binol in 40 ml of acetonitrile was reacted overnight at room temperature in the dark with 0.80 g (5 mmol) of bromine. The standard workup was used. Evaporation of the solvent gave a quantitative yield of a yellow oil which could not be distilled without decomposition. However, the NMR of the oil was that of a pure compound assigned the structure 2,4-dibromo-1,1-diphenyl-1-butanol (V): NMR (CCl_4) δ 2.00 (m, 1 H), 2.30 (m, 1 H), 2.82 (s, 1 H, OH), 3.58 (m, 2 H), 5.47 (dd, 1 H, J = 6 and 1 Hz), 7.2–7.7 (m, 10 H); IR (neat) 3560 cm^{-1}(OH).

Anal. Calcd for $C_{16}H_{16}OBr_2$: mol wt, 383.9543. Found: mol wt, 383.9548.

B. With Hydrobromic Acid. A solution of 2.0 g (0.9 mmol) of diphenylcyclopropylcarbinol in 20 ml of benzene was stirred with 25 ml of 48% hydrobromic acid for 1 h at room temperature. The reaction mixture was washed with water and dilute sodium bicarbonate. The solvent was evaporated, yielding 2.3 g (88%) of light yellow oil, 4-bromo-1,1-diphenyl-1-butene (VII). Purification by high-vacuum short-path distillation gave a product pure by NMR: NMR (CCl_4) δ 2.68 (q, 2 H), 3.40 (t, 2 H), 6.12 (t, 1 H), 7.25 (m, 10 H).

Anal. Calcd for $C_{16}H_{15}Br$: mol wt, 286.0357. Found: mol wt, 286.0364.

C. Reaction with Acetic Acid. A solution of 1.12 g (5 mmol) of diphenylcyclopropylcarbinol in 40 ml of glacial acetic acid was treated with one drop of trifluoroacetic acid at 80 °C for 3 h. The standard workup was used. The product was a slightly brown oil which gave the NMR spectrum expected for pure 4-acetoxy-1,1-diphenyl-1-butene:[2] NMR ($CDCl_3$) δ 2.02 (s, 3 H), 2.44 (t, 1 H, J = 6 Hz), 2.50 (t, 1 H, J = 6 Hz), 4.16 (t, 2 H, J = 6 Hz), 6.18 (t, 1 H, J = 6 Hz), 7.38 (m, 10 H).

Other Reactions. A. 1,2,4-Tribromo-1,1-diphenylbutane. A 5% solution of bromine in carbon tetrachloride was added slowly and dropwise to a solution of 500 mg of 4-bromo-1,1-diphenyl-1-butene (VII) in ca. 10 ml of carbon tetrachloride until the color persisted. The solution was washed with dilute sodium sulfite and the solvent evaporated. Attempted short-path distillation led to decomposition of the product. However, the whole crude product had the NMR of a single pure compound and gave the correct high-resolution MS for $C_{16}H_{15}Br_3$. The structure was assigned as 1,2,4-tribromo-1,1-diphenylbutane (IX) based on the NMR (CCl_4): δ 2.1 (m, 1 H), 2.95 (m, 1 H), 3.70 (m, 2 H), 5.52 (dd, 1 H, J = 7 and 2 Hz), 7.65 (m, 10 H).

Anal. Calcd for $C_{16}H_{15}Br_3$: mol wt, 447.9364. Found: mol wt, 447.9374.

B. Reaction of VII with Bromine in Acetic Acid. The following experiment was carried out in the MH-100 NMR in a standard 5-mm tube. A mixture of ca. 80 mg of VII in 0.6 ml of perdeuterioacetic acid was treated with slightly more than 1 equiv of bromine. The NMR spectrum changed quickly to that of the tribromide IX. No trace of the dibromo acetate IV was evidenced.

C. Reaction of VII with Acetyl Hypobromite. A solution of acetyl hypobromite in carbon tetrachloride was generated as described by Rolston and Yates[7] from 1.5 g of silver acetate. A solution of 1.0 g of VII in 10 ml of carbon tetrachloride was added at −20 °C. After warming to room temperature, the reaction mixture was filtered, washed, and concentrated to give 1.4 g of crude product which analyzed by NMR as 72% of dibromo acetate IV, and 28% of the tribromide IX.

