solvent removed from the filtrate to yield an oil which crystallized on the addition of 3 mL of 95% ethanol, wt 1.04 g (3.75 mmol, 75%), mp 94–96 °C. Recrystallization from 95% ethanol yielded an analytical sample: mp 95–96 °C; IR (KBr) 3010, 2960, 2940, 2880, 1720 (C=O), 1470, 1350, 1098, 1050, 1026, 1018, 980, 765, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.9–7.3 (m, 4, *o*-disubstituted Ar), 7.20 (s, 5, Ph), 6.81 (d, 1, =CHPh, *J* = 12.2 Hz), 5.92 (d, 1, =CHC, *J* = 12.2 Hz), 4.18–3.63 (m, 3, OCH$_2$CH$_A$N),[13] 3.50–2.88 (m, 1, CH$_B$N).[13]

Anal. Calcd for C$_{18}$H$_{15}$NO$_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.23; H, 5.54; N, 5.04.

Registry No. **1a**, 100-52-7; **1b**, 104-88-1; **1c**, 104-87-0; **1d**, 123-11-5; **1e**, 555-16-8; **1f**, 99-61-6; **3a**, 74591-93-8; **3b**, 74591-94-9; **3c**, 74591-95-0; **3d**, 74591-96-1; **3e**, 74591-97-2; **3f**, 74591-98-3; **4a**, 74591-99-4; **4b**, 74592-00-0; **4c**, 74592-01-1; **4d**, 74592-02-2; **4e**, 74609-62-4; **4f**, 74592-03-3; **5a**, 74592-04-4; **5b**, 74592-05-5; **6a**, 74592-06-6; **6b**, 74592-07-7; **7**, 74592-08-8; **8**, 74592-09-9; *N*-(3-bromopropyl)phthalimide, 5460-29-7; triphenyl(3-phthalimidopropyl)phosphonium bromide, 7743-29-5; phenylacetylene, 536-74-3; *N*-(2-bromoethyl)-phthalimide, 574-98-1; *trans*-*p*-chlorocinnamaldehyde, 1075-77-0; 1-nitro-4-(*p*-chlorophenyl)-1,2-butadiene, 74592-10-2.

Neopentyl *p*-Toluenesulfonate Solvolysis. A Study of Response to Solvent Ionizing Strength

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Much experimental and theoretical evidence has been collected to support the contention that cyclopropyl-carbinyl derivatives solvolyze with σ-participation, leading to the formation of a set of rapidly equilibrating non-classical cationic intermediates.[2,3] Although controversy continues to surround the precise nature of these cationic intermediates,[2c,3c] the present understanding[3,4] indicates that, unlike the neophyl system,[5] delocalization of charge in the carbocation-like transition state takes place not by bridging[6] but via a greatly enhanced hyperconjugative

interaction between the 2p (C$^+$) orbital and the exocyclic ring orbitals.[3c,7]

Recently,[4a] we proposed an experimental procedure for distinguishing between delocalization of charge by enhanced hyperconjugation and delocalization of charge by bridging. The procedure adopted was an extension of the test used by Winstein to establish the existence of discrete k_Δ and k_s pathways in the solvolysis of 2-phenyl-1-ethyl-OTs,[5] *n*-Pr-OTs,[8] and related systems.[9] Specifically, the rates of solvolysis of cyclopropylcarbinyl-OPms were plotted against the solvolysis rates (k_t) of neophyl-OTs.

It was found that such a plot yielded not a quantitative correlation, as reported by Winstein for substrates solvolyzing by the k_Δ pathway,[5,8,9] but instead yielded a dispersion with lines of different slopes for ethanol/water on the one hand and the carboxylic acids formic and acetic on the other. On the basis of the mechanistic significance assigned to k_t for neophyl-OTs (delocalization of charge in a carbocation-like transition state by bridging) and the predominantly k_Δ process followed in the solvolysis of cyclopropylcarbinyl-OPms,[4a] we ascribed the dispersion to the special properties (delocalization of charge by enhanced hyperconjugation) of the cyclopropylcarbinyl system.

