(two s, 3 each), 4.72 (t of d, $J$ = 4.5, 10.0 Hz, 1), and 5.10 ppm (m, 1).

The cis epoxy ether **11** reacted very rapidly (1 min) to give the product distribution shown in eq 4 in overall 95% yield. The acetate of **12** had nmr $\delta$ 0.85 (d, $J$ = 7 Hz, 3), 0.9–2.1 (m, 7), 2.02 (s, 3), 3.31 (s, 3), 3.48 (m, 1), and 4.38 ppm (d of d, $J$ = 1.4, 10.1 Hz, 1). The acetate of **13** had nmr $\delta$ 0.97 (d, $J$ = 7 Hz, 3), 0.9–2.3 (m, 7), 1.98 (s, 3), 2.75 (t of d, $J$ = 4.7, 11 Hz, 1), 3.31 (s, 3), and 4.38 ppm (t of d, $J$ = 4.7, 11 Hz, 1).

The trans epoxy ether **14** after 3 hr at −5° and 2.5 hr at 25° gave 83% of a mixture having the composition shown in eq 5. The acetate of **15** had nmr $\delta$ 0.90 (d, $J$ = 7 Hz, 3), 0.9–2.2 (m, 7), 2.00 (s, 3), 3.01 (m, 1), 3.22 (s, 3), and 4.48 (t, $J$ = 10 Hz, 1). The acetate of **16** had $\delta$ 0.94 (d, $J$ = 7 Hz, 3), 0.9–2.1 (m, 7), 1.96 (s, 3), 3.29 (s, 3), 3.33 (m, 1), and 4.74 ppm (t of d, $J$ = 4.3 and 10.0 Hz, 1).

*cis*-2,3-Epoxycyclohexyl acetate (**17**) after 40 min at −7° gave 89% of a mixture containing 6% unreacted **17**, 29% of **6**[12] (identical with material formed in eq 2), 7% of a compound assumed to be **18** (see below), and 59% of an approximately equal mixture (by nmr, unresolved by vpc) of **19** and **21**.

This mixture was treated with acetic anhydride in pyridine, giving 93% of **6** diacetate and 7% of **7** diacetate. Combining these data allowed the determination of the product distribution shown in eq 6.

The stereospecific trans opening of the epoxide ring by lithium dimethylcuprate was evident from the mutually exclusive formation of products in, *e.g.*, eq 2 (and 6) *vs.* 3 and 4 *vs.* 5.

**Registry No.**—**1**, 5369-63-1; **2**, 34849-39-3; **3**, 42282-48-4; **5**, 26828-72-8; **6** diacetate, 42282-50-8; **7** diacetate, 42282-51-9; **8**, 26828-73-9; **9** diacetate, 42282-53-1; **10** diacetate, 42282-54-2; **11**, 17208-68-3; **12** acetate, 42282-56-4; **13** acetate, 42282-57-5; **14**, 2699-17-4; **15** acetate, 42282-59-7; **16** acetate, 42282-60-0; lithium dimethylcuprate, 15681-48-8.

(12) J. Klein and E. Dunkelblum, *Tetrahedron*, **24**, 5701 (1968).

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# Dehydrochlorination–Decarbonylation of 2-Chloro-1,3-dicarbonyl Compounds, a Method for Ring Contraction

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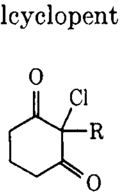
*Received July 6, 1973*

Treatment of 2-chloro-2-alkylcyclohexane-1,3-diones (**1**) with sodium carbonate in hot xylene leads to 2-alkylcyclopentenones (**3**). This new method for the construction of cyclopentenones was used in efficient syntheses of methyl jasmonate and jasmone.[1] It was applied subsequently in the preparation of other cyclopentenones on the way to prostaglandins.[2,3] To survey the applicability of the new reaction, we investigated the behavior of an $\alpha$-chloro-$\beta$-ketoaldehyde and two $\alpha$-chloro-$\beta$-keto esters.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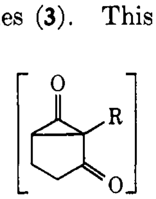
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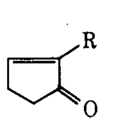
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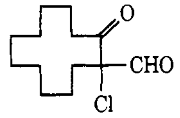
Chlorination of 2-formylcyclododecanone with *tert*-butyl hypochlorite in chloroform solution gave the crystalline chloride **4**, whose reaction with suspended sodium carbonate in boiling xylene was slow, requiring 45 hr. The resulting cycloundecene-1-carboxaldehyde (**6**) was separated from minor amounts of 2-chlorocyclododecanone by chromatography.

