frohneberg, *Chem. Ber.*, **42**, 272 (1909).

[16] F. G. Hollinen and F. G. Mann, *J. Chem. Soc.*, 1634 (1947).

o,o'-**Bis(methoxymethyl)triphenylcarbinol (Ip)** was obtained in 100% yield from *o*-bromobenzyl methyl ether (2 equiv) and ethyl benzoate (1 equiv), mp 145–147°. *Anal.* Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.69; H, 7.02.

o,o',o''-**Tris(methyloxymethyl)triphenylcarbinol (Iq)** was obtained in 48% yield from *o*-bromobenzyl methyl ether (3 equiv) and diethyl carbonate (1 equiv), mp 122.5–123.8°. *Anal.* Calcd for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 76.45; H, 7.23.

o-**(Thiomethoxymethyl)triphenylcarbinol (Ia)** was obtained in 41% yield from *o*-bromobenzyl methyl sulfide (1 equiv) and benzophenone (1 equiv), mp 112.5–113.5°. *Anal.* Calcd for $C_{21}H_{20}OS$: C, 78.71; H, 6.28; S, 10.00. Found: C, 79.14; H, 6.36; S, 9.74.

o,o',o''-**Tris(thiomethoxymethyl)triphenyl carbinol (Ic)** was obtained in 53% yield from *o*-bromobenzyl methyl sulfide (3 equiv) and diethyl carbonate (1 equiv), mp 76–78°, second mp 91–92°, after ether extraction, alumina chromatography, and crystallization from hexane. *Anal.* Calcd for $C_{25}H_{28}OS_3$: C, 68.14; H, 6.40; S, 21.83. Found: C, 68.37; H, 6.37; S, 21.47.

o-**Mono-*n*-propyltriphenylcarbinol (Ir)** was obtained in 60% yield from *o*-bromopropylbenzene (1 equiv) and benzophenone (1 equiv), mp 71.8–73.0° after ether extraction, alumina chromatography, and crystallization from hexane. *Anal.* Calcd for $C_{22}H_2O$: C, 87.42; H, 7.29. Found: C, 87.57; H, 7.59.

o,o'-**Bis-*n*-propyltriphenylcarbinol (Is)** was obtained in 52% yield from *o*-bromopropylbenzene (2 equiv) and ethyl benzoate (1 equiv), mp 49–51° after ether extraction, vacuum distillation, and slow crystallization. *Anal.* Calcd for $C_{25}H_{28}O$: C, 87.21; H, 8.14. Found: C, 87.35; H, 8.53.

o,o',o''-**Tris-*n*-propyltriphenylcarbinol (It)** was obtained in 24% yield from *o*-bromopropylbenzene (3 equiv) and diethyl carbonate (1 equiv), mp 66.5–78.5° after ether extraction, alumina chromatography, and crystallization from hexane. *Anal.* Calcd for $C_{28}H_{34}O$: C, 87.05; H, 8.81. Found: C, 86.78; H, 9.12.

o-**(Thiomethoxymethyl)-*p'*-methoxytriphenylcarbinol (Id)** was obtained in 16% yield from *o*-bromobenzyl methyl sulfide (1 equiv) and *p*-methoxybenzophenone (1 equiv), mp 87–89° after ether extraction, alumina chromatography, and crystallization from hexane. *Anal.* Calcd for $C_{23}H_{22}O_2S$: C, 75.39; H, 6.33; S, 9.15. Found: C, 75.39; H, 6.57; S, 9.01.

o,o'-**Bis(thiomethoxymethyl)-*p''*-methoxytriphenylcarbinol (Ie)** was obtained in 47% yield from *o*-bromobenzyl methyl sulfide (2 equiv) and ethyl *p*-anisate (1 equiv), mp 110–111° after ether extraction, alumina chromatography, and crystallization from hexane. *Anal.* Calcd for $C_{24}H_{26}O_2S_2$: C, 70.21; H, 6.38; S, 15.62. Found: C, 70.34; H, 6.48; S, 15.56.

