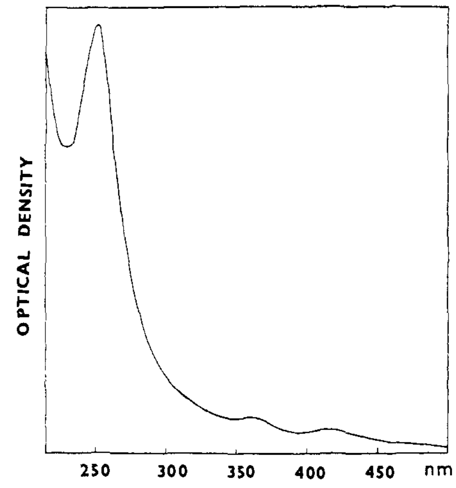


Figure 1. Absorption spectrum of the Te_n^{n+} cation.

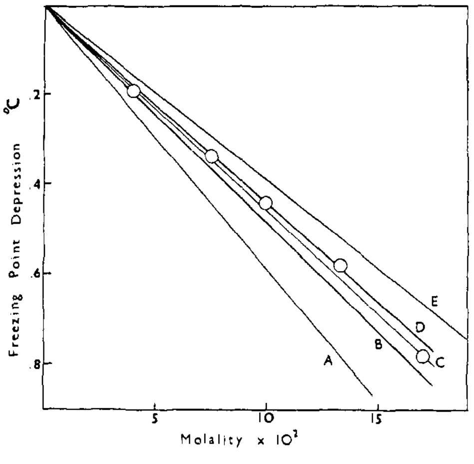


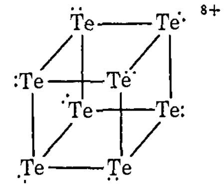
Figure 2. Freezing-point depressions for solutions of $TeSO_3F$ in fluorosulfuric acid: A, Te_2^{2+}; B, Te_4^{4+}; C, Te_6^{6+}; D, Te_8^{8+}; E, $Te_\infty^{\infty+}$.

after making allowance for a small amount of oxidation of tellurium by the solvent to red Te_4^{2+}, 2.1 mol of $S_2O_6F_2$ was required to oxidize tellurium to the yellow species, which has a strong characteristic absorption at 250 nm and two very weak absorptions at 360 and 420 nm (Figure 1). On the basis of this result we conclude that tellurium is in the 1+ oxidation state in this species and is presumably either Te^+ or a polyatomic cation such as Te_2^{2+}, Te_3^{3+}, Te_4^{4+}, etc.

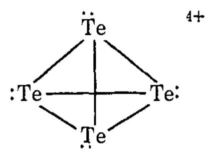
Antimony pentafluoride has been found to react with tellurium at −23° in liquid sulfur dioxide to give a red sulfur dioxide-soluble product and a small amount of a yellow sulfur dioxide-insoluble product. The red compound was shown to be $Te_4^{2+}(Sb_2F_{11}^-)_2$. On heating the yellow compound at approximately 100° a white sublimate of SbF_3 was obtained. After all the SbF_3 had sublimed off the remaining material had an analysis corresponding to the formula $TeSbF_6$. The infrared spectrum of the compound showed the characteristic SbF_6^- peak at 699 cm^{-1} and a solution in $HSO_3F–SbF_5$ had the characteristic absorption spectrum of the tellurium(1+) species shown in Figure 1.

