group in place of *p*-methoxyphenyl, but possibly in the other position because of much smaller F^{19} chemical shift difference between the trifluoromethyl groups. The steric bulk of the *t*-butyl group could change the orientation in addition.

8. With Aluminum Chloride.—A solution of 2.70 g (0.010 mol) of quinonemethide **1a** in methylene chloride was added to 1.33 g (0.010 mol) of anhydrous aluminum chloride in 15 ml of methylene chloride. After about one-third of the quinonemethide solution was added, a dark green color developed, and a mild exothermic reaction was noted. After addition was complete, the solution was stirred for about 1 hr and filtered under nitrogen to separate a white precipitate, 0.88 g. The greenish black mother liquor was evaporated under nitrogen leaving 2.84 g of a tan solid streaked with green. The ir and nmr spectra of these two solids were almost identical and showed the same proton nmr spectra as the starting quinonemethide but with a chemical shift to lower field. In the ir spectra, the carbonyl absorption at 1640 cm^{-1} was weak and broad. The first precipitate above was hydrolyzed in water and extracted into methylene chloride; it was shown by melting point, mixture melting point, and infrared and nuclear magnetic resonance spectra to be the benzyl chloride **2a**.

Notes

Perhalo Ketones. XIV.[1]

7,7-Bis(trifluoromethyl)quinonemethide

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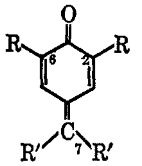
Received December 27, 1967

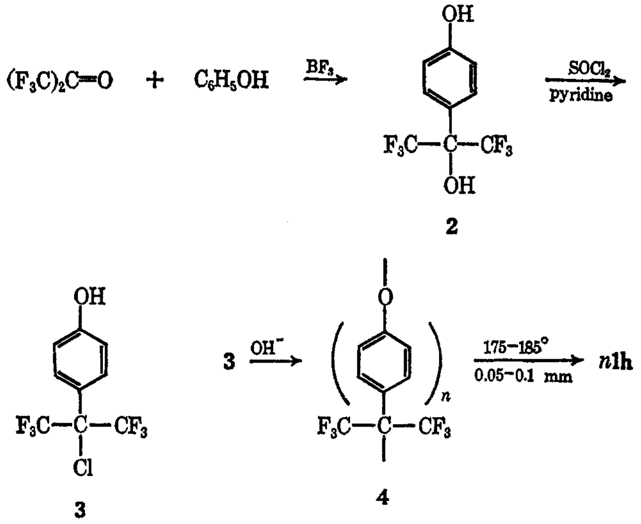
Although *p*-benzoquinonemethides (**1**) containing highly conjugated systems, such as **1i**, are stable,[2] those in which R′ is hydrogen or alkyl have required the presence of alkyl groups in the 2,6 positions to permit isolation in dilute solution. Thus, 2,6-di-*t*-butylquinonemethide with no C-7 substituents (**1a**) could be prepared only in dilute solution, and dimerized on attempted isolation.[3] 2,6-Di-*t*-butyl-7,7-dialkylquinonemethides (**1b**)[4] and 2,6-dimethyl-7,7-dicyanoquinonemethide (**1c**)[5] have been isolated as stable compounds. Sheppard[6] has recently prepared fluoroalkylquinonemethides with R′ = $-CF_3$ or $-CF_2Cl$, and with R = CH_3 or *t*-butyl (**1d**, **e**, and **f**), and has found them to be stable at temperatures even considerably above room temperature. He concluded that the presence of alkyl substituents in the 2,6 positions was essential for stability. We wish to report the preparation and isolation of 7,7-bis(trifluoromethyl)quinonemethide (**1h**), a compound without 2,6 substitution but stable at room temperature in pure form for a short time, and for at least several weeks in solution.



1a, R = *t*-butyl; R′ = H
b, R = *t*-butyl; R′ = alkyl
c, R = CH_3; R′ = CN
d, R = CH_3; R′ = CF_3
e, R = *t*-butyl; R′ = CF_3
f, R = CH_3; R′ = CF_2Cl
g, R = Br; R′ = CF_3
h, R = H; R′ = CF_3
i, R = H; R′ = C_6H_5

Compound **1h** was prepared from phenol and hexafluoroacetone *via* **2**[7] and **3**[8] (Scheme I).