o,o'-**Bis(thiomethoxymethyl)-tri-*p*-anisylcarbinol (If)** was obtained from 2-bromo-5-methoxy-α-thiomethoxytoluene (2 equiv) and ethyl *p*-anisate (1 equiv) as an oil which was converted into the perchlorate (IIf ClO_4^-) without further purification.

o-*n*-**Butyltriphenylcarbinol (Iu)** was obtained in 30% yield from *o*-bromo-*n*-butylbenzene (1 equiv) and benzophenone (1 equiv), mp 58–59° after ether extraction, chromatography on alumina, and crystallization from hexane. *Anal.* Calcd for $C_{23}H_{24}O$: C, 87.34; H, 7.84. Found: C, 87.16; H, 7.72.

p-**Dimethylaminotriphenylcarbinol (Ig)** was obtained in 51% yield from ethyl *p*-dimethylaminobenzoate and excess phenyllithium, mp 83.5–85° after crystallization from hexane. *Anal.* Calcd for $C_{21}H_{21}NO$: C, 83.17; H, 6.93; N, 4.62. Found: C, 83.20; H, 6.57; N, 4.62.

o-**(Thiomethoxymethyl)-*p'*-dimethylaminotriphenylcarbinol (Ih)** was obtained in 40% yield from *o*-bromobenzyl methyl sulfide (1 equiv) and *p*-dimethylaminobenzophenone (1 equiv), mp 115–117° after ether extraction, chromatography on *basic* alumina, and crystallization from hexane with Norite treatment. *Anal.* Calcd for $C_{23}H_{25}NOS$: C, 75.98; H, 6.95. Found: C, 75.43; H, 7.40.

o,o'-**Bis(thiomethoxymethyl)-*p''*-dimethylaminotriphenylcarbinol (Ii)** was obtained in 70% yield from *o*-bromobenzyl methyl sulfide (2 equiv) and ethyl *p*-dimethylaminobenzoate (1 equiv), mp 121.50 123.5° on crystallization from benzene--hexane.[17] *Anal.* Calcd for $C_{25}H_{29}NOS_2$: C, 70.92; H, 6.86; N, 3.31. Found: C, 71.10; H, 7.03; N, 3.54.

o,o'-**Bis-*n*-propyl-*p''*-dimethylaminotriphenylcarbinol (Ij)** was obtained in 72% yield from *o*-bromo-*n*-propylbenzene (2 equiv) and ethyl *p*-dimethylaminobenzoate (1 equiv) as an oil after ether extraction and chromatography. The nmr spectrum was in accord with this structure, and the compound was converted directly into its perchlorate (IIj ClO_4^-).

o,o'-**Bis(methoxymethyl)-*p''*-dimethylaminotriphenylcarbinol (Iv)** was obtained in 72% yield from *o*-bromobenzyl methyl ether (2 equiv) and ethyl *p*-dimethylaminobenzoate (1 equiv), mp 127.50 128.5° after ether extraction, alumina chromatography, and crystallization from hexane with Norite treatment. *Anal.* Calcd for $C_{25}H_{29}NO_3$: C, 76.68; H, 7.48. Found: C, 76.65, 76.74; H, 7.75, 7.78.

o,o'-**Bis(thiomethoxymethyl)-*p''*-(4-morpholinyl)triphenylcarbinol (Ik)** was obtained in 49% yield from *o*-bromobenzyl methyl sulfide (2 equiv) and ethyl *p*-(4-morpholinyl)benzoate (1 equiv), mp 144–145° after crystallization from ethanol. *Anal.* Calcd for $C_{27}H_{32}NO_2S_2$: C, 69.48; H, 6.92. Found: C, 69.52; H, 6.80.

o-**Thiomethoxytriphenylcarbinol (Iw)** was obtained in 97% yield from *o*-bromothioanisole (1 equiv) and benzophenone (1 equiv), mp 94–96°. *Anal.* Calcd for $C_{20}H_{18}OS$: C, 78.38; H, 5.93. Found: C, 78.08; H, 6.16.