Reaction of tellurium with excess sulfur trioxide at room temperature for several days gave a yellow compound, which after removal of excess SO_3 had an analysis corresponding to the composition $Te_2S_3O_{10}$. A solution of this compound in 30% oleum gave an identical spectrum to that shown in Figure 1. Both solid materials and their solutions in acid had a characteristic strong Raman frequency at 199 cm^{-1}. The compositions of these compounds confirm that tellurium is in the 1+ oxidation state. Magnetic measurements showed that the cation is diamagnetic. Presumably, therefore, odd electron species such as Te^+ and Te_3^{3+} can be ruled out and the most likely possibilities would appear to be Te_2^{2+}, Te_4^{4+}, Te_6^{6+}, or Te_8^{8+}. Determination of the exact molecular weight of this new tellurium cation has proved difficult. It was found that if tellurium was oxidized by $S_2O_6F_2$ in solution in HSO_3F at −23° no oxidation of tellurium to the red Te_4^{2+} by the solvent occurred, and a quantitative reaction between 2 mol of tellurium and 1 mol of $S_2O_6F_2$ gave a dark yellow-brown solution, which on addition of sulfur dioxide precipitated a bright yellow compound. Unfortunately this compound was not stable above −75° but we presume that it is $TeSO_3F$. It was however found possible to make some freezing-point depression measurements on solutions of this compound in HSO_3F. The results are compared with calculated curves for Te_2^{2+}, Te_4^{4+}, etc., in Figure 2. It is clear that the ion cannot be Te_2^{2+}, but the scatter of the experimental results resulting from the considerable experimental difficulties associated with these measurements and the small differences between the freezing-point depressions produced by the higher polymeric species make it difficult to distinguish between the various possibilities such as Te_4^{4+}, Te_6^{6+}, and Te_8^{8+}. The results in Figure 2 agree best with the octameric formulation Te_8^{8+} for which it would appear reasonable to propose the interesting cubic structure I. However, the other possibilities Te_4^{4+} and Te_6^{6+} cannot be ruled out. On the assumption that these clusters contain normal two-electron bonds they would be expected to have tetrahedral and trigonal prism structures, respectively (II and III). Te_4^{4+} is isoelectronic with tetrahedral P_4.

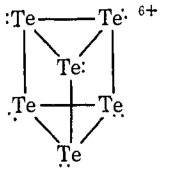
Studies of the vibrational spectra and attempts to obtain X-ray crystallographic data on the compounds continue in order to obtain definite structural information on this novel cation.



I



II



III

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Received December 19, 1969

Solvolysis Reaction of Triarylhaloallenes

Sir:

The current interest in vinyl cations derived from solvolysis reactions is indicated by the flurry of publications in this area in recent months. The substrates

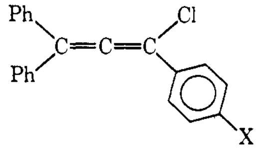
Table I. Rates of Reaction of Triarylchloroallenes in Aqueous Acetone

Compd	Temp, °C	DMK–H_2O (v/v)	10^4k, sec^{-1} [a]
1a	26.08 ± 0.02	80:20	0.542 ± 0.005
		70:30	1.82 ± 0.02
		60:40	5.65 ± 0.03
	45.00 ± 0.02	80:20	4.33 ± 0.03
1b	26.08 ± 0.02	90:10	2.37 ± 0.02
		80:20	19.5 ± 0.72

[a] Determined conductometrically in triplicate. Good first-order plots were obtained to 90% reaction. Experimental infinity values were within 1% of the computer-calculated infinity values which provided the best least-squares fit of the data.

encountered in these reports range from aryl-substituted vinyl halides[1] to less complex vinyl derivatives such as 2-bromo-1,3-butadienes,[2] cyclopropyl-1-haloethylenes,[3] haloenamines,[4] and alkyl-substituted vinyl esters.[5]

It is well known that allylic halides undergo solvolytic reactions at a rate greater than that of their saturated analogs due to charge delocalization through the three-carbon π system.[6] Grob and Spaar recently noted that adjacent π bonds apparently render vinyl halides such as 2-bromo-1,3-butadiene also more reactive.[2] We have undertaken an investigation to determine whether allenyl halides, the "unsaturated" analogs of the allyl system, exhibit similar behavior under solvolytic conditions and wish to report that triarylchloroallenes **1a** and **1b** undergo a facile solvolysis reaction in aqueous acetone at 25°. These results are given in Table I.