Scheme I



The structure of 7,7-bis(trifluoromethyl)quinonemethide (**1h**) is quite clear from its infrared and nmr spectra. In carbon tetrachloride solution its infrared spectrum exhibited bands at 6.1 and 6.2 μ ascribed to the conjugated carbonyl group,[3,6] and strong C–F absorption in the 8–9-μ region.

Its nmr spectrum in carbon tetrachloride solution consisted of AA′BB′ spin pattern (of an $AA'BB'X_3X_3'$ system) with A calculated δ 7.68 and B at δ 6.59 (J_{AB} = 10.5 Hz). The A portion shows fine structure due to coupling with the CF_3 groups: $(J_{AX} \cong J_{AX'} \cong J_{A'X} \cong$

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[1] Perhalo Ketones. XIII: R. E. A. Dear, E. E. Gilbert, *J. Org. Chem.* **33**, 819 (1968).

[2] A. Bistrzycki and C. Herbst, *Ber.*, **36**, 2335 (1903).

[3] J. D. McClure, *J. Org. Chem.*, **27**, 2365 (1962); L. J. Filar and S. Winstein, *Tetrahedron Lett.*, **25**, 9 (1960).

[4] A. Hubele, H. Suhr, and U. Heilmann, *Ber.*, **95**, 639 (1962); C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **78**, 3797 (1956).

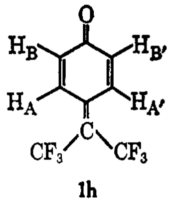
[5] H. H. Takimoto, G. C. Denault, and L. O. Krbechek, *J. Org. Chem.*, **29**, 1899 (1964).

[6] W. A. Sheppard paper presented at the Fourth International Fluorine Symposium, Estes Park, Colo., July 24–28, 1967.

[7] B. S. Farah, E. E. Gilbert, M. Litt, J. A. Otto, and J. P. Sibilia, *J. Org. Chem.*, **30**, 1003 (1965).

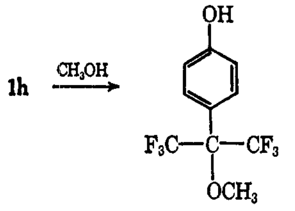
[8] I. L. Knunyants, C. Ching-Yun, N. P. Gambaryan, and E. M. Rokhlin, *Zh. Vses. Khim. Obshch.*, **5**, 114 (1960); *Chem. Abstr.*, **54**, 20962 (1960).

$J_{A'X'} \leq 2$ Hz) (width at approximately one-half peak height); $J_{AA'}$, $J_{BB'}$, $J_{AB'} \cong J_{A'B}$ were not calculated; $J_{BX} \cong J_{BX'} \cong J_{B'X} \cong J_{B'X'} \cong 0$. The ^{19}F nmr spectrum of **1h** showed a partially resolved complex multiplet at 57.6 relative to $CFCl_3$ with spacings of 0.70 Hz. This reaction sequence, except for the last step, is the same as that employed by Sheppard for preparing compounds **1d**, **e**, and **f**, since those quinonemethides are stable in the presence of base. He observed, however, that only polymer resulted during an attempted similar preparation of **1g**; this was also noted by us in the attempted basic conversion of **3** into **1h**. We then found that polymer **4** could be thermally depolymerized to **1h** at low pressure, the product being trapped at liquid nitrogen temperature. This technique may be applicable to the preparation of other base-sensitive quinonemethides.



1h

Compound **1h** is an orange-yellow solid at liquid nitrogen temperature, melting at room temperature to an orange liquid with a spicy odor, properties also characteristic of compounds **1d**, **e**, and **f**. At room temperature, pure **1h** soon polymerizes. As expected,[6] **1h** reacts with methanol at room temperature.

