Table I. Enantioselective Protonation of Enolate **4**

entry	substrate	reaction cond (equiv; °C; min)	% ee **5**	% dist yield **5**
1	**1**	(1) *n*-BuLi (1,2; −78 → 15; 30)	58(*S*)	60[a]
		(2) C_3H_5MgCl (1.3; 15 → 35; 20)		
		(3) (+)-**7**(H) (2.0; −50 → −10; 60)		
2		(3)[b] (−)-**8**(H) (2.0; −50 → −10; 60)	70(*S*)	60[a]
3	**3**	(1) C_3H_5MgCl (1.2; −78 → 35; 30)	16(*R*)	*c*
		(2) (−)-**8**(H) (1.5; −50 → −10; 60)		
4		(2)[b] MeOLi (1.0; 35; 30)	70(*S*)	75
		(3) (−)-**8**(H) (2.0; −50 → −10; 60)		
5		(2)[b] (−)-**8**(Li) (1.0; 20; 30)	84(*S*)[e]	73[e]
		(3) (−)-**8**(H) (2.0; −50 → −10; 60)[d]	>98(*S*)[f]	48[f]
6		(2)[b] (+)-**8**(Li) (1.0; 20; 30)	84(*R*)[g]	73[g]
		(3) (+)-**8**(H) (2.0; −50 → −10; 60)	>98(*R*)[g]	48[g]
7		(2)[b] (−)-**8**(Li) (1.0; 20; 30)	63(*R*)	*c*
		(3) (+)-**8**(H) (2.0; −50 → −10; 60)		
8		(2)[b] (−)-**8**(Li) (1.0; 20; 30)		
		(3) *t*-BuOH (2.0; −78 → 0; 60)	62(*S*)	70

[a] See footnote 13. [b] (1) (and (2)) as above. [c] Yield not determined. [d] Use of 1.3 equiv of (−)-**8**(H) gave 78% ee. [e] Procedure (entry 5): ketene **3** (10 g, 66.6 mmol) in THF (200 mL) was sequentially treated with C_3H_5MgCl (in THF), (−)-**8**(Li) (from (−)-**8**(H) + *n*-BuLi (1.0 equiv) in THF), and (−)-**8**(H) (for equiv; °C; min, see Table I). The reaction mixture was poured into aqueous NH_4Cl/ice and extracted (Et_2O), and the organic phase was treated with 5% aqueous HCl. The combined aqueous phases were washed (Et_2O), basified (20% aqueous KOH), and extracted (Et_2O) to afford (−)-**8**(H) (98% distilled yield). The ketone mixture obtained from the organic extracts was distilled (bulb-to-bulb, 70 °C (oven), 0.5 Torr; 9.7 g) and isomerized (Al_2O_3, Et_2O, 20 °C, 1 h;[12] or *p*-TsOH/toluene, 20 °C, 15 h) to afford (*S*)-(−)-**5** (9.3 g, 73%) containing ~5% of isomeric butenones ($[\alpha]^{20}_D$ ($CHCl_3$, *c* 4.0) −396°). [f] Enantiomerically pure (*S*)-(−)-**5** [(6.13 g, 48%), $[\alpha]^{20}_D$ ($CHCl_3$, *c* 4.0) −488°; mp 27.5–28 °C] was obtained by repeated crystallization (pentane). [g] Same procedure as above, see *e* and *f*; (*R*)-(+)-**5**: $[\alpha]^{20}_D$ ($CHCl_3$, *c* 3.6) +487°; mp 27.5–28 °C.

to protonation. Much to our surprise, protonation of the ligand- and lithium-free enolate **4** (M = MgCl) afforded (*R*)-(+)-**5** (16% ee) as the major enantiomer (Table I, entry 3). On the other hand, addition of 1 equiv of MeOLi prior to protonation (Table I, entry 4), thus restoring the conditions present when starting from ester **1** (Table I, entry 2), furnished (*S*)-(−)-**5** with 70% ee. Next, enolate **4** (M = MgCl, from ketene **3**) was treated with (−)-**8**(Li) and protonated with (−)-**8**(H) to afford (*S*)-(−)-**5** with 84% ee (>98% ee after crystallization[4]) (Table I, entry 5). These results represent the highest ee yet reported for enantioselective enolate protonation and can be considered as the result of a double stereodifferentiation.[16] Interestingly, protonation of the same species with (+)-**8**(H) (Table I, entry 7) gave (*R*)-(+)-**5** (63% ee), whereas protonation with an achiral proton source (*tert*-butyl alcohol) gave (*S*)-(−)-**5** with 62% ee (Table I, entry 8). In addition, the use of (+)-**8**(Li) and (+)-**8**(H) (Table I, entry 6) allowed the synthesis of (*R*)-(+)-**5** (84% ee;[16] >98% ee after crystallization[4]).