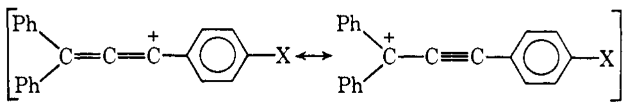


1a, X = H
b, X = CH_3O

Triphenylchloroallene[7] resulted from the action of $SOCl_2$ on 1,1,3-triphenylpropyn-1-ol according to the procedure of Jacobs and Fenton.[8] The precursor alcohol was prepared in good yield according to the procedure of Olah and Pittman[9] using phenylethynyllithium and benzophenone in hexane. In a similar manner 1-chloro-1-(*p*-methoxyphenyl)-3,3-diphenylallene (**1b**) was prepared.[10] The effect of solvent composition on the rate of solvolysis of triphenylchloroallene corresponds to $m = 0.69$, a value comparable to those obtained in the solvolysis of isopropenyl trifluoromethanesulfonate ($m = 0.52$)[5c] and trianisylvinyl halides ($m = 0.34$–0.53).[1c] Since limited data are available on solvent effects in vinyl cation solvolysis, further comment seems unwarranted. The activation parameters calculated from the temperature dependence of the rate of solvolysis are consistent with the data reported by Miller and Kaufman on 2,2-diphenyl-1-anisyliodoethylene ($\Delta S^{\ddagger} = -16.3$ eu).[1b] Such a calculation for triphenylchloroallene in 80:20 acetone–water gives $\Delta H^{\ddagger} = 20.1$ kcal/mol and $\Delta S^{\ddagger} = -10.9$ eu.[11]

When triphenylchloroallene is treated with an excess of 5% ethanolic silver nitrate solution, silver chloride is precipitated immediately at room temperature. Silver ion is not a necessary catalyst for the reaction, however, as the data in Table I indicate. When this haloallene is allowed to react at room temperature in 70:30 (v/v) aqueous acetone for 2 days, 1,1,3-triphenylpropyn-1-ol is isolated in 90% yield. No evidence of carbonyl absorption in the infrared spectrum of the product is detected.

The effect of an electron-releasing group on the reaction should be noted. If the data for **1a** and **1b** in 80% acetone are plotted *vs.* σ^+, a ρ of -2.0 is obtained. This is consistent with an intermediate carbonium ion, **2**, in which substantial delocalization of the positive charge to the 3 position exists.



2

These data thus represent the first convincing evidence that the solvolysis of aryl-substituted chloroallenes does indeed proceed through a resonance-stabilized vinyl cation as Jacobs and Fenton had earlier postulated.[7] They observed that the hydrolysis of several aryl-substituted haloallenes yielded the corresponding propargyl alcohols rather than α,β-unsaturated ketones. This is in contrast to their report that attempts to crystallize triphenylbromoallene from aqueous methanol yielded 1,3,3-triphenyl-2-propen-1-one. We are examining this discrepancy.

Based on the meager data in the literature, it is difficult to assess clearly the effect of the allylic π bond in allenyl halides. Extrapolations through 100° as well as through solvent and leaving group changes are too severe to be meaningful. We are currently examining the behavior of other model systems which should provide the answer to this question. It seems reasonable that the stability of the allenyl cation formed from triphenylchloroallene should be derived chiefly from the delocalization of positive charge over the three-carbon system, thereby allowing further delocalization into the aromatic rings at the propargylic position. The preferential reaction of solvent at this position adds support to this conclusion. On the other hand, Olah and coworkers[9] and Richey and coworkers[12] have reported that the nmr and uv spectra of several alkynylcarbonium ions indicate a strong contribution from allenyl cation forms. The enhancement of the rate of solvolysis by a *p*-methoxy group observed in our work may be interpreted as supporting their conclusion. We are exploring the charge distribution of the cation

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(1) (a) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964); (b) L. L. Miller and D. A. Kaufman, *J. Am. Chem. Soc.*, **90**, 7282 (1968); (c) Z. Rappoport and A. Gal, *ibid.*, **91**, 5246 (1969).

(2) C. A. Grob and R. Sparr, *Tetrahedron Letters*, 1439 (1969).

(3) (a) S. A. Sherrod and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 2115 (1969); (b) M. Hanack and T. Bassler, *ibid.*, **91**, 2117 (1969).

(4) S. J. Huang and M. V. Lessard, *ibid.*, **90**, 2432 (1968).

