Solvolysis of 1-Bromomethyltriptycene. An Unusually Unreactive Bromide

JAMES W. WILT* AND THOMAS P. MALLOY[1]

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

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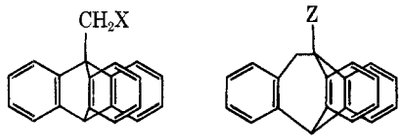
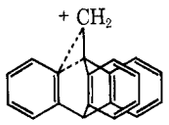
Our interest[2] in the inductive effect of the phenyl group apart from its resonance effect led us to study the solvolysis of the title compound **1**-Br. A phenonium ion type of stabilization for the ion **2** logically produced upon solvolysis of **1**-Br is precluded geometrically. It was hoped, therefore, that the solvolytic reactivity of **1**-Br would reflect rather the inductive influence of these rings upon the stability of **2**. Interestingly, deamination of amine **1**-NH_2 in acetic acid has recently been shown[3] to give "homotriptycene" derivatives **3** by an astounding 1,2-aryl shift that seemingly demands a σ-bonded precursor such as **4**. Whether such a rearrangement would also attend the solvolysis of **1**-Br was an additional point of interest in this study.



1, X = cited function
2, X = +

3, Z = OH, OAc



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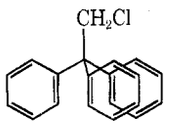

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The synthesis of **1**-Br followed reported procedures used for similar compounds. The synthesis and other relevant reactions are described in the Experimental Section.

Bromide **1**-Br was extraordinarily unreactive under typical solvolysis conditions,[4] but reaction in *m*-cresol[5] at elevated temperatures was finally achieved. First-order kinetic behavior was observed to the limit studied (~80%). The kinetic and activation parameter data are collected in Table I. The solvolysis of highly reactive[6] 2-chloro-1,1,1-triphenylethane (**5**) was studied also for comparison.

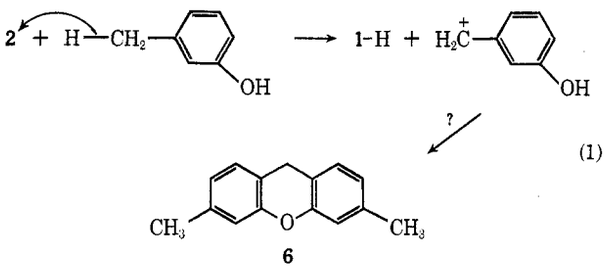
The sole identifiable solvolysis product from **1**-Br was 1-methyltriptycene (**1**-H), isolated in 31% yield. Importantly, however, the solvent-derived product, 3,6-dimethylxanthene (**6**), was isolated in 16.5% yield.

TABLE I
SOLVOLYSIS DATA IN *m*-CRESOL

Halide	Temp, °C	k_1, sec^{-1} [a]	ΔH^*, kcal mol^{-1}	ΔS^*, eu
1-Br	325[b]	4.47×10^{-5}		
	360	6.25×10^{-5}		
	370	1.01×10^{-4}		
	25[c]	4.13×10^{-19}	35.2	−23.9
5[d]	65[e]	3.65×10^{-5}		
	77	1.11×10^{-4}		
	90	2.97×10^{-4}		
	25[c]	6.15×10^{-7}	20.1	−19.7

[a] Precision ±5%. [b] ±1°. [c] Calculated from data at other temperatures. [d] In the presence of 2,4-lutidine. [e] ±0.2°.

A control experiment showed that **6** was not formed in the absence of **1**-Br. Only triphenylethylene was observed as the product from **5**. The sluggish behavior of **1**-Br, the absence of homotriptycyl products, and the formation of **1**-H imply that ion **2** is a highly reactive species formed with considerable difficulty. We suggest that **1**-H was formed *via* hydride transfer from the solvent (eq 1), although this is admittedly conjectural. Nonetheless, xanthene **6** does result from *m*-cresol and acids or bases at elevated temperatures[7] and its formation here lends some credibility to an ionic process leading to **1**-H.



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Homolysis of **1**-Br into radicals is also a possible reaction pathway, although the process was insensitive to the presence of oxygen. We feel, moreover, that the kinetic ΔH^* value is too low[8] for such a process (if nonchain) and that the reaction is more likely a heterolytic one.

The remarkable 10^{12}-fold difference in reactivity at 25° between **1**-Br and **5** deserves some comment. A minimal value of *ca.* $10^{-2.7}$ per aromatic ring for inductive retardation[9] seems inordinately large.[10] Some of the extra retardation may likely be the result of lost solvent stabilization of **2**. A Dreiding model of **2**, as depicted in **7**, indicated peri-type steric hindrance about the cationic center by the adjacent aromatic hydrogens.