Although enolates are known to form aggregates,[17] deaggregation and chelation[6b,17bc] should also be considered for the understanding of enolate chemistry. In particular, the dichotomy observed when apparently the same enolate **4** (with or without lithium alkoxide) is protonated with (−)-**8**(H) (Table I, entries 3, 4, and 5) leads us to the conclusion that the formation of a mixed lithium–magnesium 1:1 complex between **4** and an alkoxide is a prerequisite for high enantioselectivity.[18] Moreover, the protonation with *tert*-butyl alcohol (Table I, entry 8) constitutes the first example of substantial chirality induction via an in situ formed chiral enolate–alkoxide complex.[19] At present, it is premature to present a detailed mechanistic rationale for the observed enantioselectivity; nevertheless, it is evident that the protonating species does not undergo fast proton exchange with the chelated alkoxide: otherwise the experiment with (−)-**8** (Li) as ligand and (+)-**8**(H) as proton source (Table I, entry 7) would have given essentially racemic **5** (ee ≤33%). On the other hand, exchange processes between Li and Mg are rapid: indeed, in a crossover experiment, the lithium enolate **4** (M = Li; from **6** + MeLi in THF) was treated with the magnesium alkoxide (−)-**8**(MgCl) (from (−)-**8**(H) + C_3H_5MgCl) and subsequently protonated with (−)-**8**(H) to afford (*S*)-(−)-**5** with 84% ee. Thus, the same mixed lithium–magnesium complex is obtained, independent of the origin of Li and Mg. The analogous magnesium-free–lithium complex shows lower enantiofacial discrimination (65% ee), and the lithium-free–magnesium complex is ineffective (10% ee).

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[17] (a) Seebach, D. *Proc. R. A. Welch Foundation Conf.* **1984**, *27*, 93. (b) Polt, R.; Seebach, D. *Helv. Chim. Acta* **1987**, *70*, 1930. Laube, T.; Dunitz, J. D.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1373. Seebach, D.; Amstutz, R.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2622. Strazewski, P.; Tamm, C. *Helv. Chim. Acta* **1986**, *69*, 1041. (c) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 5539.

[18] Ongoing work confirms the importance of alkoxide ligands: replacement of MeOLi (see Table I, entry 4) by *t*-BuOLi affords **5** with 79% ee.

[19] The asymmetric induction reported by protonation of an aminoester enolate–chiral amine ($R_1{}^*R_2NH$) complex with an achiral proton source is rather poor (6–24%): ref 6b. See, also: Wasmuth, D.; Seebach, D. *Angew. Chem.* **1981**, *93*, 1007. Hogeveen, H.; Menge, W. M. P. B. *Tetrahedron Lett.* **1986**, *27*, 2767 and references cited therein.

Allylic Radicals in Cyclization Reactions

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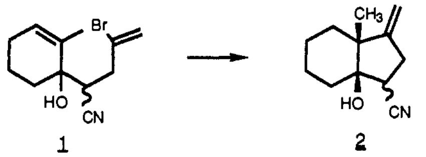
One important attribute of the vinyl radical cyclization (e.g., **1** → **2**)[1] is that the vinyl functionality is retained in the resulting ring and allows for varied subsequent chemical transformations. Another extension of the synthetic usefulness of radical cyclization reactions would result if allylic radicals could be involved in cyclization processes. It is this possibility that we address here.



1 2

We now show that allylic radicals, although clearly less reactive than their saturated or vinylic counterparts,[2,3] can provide a route complementary to a number of recently described organometallic[4] and Lewis acid[5] processes, to vinyl cyclopentane systems.