While differences in leaving-group solvation and ion return were deduced to be unlikely explanations for the observed data,[4a] the possibility remains that the dispersion could be due to a different response to medium effects by a phenyl and an alkyl neighboring group.[10] Therefore, an important addition to the previous study is its extension to a primary alkyl substrate whose solvolysis is assisted exclusively by neighboring alkyl participation.

In solvolysis reactions, neopentyl-OTs is a rather good model for a primary alkyl substrate solvolyzing via the k_Δ pathway.[12] Although it is thought that it solvolyzes with alkyl participation without nucleophilic solvent participation,[12,13] the rates of solvolysis of neopentyl-OTs in both ethanol/water and carboxylic acid solvents have not been analyzed for correlation with those of neophyl-OTs. In this paper we report the results of such an analysis which further support the use of the proposed experimental procedure as a probe for distinguishing between delocalization of charge by enhanced hyperconjugation and delocalization of charge by bridging in solvolytic transition states.

In the course of this study we also confirmed the earlier conclusion that the solvent dispersion was not due to differences in leaving-group solvation.

The first-order rate constants for solvolysis of neopentyl

(1) Taken in part from the M.S. thesis submitted to Louisiana Tech University, 1980.

(2) For reviews see the following: (a) H. G. Richey, Jr., "Carbonium Ions", G. A. Olah and P. v. R. Schleyer, Eds., Vol. III, Wiley-Interscience, New York, 1972, Chapter 25; (b) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, ref 2a, Chapter 26; (c) H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, 1977, Chapter 5.

(3) For more recent investigations see the following: (a) G. A. Olah, R. J. Spear, P. C. Hiberty, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 7470 (1976); (b) J. S. Staral, I. Yavari, J. D. Roberts, G. K. Prakash, D. J. Donavan, and G. A. Olah, *ibid.*, **100**, 8016 (1978); (c) J. S. Staral and J. D. Roberts, *ibid.*, **100**, 8018 (1978).

(4) (a) D. D. Roberts and R. C. Snyder, Jr., *J. Org. Chem.*, **44**, 2860 (1979); (b) W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **96**, 302 (1974); (c) W. J. Hehre, *Acc. Chem. Res.*, **8**, 369 (1975); (d) G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.*, **97**, 1539 (1975).

(5) A. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 6546 (1968).

(6) (a) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952); (b) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (c) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5244 (1970); (d) H. C. Brown and C. J. Kim, *ibid.*, **93**, 5765 (1971).

(7) (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Am. Chem. Soc.*, **92**, 829 (1970); (b) D. F. Eaton and T. G. Traylor, *ibid.*, **96**, 1226 (1974); (c) G. A. Olah and G. Liang, *ibid.*, **97**, 6803 (1975); (d) B. A. Levi, E. S. Blurock, and W. J. Hehre, *ibid.*, **101**, 5537 (1979).

(8) I. Lazdins Reich, A. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **91**, 5635 (1969).

(9) A. Diaz and S. Winstein, *J. Am. Chem. Soc.*, **91**, 4300 (1969).

(10) Previously, we found[11] that a series of substituents (including methyl) had the same response to medium effect as phenyl, but this was essentially in a carboxylic acid solvent series. The rates of solvolysis in aqueous alcohols were not investigated.

(11) D. D. Roberts and Chum-Hsiang Wu, *J. Org. Chem.*, **39**, 1570 (1974).

(12) S. H. Liggero, R. Sustmann, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4571 (1969).

(13) Hoffmann[14a] and Mosher[14b] have demonstrated that the solvolysis of neopentyl tosylate in ethanol/water solvents gives rise to some k_s pathway products, but the amount is less than 10%.

(14) (a) G. M. Fraser and H. M. R. Hoffmann, *Chem. Commun.*, 561 (1967); (b) G. Solladie, M. Muskatirovic, and H. S. Mosher, *ibid.*, 809 (1968).