o,o'-**Bis(thiomethoxy)triphenylcarbinol (Ix)** was obtained in 92% yield from *o*-bromoanisole (2 equiv) and ethyl benzoate (1 equiv), mp 146–148°. *Anal.* Calcd for $C_{21}H_{20}OS_2$: C, 71.58; H, 5.73. Found: C, 71.24; H, 5.81.

p-**Thiomethoxytriphenylcarbinol (Iy)** was obtained in 67% yield from *p*-bromothioanisole (1 equiv) and benzophenone (1 equiv) after molecular distillation as an oil with bands in the nmr at δ 7.8–6.7 (14.5 protons), 2.9 (1 proton), and 2.35 (3 protons).

p,p'-**Bis(thiomethoxy)triphenylcarbinol (Iz)** was obtained in 65% yield from *p*-bromothioanisole (2 equiv) and ethyl benzoate (1 equiv), mp 112–113.5° after crystallization from hexane–2-butanone. *Anal.* Calcd for $C_{21}H_{20}OS_2$: C, 71.58; H, 5.73. Found: C, 71.42, 71.76; H, 5.42, 5.52.

o-**(Methanesulfonylmethyl)triphenylcarbinol (Il)** was prepared in 71% yield by treating a 2% solution of Ia in CH_2Cl_2 with excess O_3 at Dry Ice temperature for 6 min, followed by solvent removal and silica gel chromatography, mp 154.5–155.5° after crystallization from aqueous ethanol. *Anal.* Calcd for $C_{21}H_{20}O_3S$: C, 71.59; H, 5.68. Found: C, 71.80; H, 5.78.

The infrared spectrum showed sulfone bands at 1120 and 1290 cm^{-1}, and the nmr spectrum showed aromatic protons at δ 7.5–6.4 (15 H), and singlets at 4.3 (2.1 H) and 2.7 (3 H).

o,o'-**Bis(methanesulfonylmethyl)triphenylcarbinol (Im)** was obtained by ozone oxidation of Ib, or with excess *m*-chloroperbenzoic acid in $CHCl_3$ in 63% yield, mp 209–210° after crystallization from hexane. *Anal.* Calcd for $C_{23}H_{24}O_5S_2$: C, 62.16; H, 5.41. Found: C, 62.22, 62.17; H, 5.43, 5.64.

The infrared spectrum had peaks at 1125 and 1300 cm^{-1}, and the nmr spectrum was as expected.

o,o',o''-**Tris(methanesulfonylmethyl)triphenylcarbinol (In)** was obtained by oxidation of Ic with either O_3 or *m*-chloroperbenzoic acid, mp 243–245° dec after crystallization from ethanol–acetone. *Anal.* Calcd for $C_{25}H_{28}O_7S_3$: C, 55.97; H, 5.22. Found: C, 55.61, 55.41; H, 5.19, 5.18.

The infrared spectrum showed bands at 1280 and 1120 cm^{-1}. The nmr spectrum (DMSO-d_6) shows aromatic absorption from δ 8.0 to 6.1 (12 H), an AB quartet at 5.15 and 4.15 (J_{AB} = 18 cps, 6 H), and singlets at 3.17 (1 H) and 3.05 (9 H).

Triarylmethyl Perchlorates. Nmr spectra and electronic spectra are presented in detail in the accompanying paper.

o-**(Thiomethoxymethyl)triphenylmethyl Perchlorate (IIa).** To a solution of 0.85 g of Ia in 10.5 ml of acetic anhydride at 0° was added, dropwise, 0.87 ml of 71% $HClO_4$. Addition of 25 ml of anhydrous ether to the resulting orange solution and storage at −20° for 22 hr afforded 0.93 g (86%) of white solid, mp 197.0–197.3° (sealed capillary; the solid turns black at 195°). *Anal.* Calcd for $C_{21}H_{19}ClO_4S$: C, 62.61; H, 4.75; Cl, 8.80; S, 7.96. Found: C, 62.67, 62.51; H, 5.11, 4.88; Cl, 8.88, 8.62; S, 8.03, 7.86.