D. Treatment of the Dibromo Acetate IV with Hydrogen Bromide in Acetic Acid. A solution of approximately 200 mg of the dibromo acetate IV in 1 ml of acetic acid was treated by bubbling in hydrogen bromide at room temperature for 2 min. After standing overnight the reaction mixture was worked up in the usual way. An NMR analysis of the product indicated that it was the dibromo olefin VI contaminated with a trace of the dibromo alcohol V.

E. Reactions Which Failed to Yield Product. The following reactions were attempted but only starting material was recovered: (1) Repeated attempts were made to acetylate the DPCC I and the dibromo alcohol V. Among these may be listed acetic anhydride and acetyl chloride both with and without pyridine. (2) The dibromo alcohol V did not react on standing with acetic acid. Catalysis by either small amounts of trifluoroacetic acid or 70% perchloric acid did not alter the starting material.

Acknowledgment. Grateful appreciation is extended to the Robert A. Welch Foundation for their support of this work.

Registry No.—I, 5785-66-0; IV, 61076-21-9; V, 61076-22-0; VI, 51752-40-0; VII, 6078-95-1; IX, 61076-23-1; bromine, 7726-95-6; 4-acetoxy-1,1-diphenyl-1-butene, 24104-21-0; acetyl hypobromite, 4254-22-2.

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Structural Effects in Solvolytic Reactions. 19. The Relative Electron Releasing Capability of Methyl, Phenyl, and Cyclopropyl Groups as Measured by the Tool of Increasing Electron Demand

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The rates of solvolysis of aryldimethylcarbinyl (*tert*-cumyl) and 1-aryl-1-phenyl-1-ethyl *p*-nitrobenzoates with representative substituents in the aryl ring were determined in 80% aqueous acetone in order to test, by the application of the tool of increasing electron demand, the relative capability of methyl, phenyl, and cyclopropyl groups to stabilize a carbonium ion center. The *tert*-cumyl system yields a ρ^+ of −4.72 and the 1-aryl-1-phenyl-1-ethyl system yields one of −3.23. These data, together with the earlier reported value of ρ^+ for 1-aryl-1-cyclopropyl-1-ethyl system, −2.78, reveal that the relative electron releasing abilities of these groups increase in the order methyl < phenyl < cyclopropyl, supporting the conclusions reached earlier based on both rate and equilibria studies, but in direct contradiction to conclusions based on ^{13}C NMR shifts.

The extent and the consequences of the stabilization of carbonium ion centers by attached groups have received considerable attention in recent years. For many years, the main tool in such studies has been the solvolytic behavior of appropriate derivatives. With the advent of ^{13}C NMR and the ability to prepare and observe carbonium ions under stable ion conditions, workers in the field have utilized ^{13}C shifts to estimate electron densities at the carbonium carbon and to

Table I. Rates of Solvolysis of *tert*-Cumyl and 1-Aryl-1-phenyl-1-ethyl *p*-Nitrobenzoates and Related Derivatives in 80% Aqueous Acetone

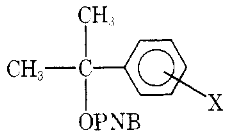
Registry no.	System	Substituent in aryl	$k_1 \times 10^6$, s^{-1}			$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
			T_1, °C	T_2, °C	25 °C		
23852-76-8	1	p-CH$_3$O			372		
23852-75-7		p-CH$_3$	577 (75)	37.5 (50)	1.54^a	23.8	−5.1
7429-06-3		p-H	391 (100)	33.6 (75)	0.072^a	24.8	−8.2
40543-93-9		p-CF$_3$	238 (150)	25.7 (125)	$8.36 \times 10^{-5\,a}$	29.2	−6.7
60921-48-4		3,5-(CF$_3$)$_2$	219 (175)	22.2 (150)	$7.50 \times 10^{-7\,a}$	33.9	−0.3
60921-49-5	2	p-CH$_3$O			322^b		
60921-50-8		p-H	320 (75)	20.0 (50)	0.785^{b,c}	24.2	−5.3
60921-51-9		p-CF$_3$	107 (100)	7.36 (75)	$8.95 \times 10^{-3\,a}$	27.1	−4.5
60921-52-0		3,5-(CF$_3$)$_2$	126 (125)	10.2 (100)	$4.31 \times 10^{-4\,a}$	29.1	−3.8
41327-36-0	3^d	p-CH$_3$O			33 000		
41327-37-1		p-H	8.91 (0)		241	20.8	−5.5
41327-38-2		p-CF$_3$	83.8 (50)		3.88	22.9	−6.4
41327-39-3		3,5-(CF$_3$)$_2$	111 (75)	7.42 (50)	0.315^a	23.6	−9.1