For instance, under the standard cyclization conditions (0.005 M benzene solution of 1.1 equiv of tributylstannane and 0.1 equiv of AIBN, reflux 1–2 h) the allylic bromide **3** as well as its isomer **4**[6] cyclized readily (80% yield) to give a mixture of **5**, **6**, and **7**

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[1] Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321.

[2] The allyl delocalization energy has recently been estimated to be 14.0–14.5 kcal/mol (Korth, H.-G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483).

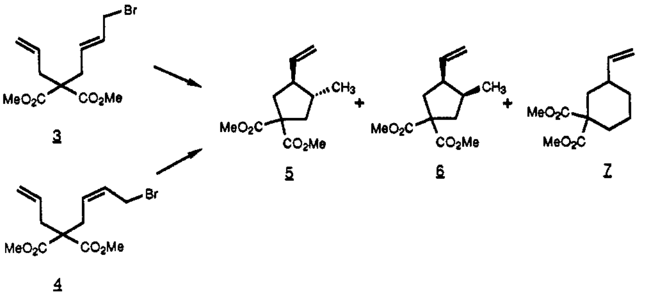
[3] For isolated examples of cyclizations which involve allylic radicals produced by intramolecular hydrogen transfer to an alkoxy or a vinyl radical, see: Lathbury, D. C.; Parsons, P. J.; Pinto, I. *J. Chem. Soc., Chem. Commun.* **1988**, 81. Johns, A.; Murphy, J. A. *Tetrahedron Lett.* **1988**, *29*, 837.

[4] (a) Felkin, H.; Umpleby, J. D.; Hagaman, E.; Wenkert, E. *Tetrahedron Lett.* **1972**, *13*, 2285. (b) Lennon, P.; Rosenblum, M. *J. Am. Chem. Soc.* **1983**, *105*, 1233. (c) Oppolzer, W.; Jacobsen, E. J. *Tetrahedron Lett.* **1986**, *27*, 1141.

[5] (a) Majetich, G.; Defauw, J.; Hull, K.; Shawe, T. *Tetrahedron Lett.* **1985**, *26*, 4711. (b) Schinzer, D.; Solyom, S.; Becker, M. *Tetrahedron Lett.* **1985**, *26*, 1831. (c) Schinzer, D.; Allagiannis, C.; Wichmann, S. *Tetrahedron* **1988**, *44*, 3851.

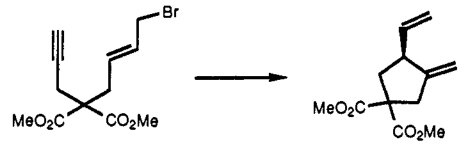
[6] The dialkyl malonates **3**, **4**, and **8** were prepared by malonic ester alkylation (NaH, THF, 0 °C) with the appropriate allylic or propargylic substrates.

in the ratio of 59:31:9,[7] respectively. As expected, formation of the cyclopentanes **5** and **6** outweighed (9.6:1) that of the cyclohexane **7**.



3, 4, 5, 6, 7

Allylic radicals are also sufficiently reactive to cyclize into a triple bond. The cyclization of **8** to **9**[8] (62% yield) represents an interesting construction of a skipped diene system embodying an exocyclic methylene.



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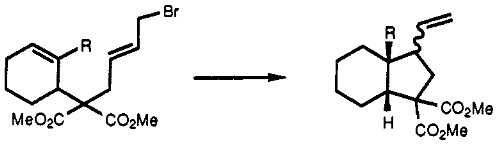
Cyclization of allylic radicals suitably positioned on a cycloalkene leads to the formation of vinyl substituted cis bicyclic systems. Cyclization of **10**[9] proceeded in high yield (86%) to give

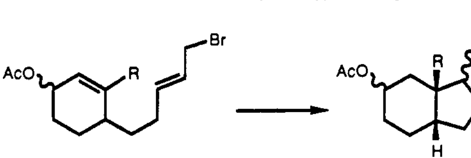


10, R=H
12, R=CH_3

11, R=H
13, R=CH_3

predominantly (2.4:1) the β-vinyl isomer of the cis hydrindane **11**.[10] It is of considerable interest that cyclization of **12** also proceeded in excellent yield (92%) to give the angularly methylated cis hydrindane derivative **13**,[11] in which the β-vinyl isomer again predominated over its epimer (3:1 β:α).