*tert*-Butyl hypochlorite served again in the chlorination of 2-carbomethoxycyclohexanone. The resulting chloride **7** (84%) on dehydrochlorination–decarbonylation with sodium carbonate in hot xylene afforded 1-carbomethoxycyclopentene (**9**) in 71% yield.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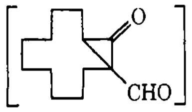
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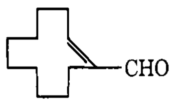
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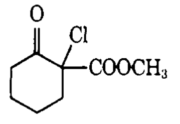
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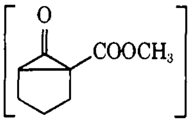
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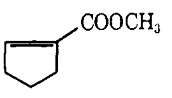

9

To study the behavior of an aliphatic $\alpha$-chloro-$\beta$-keto ester, compound **10** was prepared by standard procedures. When a solution of **10** was heated in xylene over sodium carbonate, gas evolution ceased in 6 hr. Owing to the air sensitivity of some of the products, the isolation of four pure substances by chromatography was accompanied by heavy losses. The least polar, liquid material was identified as methyl (*E*)-2-phenylcinnamate (**23**, 6%) by hydrolysis to the known carboxylic acid **24**. It was followed by crystalline 1-phenyl-2-indanone (**19**, 21%). The more polar fractions contained 2-methoxy-5-oxo-3,4-diphenyl-2,5-dihydrofuran (**22**, 5%) and 2-methoxy-4-oxo-3,5-diphenyl-4,5-dihydrofuran (**16**, 14%) whose structures were deduced from spectral properties (see Experimental Section).

The products observed in the dehydrochlorination–decarbonylation of the three cyclic chlorides **1**, **4**, and **7** appear to originate from the cyclopropanones **2**, **5**, and **8** by thermal, nonconcerted elimination of carbon monoxide. Earlier work on the pyrolysis of 2-acetoxy-1,3-cyclohexanediones[4] and medium-ring 2-acetoxy ketones[5] as well as investigations on the thermolysis of 3-cyclopropyl-3-oxopropanoates[6] support this hypothesis. Thermally allowed, energetically more favorable disrotatory ring opening of these cyclopropanones to the corresponding cis–cis oxyallyl dipoles,[7] if it occurs, is nonproductive and reversible.[8] An entirely different situation prevails in the aliphatic case **10**. Two of the four phenyl-stabilized oxyallyl ions **12–15**, produced either directly from the enolate by ionization or, less likely, by disrotatory ring opening of the two diastereomeric cyclopropanones **11**, can cyclize to the

(1) G. Büchi and B. Egger, *J. Org. Chem.*, **36**, 2021 (1971).

(2) J. Bagli and T. Bogri, *Tetrahedron Lett.*, 3815 (1972).

(3) F. Kienzle, G. Holland, J. L. Jernow, S. Kwoh, and P. Rosen, *J. Org. Chem.*, **38**, 3440 (1973).

(4) T. A. Spencer, A. L. Hall, and C. Fordham v. Reyn, *J. Org. Chem.*, **33**, 3369 (1968).

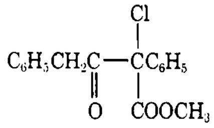
(5) R. G. Carlson and J. H. Bateman, *J. Org. Chem.*, **32**, 1608 (1967).

(6) W. F. Berkowitz and A. A. Ozorio, *J. Org. Chem.*, **36**, 3787 (1971).

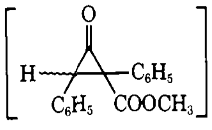
(7) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH, Weinheim/Bergstr., Germany, 1971, p 46.

(8) Compare the facile thermal racemization of optically active *trans*-2,3-di-*tert*-butylcyclopropanone with its slow decarbonylation: D. B. Sclove, J. F. Pazos, R. L. Camp, and F. D. Greene, *J. Amer. Chem. Soc.*, **92**, 7488 (1970).