[a] Calculated from rates at higher temperatures. [b] Calculated by multiplying the rate of the benzoate by the factor 20.8 (ref 10). [c] Lit.[4b] $k_1^{25} = 6.81 \times 10^{-8}$ s^{-1}. [d] Reference 9.

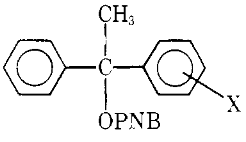
deduce therefrom the relative electron releasing properties of various groups to the carbonium carbon. For example, from a study of the ^{13}C shifts of the carbonium carbon in the *tert*-butyl cation, the phenyldimethyl, and the cyclopropyldimethyl carbonium ions, Olah and White proposed that electron release from these groups to an electron deficient center increases in the order methyl < phenyl > cyclopropyl.[3] But there are much rate[4] and equilibrium data[5,6] that indicate that the electron release follows the order methyl < phenyl < cyclopropyl.

The tool of increasing electron demand[7,8] offers considerable promise for arriving at an objective conclusion in cases where such ambiguity is present. It is possible to estimate the magnitude of the electron density at the developing electron deficient center by observing the effect of substituents in the aromatic ring (ρ^+). The quantitative aspects of the Hammett treatment facilitate realizing a quantitative estimate of the electron deficiency at the developing carbonium ion center. Numerous systems have now been subjected to this test, yielding consistent unambiguous results.[8]

We therefore decided to apply this tool to examine the electron releasing properties of methyl, phenyl, and cyclopropyl. This was achieved by synthesizing and determining the rates of solvolysis of representative derivatives of two systems (**1**, **2**) for comparison with the data already available for the third (**3**).[9]



1



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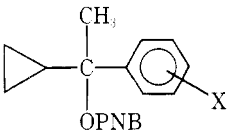


3

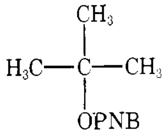
Results

Synthesis. The synthesis of 1-aryl-1-cyclopropyl-1-ethyl *p*-nitrobenzoates (**3**) was described earlier.[9] The *tert*-cumyl alcohols (**1**-OH) were synthesized by the addition of the appropriate Grignard reagents to acetone. Similarly, the addition of the Grignard reagents to acetophenone furnished **2**-OH. The alcohols were converted to *p*-nitrobenzoates by successive treatment with *n*-butyllithium and *p*-nitrobenzoyl chloride. The properties of the *p*-nitrobenzoates are summarized in Table III.

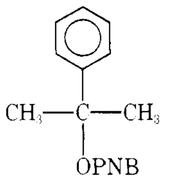
Kinetic Studies. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% aqueous acetone following the standard titrimetric procedure. 1-*p*-Anisyl-1-phenyl-1-ethyl *p*-nitrobenzoate (**2**, X = *p*-OCH$_3$) was too unstable to be isolated; hence, the benzoate was prepared and solvolyzed and the rate of the *p*-nitrobenzoate was calculated by multiplying the rate of the benzoate by the factor 20.8.[10] The rate data, together with activation parameters, are tabulated in Table I.