The nmr spectrum (SO_2) shows aromatic protons at δ 7.7–7.4 (14 H), an AB quartet at 5.09 and 4.53 (J_{AB} = 16 cps, 2.1 H), and a singlet at 2.45 (2.9 H).

o-**(Thiomethoxymethyl)-*p'*-methoxytriphenylmethyl perchlorate (IId)** was prepared similarly, mp 171.5–172°. *Anal.* Calcd for $C_{22}H_{21}ClO_5S$: C, 61.04; H, 4.89; Cl, 8.19; S, 7.38. Found: C, 60.36; H, 5.04; Cl, 7.98; S, 7.22.

o-*n*-**Butyltriphenylmethyl perchlorate (IIu)** was prepared similarly, mp 105–107°. *Anal.* Calcd for $C_{23}H_{23}ClO_4$: C, 69.26; H, 5.77; Cl, 8.91. Found: C, 69.07; H, 5.95; Cl, 9.00.

o,o'-**Bis-*n*-propyl-*p''*-dimethylaminotriphenylmethyl Perchlorate (IIj).** To a solution of 1.15 g of Ij in the minimum amount of ethanol was added 2.0 g of 70% perchloric acid. From the result-

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(17) This compound and all other *p*-dimethyaminotriphenylcarbinols described in this paper are difficult to handle and purify since they are extremely sensitive to acid, even that found in alumina, Norite, or in laboratory air.

ing red solution, 1.0 g of an orange solid was precipitated by the addition of ether. This material was recrystallized twice from acetonitrile–ether to give 0.73 g of an orange solid, mp 175–178°. *Anal.* Calcd for $C_{27}H_{32}NClO_4$: C, 68.99; H, 6.88. Found: C, 69.01, 68.99; H, 7.19, 7.04.

o,*o*′-**Bis(thiomethoxymethyl)tris-*p*-anisylmethyl perchlorate (IIf)** was prepared similarly, except that water was added to the ethanol solution rather than ether, to yield a pink solid, mp 96–100°. *Anal.* Calcd for $C_{26}H_{29}S_2ClO_7$: C, 56.45; H, 5.30. Found: C, 56.45, 56.74; H, 5.57, 5.42.

Triarylmethyl trifluoracetates were prepared from the corresponding carbinols by shaking with trifluoroacetic anhydride for 40–60 hr, removing the dense anhydride phase, and vacuum drying. They were used for nmr studies without further purification; in several cases sharp-melting solids were obtained.

α,α-Diphenyldihydroisobenzofuran (IV) was prepared by heating 2.6 g of *o*-(methoxymethyl)triphenylcarbinol (Io) with 1.5 ml of acetyl chloride and 3.0 ml of benzene for 3 hr, then stirring at room temperature for 2 days. Volatile material was evaporated and the solid residue recrystallized from hexane to yield 1.4 g (62%) of a product, mp 99–101°. *Anal.* Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 87.74; H, 5.94. The nmr spectrum showed aromatic absorption at δ 7.6–7.0 (14.5 H) and a singlet at 5.12 (2 H).

o-**(Thiomethoxymethyl)benzophenone (IIIa)** was prepared in 51% yield by reaction of *o*-bromobenzyl methyl sulfide (1 equiv) with butyllithium (1 equiv) in ether for 1 hr, followed by reaction overnight with benzonitrile (1 equiv) and overnight hydrolysis of the resulting imine in 30% H_2SO_4 at 90°, mp 54–55° after extraction, alumina chromatography, and crystallization from ethanol. *Anal.* Calcd for $C_{15}H_{14}OS$: C, 74.33; H, 5.83. Found: C, 74.32; H, 5.84.