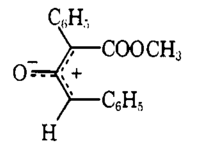
ketene acetal **16** while three could cyclize to the keto esters **17** and **18**, both of which are expected to undergo decarbomethoxylation to **19** in the reaction medium.


$C_6H_5CH_2\underset{O}{\underset{\|}{C}}-\underset{COOCH_3}{\overset{Cl}{C}}C_6H_5$

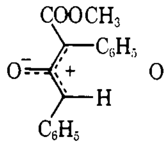
**10**



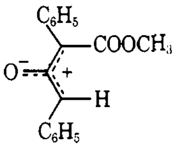
**11**



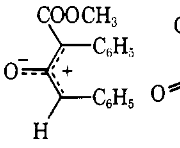
**12**



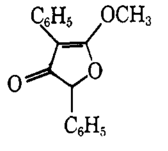
**13**



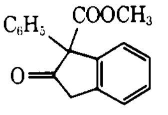
**14**



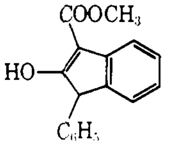
**15**



**16**



**17**



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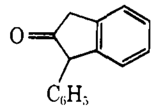
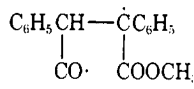
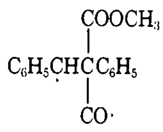


**19**

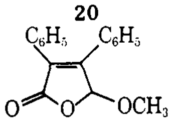
The cyclopropanones **11** are, however, attractive intermediates to rationalize the production of the two minor products. Methyl (*E*)-2-phenylcinnamate (**23**)


$C_6H_5\underset{CO\cdot}{CH}-\underset{COOCH_3}{C}C_6H_5$

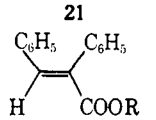
**20**


$C_6H_5\underset{\cdot}{C}H\underset{CO\cdot}{\overset{COOCH_3}{C}}C_6H_5$

**21**



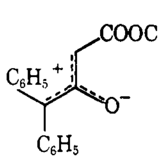
**22**



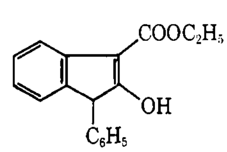
**23**, R = $CH_3$
**24**, R = H

results from decarbonylation of either diradical **20** or **21**. Recyclization of the former could lead to the $\beta$-butenolide and thence to the more stable $\alpha$-butenolide **22** actually observed.

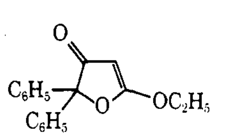
Our findings seem to be closely related to some of Kende's.[9] He found that thermal decomposition of ethyl diazoacetate in diphenylketene gave the indanone **26** and the ketene acetal **27** and hypothesized that these



**25**



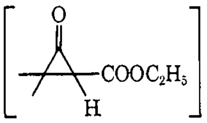
**26**



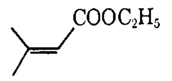
**27**

products originate from the oxyallyl intermediate **25**. Addition of ethyl diazoacetate to dimethylketene, on the other hand, yielded ethyl $\beta,\beta$-dimethylacrylate (**29**) and the $\beta$-butenolide **30**. The cyclopropanone **28** was postulated to be the critical intermediate and its transformation to the two products **29** and **30** is analogous to the conversion of **11** to **22** and **23**.

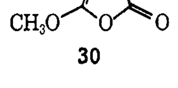
In summary, the dehydrochlorination–decarbonylation of 2-chloro-1,3-dicarbonyl compounds is a useful procedure for ring contraction, affording $\alpha,\beta$-unsaturated cyclic ketones, aldehydes, and esters. It seems to be of no preparative value in the aliphatic series because reactions other than decarbonylation take place more readily. Efforts to decarbonylate the chloro diketone **31** failed and the method does not seem to serve in the synthesis of cyclobutenones.