Discussion

It was previously concluded from a study of the solvolysis of *tert*-butyl, *tert*-cumyl, and cyclopropyldimethylcarbinyl *p*-nitrobenzoates (**4**, **5**, **6**) that the electron releasing ability of methyl, phenyl, and cyclopropyl increases in the order methyl < phenyl < cyclopropyl.[4] Relief of B strain is not a significant factor in the major changes in the rates of solvolysis of these derivatives.[4] Hence the observed rate enhancement is attributed to the greater effectiveness of phenyl and cyclopropyl groups in delocalizing the positive charge. Clearly, according to these results, cyclopropyl is far more efficient than phenyl in delocalizing such charge. Olah and co-workers previously examined the ^{13}C chemical shifts for the carbonium ion carbon in **4**, **5**, and **6** and concluded from the observed values that the phenyl (δ ^{13}C$^+$ 254.8 ppm) must be more electron releasing than the cyclopropyl group (δ ^{13}C$^+$ 280.8

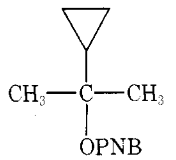


4



5

	4	**5**
Rel rate (25°C)	1.00	969
δ ^{13}C$^+$	328.8	254.8



6

	6
Rel rate (25°C)	503 000
δ ^{13}C$^+$	280.8

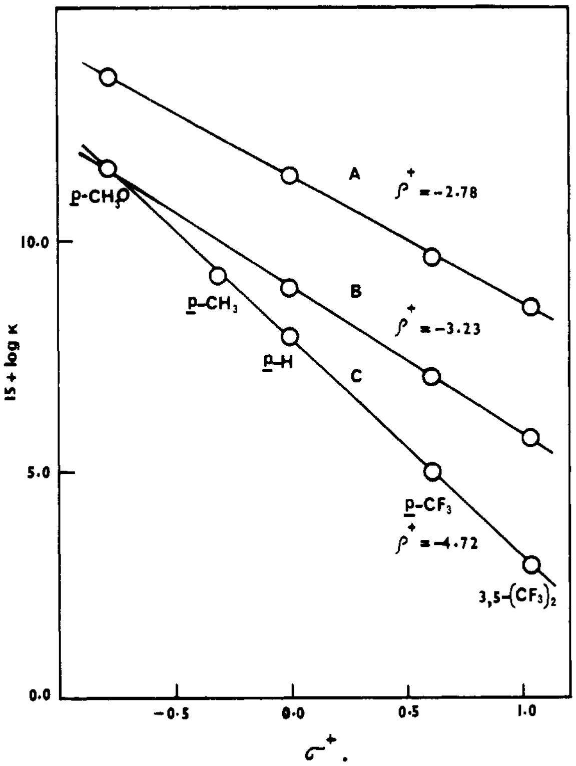


Figure 1. Log k–σ^+ plot for the solvolysis of (A) 1-aryl-1-cyclopropyl-1-ethyl, (B) 1-aryl-1-phenyl-1-ethyl, and (C) *tert*-cumyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C.

Table II. Relative Solvolytic Reactivities of *tert*-Cumyl, 2-Aryl-3-methyl-2-butyl, 1-Aryl-1-phenyl-1-ethyl, and 1-Aryl-1-cyclopropyl-1-ethyl *p*-Nitrobenzoates in 80% Aqueous Acetone

Substituent in aryl	Relative rate 1	9^a	2	3
p-CH$_3$O	1.00	0.20	0.87	89
p-H	1.00	0.13	10.9	3 350
p-CF$_3$	1.00	0.16	107.0	46 400
3,5-(CF$_3$)$_2$	1.00	0.19	575.0	420 000

[a] Registry no. are, respectively, 41327-33-7, 41366-66-9, 41327-34-8, 41327-35-9.

Table III. Properties of *p*-Nitrobenzoates

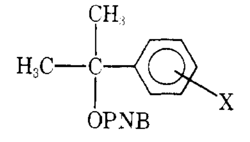
System	Substituent in aryl	Mp, °C	Anal.
1	p-CH$_3$O	90 dec^a	C, H, N
	p-CH$_3$	106–107.4^b	C, H, N
	p-H	133–134^c	
	p-CF$_3$	110.5–111^d	C, H, N, F
	3,5-(CF$_3$)$_2$	89	C, H, N, F
2	p-H	135 dec	C, H, N
	p-CF$_3$	121.5–122	C, H, N, F
	3,5-(CF$_3$)$_2$	138–139	C, H, N, F

[a] Lit.[15] mp 83–84 °C. [b] Lit.[15] mp 108–109 °C. [c] Lit. mp 136–137 °C: L. F. King, *J. Am. Chem. Soc.*, **61**, 2383 (1939). [d] Lit.[15] mp 110–111 °C.

ppm).[4,11] Hence, the observed solvolytic results fail to correlate with the ^{13}C shifts, although it has been proposed that such shifts do indeed provide a measure of the electron density in such ions.[4,12] Consequently, there exists a major discrepancy between the results realized in solvolytic studies and the conclusions based on ^{13}C shifts as to the relative ability of the phenyl and cyclopropyl groups in stabilizing the carbonium ion center.