The cyclizations just recorded are undoubtedly facilitated by the presence of a *gem*-diester group in the cyclizing chain. That allylic radical cyclization can still occur in the absence of that help is shown by the moderately successful (58% yield) cyclization of **14**[12] to **15** (4:1 β:α).[13] A mixture of dimers of the allylic radical

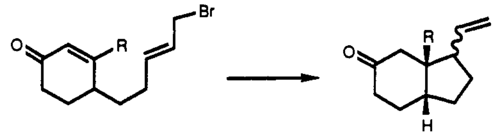


14, R=H
16, R=CH_3

15, R=H
17, R=CH_3

from **14** was also produced (15%) as were the products of simple reduction (14%). Not surprisingly, dimer formation competed even more successfully (35%) in the allyl radical cyclization starting with the methylated cyclohexene **16**. There was also much reduction of the initial allylic radical (39%), in addition to a low yield (19%) of the desired bicyclic system **17**.

That cyclization took place to some extent, even without the gem substituents of **12**, suggested that the reaction should be especially successful in the presence of an electron-deficient olefin acceptor. This was verified by cyclizing **18**[14] to the indanone **19** (4:1 β:α)[15] in 93% yield. Cyclization of **20** to form a quaternary carbon also produced a respectable 59% yield of **21** (5:1 β:α).[16]



18, R=H
20, R=CH_3

19, R=H
21, R=CH_3

We finally address the obvious question whether the reactions just described are under kinetic or thermodynamic control: to what extent are the ratios of the various cyclic isomers obtained determined by the intrusion of reversibility?[17] The relative stability of the allylic radicals involved here certainly make such reversibility conceivable. This possibility is supported by the finding that in many of the cases we studied (**3**, **10**, **12**, **18**, and **20**), the proportion of the more to the less stable of the vinyl epimers produced in the allylic cyclizations increased (71:29 β:α to 86:14 β:α, a factor of 2.5, in the case of **10**) when triphenyl- or tributylgermane[18] was used, rather than tributylstannane, to increase the lifetime of the cyclized radical.[19]

We have carefully studied the question of reversibility in the particular case of **3**, by the obvious expedient of generating the two possible isomeric radicals that cyclization of **3** would produce.

When the "*cis*"-bromomethylcyclopentane **22** (20:1 cis:trans)[20] was subjected to standard "cyclization" conditions (86% yield), some crossover from the radical corresponding to **22** to that of the radical related to **23** occurred, but the cis isomer **6** was the

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[7] Ratios were determined by capillary VPC and compared with authentic samples prepared from the mixture of exocyclic methylene relatives of **5**, **6**, and **7** (ref 1) by ozonolysis and separation of the five- and six-membered ring ketones by flash chromatography (Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923). The ketones were then separately reconverted to the exocyclic methylenes (Zn, CH_2Br_2, $TiCl_4$) (Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1978**, *19*, 2417), hydroborated, and oxidized to the primary alcohols. These alcohols were oxidized to the aldehydes and converted to **5**–**7** via Wittig reaction. Significant ^1H NMR resonances (400 MHz, $CDCl_3$ unless otherwise stated) are as follows: **5**, 5.63 (1 H, ddd, J = 17.1, 10.2, 7.9 Hz), 4.98–5.07 (2 H, m), 0.98 (3 h, d, J = 6.3 Hz); **6**, 5.74 (1 H, ddd, J = 16.8, 9.6, 8.2 Hz), 4.98–5.04 (2 H, m), 0.87 (3 H, d, J = 7.0 Hz) which are in agreement with the relevant values of the related substances reported by Rosenblum (ref 4b).

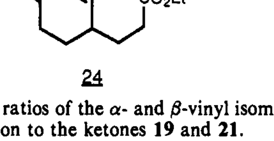
[8] **9**, 5.65 (1 H, ddd, J = 17.5, 9.6, 8.0 Hz), 5.05–5.10 (2 H, m), 4.83 and 4.99 (2 H, 2 dd, J = 2.3, 4.7 Hz), 3.75 and 3.73 (6 H, 2 s).

