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Vinyl Cations. 19.[1] Preparation and Solvolysis of (1-Bromo-1-arylmethylene)cyclopropanes. Effect of *p*-Aryl Substituents on the Generation of Stabilized Vinyl Cations

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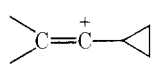
Vinyl cation intermediates are now readily available in solvolysis reactions either through heterolysis of vinyl substrates or triple bond participations.[2] Although vinyl cations are generally less stable than the corresponding saturated carbenium ions,[3] recent studies have given evidence for their formation.

Thus, in the solvolysis of simple alkyl vinyl derivatives the choice of a more reactive leaving group (e.g., arylsulfonates[4] or, even better, the "super leaving groups" triflate[5] and nonaflate[6]), or the stabilization of the positive charge by electron-releasing neighboring groups (e.g., vinyl,[7] aryl,[7,8] cyclopropane[9]) have favored the generation of this challenging intermediate.

In the particular case of a cyclopropane ring, it appears possible to stabilize a positive charge in two ways.

In the vinyl cation **1** the cyclopropane ring is directly attached to the positive center. In the vinyl cation **2**, the β carbon atom of the vinyl double bond is in the cyclopropyl ring.



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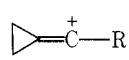


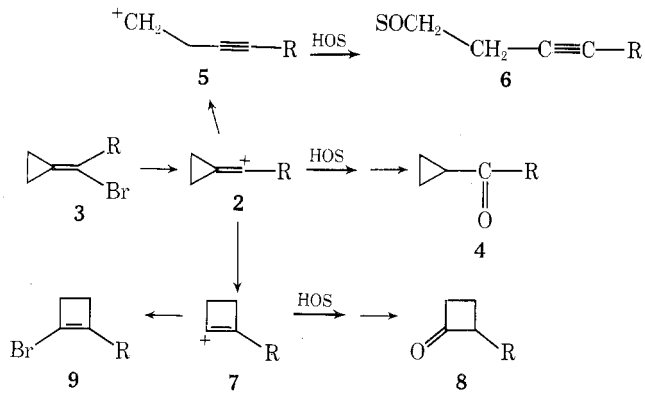
2

Vinyl cation **1** appears analogous to the cyclopropyl carbinyl cation, where the stabilizing effect of the cyclopropyl group is well established.[10] Vinyl cation **2** was first proposed by us as an intermediate in the homopropargyl rearrangement;[11] its high stability, arising from its special geometry (favorable overlapping of the vacant p orbital with the cyclopropane bonds and short C–C distance of the double bond), was confirmed by MO calculations.[12] If we consider now the generation of the vinyl cation **2** by the solvolysis of (halomethylene)cyclopropanes **3**, the reaction products given in Scheme I are possible.

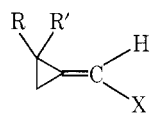
Besides direct substitution by solvent leading to the cyclopropyl ketone **4**, the cyclopropylidenemethyl cation **2** is able to undergo either a homopropargylic rearrangement to give the homopropargyl cation **5** and then **6**, or a ring enlargement to the cyclobutenyl cation **7** and formation of the cyclobutanone **8**.

We have previously reported the generation of primary cyclopropylidene methyl cations **2** (R = H) through the solvolysis reactions of vinyl halides **10**. If the cyclopropane ring is substituted by one or two methyl groups (**10a, 10b**)

Scheme I



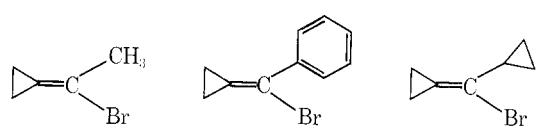
the corresponding primary vinyl cations undergo partial rearrangement to the corresponding homopropargyl cat-



10a, R = R′ = CH_3; X = Cl
b, R = CH_3; R′ = H; X = Br
c, R = R′ = H; X = Br

ions (secondary and tertiary derivative of ion **5**).[13,14] The (1-bromomethylene)cyclopropane **10c** solvolyzes to cyclobutanone as the only solvolysis product,[15] involving a rearrangement of the labile primary vinyl cation **2** into a nonclassical stabilized cyclobutenyl cation **7**.[12]

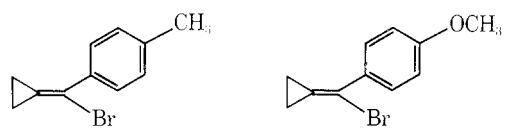
Further work has led to the generation of secondary vinyl cations **2** (R ≠ H) through the solvolysis of the (bromomethylene)cyclopropanes **11, 12,** and **13** in order to ob-