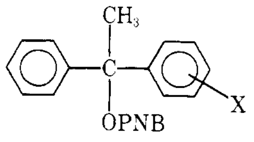
An alternative approach for testing this discrepancy is to apply the tool of increasing electron demand. After all, this tool has provided consistent unambiguous results in numerous systems. The determination of ρ^+ in **1**, **2**, and **3** makes it possible to evaluate the effectiveness of these groups in stabilizing the carbonium ion, utilizing ρ^+ as a measure of the electron demand in the transition state.

The value of ρ^+ for the solvolysis of *tert*-cumyl *p*-nitrobenzoates in 80% aqueous acetone is −4.72 (correlation coefficient 0.999).[13-15] The 1-aryl-1-phenyl-1-ethyl *p*-nitrobenzoates (**2**) yield ρ^+ of −3.23 (correlation coefficient 0.999) and the 1-aryl-1-cyclopropyl-1-ethyl *p*-nitrobenzoates (**3**) yield one of −2.78[9] (Figure 1). Hence, ρ^+ for the cyclopropyl system is more positive than for the phenyl system, thereby reaffirming the greater ability of the cyclopropyl group over the phenyl group in delocalizing the charge.



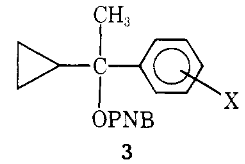
1

ρ^+ -4.72



2

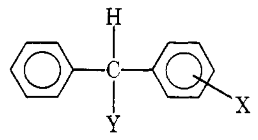
ρ^+ -3.23



3

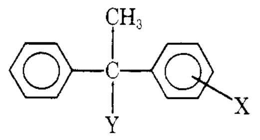
ρ^+ -2.78

It is of interest to examine by means of this tool the relative electron releasing effect of hydrogen as a substituent at the carbonium ion center. The value of ρ^+ for the benzhydryl system (**7**) is −3.72, considerably more negative than ρ^+ for the diarylmethyl system (−3.23), which in turn is more negative than ρ^+ (−2.52) for the triarylmethyl system (**8**).[16,17] Thus, the electron releasing properties, as measured by this tool, increase hydrogen < methyl < phenyl. The three aromatic groups of **8** delocalize the charge more effectively than the two aromatic groups of **7** or the two aromatic and one methyl group of **2**. It should be noted that the ρ^+ for 1-cyclopropyl-1-aryl-1-ethyl system (**3**) approaches the value observed for the triarylmethyl system (**8**). Consequently, a cyclopropyl group plus a methyl group is nearly as effective as two phenyl groups in delocalizing charge to the electron deficient center.



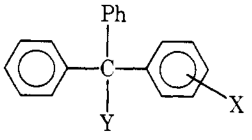
7

ρ^+ -3.72



2

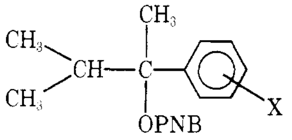
ρ^+ -3.23



8

ρ^+ -2.52

A comparative study of the rates of solvolysis of the 1-aryl-1-phenyl-1-ethyl system (**2**) and of the 1-aryl-1-cyclopropyl-1-ethyl system (**3**) with the closely related *tert*-cumyl and 2-aryl-3-methyl-2-butyl systems (**9**) (ρ^+ = −4.76[9]) is



9 $\rho^+ = -4.76$

presented in Table II. Thus the electron releasing power of an isopropyl group is similar to that of a methyl group. With increasing electron demand at the cationic center, the rate enhancement observed for **3** is much greater than that observed for **2**. This is in agreement with the greater stabilizing effect of the cyclopropyl group compared with the phenyl group.