The infrared spectrum has carbonyl absorption at 1650 cm^{-1}, and the nmr shows aromatic protons at δ 7.9–7.1 (10 H), and singlets at 3.8 (1.9 H) and 1.83 (3.0 H).

o,*o*′-**Bis(thiomethoxymethyl)benzophenone (IIIb)** was prepared in low (7%) yield by treating the *o*-lithiobenzyl methyl sulfide solution with solid CO_2, added in small portions, and separation of the neutral from the acidic products, mp 73–74° after alumina chromatography and crystallization from ethanol. *Anal.* Calcd for $C_{17}H_{18}OS_2$: C, 67.50; H, 6.01. Found: C, 67.60; H, 5.94.

The nmr spectrum showed aromatic protons at δ 7.6–7.2 (8.3 H), and singlets at 4.00 (4.0 H) and 1.99 (6.0 H).

o-**(Methanesulfonylmethyl)benzophenone (IIIl)** was formed in 60% yield by oxidation of IIIa with excess *m*-chloroperbenzoic acid. After neutral alumina chromatography the oil was homogeneous by tlc and vpc. *Anal.* Calcd for $C_{15}H_{14}O_3S$: C, 65.66; H, 5.15. Found: C, 65.50; H, 5.37.

The nmr spectrum showed absorption at δ 8.0–7.2 (9.4 H), and singlets at 4.62 (1.9 H) and 2.79 (3.0 H).

o,*o*′-**Bis(methanesulfonylmethyl)benzophenone (IIIm)** was formed similarly in 85% yield from IIIb, mp 210–212° after crystallization from ethanol. *Anal.* Calcd for $C_{17}H_{18}O_5S_2$: C, 55.71; H, 4.96. Found: C, 56.22; H, 5.06.

The infrared spectrum showed bands at 1660, 1125, and 1280 cm^{-1}. The nmr spectrum showed aromatic absorption at δ 7.7–7.3 (8.3 H), and singlets at 4.80 (3.8 H) and 2.85 (6.0 H).

o,*o*′-**Bis-*n*-propylbenzophenone (IIIs).** A mixture of 12.4 ml of a 15% (by weight) solution of *n*-butyllithium in hexane and 3.7 g (0.019 mol) of *o*-bromo-*n*-propylbenzene in 10 ml of anhydrous ether was treated with 0.6 g (0.0093 mol) of ethyl formate in the standard fashion. Normal work-up by ether extraction yielded 2.5 g of yellow solid.

This material was dissolved in 20 ml of acetone and treated at a −5° with 3.5 ml of 2.67 *M* Jones reagent. Addition of isopropyl alcohol to reduce the excess chromic acid, addition of 100 ml of water, and ether extraction gave 2.1 g of a yellow oil. Rough vacuum distillation using a Hickman still followed by preparative vapor phase chromatography on a 4 ft × $^3/_8$ in., 25% SE 30 column at 250° yielded 0.50 g (20%) of product, whose nmr spectrum ($CDCl_3$) consisted of complex absorption at δ 7.8–6.8 and multiplets centered at δ 2.8, 1.65, and 0.9, with relative areas of 8.2:3.8:4.05:6.0, respectively. *Anal.* Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.56; H, 8.06.

Decomposition of Io in Acid. When Io dissolved in 60% H_2SO_4, a yellow solution of the cation IIo was produced, as evidenced by its electronic and nmr spectra, and immediate quenching of this solution with $NaHCO_3$ led to quantitative recovery of Io. On standing for 24 hr, a solution of Io in CF_3CO_2H deposited a solid in 72% yield identified as 9-phenylanthracene, mp 153–155° (lit.[18] 156°), by the identity of its ultraviolet spectrum with that reported.[19] *Anal.* Calcd for $C_{20}H_{14}$: C, 94.49; H, 5.51. Found: C, 94.32; H, 5.44.

Solutions of IIp and IIq in H_2SO_4 were similarly unstable, but the products were not characterized.

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