11 **12** **13**

tain additional stabilization of the positive charge by electron-releasing substituents.[16,17] As expected, the kinetic data and product analysis have evidenced the formation of stabilized cyclopropylidenemethyl cation intermediates such as **2**.[17]

We report here the syntheses and the solvolysis reactions of the (1-bromo-1-arylmethylene)cyclopropanes **14** and **15**



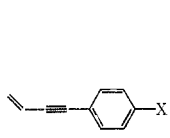
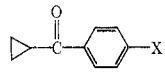
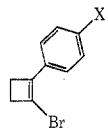
14 **15**

in which the phenyl ring is substituted by a *p*-methyl and a *p*-methoxy group, respectively, in order to study the increase in the stabilization of the intermediate vinyl cations induced by the increased electron-releasing effect of such para substituents.

Syntheses. The syntheses of the vinyl bromides **14** and **15** were carried out via the methylenecyclopropanes **16** and **20.**

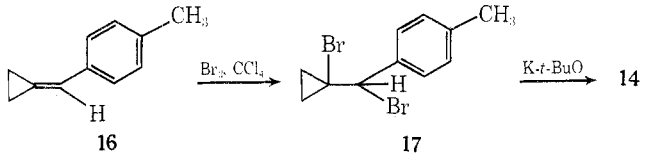
(1-*p*-Tolylmethylene)cyclopropane (**16**) was prepared in 70% yield by the Wittig reaction of *p*-methylbenzaldehyde with cyclopropyltriphenylphosphonium bromide (from 1,3 dibromopropane and triphenylphosphine), as recently reported for the synthesis of benzylidenecyclopropane.[16,18]

Table I
Solvolysis Products (Percent) of (1-Bromoarylmethylene)cyclopropanes 12, 14, and 15[d]

	Solvent	Reaction time, hr	 22	 23	 24	Others
12[16]	EtOH–H_2O (80:20)	24	48	52		
	Trifluoroethanol	4	55			Seven unknown compounds
14	EtOH–H_2O (80:20)	48	31	49	8	12[c]
	Acetone–H_2O (60:40)	24		84	4	12[c]
	Trifluoroethanol	4	64	23[a]		13[b]
15	EtOH–H_2O (80:20)	48	34	54	4	8[c]
	Acetone–H_2O (60:40)	48	51	37	6	6[c]
	Trifluoroethanol	4	29	58[a]	8	5[c]

[a] As trifluoroethanol ketal. [b] As trifluoroethyl enol ether. [c] Brominated derivatives of 23 from ir and mass spectra. [d] Temperature 80°, buffered with 1.1 equiv of triethylamine.

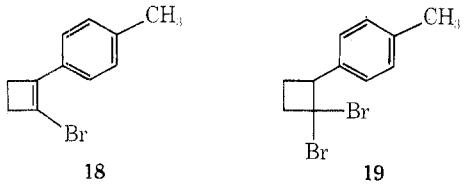
The bromination of **16** in carbon tetrachloride at −5° gave the dibromide **17**. The dehydrobromination with KOH and



16 17

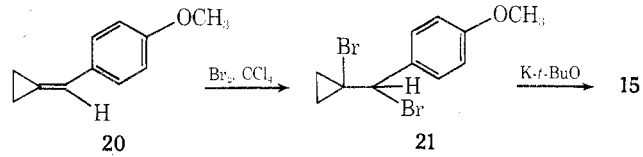
sea sand was successful for the preparation of **12**;[16] treated under the same conditions the dibromide **17** underwent ring opening to form olefinic derivatives. The addition of the dibromide **17** to potassium *tert*-butoxide in dimethyl sulfoxide gave, after hydrolysis and pentane extraction, the expected vinyl bromide **14** in 15% yield as shown by NMR spectroscopy. However, attempted purification by distillation or sublimation in vacuo led to a rearranged product.