(5) (a) P. E. Peterson and R. J. Kamat, *ibid.*, **91**, 4152 (1969); (b) P. E. Peterson and J. E. Indelicato, *ibid.*, **90**, 6515 (1968); (c) P. J. Stang and R. Summerville, *ibid.*, **91**, 4600 (1969); (d) P. E. Peterson and J. E. Indelicato, *ibid.*, **91**, 6194 (1969).

(6) C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

(7) The characteristic allenic stretch was observed at 1910 cm^{-1}.

(8) T. L. Jacobs and D. M. Fenton, *J. Org. Chem.*, **30**, 1808 (1965).

(9) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5632 (1965).

(10) The characteristic allenic stretch was observed at 1929 cm^{-1}.

(11) Calculated at 25.0°.

(12) H. G. Richey, J. C. Phillips, and L. E. Rennick, *J. Am. Chem. Soc.*, **87**, 1381 (1965).

formed in this solvolysis reaction by making appropriate structural modifications.

Acknowledgment. The authors express appreciation to the Faculty Research Fellowship program of the College of William and Mary for support of this research.

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Syntheses *via* Dihydro-1,3-oxazines. X. A Versatile Ketone Synthesis Involving Stepwise Alkyl or Aryl Introduction

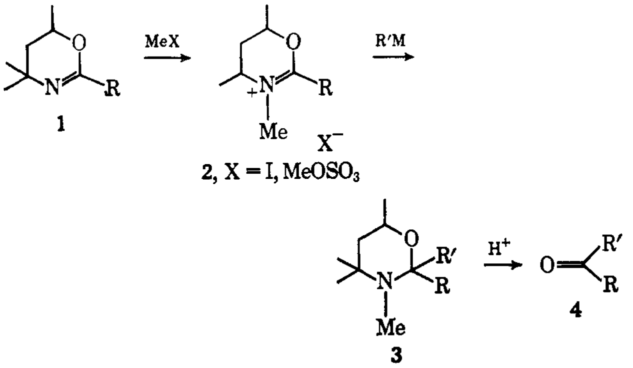
Sir:

We report a synthesis of alkyl and aryl ketones (**4**) originating from the versatile dihydro-1,3-oxazine system[1] (**1**) which involves addition of organometallics to the N-methyl quaternary salts **2** followed by hydrolytic cleavage. It was recently demonstrated that the dihydro-1,3-oxazine ring is inert to organometallics[2] and that this property afforded a novel protecting group against such reagents. It appeared to us that the facile elaboration of the 2-alkyl substituent in dihydro-1,3-oxazines by use of strong bases (*e.g.*, butyllithium) and alkyl halides[4] would provide considerable scope in constructing various ketones if the C=N link in the oxazine could be induced to add an appropriate organometallic. Various attempts to increase the reactivity of the C=N bond toward nucleophillic reagents (RMgX, RLi) by the use of BF_3, R_3B, or Et_3Al failed to provide the adduct in any appreciable amount.[5] The desired result was finally realized by addition of methyl iodide to **1** followed by introduction of the organometallic which was allowed to react at room temperature. In this fashion, the N-methyl quaternary salts[6] were indeed receptive to organometallic addition to the C=N link, and some typical examples of ketones prepared are given in Table I. The dihydro-1,3-oxazines utilized in this study were all prepared by techniques previously described for synthesizing aldehydes.[7] There were differences in behavior noted between several Grignards and their corresponding lithium derivatives. The Grignard generally gave higher yields of the adducts **3** than their organolithium counterpart, whereas phenyl and *t*-butyl Grignard reagents failed to react at all. On the other hand, *t*-butyllithium added successfully to the oxazine quaternary salts producing, after hydrolysis, the corresponding *t*-butyl ketones. The phenyl ketones could be obtained by employing the 2-phenyloxazine (**1**, R = Ph) and an appropriate organometallic. A study to extend this method to the synthesis of α,β-unsaturated ketones is currently under way.[3]