(15) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

(16) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

Table I. Summary of Solvolysis Rate Constants for Neopentyl and Neophyl Arenesulfonates

substrate	solvent[a]	temp, °C	k_t,[b,c] s⁻¹	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
neopentyl-OTs	EtOH	75	$(2.7 \pm 0.08) \times 10^{-8}$	26.1 (±0.2)	−18.3 (±0.1)
		100	$(3.6 \pm 0.07) \times 10^{-7}$ [d]		
	90% EtOH	75	$(9.6 \pm 0.09) \times 10^{-8}$	28.6 (±0.1)	−8.9 (±0.2)
		100	$(1.60 \pm 0.02) \times 10^{-6}$		
	80% EtOH	75	$(2.6 \pm 0.05) \times 10^{-7}$	28.4 (±0.1)	−7.5 (±0.1)
		100	$(4.30 \pm 0.02) \times 10^{-6}$		
	70% EtOH	90	$(3.6 \pm 0.05) \times 10^{-6}$	28.7 (±0.1)	−4.6 (±0.1)
		65	$(1.80 \pm 0.02) \times 10^{-7}$		
	AcOH	74.7	8.32×10^{-8} [e]		
		99.6	1.6×10^{-6} [e]		
	HCOOH	50	8.51×10^{-7} [f]		
		75	1.89×10^{-5} [f]		
neophyl-OTs	90% EtOH	50	$(1.05 \pm 0.02) \times 10^{-6}$	24.8 (±0.3)	−9.5 (±0.1)
		75	$(1.80 \pm 0.01) \times 10^{-5}$		
	80% EtOH	50	2.7×10^{-6} [g]		
		70	$(2.86 \pm 0.02) \times 10^{-5}$		
	70% EtOH	50	$(5.78 \pm 0.03) \times 10^{-6}$	23.1 (±0.1)	−11.2 (±0.1)
		75	$(8.2 \pm 0.1) \times 10^{-5}$		
neophyl-OPms	EtOH	75	$(8.7 \pm 0.05) \times 10^{-7}$	27.0 (±0.4)	−9.0 (±0.6)
		85	$(2.8 \pm 0.05) \times 10^{-6}$		
	90% EtOH	50	$(1.1 \pm 0.05) \times 10^{-7}$	28.7 (±0.2)	−1.9 (±0.1)
		75	$(2.9 \pm 0.08) \times 10^{-6}$		
		85	$(9.1 \pm 0.09) \times 10^{-6}$		
	80% EtOH	50	$(2.9 \pm 0.09) \times 10^{-7}$	27.4 (±0.2)	−4.0 (±0.2)
		75	$(6.8 \pm 0.05) \times 10^{-6}$		
		85	$(2.1 \pm 0.05) \times 10^{-5}$		
	70% EtOH	50	$(7.5 \pm 0.03) \times 10^{-7}$	25.8 (±0.2)	−7.1 (±0.3)
		75	$(1.4 \pm 0.05) \times 10^{-5}$		
	AcOH	50	$(1.6 \pm 0.09) \times 10^{-7}$	25.4 (±0.4)	−6.0 (±0.5)
		75	$(4.00 \pm 0.02) \times 10^{-6}$		
		85	$(9.9 \pm 0.4) \times 10^{-6}$		
	HCOOH	40	$(1.07 \pm 0.03) \times 10^{-5}$	27.1 (±0.3)	−0.4 (±0.4)
		50	$(4.2 \pm 0.1) \times 10^{-5}$		
		60	$(1.3 \pm 0.04) \times 10^{-4}$		

[a] Percent by volume of alcohol in aqueous alcohol mixtures. [b] Errors reported as one standard deviation from the mean. [c] In most cases, the reported rate constants are averages of duplicate runs. [d] Compares with a value of 4.0×10^{-7} s⁻¹ reported by Winstein and Marshall.[15] [e] Reference 6a. [f] Reference 15. [g] Reference 16.

Table II. Summary of Solvent Parameters Derived from the mY Equation[18]

substrate	m_{EW}	m_{AF}	$[k_{EW}/k_{AcOH}]_Y$	$[k_{EW}/k_{HCOOH}]_Y$
neophyl-OTs[a,b]	0.39	0.59	0.37	0.07
neophyl-OPms[c,d]	0.47	0.66	0.35	0.07
neopentyl-OTs[c,d]	0.52	0.56	0.48	0.18

[a] Reference 22. [b] 75 °C. [c] Calculated from data listed in Table I. [d] 45 °C.

and neophyl arenesulfonates in selected solvents are collected in Table I. The course of reaction was followed by titrating the liberated arenesulfonic acid and in all cases the reaction followed strictly a first-order kinetic law up to at least 75% conversion, furnishing, within experimental error,[17] 100% of the theoretical amount of acid present.