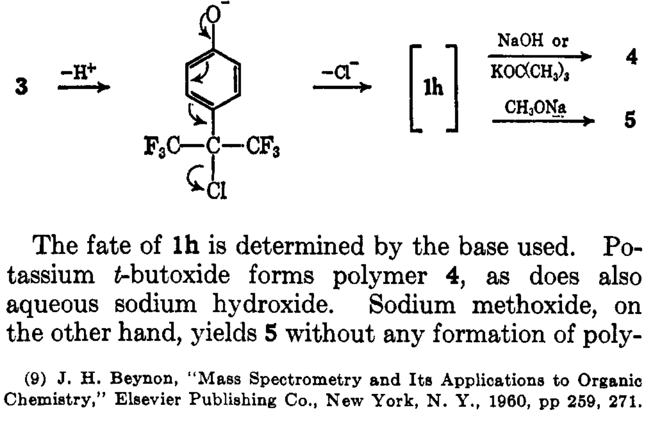


5

The mass spectrum obtained from the thermal decomposition of the polymer **4** at 200° showed a parent ion of *m/e* 242 $(\mathbf{1h})^+$ and a characteristic fragment ion of *m/e* 214, presumably 6,6-bis(trifluoromethyl)fulvene; corresponding to the loss of CO. Similar cracking patterns are reported for cyclic ketones such as anthraquinone and fluorenone.[9]

The conversion of **3** into **4** is thought to take the course given in Scheme II.

SCHEME II



The fate of **1h** is determined by the base used. Potassium *t*-butoxide forms polymer **4**, as does also aqueous sodium hydroxide. Sodium methoxide, on the other hand, yields **5** without any formation of polymer. The unusually high reactivity of the chlorine atom in **3** was shown by the fact that compound $C_6H_5C(CF_3)_2Cl$ (**6**) failed to form an analogous derivative, even under much more drastic conditions.

Experimental Section

Melting and boiling points are uncorrected. The proton nmr spectra were obtained on a Varian A-60 spectrometer with tetramethylsilane as an internal reference; ^{19}F spectrum was run on a Hitachi Perkin-Elmer Model R-20 spectrometer at 56.4 Mc; the infrared spectrum was run on a Perkin-Elmer Model 521 spectrophotometer. The microanalyses were carried out in this laboratory's Analytical Department by Mr. G. Mohler and Schwarzkopf Microanalytical Laboratory.

Hexafluoroacetone and phenol–boron trifluoride complex were obtained from Industrial Chemicals Division, Allied Chemical Corp., Morristown, N. J.

1-(2-Hydroxyhexafluoro-2-propyl)-4-hydroxybenzene (**2**).—Phenol–boron trifluoride complex (128 g, comprising 1.0 mol of phenol and 0.5 mol of boron trifluoride) and toluene (100 ml) were mixed and hexafluoroacetone (bp −28°) was slowly admitted with efficient stirring as fast as reaction occurred; the presence of excess ketone was indicated by refluxing. The ketone (150 g, 0.90 mol) was introduced over 8 hr at 30–35°. The mixture was stirred at room temperature overnight, and then diluted with 600 ml of hexane. The crude dark brown residue was filtered, washed with *n*-hexane, and recrystallized from toluene (decolorizing carbon) to give 103 g (43%) of product, mp 120–123.5°. A second recrystallization from *n*-hexane gave **2**, mp 122–123.5° (lit. mp 127–130°,[7] 122.5–123.5° [8]).

1-(2-Chlorohexafluoro-2-propyl)-4-hydroxybenzene (**3**).—To a mixture of **2** (52 g, 0.20 mol) and pyridine (4 g) at room temperature was added excess thionyl chloride (80 g, 0.66 mol) dropwise (10 min). The mixture was then heated slowly to 105° over a period of 1 hr and maintained at 105 ± 1.0° for 45 min. Excess thionyl chloride was removed under reduced pressure and the resulting residue diluted with 1 l. of ice water to give 55.5 g (99%) of crude product. Two recrystallizations from carbon tetrachloride gave pure **3** as white needles, mp 107–111° (lit.[8] mp 112–112.5°).

Anal. Calcd for $C_9H_5F_6OCl$: C, 38.78; N, 1.79; Cl, 12.75. Found: C, 38.54; N, 1.92; Cl, 12.9.

Polymeric 7,7-Bis(trifluoromethyl)quinonemethide (**4**).—To a mixture of **3** (5.6 g, 0.02 mol) and potassium *t*-butoxide (2.5 g, 0.022 mol) at room temperature was added 40 ml of *t*-butyl alcohol. The resulting reaction mixture was refluxed 1 hr, cooled to room temperature, and filtered through a sintered glass filter. The crude product was washed with hot water overnight (Soxhlet apparatus) to remove potassium chloride, and air dried to give 4.8 g (99%) of crude **4** as an amorphous white powder. In a capillary tube it softened and melted between 175 and 185°.

Anal. Calcd for $C_9H_4F_6O$: C, 44.6; H, 1.60. Found: C, 44.4; H, 1.74.