Table I. Formation of Ketones from Dihydro-1,3-oxazines

Dihydro-1,3-oxazine (**1**), R	R′M	Yield of ketone **4**, %[a,k]	2,4-DNP mp, °C (lit.)
$PhCH_2CH_2$	EtMgBr	78	108–115[b]
$PhCH_2CH_2$	*n*-BuMgBr	71[c]	118–120 (130)[d]
	n-BuLi	51	
$PhCH_2CH_2$	*t*-BuLi	29[e]	175–176 (179)[f]
Ph	EtMgBr	70	190 (191)[g]
$CH_2{=}CHCH_2C(Ph)H$	MeMgBr	56	121–123 (123)[h]
Cyclopropyl	*n*-BuMgBr	35[i]	108–110 (112)[j]

[a] Yields are based on 2-substituted 5,6-dihydro-1,3-oxazine. [b] Semicarbazone derivative, I. Heilbron, "Dictionary of Organic Compounds," Oxford Press, New York, N. Y., 1965, reports mp 82, 132, 100–135°. [c] Mass spectrum, found: M 190; $C_{13}H_{18}O$ requires M 190. [d] I. N. Nazarov and L. I. Shmonina, *Zh. Obshch. Khim.*, **20**, 1114 (1950); *Chem. Abstr.*, **44**, 9460*i* (1950). [e] Mass spectrum, found: M 190; $C_{13}H_{18}O$ requires M 190. [f] E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, **72**, 222 (1950). [g] A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co. Ltd., London, 1957. [h] M. Mousseron, R. Jacquier, and H. Christol, *Bull. Soc. Chim. France*, 346 (1957). [i] Mass spectrum, found: M 126; $C_8H_{14}O$ requires M 126. [j] M. Julia, S. Julia, and T. S. Yu, *Bull. Soc. Chim. France*, 1849 (1961). [k] All products exhibited ir and nmr spectra in total agreement with assigned structure.



A typical procedure for this ketone synthesis is illustrated by the preparation of 1-phenyl-3-pentanone (**4**, R = CH_2CH_2Ph; R′ = Et). A mixture of 2-phenethyl-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine[7] (2.31 g)

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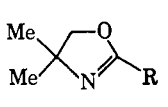
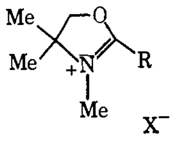
(1) Dihydro-1,3-oxazines have been reported as vehicles for the synthesis of various aldehydes, ketones, and carboxylic acids: A. I. Meyers and A. C. Kovelesky, *J. Am. Chem. Soc.*, **91**, 5887 (1969), and references cited therein.

(2) A. I. Meyers, I. R. Politzer, B. K. Bandlish, and G. R. Malone, *ibid.*, **91**, 5886 (1969). The 2-oxazolines[3] are also useful and, in some respects, superior to the dihydro-1,3-oxazines as protecting groups.

(3) Further investigation into the chemistry of related systems (*i.e.*, the 2-oxazoline A and its N-methyl derivative B) have proven that they have comparable synthetic utility toward the synthesis of ketones, acids, esters, and aldehydes. This work will be reported at a later date.



A



B

(4) A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzer, *J. Am. Chem. Soc.*, **91**, 763 (1969).

(5) In most cases trace amounts of the 2,2-dialkyltetrahydro-1,3-oxazine (**3**) were detected, but the major paths were usually reaction with the complexing moiety.

(6) It was found that the *in situ* preparation of the methiodide or N-methyl methosulfate were of approximately equal value and that neither derivative had to be removed from the reaction vessel or purified before addition of the organometallic.

(7) For example, **1** (R = $PhCH_2CH_2$) was obtained in 95% yield from the lithio salt of **1** (R = Me) and benzyl bromide; **1** (R = $CH(Ph)CH_2CH{=}CH_2$) was obtained from the lithio salt of **1** (R = CH_2Ph) and allyl bromide; **1** (R = cyclopropyl) was obtained from **1** (R = Me), 1-chloro-2-bromoethane, and 2.0 equiv of butyllithium; **1** (R = Ph) was obtained using 2-methyl-2,4-pentanediol, benzonitrile, and 96% sulfuric acid. Preparative details for these transformations have been published (A. I. Meyers, *et al.*, *Org. Proc. Prep.*, **1**, 193, 213 (1969); J. J. Ritter and E. J. Tillmanns *J. Org. Chem.*, **22**, 839 (1957)).