The vinyl bromide **14** was finally obtained in 76% yield by stirring a mixture of the dibromide **17** and 1.5 equiv of potassium *tert*-butoxide in pentane for 10 min at 0°. After the usual work-up, **14** was purified by several recrystallizations from pentane. Unlike the (1-bromo-1-phenylmethylene)cyclopropane **12**, the vinyl bromide **14** cannot be purified by gas chromatography; on heating to 100° for 15 min **14** undergoes a quantitative ring enlargement, probably into 1-bromo-2-*p*-tolylcyclobutene (**18**) from mass spectra and NMR evidence. In the same way, on heating to 150° for 60 min the dibromide **17** undergoes a nearly quantitative ring enlargement into the 1,1-dibromo-2-*p*-tolylcyclobutane (**19**).



18 19

(1-*p*-Anisylmethylene)cyclopropane (**20**) was prepared from 1,3-dibromopropane, triphenylphosphine, and *p*-anisaldehyde in 60% yield. The bromination of **20** in carbon tetrachloride at −5° gave the labile dibromide **21**, which without further purification was readily dehydrobrominated by stirring it for 10 min at 0° with 1.5 equiv of potassium *tert*-butoxide in pentane. The vinyl bromide **15** was obtained in 82% yield; although attempts at crystallization were unsuccessful, NMR examination and gas chromatographic analysis show it to be more than 95% pure, contaminated only by the rearrangement product 1-bromo-2-*p*-anisylcyclobutene.



20 21

Results and Discussion

The (bromomethylene)cyclopropanes **14** and **15** were solvolyzed in solvents of different ionizing power and nucleophilicity. For each run, the products were separated by gas chromatography and their structures unequivocally proven by ir, NMR, and mass spectroscopy. The solvolysis rates were measured by automatic continuous titration, and compared with the reaction rates of the parent vinyl bromide **10c**.

The vinyl bromides **12**, **14**, and **15**, as shown in Table I, solvolyze mainly with formation of the cyclopropylaryl ketones **23** and the but-3-en-1-yne derivatives **22**, as well as a few percent of the four-membered ring vinyl bromides **24**.

A secondary vinyl cation **25**, stabilized by both the adjacent cyclopropane and aryl rings, can explain the results of the solvolyses as shown in Scheme II.

Trapping of **25** by the solvent led to the expected cyclopropyl ketones **23**. However, an astonishing result in this case was the formation of the 3-buten-1-yne derivative **22**. Such a rearrangement would imply the homopropargylic rearrangement of a highly stabilized secondary vinyl cation **25** into the less stable primary cation **26**, followed by the formation of the eneyne **22**.

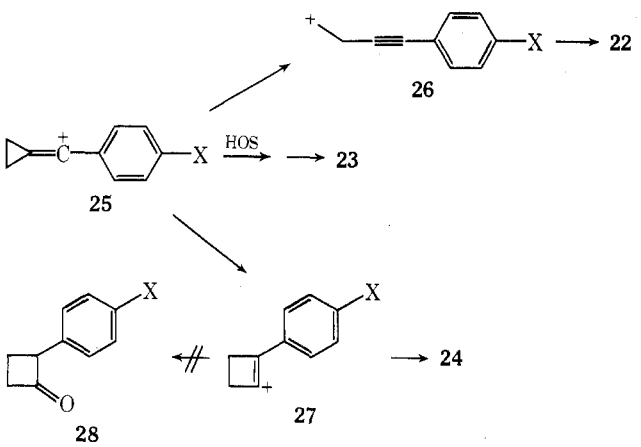
It must be noted that the eneynes **22** were not detected in the products of unbuffered solvolysis. Thus, for example, the solvolysis of the vinyl bromide **15** in aqueous EtOH (80:20) at 80° for 48 hr, without any buffer (NEt_3), led

Table II
Solvolysis Rates of the Vinyl Bromides 12, 14, and 15 in 80% Aqueous Ethanol at pH 6.88[a]

	Temp, °C	10^5k, sec^{-1}	k_{rel}
12[16]	80	2.60 ● 0.09	1
14	80 (extrapolated)	11.95	4.60
	74.5	6.91 ± 0.02	
	60	1.49 ± 0.04	
15	80 (extrapolated)	658	253
	38.7	8.68 ± 0.11	
	17.7	2.72 ± 0.15	
29a	100.0	4.2×10^{-4}	1
29b	100.1	3.60	8.5×10^3

[a] For 12 at 120°, E_a = 25.9 kcal/mol; for 14 and 15 at 80°, E_a = 24.42 and 23.05 kcal/mol; for 29a and 29b at 100°, E_a = 34.1 and 27.8 kcal/mol, respectively.