The solvent parameters derived from the mY equation of Winstein and Grunwald[18] are useful tools for evaluating the mechanism of a solvolysis reaction. Accordingly, we have collected the values of m_{EW}, m_{AF}, $[k_{EW}/k_{AcOH}]_Y$, and $[k_{EW}/k_{HCOOH}]_Y$ for solvolysis of neopentyl and neophyl arenesulfonates in Table II. In all cases the listed m values are well within the range observed for substrates solvolyzing with predominant neighboring-group participation.[16,19] Also the magnitudes of $[k_{EW}/k_{AcOH}]_Y$ and

$[k_{EW}/k_{HCOOH}]_Y$ observed for the solvolysis of both neophyl-OPms and neopentyl-OTs are within the range proposed by Schleyer[22] for solvolysis of arenesulfonates occurring without nucleophilic solvent assistance and internal return.

When log k_t values for neophyl-OPms are plotted against log k_t for neophyl-OTs in various solvents, a good linear correlation is observed (see Figure 1).[23] This result clearly establishes that the response of the pemsylate (OPms) leaving group to solvent ionizing strength closely parallels that of the tosylate (OTs) leaving group. As a consequence, it can be concluded that the deceleration realized with the pemsylate group is largely electronic in origin.

Of greater interest is the plot of log k_t values for neopentyl-OTs against those of neophyl-OTs in various solvents. As can be seen from Figure 2, the rate data for neopentyl-OTs, in sharp contrast to that of cyclopropylcarbinyl arenesulfonates, are correlated with log k_t values for neophyl-OTs by a single line.[24] This result clearly

(17) The more slowly reacting ethanolyses were followed only to 10–40% reaction.

(18) (a) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956); (c) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, 1962, pp 45–47, 63–65.

(19) The higher m values of neophyl-OPms relative to those of neophyl-OTs can be attributed to the well-known inverse relationship between m values and the ability of leaving groups to disperse developing negative charge.[20,21]

(20) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **79**, 1608 (1957).

(21) J. L. Fry, C. J. Lancelot, L. K. M. Lim, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2538 (1970).

(22) T. W. Bentley and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7658 (1976).

(23) The slope of the least-squares line is 0.97 with a correlation coefficient of 0.997.

Table III.   Solvolysis Rates $(-\log k_t)^a$ for Selected Substrates in Various Solvents^b at 45 ° C

substrate	100% E	90% E	80% E	70% E	AcOH	HCOOH
neophyl-OTs	6.90^c	6.30^d	5.90^d	5.5^d	6.30^c	3.89^e
neophyl-OPms	7.70^d	7.25^d	6.86^d	6.38^d	7.10^d	4.66^f
neopentyl-OTs	9.18^d	8.65^d	8.25^d	7.8^d	8.70^d	6.37^d

^{a} In s^{-1}. ^{b} E = aqueous ethanol. ^{c} Calculated from data at higher temperatures contained in ref 6a. ^{d} Extrapolated from data listed in Table I. ^{e} Calculated from data at higher temperatures contained in ref 5. ^{f} Interpolated from data listed in Table I.
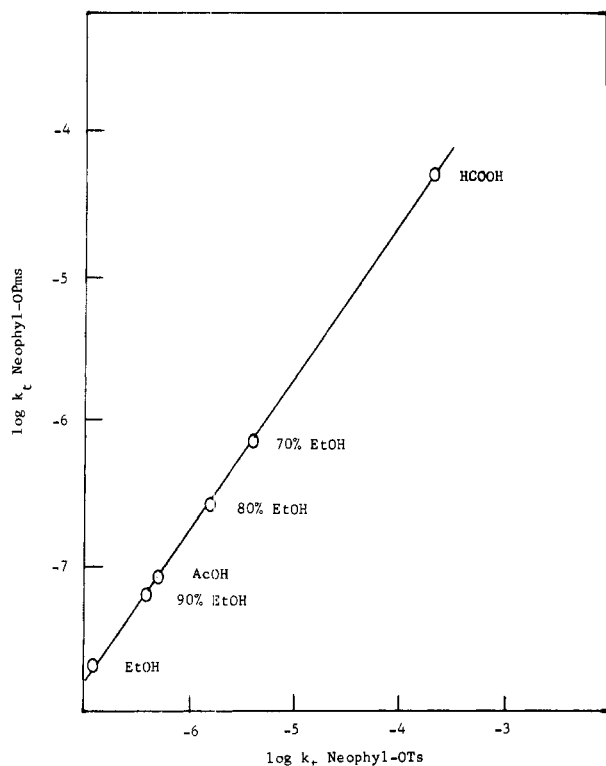