The rearrangement reported[3] with **1**-NH_2 may be allowed in its case because no hydride donor was present to trap ion **2**. In fact, deamination of **1**-NH_2 with nitrosyl chloride[3] gave some unrearranged **1**-Cl, pos-

(1) National Science Foundation Trainee, 1968–1970.

(2) J. W. Wilt, H. F. Dabek, Jr., J. P. Berliner, and C. A. Schneider, *J. Org. Chem.*, **35**, 2402 (1970).

(3) S. J. Cristol and D. K. Pennelle, *ibid.*, **35**, 2357 (1970). We thank Professor Cristol for information on this work prior to its publication.

(4) Apropos of this, Cristol and Pennelle[3] reported that **1**-Cl was unchanged upon treatment with silver acetate in acetic acid for 24 hr at 210°.

(5) *Cf.* K. B. Wiberg and B. R. Lowry, *J. Amer. Chem. Soc.*, **85**, 3188 (1963). Bromide **1**-Br is in fact comparable in reactivity (or lack thereof) to the *bridgehead* halides studied by these workers.

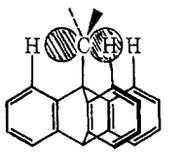
(6) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952), studied the corresponding tosylate and developed the basis for understanding in this area.

(7) *Inter alia*, *cf.* C. Graebe, *Ber.*, **16**, 862 (1883); R. Möhlau, *ibid.*, **49**, 168 (1916). See also S. Wawzonek in "Heterocyclic Compounds," Vol. 2, R. C. Elderfield, Ed., Wiley, New York, N. Y., 1951, p 453.

(8) D(C–Br) is normally 65–70 kcal mol^{-1} in the gas phase, much above the ΔH^* value for **1**-Br. We seriously doubt that some type of "solvation" phenomenon could lower the enthalpy by 30 kcal mol^{-1}.

(9) The tosylate related to **5** is *ca.* 10^4-fold more reactive in acetolysis (50°) than is neopentyl tosylate,[6] undoubtedly because of anchimeric assistance. The 10^{-12} rate found for **1**-Br relative to **5** places **1**-Br roughly at 10^{-8} relative to neopentyl tosylate, or *ca.* $10^{-2.7}$ slower per aromatic ring. Because **5** is undoubtedly somewhat slower in solvolysis than its related tosylate, this extrapolation really gives a minimal value for this "inductive retardation."

(10) A value of *ca.* 10^{-1} seems more likely.[2]



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sibly by capture of 2 prior to rearrangement by chloride ion. In our case, 2 upon formation is surrounded by a potential hydride donor solvent and formation of 1-H is thereby favored, all the more so because eq 1 should be sizably exothermic.

Finally, the relationship of 1-Br to 5 is reminiscent of the similar relationship between 1-triptycyl and triphenylmethyl halides[11] and demonstrates once more the dramatic effect of pinning back the aromatic rings in these compounds.

Experimental Section

General.—Microanalyses were done by Micro-Tech Laboratories, Skokie, Ill., and by M-H-W Laboratories, Garden City, Mich. Spectral data were obtained on Varian A-60A (nmr, $CDCl_3$ solutions) and Beckman IR-5A (ir, KBr discs) instruments.

1-Bromomethyltriptycene (1-Br).—Reaction of yellow 9-bromomethylanthracene, mp 145–147° (lit.[12] mp 137.5–142° dec), anthranilic acid, and isoamyl nitrite in dioxane, as described for similar preparations,[13] led to colorless 1-Br: 39.5% on a 22-mmol scale; mp 217–218.5° from benzene–petroleum ether (bp 30–60°); nmr δ 7.5 (m), 7.0 (m, ArH), 5.37 (s, bridgehead H), 4.85 (s, CH_2Br).

Anal. Calcd for $C_{21}H_{15}Br$: C, 72.63; H, 4.35. Found: 72.61; H, 4.31.

Crude product from this reaction was yellow. Purification was tedious, requiring chromatography on silica gel for final processing. Use of carboxybenzenediazonium chloride[14] as the benzyne precursor in this reaction gave 1-Br contaminated with 1-Cl (82.5:17.5), probably *via* some prior conversion of 9-bromomethylanthracene to its 9-chloro analog by chloride ion displacement. Chloride 1-Cl was apparent from its $-CH_2Cl$ resonance at δ 5.07.[3]

2-Chloro-1,1,1-triphenylethane (5).—The chloride was prepared as reported,[15] mp 99–101° (lit.[14] mp 101.0–101.8°), nmr δ 7.33 (s, ArH), 4.67 (s, CH_2Cl).