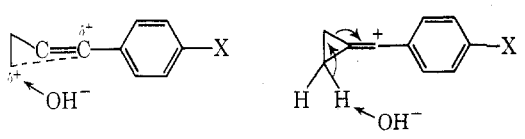
Scheme II



mainly to the ketone **23**, besides the rearranged derivatives **24** and some unknown compounds. We have determined that the vinyl bromides **14** and **15** do not undergo ring opening by the direct action of bases (K-*t*-BuO in pentane, NEt_3, etc.) implying, then, that this base-induced rearrangement occurs during the heterolysis of the C–Br bond of the initial vinyl bromides.

The direct attack by base on the delocalized positive charge at one of the cyclopropyl carbons as envisaged by Bergman and Kelsey to take into account the ring opening of the 1-cyclopropyl propenyl cation[19] or the base-induced proton elimination at one of the cyclopropyl carbons, and concurrent ring opening as shown in Scheme III appears likely in this case.

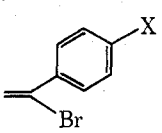
Scheme III



The fact that 2-aryl cyclobutanones **28** are not observed among the products of the solvolysis of the vinyl bromides **12**, **14**, and **15** would imply that the ring enlargement **25** → **27** is also unlikely. However, we have found that the rearranged 1-bromo-2-methylcyclobutene (65–70%), along with 2-methylcyclobutanone (15–30%), were the main products from the solvolysis of (1-bromo-1-methylmethylene)cyclopropane.[17] On the other hand, considering the thermal behavior of the vinyl bromides **14** and **15**, which undergo, on simple heating, ring enlargement with simultaneous internal return (vide supra), the formation of larger amounts of 1-bromo-2-aryl cyclobutenes **24** could be expected in this case.

Finally, the total absence of cyclobutanone derivatives in the solvolysis products of vinyl bromides **12**, **14**, and **15** (it must be remembered that 1-bromomethylenecyclopropane itself led to cyclobutanone as the sole solvolysis product[15]) illustrates clearly here the importance of the classical stabilizing effect of the aromatic ring (phenyl, *p*-tolyl, *p*-anisyl) on the positive charge of the secondary vinyl cations **25**.

The solvolysis rates of the vinyl bromides **12**, **14**, and **15** are given in Table II. As expected, the rates increase with the increasing electron-releasing ability of the substituent in the para position of the aromatic ring: the vinyl bromide **14** reacted 4.6 times faster than the nonsubstituted compound **12** owing to the inductive effect of the para methyl group. The effect of a para methoxy group was strongly marked, **15** reacting 253 times faster than the parent compound **12** under the same conditions. Such a substituent effect on the solvolysis rates strongly suggests a unimolecular ionization process and the formation of an intermediate vinyl cation (i.e., **25**). In comparison, the solvolysis rates of the α-bromostyrenes **29** at 100° in 80% aqueous ethanol are



29a, X = H
b, X = OCH_3

shown in Table II as previously reported by Grob and Cseh.[7a]

The contribution of the three-membered ring to the stabilization of the intermediate vinyl cation **25** is reflected by the higher reactivity of the vinyl bromide **12** compared to α-bromostyrene (**29a**) (at 100°, $k_{12}/k_{29a} = 3.6 \times 10^4$) and also by a relatively less marked rate enhancement due to the added effect of a para methoxy group (compare k_{15}/k_{12} = 253 and k_{29b}/k_{29a} = 8.500). The kinetic data for the solvolyses of various 1-substituted (1-bromomethylene)cyclopropanes are given in Table III. An increase in the solvolysis rates (implying an increase in the stabilization of the intermediate vinyl cation) is clearly observed when the carbon of the vinyl bromide which will become positively charged is successively substituted by a more powerful electron-releasing group. Changing from a methyl (**11**) to a phenyl (**12**) to a *p*-tolyl (**14**) or to a *p*-anisyl (**15**) and most markedly when changing from a primary vinyl bromide (**10c**) to a secondary vinyl bromide with suitable electron-donating substituents, a rate increase of five powers of ten is observed.