Figure 1. Plot of log k_t (neophyl-OPms) against log k_t (neophyl-OTs) in various solvents at 45 °C. Data taken from Table III.

Figure 2. Plot of log k_t (neopentyl-OTs) against log k_t (neophyl-OTs) in various solvents at 45 °C. Data taken from Table III.

demonstrates a similar response to medium effects by phenyl and alkyl neighboring groups. More importantly, it strongly supports our contention that delocalization of charge in solvolytic transition states by enhanced hyperconjugation can be detected by a graphical analysis of solvolysis rates in aqueous ethanol and carboxylic acid solvents (see Table III).

Other tests of this contention are under study and will be reported subsequently.

Experimental Section

2-Methyl-2-phenyl-1-propanol (neophyl alcohol) was prepared by a published procedure[25] in 70% yield. Identity was established by conversion to the known *p*-toluenesulfonate derivative, mp [after one recrystallization from petroleum ether (bp 30–60 °C)] 74.0–74.5 °C (lit.[6a] mp 74–75 °C).

Neophyl pentamethylbenzenesulfonate (neophyl-OPms) was prepared several times according to established procedure.[4a] In a typical run, pentamethylbenzenesulfonyl chloride (4.5 g, 18 mmol) was added all at once to a hand-stirred solution of neophyl alcohol (2.65 g, 18 mmol) in 30 mL of dry pyridine (spectrophotometric grade, Aldrich Chemical Co.) cooled to 0 °C. After standing 24 h at about 5 °C, the mixture was carefully hydrolyzed by the slow addition of 20 mL of cold water (reaction temperature
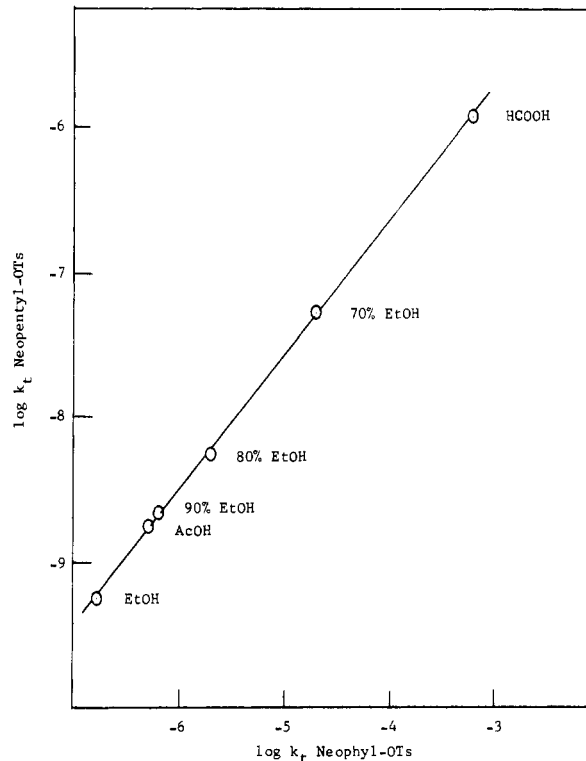
maintained between 0 and 5 °C) followed by the addition of cold, dilute HCl (reaction temperature maintained between 0 and 10 °C) to acidify the mixture. The precipitated ester was separated on a Buchner funnel and washed several times with cold, dilute HCl, several times with cold water, and then cold petroleum ether (bp 30–60 °C). After the solid was air-dried, a crude yield of 4.6 g (71%) of white needles (mp 117–120 °C) was obtained. Recrystallization from a 10:1 mixture of hexane–benzene gave 3.1 g (48%) of the purified product, mp 119–120 °C. Anal. Calcd for $C_{21}H_{28}O_3S$: C, 69.96; H, 7.83. Found: C, 69.92; H, 7.91.