[9] **10** and **12** were prepared by alkylation (NaH, THF, 0 °C) of the cyclohexenyl malonates which were prepared by Pd-catalyzed alkylation of the corresponding allylic acetates (cf. Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730).

[10] **11β**, 5.54 (1 H, ddd, J = 16.9, 10.1, 8.5 Hz), 4.93–5.01 (2 H, m), 3.72 and 3.69 (6 H, 2 s); **11α**, 5.85 (1 H, ddd, J = 17.1, 10.2, 7.9 Hz), 3.73 and 3.69 (6 H, 2 s).

[11] **13β**, 5.61 (1 H, ddd, J = 17.0, 10.3, 8.1 Hz), 4.98–5.07 (2 H, m), 3.73 and 3.69 (6 H, 2 s), 0.72 (3 H, s).

[12] **14** was prepared from **24** (Elliott, M. L.; Urban, F. J. *J. Org. Chem.* **1985**, *50*, 1752) in 10 steps ($NaBH_4$, $CeCl_3$, MeOH/TBDMSCl, imidazole, CH_2Cl_2/LAH/Swern/Wittig/DIBAL/2-methoxypropene, PPTS, CH_2Cl_2/Ac_2O, pyridine, CH_2Cl_2/PPTS, EtOH/CBr_4, PPh_3, CH_2Cl_2). **16** was similarly prepared from **25** (Johnson, W. S.; McCarry, B. E.; Markezich, R. L.; Boots, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 352) by steps 1 and 2 (above) followed by hydroboration/oxidation (9-BBN/$^-$OOH) and then steps 4–10.



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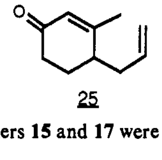

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[13] The ratios of the α- and β-vinyl isomers **15** and **17** were determined after oxidation to the ketones **19** and **21**.

[14] **18** and **20** were prepared in the same manner as were **14** and **16**, only oxidized (MnO_2, $CHCl_3$) rather than acylated.

[15] **19β**, 5.66 (1 H, ddd, J = 17.1, 9.9, 7.8 Hz), 4.95–5.04 (2 H, m).

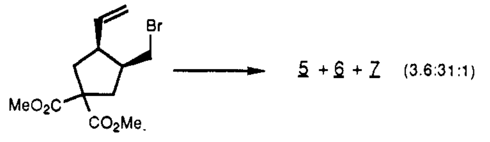
[16] **21β**, 5.68 (1 H, ddd, J = 16.8, 10.4, 8.2 Hz), 4.98–5.05 (2 H, m), 0.86 (3 H, s); **21α**, 0.97 (3 H, s). For comparison, see ref 5b and 5c.

[17] (a) Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386. (b) Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525. (c) Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1986**, *27*, 4529.

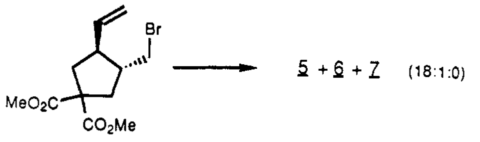
[18] Kuivila, H. G.; Beumel, O. F., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 1246.

[19] Tributylgermane is poorer hydrogen donor than is tributylstannane. Cf. Ingold, K. U. et al. *J. Am. Chem. Soc.* **1985**, *107*, 4594.

[20] **22** and **23** were prepared from **9** by chromatographic separation of the monohydroboration/oxidation (9-BBN/$^-$OOH) products and further separation of the cis and trans alcohols. These alcohols were then separately tosylated (TsCl, pyr, DMAP, CH_2Cl_2) and converted to the bromides (LiBr, CH_3CN).



22 (20.1)



23 (14.1)

major product (9:1 cis to trans). Significantly, however, a small amount (2.2%) of the cyclohexyl isomer 7 was produced. As expected, the stereochemistry of bromomethylcyclopentane 23 (14:1 trans to cis) was not significantly altered upon reaction with stannane to give 5 as the major product (18:1 trans to cis). We conclude that there is a real, but small, intrusion of reversibility in allylic radical cyclizations, but that it does not appear sufficient to explain the difference in stereochemical results observed when germanes rather than stannanes are used to bring about cyclization.