It must be mentioned that the high rate enhancement we

Table III
Comparison of the Solvolysis Rates of (1-Bromomethylene)cyclopropane Derivatives in 80% Aqueous Ethanol at 100°

	k, sec^{-1}	k_{rel}	m
10c[17]	7.1×10^{-8} [a]	1	0.53[b]
11[17]	6.6×10^{-5}	10^3	0.64[c]
12[16]	1.54×10^{-4}	2.2×10^3	
14	7.65×10^{-4} [a]	1.08×10^4	0.85[d]
15	3.78×10^{-2} [a]	5.32×10^5	
13[9c,17]	6.4×10^{-3} [a]	1.11×10^5	0.89[a]

[a] Extrapolated. [b] At 130°. [c] At 90°. [d] At 74.5°. [e] At 48.8°.

expected for (1-bromo-1-cyclopropylmethylene)cyclopropane (**13**[9c,17]) is of the same order (10^5 times faster than the parent compound **10c**) as that gained with the vinyl bromide **15** (effect of an added *p*-anisyl substituent).

Finally the intermediate formation of the vinyl cation **25** was supported by two other findings. A criterion for the occurrence of **25** was the high sensitivity of the reaction rates to the ionizing power of the solvent; e.g., at 74.5°, the vinyl bromide **14**, reacted 26 times faster in 50% aqueous ethanol ($k = 1.77 \pm 0.02 \times 10^{-3}$ sec^{-1}) than in 80% ethanol, corresponding to a Winstein–Grunwald m value of 0.85, which, together with that for **13** ($m = 0.89$[9c,17]), is one of the highest m values determined up to now for a reaction involving a vinyl cation. (See Table III.)

For the vinyl bromides **12, 14,** and **15,** the plots of log k_x/k_H correlated linearly with Brown σ^+ substituent constants with a ρ value of −2.8. Compared to the values obtained in the solvolysis of α-arylvinyl substrates such as **29a,** and **29b** ($\rho = -6.6$[7d]) this value appears small. However, it is normal when one considers the delocalization of the positive charge of the vinyl cation **25** over the adjacent cyclopropane ring.

Experimental Section

A. Synthesis of (1-Bromo-1-*p*-tolylmethylene)cyclopropane (14). (1-*p*-Tolylmethylene)cyclopropane (16). A suspension of 108.4 g (0.4 mol) of triphenylphosphine in 70 ml of absolute xylene was treated with 80.8 g (0.4 mol) of 1,3-dibromopropane. The mixture was heated at reflux for 16 hr and left at room temperature overnight. The precipitated salt was removed by filtration, washed three times with 50 ml of dry ether, and dried at 50° under vacuum. The salt, 180 g (mp 217°), was obtained in 95% yield.[18c]

A suspension of 47.3 g (0.1 mol) of the phosphonium salt in 200 ml of dry 1,2-dimethoxyethane was treated with 9.6 g of NaH (50% in suspension in oil, 0.2 mol). The mixture was stirred at room temperature for 8 hr, and then was treated dropwise with 12.02 g (0.1 mol) of *p*-methylbenzaldehyde (freshly distilled) and 5 drops of absolute ethanol. The mixture was stirred for 5 hr at room temperature and then 8 hr at 60°. After cooling, the triphenylphosphine oxide was removed by filtration and the filtrate was concentrated by distillation of the solvent followed by a short-path vacuum distillation of the product. Fractional distillation of the crude distillate yielded 9.9 g (68.5%) of **16** (liquid): bp 58° (0.2 mm); NMR (CCl_4) δ 1.13 (m, 4 H), 2.30 (s, 3 H), 6.60 (m, 1 H), 6.90–7.35 ppm (q, 4 H); MS M^+ *m/e* (rel intensity) 144 (19, 5), 143 (13), 129 (100).

(1,2-Dibromo-1-*p*-tolylmethylene)cyclopropane (17). A solution of 4.32 g (0.03 mol) of **16** in 40 ml of carbon tetrachloride was cooled to −5°, then treated dropwise with 4.8 g (0.03 mol) of bromine. The mixture was washed with aqueous Na_2SO_3 solution and with NaCl-saturated water and dried over $CaCl_2$. The solvent was removed under vacuum, followed by a short-path distillation, yielding 8.65 g (95%) of the liquid dibromide **17**: bp 94° (0.5 mm); NMR (CCl_4) δ 1.30 (s, 4 H), 2.32 (s, 3 H), 5.06 (s, 1 H), 7.05–7.45 ppm (q, 4 H); MS M^+ *m/e* (rel intensity) 302 (6), 304 (12), 306 (5), and 105 (100).