Neophyl *p*-toluenesulfonate (neophyl-OTs) was prepared from neophyl alcohol and *p*-toluenesulfonyl chloride, as described above, in 87% yield, mp (after one recrystallization from hexane) 74.0–74.5 °C (lit.[6a] mp 74–75 °C).

Neopentyl *p*-toluenesulfonate (neopentyl-OTs) was prepared from neopentyl alcohol (Aldrich Chemical Co.) and *p*-toluenesulfonyl chloride, as described above, in 87% yield, mp (after one recrystallization from a 17:1 mixture of hexane–benzene) 47–48 °C (lit.[6a] mp 48–49 °C).

Solvents were prepared as previously described.[4a]

Rate Measurements. The rates of solvolysis were followed titrimetrically. Reaction solutions of neophyl-OPms were 0.02 M while those of neophyl-OTs and neopentyl-OTs were 0.03 M. Rate measurements were accomplished by the ampule technique. In a typical run, 5-mL aliquots of the reaction solution[26] were sealed under nitrogen in 10-mL ampoles, thermostated in a

(24) The slope of the least-squares line is 0.92 with a correlation coefficient of 0.995.

(25) (a) F. C. Whitmore and A. R. Lux, *J. Am. Chem. Soc.*, **54**, 3448 (1932); (b) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice-Hall, pp 26–27, 1264–1273 (1954).

(26) The esters dissolved within a few minutes in all solvents except formic acid. To effect dissolution in this solvent, the ester was dissolved in 8 drops of ethyl acetate before the addition of the formic acid. As measured in our laboratory, this quantity of ethyl acetate has no effect on the observed rates of such formolysis reactions.

constant-temperature bath held to ±0.05 °C of reaction temperature, and then, at appropriate times, titrated as previously described.[4a]

Treatment of Kinetic Data. The thermodynamic activation parameters were calculated by regression analysis on an IBM 370 computer. The linear correlations, slope values, and correlation coefficients were also calculated by IBM 370 computer regression analysis.


Tetramethyl-1,2,3,4,5-hexapentaene[1]

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Peculiar conjugation effects and unusual reactivity have long been associated with the cumulenes, an interesting family of highly unsaturated hydrocarbons.[2] In the parent series, C_nH_4, a proclivity for polymerization has prevented isolation of all but the smallest members (n = 2, 3, 4).[3] Study of the more extended cumulenes, therefore, has necessarily focused on derivatives in which stabilizing groups have replaced the hydrogen atoms.[2] We report here a short, convenient procedure for preparing and purifying the title compound (**1**), an extended cumulene substituted only by methyl groups.
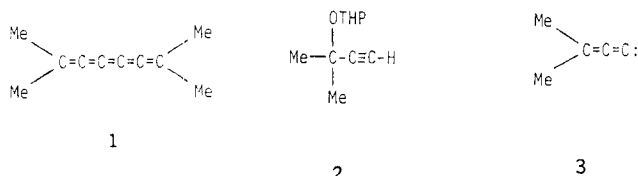
The tetrahydropyranyl ether of 3-methyl-1-butyn-3-ol (**2**) can be cleanly deprotonated with ethylmagnesium chloride to give a solution of the corresponding acetylide which is stable under ordinary conditions. Subsequent treatment with a catalytic amount of cuprous chloride, however, induces a γ-elimination which leads to the formation of cumulene **1**, presumably via a copper carbenoid related to **3**.[4] Chromatography on silica gel provides a yellow pentane solution of pure **1** which was characterized by hydrogenation to 2,7-dimethyloctane (Rh/alumina/−78 °C) and by spectroscopic means: ^{1}H NMR (CDCl$_3$) δ 1.95 (s); UV max (EtOH) 214, 226, 306, 320 nm (relative ε 29, 100, 17, 19).

It is interesting to note the large downfield shift of the methyl hydrogen NMR signal of **1** relative to that of tetramethylethylene (δ 1.67). The magnitude of this downfield shift appears to correlate with the number of double bonds in the tetramethyl cumulene family.[5] The longer wavelength UV absorptions of **1** relative to those of lower homologues[5] likewise reflect the more extended π system in **1**.