7,7-Bis(trifluoromethyl)quinonemethide (**1h**).—Finely powdered polymer **4** (0.5 g, 0.002 mol) was outgassed by heating in a Wood's metal bath up to 175° at 0.05 mm. The temperature was then slowly raised to 190–195° and held there for 1 hr to effect depolymerization to **1h**, which was trapped as an orange-yellow solid at liquid nitrogen temperature. With maintenance of vacuum, the trap containing the crude **1h** was warmed to room temperature, whereupon **1h** is distilled into a second cold trap. Conversions to **1h** in several runs were 60–70%, with 0 15–0.20 g of solid distillation residue. For spectral study, it was briefly exposed to air as it was dissolved in carbon tetrachloride.

1-(2-Methoxyhexafluoro-2-propyl)-4-hydroxybenzene 5).—A mixture of **3** (1.4 g, 0.005 mol), sodium methoxide (1.1 [illegible] 0.020 mol), and absolute methanol (20 ml) was heated at reflux with stirring for 2 hr (Drierite trap). After cooling to room temperature, 5 ml water was added. The clear solution was acidified with concentrated hydrochloric acid, diluted with 200 ml of ice water, stirred for 30 min and filtered to give 1.1 g (80%) of crude **5**. One recrystallization from petroleum ether, bp 30–60°, gave pure product, mp 79–83°.

Anal. Calcd for $C_{10}H_8F_6O_2$: C, 43.8; H, 2.92. Found: C, 43.74; H, 3.00.

The nmr spectrum (deuteriochloroform) displayed the characteristic signal for the methoxyl protons at δ 3.47 (three protons, J = 1 Hz, septet, tentative), a broad singlet at δ 5.28

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(9) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, pp 259, 271.

(one proton), and the aromatic multiplet at δ 6.8–7.2 (four protons). Compound **5** was also prepared by dissolving **1h** in methanol and evaporating to dryness.

(2-Chlorohexafluoro-2-propyl)benzene (6).—A mixture of (2-hydroxyhexafluoro-2-propyl)benzene[10] (100 g, 0.41 mol), thionyl chloride (100 g, 0.83 mol), and pyridine (5 ml) was refluxed with stirring for 48 hr. After cooling to room temperature, 500 ml of ice water and 500 ml of 1 *N* potassium hydroxide were added. The lower organic layer was separated and the aqueous layer was extracted with 100 ml of methylene chloride. The organic layers were combined, dried over anhydrous magnesium sulfate, and distilled at atmospheric pressure to give 69.5 g (65%) of **6**, bp 159°.

Anal. Calcd for $C_9H_5F_6Cl$: Cl, 13.5. Found: Cl, 13.7.

Attempted Reaction of 6 with Sodium Methoxide.—A mixture of **6** (16 g, 0.061 mol), sodium methoxide (6.5 g, 0.12 mol), and 120 ml of absolute methanol was heated at reflux for 24 hr with stirring, cooled to room temperature, acidified with concentrated hydrochloric acid, and diluted with 1 l. of water. The lower organic layer was separated. The aqueous layer was extracted with 50 ml of methylene chloride and the two organic layers were combined. After drying over anhydrous magnesium sulfate, the solution was distilled at atmospheric pressure to give 9.6 g of unchanged **6**, bp 158–160°, with no evidence for the formation of the desired methoxyl compound.

Registy No.—**1h**, 16878-48-1; **5**, 16878-49-2; **6**, 16878-50-5.

Acknowledgment.—The author wishes to express his gratitude to Dr. E. E. Gilbert and Professors J. Meinwald and M. Litt for helpful discussions and to Dr. B. B. Stewart for his help in interpreting the nmr data.

[10] B. S. Farah, E. E. Gilbert, and J. P. Sibilia, *J. Org. Chem.*, **30**, 998 (1965).