1,1-Dibromo-2-*p*-tolylcyclobutane (19). The dibromide **17** (1 g, 3.3×10^{-3} mol) was placed in a 5-ml flask and heated at 150° for 60 min. After cooling, the pale yellow liquid product was examined spectroscopically: NMR (CCl_4) δ 2.42 (s, 3 H), 3.10 (t, 2 H) 3.63 (t, 2 H) (J_{AB} = 6.5 Hz), 6.80 (s, 1 H), 7.0–7.6 ppm (q, 4 H); MS M^+ *m/e* (rel intensity) 302 (24), 304 (37), 306 (24), and 130 (100).

Analytical gas chromatography (2 m, 10% SE-30, 150°, N_2 30 ml/min) showed only a single product.

(1-Bromo-1-*p*-tolylmethylene)cyclopropane (14). A mixture of 2 g (6.6×10^{-3} mol) of the dibromide **17**, 1 g of finely powdered KOH, and 1 g of sea sand was heated to 100° with stirring, under vacuum (0.1 Torr). No reaction was observed. The mixture became black, and under higher vacuum a distillate was collected, bp 63° (0.025 mm). The NMR of the distillate showed the complete disappearance of the cyclopropane proton signals and the formation of some olefinic derivatives.

To a mixture of 2.24 g (0.02 mol) of K-*t*-BuO in 20 ml of dry dimethyl sulfoxide (freshly distilled over calcium hydride) was added with stirring 3.04 g (0.01 mol) of the dibromide **17**. During the addition the mixture was cooled by immersion of the flask in ice water. Then the mixture was stirred at room temperature for 2 hr, hydrolyzed with 160 ml of water, and extracted with pentane. The pentane phase was washed three times with 20 ml of water, dried over $CaCl_2$, and concentrated under vacuum. From the residue, cooled in the freezer (−20°) overnight, 0.33 g (15% yield) of pure crystalline **14** was isolated by filtration.

To a solution of 3.04 g (0.010 mol) of the dibromide **17** in 10 ml of pentane was added at 0° a suspension of 1.68 g (0.015 mol) of K-*t*-BuO in 20 ml of pentane. The mixture was stirred at room temperature for 10 min and quickly hydrolyzed with 20 ml of water and extracted with pentane. The pentane phase was washed three times with 10 ml of water and dried over Na_2SO_4. Removing the solvent on a rotary evaporator gave 1.7 g (76%) of a pale yellow solid. Two recrystallizations from pentane gave the pure (1-bromo-1-*p*-tolylmethylene)cyclopropane (**14**): mp 53.4°; NMR (CCl_4) δ 1.18–1.88 (m, 4 H), 2.35 (s, 3 H), 7.04–7.68 ppm (q, 4 H); MS: M^+ *m/e* (rel intensity) 224 (9), 222 (9), and 128 (100).

Anal. Calcd for $C_{11}H_{11}Br$: C, 59.21; H, 4.96; Br, 35.81. Found: C, 57.87; H, 4.96; Br, 34.97.

1-Bromo-2-*p*-tolylcyclobutene (18). The vinyl bromide **14** (10 mg) was placed in a NMR tube and heated at 100° for 15 min. After cooling, CCl_4 was added. The NMR spectrum showed δ 2.35 (s, 3 H), 2.98 (t, 2 H), 3.48 (t, 2 H) (J_{AB} = 6.5 Hz), 6.85–7.65 ppm (q, 4 H); MS M^+ *m/e* (rel intensity) 224 (30), 222 (30), and 128 (100).

B. Synthesis of (1-Bromo-1-*p*-anisylmethylene)cyclopropane (15). (1-*p*-Anisylmethylene)cyclopropane (20). 20 can be prepared analogously to **16** by the Wittig reaction of cyclopropyltriphenylphosphonium bromide[18] with *p*-anisaldehyde. After the usual work-up **20** was obtained in 60% yield (liquid): bp 72–74° (0.1 mm); NMR (CCl_4) δ 0.9–1.50 (m, 4 H), 3.72 (s, 3 H), 6.60 (s, 1 H), 6.65–7.35 ppm (q, 4 H); MS M^+ *m/e* (rel intensity) 160 (83), 159 (100), 145 (83), 129 (75).

(1,2-Dibromo-1-*p*-anisylmethylene)cyclopropane (21). The bromination of **20** gave, after work-up, the dibromide **21** (for the procedure, see **17**): NMR (CCl_4) δ 1.28 (m, 4 H), 3.75 (s, 3 H), 3.82 (s, 0.4 H) and 5.08 (s, 0.6 H) (two isomers), 6.75–7.50 ppm (q, 4 H); MS M^+ *m/e* (rel intensity) 318 (18), 320 (26), 322 (18), and 57 (100).