This cumulene does polymerize rapidly in the absence of solvent but can be kept for many hours in dilute solutions protected from oxygen. By working quickly, one can remove the solvent under reduced pressure and redissolve the cumulene in a different solvent without undue losses to polymerization. In CDCl$_3$ (ca. 5% solution) at 37 °C, the ^{1}H NMR signal of **1** disappears with a half-life of about 2 h; a precipitate appears, but no new ^{1}H NMR signals are observed. Bubbling oxygen through a freshly prepared NMR sample of **1** for 10 min completely destroys the cumulene.

The title compound has previously been prepared by Skattebøl by reductive dechlorination of 2,7-dichloro-2,7-dimethyl-3,5-octadiyne, although no purification method was reported.[5] The close correspondence of UV data [lit.[5] UV max (EtOH) 215, 228, 308, 321 nm (relative ε 35, 100, 20, 22)] confirms the identity of the hydrocarbons obtained by these different routes. Skattebøl reports an IR (2002 and 1625 cm^{-1}) but no ^{1}H NMR spectrum and notes that heating the polymer obtained from **1** produced an explosion on one occasion.[5] We intend by this note to supplement the sparse published information available on the title compound and to provide a procedure for its preparation and purification which other interested chemists should find easy and convenient.

Experimental Section

Tetramethyl-1,2,3,4,5-hexapentaene (1).[1] A solution of 1.680 g (10.0 mmol) of **2**[6] in 10 mL of dry THF[7] was added dropwise to 3.6 mL (10.0 mmol) of 2.79 M ethylmagnesium chloride[8] in THF. The solution was heated under reflux for 1 h and then cooled to room temperature. To the acetylide solution was added 50 mg (0.50 mmol) of anhydrous cuprous chloride.[9] The mixture was then heated under reflux for 1 h more, cooled to room temperature, and poured into dilute HCl and ice. The resulting mixture was extracted with 50 mL of ether, which was then shaken with 50 mL of saturated NaHCO$_3$, dried (MgSO$_4$), and concentrated under reduced pressure; the vacuum was released by readmitting nitrogen rather than air. The residue was rapidly taken up in minimal pentane and chromatographed on a column of silica gel (25 g), using pentane as the eluant. The yellow fraction contained pure cumulene **1** (5–10% yield); no other compounds were eluted from the column with pentane. Evaporation of the pentane under reduced pressure gave a yellow-orange solid which could be redissolved in CDCl$_3$, EtOH, THF, or other solvents with only minor losses to polymerization, provided the operation was performed quickly under nitrogen. (See text for spectra.)

Hydrogenation of 1. The pentaene (**1**) was prepared and chromatographed as above, only the yellow fraction from the column chromatography was collected in a flask flushed with nitrogen and cooled to −78 °C. When all the cumulene had been collected, 100 mg of 5% Rh/alumina was added to the pentane solution, and hydrogen gas was slowly bubbled through the mixture, still at −78 °C. The yellow color slowly faded over a period of 45 min. The mixture was allowed to warm to room temperature, and the addition of hydrogen was continued for 15 min more. The mixture was then filtered and concentrated under reduced pressure to give 41 mg (6%) of 2,7-dimethyloctane as a colorless liquid: mass spectrum, *m/e* (relative intensity) 142 (1, M$^+$), 127 (5, M − CH$_3$), 113 (no peak for M − Et), 99 (53, M − Pr),

(1) IUPAC name: 2,7-dimethylocta-2,3,4,5,6-pentaene.

(2) Fischer, H. In "The Chemistry of Alkenes"; Patai, S., Ed.; Wiley-Interscience: New York, 1964; Chapter 13.

(3) Cripps, H. N.; Kiefer, E. F. In "Organic Syntheses"; Baumgarten, H. E., Ed.; Wiley: New York, 1973; Collect. Vol. V, pp 22–4. Schubert, W. M.; Liddicoet, T. H.; Lanka, W. A. *J. Am. Chem. Soc.* **1954**, *76*, 1929–32. Ripoll, J. L. *J. Chem. Soc., Chem. Commun.* **1976**, 235–6.

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