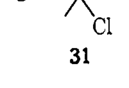
**28**



**29**



**30**



**31**

## Experimental Section

Microanalyses were performed in the Microanalytical Department of Firmenich SA, Geneva. Melting and boiling points are uncorrected. The following spectrometers were used: nuclear magnetic resonance (nmr), Varian T-60 and A-60 (peaks reported in parts per million downfield from TMS as internal standard); infrared (ir), Perkin-Elmer Model 237 and A 21; mass spectrometer (mass spectrum) Atlas CH-4; ultraviolet (uv), Cary Model 14. Vapor phase chromatography (vpc) analyses were performed on F & M 720 and Varian Aerograph 1800 instruments using silicone rubber SE-30 and Carbowax 20M columns. Thin layer chromatograms (tlc) were prepared with Merck silica gel GF 254.

**2-Hydroxymethylenecyclododecanone.**—This substance was prepared in 73% yield according to ref 10.

**2-Chloro-2-formylcyclododecanone (4).**—To a stirred solution of 21.0 g (0.1 mol) of hydroxymethylenecyclododecanone in 200 ml of dry chloroform was added dropwise under nitrogen 12.8 g (0.12 mol) of *tert*-butyl hypochlorite[11] at a temperature of −10° over a 30-min period. The mixture was stirred for an additional 2 hr at the same temperature and was then concentrated *in vacuo*. The residue consisted of 26 g of oily crystals, which were recrystallized from hexane to afford 20 g (80%) of 2-chloro-2-formylcyclododecanone (4): mp 59–61°; ir ($CHCl_3$) 1710, 1740 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 1.0–3.0 (20 H, m), 9.2 (1 H, s); mass spectrum (70 eV) *m/e* (rel intensity) $M^+$ (4.4), 209 (22), 55 (100).

**Cycloundecene-1-carboxaldehyde (6).**—A flask, equipped with a Dean-Stark trap, was charged with 50 g of glass beads, 11.0 g (0.105 mol) of anhydrous sodium carbonate, and 300 ml of xylene. After the contents had been heated under reflux for 1 hr, 2-chloro-2-formylcyclododecanone (4, 24.4 g, 0.1 mol) was added and stirring was continued at reflux under nitrogen for 45 hr. The reaction mixture was then filtered, and the filtrate was washed with water, dried ($Na_2SO_4$), and concentrated *in vacuo*. Distillation afforded 12.7 g (70%) of a 3:1 mixture of cycloundecene-1-carboxaldehyde (6) and 2-chlorocyclododecanone. These two products were separated by chromatography on a mixture of 150 g of silica gel (0.05–0.2 mm) and 50 g of silica gel GF 254, using a 1:1 mixture of benzene–chloroform as eluent. Early eluates contained 7 g of a mixture followed by 4.4 g of pure aldehyde 6: bp 78° (0.05 mm); ir ($CHCl_3$) 1680 and 1640 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 9.2 (1 H, s) and 6.2 (1 H, t, $J$ = 6 Hz); uv (EtOH) 234 nm ($\epsilon$ 14,300); mass spectrum (70 eV) *m/e* (rel intensity) 180 (10), 49 (100).

A pure sample of 2-chlorocyclododecanone was obtained by vpc collection and identified with authentic material by comparison of ir and nmr spectra.

**2-Chloro-2-carbomethoxycyclohexanone (7).**—To a stirred solution of 31.2 g (0.2 mol) of 2-carbomethoxycyclohexanone in 300 ml of dry methanol was added dropwise under nitrogen 23.7 g (0.22 mol) of *tert*-butyl hypochlorite at a temperature of −10° over a 1-hr period. After the addition was completed, the mixture was stirred for 1 hr at the same temperature and then stored overnight in the refrigerator. The next day it was stirred

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[9] A. S. Kende, *Chem. Ind.* (*London*), 1053 (1956).

[10] V. Prelog, L. Ruzicka, and O. Metzler, *Helv. Chim. Acta*, **30**, 1883 (1947).

[11] H. M. Teeter and E. W. Bell, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 125.

for an additional 3 hr at room temperature, then concentrated *in vacuo* and distilled to give 3 g of starting material and 32 g (84%) of pure 2-chloro-2-carbomethoxycyclohexanone (**7**): bp 74° (0.1 mm); ir ($CHCl_3$) 2955, 1725, and 1440 cm$^{-1}$; nmr ($CCl_4$) $\delta$ 3.80 (3 H, s) and 1.4–3.0 (8 H, m).