(1-Bromo-1-*p*-anisylmethylene)cyclopropane (15). To a solution of 3.2 g (0.010 mol) of the dibromide **21** in 20 ml of pentane was added at 0° a suspension of 1.68 g (0.015 mol) of K-*t*-BuO in 20 ml of pentane. The mixture was stirred at room temperature for 10 min. After work-up (see **14**) and removal of the solvent on a rotary evaporator 1.95 g (82%) of a pale yellow liquid was obtained which was shown to be practically pure by NMR: NMR (CCl_4) δ 1.10–1.90 (m, 4 H), 3.80 (s, 3 H), 6.70–7.75 (q, 4 H); MS M^+ *m/e* (rel intensity) 240 (10), 238 (12), and 135 (100).

Several attempts to crystallize **15** in different solvent systems were unsuccessful. The purification of **15** was achieved by preparative gas chromatography (on 1 m × 0.25 in. 10% SE-30 at 100°) and was obtained 96% pure.

Anal. Calcd for $C_{11}H_{11}OBr$: C, 55.25; H, 4.63; Br, 33.42. Found: C, 54.07; H, 4.65; Br, 32.97.

On heating over 100°, the vinyl bromide **15** underwent a rearrangement into the isomeric 2-*p*-anisyl-1-bromocyclobutene: NMR δ 3.08 (t, 2 H), 3.58 (t, 2 H), 3.75 (s, 3 H), 6.70–7.40 (q, 4 H); MS M^+ m/e (rel intensity) 240 (13), 238 (13), and 159 (100).

C. Solvolyses. Description of a Typical Product Analysis. The vinyl bromide **14** (300 mg, 1.34 mmol) was dissolved in 5 ml of EtOH–H_2O (80:20) mixture containing 135 mg (1.1 equiv) of triethylamine as buffer. The mixture was heated in a sealed tube for

48 hr at 80°. After cooling, the tube was opened and the solvent was removed on a rotary evaporator. The residue was mixed with concentrated aqueous NaCl solution and extracted three times with pentane. The pentane extract was dried over $CaCl_2$ and concentrated on a rotary evaporator. The remainder of the pentane phase was worked up by preparative gas chromatography, and each product was identified by combined GC and MS analysis.

The other solvolysis reactions were run in the same way, under the conditions reported in Table I.

Cyclopropyl *p*-tolyl ketone (23, X = CH_3):[20] NMR (CCl_4) δ 0.80–1.40 (m, 4 H), 2.25–2.85 (m, 1 H), 2.35 (s, 3 H), 7.15–7.95 (q, 4 H); MS M^+ *m/e* (rel intensity) 160 (57) and 119 (100); ir $\nu_{C=O}$ 1680 cm^{-1}.

1-*p*-Tolyl-3-buten-1-yne (22, X = CH_3): NMR (CCl_4) δ 2.40 (s, 3 H), 5.35–6.28 (m, 3 H), 7.0–7.90 (q, 4 H); MS M^+ *m/e* (rel intensity) 142 (100) and 116 (70); ir ν_{C-H} 915 and 970 cm^{-1}, $\nu_{C=C}$ 1600 and 1665 cm^{-1}, $\nu_{C\equiv C}$ 2200 cm^{-1}. The brominated derivative of **22** (X = CH_3) has been characterized by its mass spectra: M^+ *m/e* (rel intensity) 238 (8), 240 (8), and 119 (100) (p-$CH_3C_6H_4C{\equiv}O^+$) and by ir, $\nu_{C=O}$ 1710 cm^{-1}.

The trifluoroethanol ketal derivative of **23** (X = CH_3) was identified from spectroscopic data: MS M^+ *m/e* (rel intensity) 342 (4) and 243 (100); NMR (CCl_4) δ 1.25 (m, 4 H), 235 (s, 3 H), 2.30–2.50 (m, 1 H), 3.55–4.10 (q, 4 H), 7.0–7.5 (q, 4 H); ir ν[C $(OCH_2CF_3)_2$] 1160 and 1280 cm^{-1}.

Cyclopropyl *p*-anisyl ketone (23, X = OCH_3):[21] NMR (CCl_4) δ 0.75–1.40 (m, 4 H), 2.25–2.85 (m, 1 H), 3.85 (s, 3 H), 6.75–7.95 ppm (q, 4 H); MS M^+ *m/e* (rel intensity) 176 (36) and 135 (100); ir $\nu_{C=O}$ 1680 cm^{-1}.