Derivatives of Indeno[2,1-*b*]-1,4-benzothiazine

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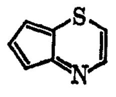
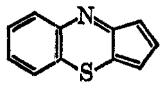
Inasmuch as the applicability of the Hückel ($4n + 2$) π-electron rule[1] to fused heterocyclic systems is still unpredictable, synthesis of systems such as **1**, **2**, and **3**,



1



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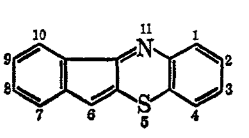
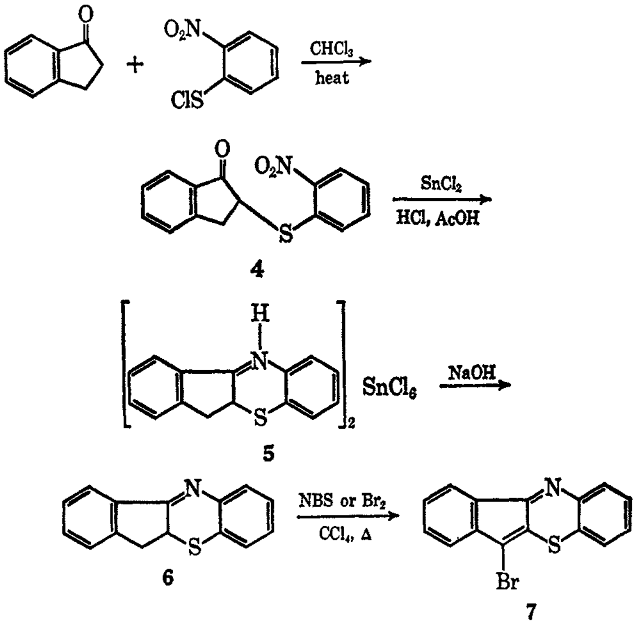


3

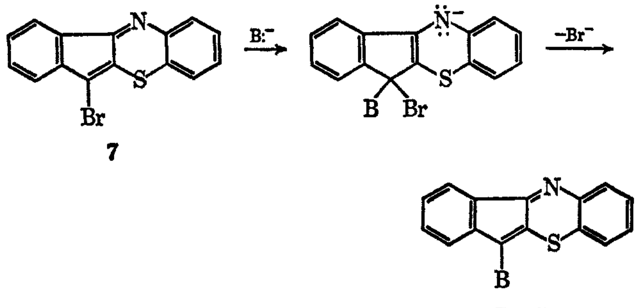
which obey the rule and may show nonclassical aromaticity, is of interest. Neither **1** nor **2** has been prepared to date. Recently, indeno[2,1-*b*]-1,4-benzothiazine (**3**) has been prepared[2] by the condensation of 1,2-indandione with *o*-mercaptoaniline, followed by dehydration. The present paper describes the preparation and properties of some derivatives of **3**.

Initially, the goal of this work was the preparation of the parent compound **3** by a different synthetic route. The approach, which used in part the Zincke procedure,[3] is outlined in Scheme I. Condensation of *o*-nitrophenylsulfenyl chloride with 1-indanone gave 2-(*o*-nitrophenylthio)indanone (**4**) in 66.3% yield. Treatment of **4** with stannous chloride in concentrated hydrochloric acid and glacial acetic acid resulted in reduction and condensation to form bis(5a,6-dihydroindeno[2,1-*b*]-1,4-benzothiazinium) hexachlorostannate(IV) (**5**), in 80.1% yield. The tin complex salt **5**, when shaken with a 10% sodium hydroxide solution, gave a 94.2% yield of 5a,6-dihydroindeno[2,1-*b*]-1,4-benzothiazine (**6**). Dehydrogenation of **6** was effected by treatment with either bromine or N-bromosuccinimide in refluxing carbon tetrachloride. However, instead of obtaining the parent compound **3**, an 84.8% yield of the monobromo derivative, 6-bromoindeno[2,1-*b*]-1,4-benzothiazine (**7**), was obtained as a deep purple solid. This result also occurred using limited amounts of bromine or N-bromosuccinimide, **7** being obtained along with unreacted **6**.

SCHEME I



The location of the bromine atom in **7** was established by the ease with which it underwent nucleophilic aromatic substitution reactions and by the products obtained from these reactions. The 6 position should be activated toward nucleophilic aromatic substitution and a bromine atom located there should be easily replaced by typical nucleophiles. This was found to be the case.



8a, B = SC_6H_5
b, B = CN
c, B = COOH

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[1] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 412–419.

[2] D. Leaver, J. Smolicz, and W. H. Stafford, *J. Chem. Soc.*, 740 (1962).

[3] T. Zincke and H. Rose, *Ann.*, **406**, 103 (1914); T. Zincke and J. Baeumer, *ibid.*, **416**, 86 (1918).