*Anal.* Calcd for $C_8H_{11}ClO_3$: C, 50.42; H, 5.81. Found: C, 50.51; H, 5.71.

**1-Carbomethoxycyclopentene (9).**—Glass beads (50 g) were added to a flask containing 19.0 g (0.1 mol) of 2-chloro-2-carbomethoxycyclohexanone (**7**), 11.0 g (0.105 mol) of anhydrous sodium carbonate, and 150 ml of dry xylene. The resulting mixture was stirred at reflux for 14 hr and was then cooled, filtered, and passed through a dry column of 200 g of silica gel. After elution of the xylene with hexane, the product was washed out with chloroform. Evaporation and distillation yielded 9.0 g (71%) of 1-carbomethoxycyclopentene (**9**): bp 57° (10 mm) [lit.[12] bp 63–65° (10 mm)]; ir ($CHCl_3$) 1700 and 1620 cm$^{-1}$; nmr ($CCl_4$) $\delta$ 6.6 (1 H, s, br), 3.6 (3 H, s), and 2.7–1.7 (6 H, m); uv (EtOH) 224 nm ($\epsilon$ 9800); mass spectrum (70 eV) *m/e* (rel intensity) M$^+$ (32), 95 (48), 64 (100).

**Methyl 2,4-diphenylacetoacetate** was prepared in 78% yield according to ref 13: mp 61–63° (lit.[13] mp 59–60°); ir 1750, 1710, 1640, and 1600 cm$^{-1}$; nmr ($CDCl_3$) $\delta$ 3.7 (3 H, s), 3.8 (2 H, s), 4.8 (1 H, s), and 7.0–7.5 (10 H, m).

**Chlorination of the Keto Ester.**—To a stirred solution of 13.4 g (0.05 mol) of the above keto ester in 150 ml of dry chloroform was added dropwise under nitrogen 65 g (0.06 mol) of *tert*-butyl hypochlorite at a temperature of −10° over a 30-min period. The reaction mixture was stored for 7 days in a refrigerator and was then concentrated *in vacuo*, and the residue was diluted with an equal amount of methanol to afford 11 g (73%) of **10**, mp 50–60°. A small sample was recrystallized from methanol: mp 64–65°; ir ($CHCl_3$) 1720 and 1740 cm$^{-1}$; nmr ($CCl_4$) $\delta$ 3.7 (3 H, s), 3.8 (2 H, s), and 6.9–7.5 (10 H, m); mass spectrum *m/e* (rel intensity) M$^+$ (1), 184 (26), 91 (100).

*Anal.* Calcd for $C_{17}H_{15}O_3Cl$: C, 67.44; H, 4.99. Found: C, 67.43; H, 4.98.

**"Decarbonylation" of the Chloride 10.**—A flask, equipped with a Dean-Stark trap, was charged with 20 g of glass beads, 3.3 g (0.031 mol) of anhydrous sodium carbonate, and 150 ml of dry xylene. After the contents had been refluxed for 1 hr, 9.0 g (0.03 mol) of the chloride **10** was added and stirring was continued at reflux under nitrogen for 6 hr. The reaction mixture was then cooled, filtered, and concentrated *in vacuo*. The dark brown residue was chromatographed on 150 g of silica gel, using a 1:1 mixture of benzene–chloroform as eluent. Early fractions gave 2.9 g of a mixture of **23** and **19** which was rechromatographed *under argon* on silica gel (0.05–0.2 mm, 30 g) using a 4:1 mixture of hexane–ether to afford 400 mg (6%) of **23**: bp 150° (0.5 mm, Kugelrohr oven); ir ($CHCl_3$) 1720 and 1600 cm$^{-1}$; nmr ($CCl_4$) $\delta$ 3.6 (3 H, s), 6.9 (1 H, s), and 7.1–7.6 (10 H, m); uv (EtOH) 221 nm ($\epsilon$ 15,700) and 287 (22,000); mass spectrum (70 eV) *m/e* (rel intensity) M$^+$ (100), 177 (77), 121 (86). Hydrolysis with aqueous potassium hydroxide gave (*E*)-2-phenylcinnamic acid, mp 175° (lit.[14] mp 173°). The following fraction (1.5 g, 21% yield) consisted of a slightly yellow, exceedingly air-sensitive liquid which crystallized at −5°. Sublimation at 40° in a high vacuum gave pure **19**: mp 50° (lit.[15] mp 49–50°); ir ($CCl_4$) 1760 cm$^{-1}$; nmr ($CCl_4$) $\delta$ 3.5 (2 H, s), 4.6 (1 H, s), and 6.9–7.3 (9 H, m); mass spectrum (70 eV) *m/e* (rel intensity) M$^+$ (30), 179 (80), 178 (100), 177 (48), 165 (25), 89 (10).