Nanosecond Laser Flash Photolytic Generation and Lifetimes in Solvolytic Media of Diarylmethyl and *p*-Methoxyphenethyl Cations

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Although carbocations are intermediates of a number of photochemical reactions,[3] there has been only limited evidence[4] from flash photolysis for their presence, and the potential of this technique for directly studying this important class has not been exploited. We report here experiments showing that the title secondary cations can be observed in aqueous and alcohol solvents, and the rates of their reactions with solvent and azide ion directly measured. We also demonstrate that, at least in the examples reported here, ground-state cations are intermediates of both photosolvolyses and alkene photoprotonations.

The diarylmethyl cations were produced by photoheterolysis,[5] with acetates and *p*-cyanophenyl ethers as precursors. Standard solvents were 20% by volume acetonitrile:water (1:4 AN:W) and trifluoroethanol (TFE). As illustrated in Figure 1, signals due to both cation and radical were typically observed. The cations, with λ_{max} at 400–500 nm, were identified by the match of these portions of the spectra with those obtained for stable cation solutions in 90% H_2SO_4. The decays of these transients were first-order, unaffected by O_2, and accelerated by azide. In addition, experiments with time-resolved conductivity detection exhibited characteristic[4d] increases in conductance in acid (release of H^+) and decreases in base (neutralization of OH^-), occurring with the same rate constants as those obtained with optical detection. The radicals were identified by their spectra[6] as well as by their second-order decay under argon with efficient scavenging by O_2. Mixtures of heterolysis and homolysis products are frequently encountered upon RX photolysis,[3a,b] and the two types of intermediate were observed with the majority of substrates we investigated (Table I). Not unexpectedly, a polar solvent was necessary for cation production. In pure AN, cations could still be observed, but the cation:radical OD ratios were only 0.1–0.2, considerably smaller than in the aqueous mixture. In CH_2Cl_2 only radical was seen. In all cases the cations were completely formed within the 20 ns laser pulse, which means that their rates of production from the precursors (including electronically excited cation) are ≥ 5×10^7 s^{-1}.

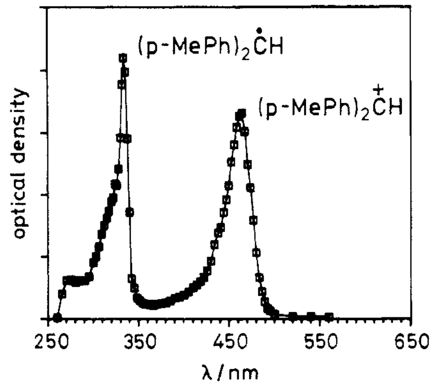

Figure 1. Transient absorption spectrum[5] measured 30–35 ns after the pulse on photolyzing $(4\text{-}MeC_6H_4)_2CHOAr$ in argon-saturated TFE. The band at 330 nm is due to $(4\text{-}MeC_6H)_2CH^{\bullet}$, that at 465 nm to $(4\text{-}MeC_6H_4)_2C^+H$.

3,4′-Dimethoxydiphenylmethyl acetate proved exceptional in so far as a strong cation signal with little radical was seen upon photolysis. This is an example of the "meta" effect, the enhancement of photoheterolysis by a *m*-MeO group.[7] This effect was sufficiently pronounced so that cation was even observed with the alcohol as the precursor, while other diarylmethanols lcking the *m*-MeO gave only a radical signal. 9-Xanthenol also produced a good cation transient. There is evidence from fluorescence spectroscopy of photoheterolysis with this system and that the cation is initially formed in the excited singlet state.[8] The cations we observed must, however, be electronically relaxed. This can be concluded from the correspondence of the transient spectra with those obtained in acid, from the independence of the spectra and decay rates on precursor, from the observation of ground-state nucleophilic selectivity[9] and substituent effects, and, with the xanthylium ion, from the agreement with a ground-state rate constant.[10]

The *p*-methoxyphenethyl cation AnC^+HCH_3 was generated by photoheterolysis of the acetate in TFE, along with a considerable yield of radical. The same cation, however with no radical, was

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[1] University of Toronto.

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