1-*p*-Anisyl-3-buten-1-yne (22, X = OCH_3): NMR (CCl_4) δ 3.75 (s, 3 H), 5.20–5.95 (m, 3 H), 6.60–6.80 (m, 4 H); MS M^+ *m/e* (rel intensity) 158 (100) and 142 (80); ir ν_{C-H} 915 and 990 cm^{-1}, $\nu_{C=C}$ 1600 and 1635 cm^{-1}, $\nu_{C\equiv C}$ 2200 cm^{-1}. The brominated derivative of **22** (X = OCH_3) was characterized from its mass spectra, M^+ *m/e* (rel intensity) 254 (5), 256 (5), and 135 (100) (p-CH_3O-$C_6H_4C{\equiv}O^+$) and from ir, $\nu_{C=O}$ 1715 cm^{-1}.

The trifluoroethanol ketal derivative of **23** (X = OCH_3) has been identified from spectroscopic data: MS M^+ *m/e* (rel intensity) 358 (40) and 259 (100); NMR (CCl_4) δ 1.30 (m, 4 H), 2.35–2.60 (m, 1 H), 3.50–4.20 (m, 7 H), 6.60–7.70 (q, 4 H); ir ν_{C-O} 1170, 1250, and 1280 cm^{-1}.

D. Kinetic Procedures. The solutions used during the kinetic runs were prepared with absolute ethanol (Fluka) and with triply distilled water. The solvolysis rates were measured by means of a Combi titrator 3 D (Metrohm AG CH-9100, Herisau, Switzerland). The pH of the solution was adjusted to 6.88. About 30 ml of solvent was transferred to the reaction vessel, which was placed in a constant-temperature bath adjusted to the appropriate temperature within a range of ±0.01°. After the stirred solution had reached thermal equilibrium, 5 mg of reactant (**14** or **15**) were added to it. The solvolysis proceeded with continual stirring. The HBr liberated during the solvolysis was automatically neutralized with 0.015 *N* NaOH solution prepared with the same aqueous ethanol solvent used for the solvolysis mixture. The titer was registered automatically on a graph, and the data were gathered in such a way that the Guggenheim method[22] could be employed for calculation of the rate constants. The errors reported were determined by means of a least-squares computer program.

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Registry No.—**10c,** 33745-37-8; **11,** 53968-63-1; **12,** 41893-65-6; **13,** 41886-92-4; **14,** 55088-78-3; **15,** 55088-79-4; **16,** 55088-80-7; **17,** 55088-81-8; **18,** 55088-82-9; **19,** 55088-83-0; **20,** 55088-84-1; **21,** 55088-85-2; **22** (X = H), 13633-26-6; **22** (X = CH_3), 30011-66-6; **22** (X = OCH_3), 55088-86-3; **23** (X = CH_3), 7143-76-2; **23** (X = CH_3) trifluoroethanol ketal derivative, 55088-87-4; **23** (X = OCH_3), 7152-03-6; **23** (X = H), 3481-02-5; **24** (X = CH_3), 55088-82-9; **24** (X = OCH_3), 55088-88-5; triphenylphosphine, 603-35-0; 1,3-dibromopropane, 109-64-8; cyclopropyltriphenylphosphonium bromide, 14114-05-7; *p*-methylbenzaldehyde, 104-87-0; K-*t*-BuO, 865-47-4; *p*-anisaldehyde, 123-11-5.

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Biological Spin Labels as Organic Reagents. Oxidation of Alcohols to Carbonyl Compounds Using Nitroxyls

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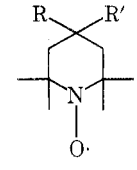
Stable nitroxyl radicals such as 4-oxotetramethylpiperidinooxy (**1,** TEMPO) are widely employed as spectroscopic probes for observing binding sites and molecular motion in macromolecules.[1,2] We report here that as a result of their remarkable redox properties, nitroxyl radicals in conjunction with an added oxidizing agent can conveniently convert a variety of alcohols to carbonyl compounds.



1a, R, R′ = =O
b, R = H; R′ = OH
c, R, R′ = H

Our interest in nitroxyls was first aroused by a report[3] that ketone **1a** was formed during the peracid oxidation of 4-hydroxy-2,2,6,6-tetramethylpiperidine (**2**) to the nitroxyl alcohol **1b.** No mechanism was proposed to account for this