Solvolysis Studies.—*m*-Cresol was purified by distillation from zinc dust, bp 50–52° (0.5 mm), homogeneous by glpc. The solvolysis was conducted on *ca.* 0.02 *M* solutions of purified 1-Br in *m*-cresol sealed in Carius tubes, following closely a reported procedure.[5] A Carius tube furnace equipped with a thermocouple for temperature measurement was used. The reactions were carried to ~80% completion and processed as reported.[5] The liberated bromide was titrated potentiometrically at 25° with standard 80% ethanolic silver nitrate (0.010 *M*), using a Leeds and Northrup Model 7402 pH meter. The kinetic data are given in Table I.

The solvolysis product from 1-Br was isolated from the titrated samples by removal of silver bromide by filtration and *m*-cresol by codistillation with water followed by chromatography of the residue on a silica gel column. Elution with petroleum ether (bp 30–60°) gave **3,6-dimethylxanthene (6)**: 16.5% based on 1-Br; mp 195–200° (lit.[16] 197.5–203.5°); ir, nmr, and uv spectra agreed with those reported;[16] mass spectrum (70 eV) *m/e inter alia*, 210 (P), 209 (P − 1), 195 (P − CH_3). Elution with benzene–petroleum ether gave **1-methyltriptycene** (1-H, 31% based on consumed 1-Br, melting point, mixture melting point with authentic sample, and nmr spectrum agreed with those reported[3]). No other characterizable products were eluted. No homotriptycyl products were detected. A control study of *m*-cresol itself at 370° for 6 hr afforded no 6. Degassed reaction conditions showed no difference.

Chloride 5 was solvolyzed analogously. Sealed ampoules containing *ca.* 0.02 *M* solutions of 5 in *m*-cresol with an equimolar amount of redistilled 2,4-lutidine added were held at various temperatures. Processing and chloride determination were as described above. See Table I for further details. From reactions taken to *ca.* 80% completion, the only product isolated (chromatography on silica gel) was **triphenylethylene**, 95% based on consumed 5, mp and mmp with authentic material 67.5–68.5°, coincidental ir and nmr spectra.

Miscellaneous.—Among the triptycenes prepared in this study were those following. Their syntheses followed standard or cited procedures and their properties are briefly reported here for documentation purposes.

1-Diazoacetyltriptycene was yellow: mp 220–222° dec; 89% from 9-triptoyl chloride and diazomethane in ether; λ 4.8, 6.14 ($COCHN_2$); nmr δ 8.02 (m, 3, peri ArH's), 7.45 (m), 7.08 (m, remaining ArH's), 5.80 (s, $-CHN_2$), 5.42 (s, bridgehead H).

Anal. Calcd for $C_{22}H_{14}ON_2$: C, 81.97; H, 4.37; N, 8.69. Found: C, 81.67; H, 4.40; N, 8.41.

1-Chloroacetyltriptycene was colorless: mp 200–202°; 85% from reaction of the diazo ketone above and hydrogen chloride[17] in tetrahydrofuran at 50°; λ 5.82 (CO); nmr δ 7.75 (m, 3, peri ArH's), 7.50 (m), 7.10 (m, remaining ArH's), 5.40 (s, bridgehead H), 4.80 (s, $-CH_2Cl$).

Anal. Calcd for $C_{22}H_{15}OCl$: C, 79.88; H, 4.57. Found: C, 80.07; H, 4.59.

1-Triptycylacetic acid was colorless: mp 298–300°; 10% from the above diazo ketone upon uv irradiation in 20% aqueous tetrahydrofuran;[18] λ 3.3 (broad) 5.82 (COOH); nmr δ 9.6 (broad s, COOH), 7.33 (m), 7.03 (m, ArH), 5.40 (s, bridgehead H), 4.03 (s, CH_2).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.23; H, 5.33.

Attempted conversion of the diazo ketone above to this acid using silver benzoate and triethylamine in methanol[19] followed by saponification gave intractable material. Reaction of silver 1-triptycylacetate with bromine in carbon tetrachloride to form 1-Br seemed partially successful. However, the easier preparation given above made further work on this reaction unnecessary.

Registry No.—1 (X = Br), 34858-83-8; **5**, 33885-01-7; *m*-cresol, 108-39-4; triphenylethylene, 58-72-0; 1-diazoacetyltriptycene, 34887-50-8; 1-chloroacetyltriptycene, 34858-85-0; 1-triptycylacetic acid, 34858-86-1.

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Intramolecular Addition of 4-Alkynyloxy Radicals

JEAN-MARIE SURZUR,* CLAUDE DUPUY, MICHÈLE PAULA BERTRAND, AND ROBERT NOUGUIER

Laboratoire associé au C.N.R.S. no. 126, Centre de St. Jerome, Université de Provence, 13—Marseille-13eme, France

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It was recently reported by Rieke and Cooke, that alkoxy radicals fail to add intramolecularly to alkynes.[1] Analysis of the photolysis products of several 4-alkynyl nitrites has provided us with evidence for the occur-

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