These results have important implications. Many different approaches are now available for establishing the relative order of stabilization of a cationic center by methyl, phenyl, and cyclopropyl groups. The earlier solvolytic and equilibrium studies revealed that the trend of delocalization of charge increases in the order methyl < phenyl < cyclopropyl.[4] From a study of the ^{13}C shifts of alkyl carbonium ions Olah concluded that a phenyl group is more effective in stabilizing a cationic center than a cyclopropyl group.[3] However, the application of the tool of increasing electron demand supports the conclusions reached earlier based on solvolysis and equilibria studies. Therefore, caution is in order at this time in utilizing ^{13}C shifts to draw conclusions as to the charge densities in carbonium ions.

Experimental Section

All melting points are uncorrected. IR spectra were taken on a Perkin-Elmer Model 137 spectrometer and NMR spectra were recorded on a Varian T-60 spectrometer.

Preparation of Tertiary Alcohols. The *tert*-cumyl alcohols were prepared by the addition of the appropriate Grignard reagents to acetone in ether. 1-Aryl-1-phenyl-1-ethylcarbinols were also similarly prepared starting from acetophenone. The following procedure for the Grignard reaction is representative. A solution of the ketone (30 mmol) in ether (25 ml) was slowly added to a solution of the Grignard reagent (32.5 mmol, prepared by reacting the aryl halide with magnesium in ether) at 0 °C. After the addition, the reaction mixture was stirred at room temperature for 1 h and then refluxed for 2 h. The reaction mixture was then decomposed with ice-cooled ammonium chloride and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and solvent evaporated. The tertiary alcohols were used for *p*-nitrobenzoate preparation without further purification.

Preparation of *p*-Nitrobenzoates. The *p*-nitrobenzoates were obtained by treating the tertiary alcohols with *n*-butyllithium and *p*-nitrobenzoyl chloride.[18] The properties and analysis of the *p*-nitrobenzoates prepared in this study are summarized in Table III.

Kinetic Procedure. The procedure employed for determining the rate constants was described earlier.[18]

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(1) Postdoctoral research associate on a grant supplied by Exxon Research and Engineering Co.

(2) Graduate research assistant on a grant (GP 31385) supported by the National Science Foundation.

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(11) More recently, Olah has taken the position from a study of ^{13}C shifts in certain secondary alkenyl cations that the electron release from methyl, phenyl, and cyclopropyl groups to an electron deficient center increases *in the order methyl ≪ phenyl ≲ cyclopropyl. G. A. Olah and* R. J. *Spear, J. Am. Chem. Soc.*, **97**, 1539 (1975).

(12) It has been pointed out that ^{13}C shifts depend upon several important factors in addition to charge density. B. V. Cheney and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 5319 (1967).

(13) The value of ρ^+ for the solvolysis of *tert*-cumyl chlorides in 90% acetone at 25 °C is -4.54[14] and for the solvolysis of *tert*-cumyl *p*-nitrobenzoates in 70% acetone at 100 °C is -3.74.[15]

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Revised Structure of the Dimer of 3,3,6,6-Tetramethylcyclohexyne

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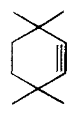
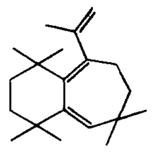
The dimerization of 3,3,6,6-tetramethylcyclohexyne has been reinvestigated and the structure of the dimer reassigned as a moncyclic conjugated enyne (3).

The dimer of 3,3,6,6-tetramethylcyclohexyne (**1**) was described by us in 1972[1] and was assigned structure **2** on the basis of spectroscopic evidence and partial degradation. The *formation of* **2** *was interpreted through dimerization of* **1** to a cyclobutadiene and subsequent rearrangement.

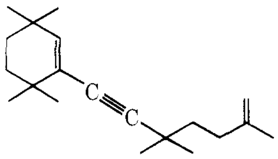


1



2

Another structure considered[1] for the dimer was **3**, which was consistent with most of the data, but the dimer lacked acetylenic infrared absorption at 2250–2270 cm^{-1}, expected for vinylacetylenes,[2] and **3** would not have been expected to give the observed acetic acid in oxidation with permanganate–periodate.



3

An intensive but unsuccessful effort to find independent