Later fractions of the original chromatogram gave compound **22**, which crystallized from ether to afford 0.39 g (5%) of crystals: mp 150°; ir ($CHCl_3$) 1770 and 1650 cm$^{-1}$; nmr ($CDCl_3$) $\delta$ 3.7 (3 H, s), 6.2 (1 H, s), 7.2–7.6 (10 H, m); uv (EtOH) 295 nm ($\epsilon$ 10,800); mass spectrum (70 eV) *m/e* (rel intensity) M$^+$ (50), 238 (34), 178 (100).

*Anal.* Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 77.04; H, 5.35.

The last fraction afforded, after trituration with ether, 1.14 g (14%) of **16**: mp 111–112°; ir ($CHCl_3$) 1690, 1610, and 1590 cm$^{-1}$; nmr ($CDCl_3$) $\delta$ 4.2 (3 H, s), 5.6 (1 H, s), and 7.1–8.2 (10 H, m); uv (EtOH) 253 nm ($\epsilon$ 22,300) and 287 (9000); mass spectrum (70 eV) *m/e* (rel intensity) M$^+$ (51), 121 (100), 89 (27).

*Anal.* Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.63; H, 5.35.

**Acknowledgments.**—We are indebted to Firmenich SA, Geneva, for generous financial support.

**Registry No.**—**4**, 42367-18-0; **6**, 42367-19-1; **7**, 42367-20-4; **9**, 25662-28-6; **10**, 42367-22-6; **16**, 42367-23-7; **19**, 24017-08-1; **22**, 42367-25-9; **23**, 36854-27-0; 2-hydroxymethylenecyclododecanone, 949-07-5; 2-carbomethoxycyclohexanone, 41302-34-5; methyl 2,4-diphenylacetoacetate, 40195-49-1.

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## A Study of 1-Substituted Benzonorbornadienes[1]

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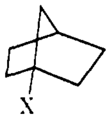
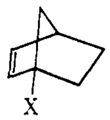
*Received March 28, 1973*

Work done on bridgehead carbinyl systems **1**,[2] **2**,[2,3] and **3**[4] has prompted us to study briefly the similar benzonorbornadiene system **4**, which has recently become available.[5–7]



1



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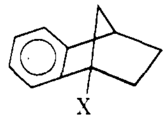

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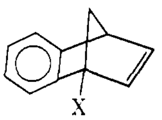

4

a, X = Br
b, X = COOH
c, X = $CH_2OH$
d, X = $CH_2OAc$
e, X = $CH_2OTs$
f, X = $CH_2OBs$

In the solvolysis of benzonorbornenyl-1-carbinyl tosylate (**3e**) Wilt and coworkers found that $\pi$ participation is precluded geometrically because of the rigid nature of the bicyclic system, preventing the twist required of the aromatic ring to achieve a phenonium ion type of geometry in the transition state for this constrained neophyl-like tosylate. They showed that tosylate **1e** solvolyzed at 50 times the rate of **3e** at 131° in acetic acid. They attributed this to the electron-withdrawing, destabilizing $-I$ effect of the aromatic ring[4] and found no phenyl migration. Bly[3] has studied brosylate **2f** and showed that acetolysis of **1f** is at least 1.3 times as rapid as that of the unsaturated tosylate **2f** at 100°, demonstrating the $-I$ effect of the double bond. They found no double-bond migration either.

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[1] This investigation was supported in part by a University of Wisconsin—Eau Claire University Research Grant.

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[7] Certain derivatives of this system have been synthesized by an entirely different route: (a) K. Wiesner and A. Philipp, *Tetrahedron Lett.*, 1467 (1966); (b) A. H. Philipp, Ph.D. Dissertation, University of New Brunswick, 1967. We thank Professor Wiesner for this information.