

# Lewis Acid Promoted Decomposition of Unsaturated $\alpha$ -Diazo Ketones. 2. A New Initiator for Polyolefinic Cationic Cyclization

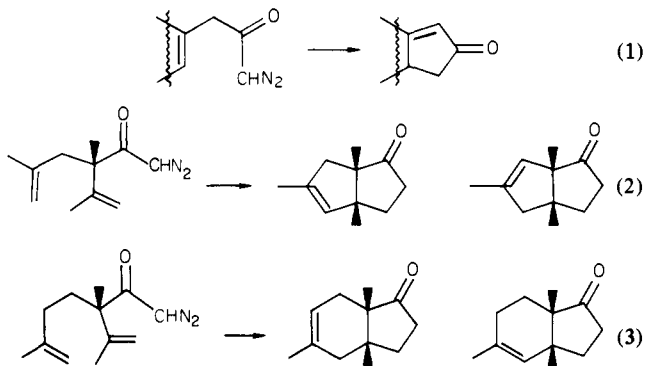
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**Abstract:** This report documents the first utilization of the unsaturated diazo ketone functionality in the initiation of polyolefinic cationic cyclizations. Specifically,  $\beta,\gamma$ -unsaturated diazo ketones **1** and **2** undergo a stereoselective Lewis acid promoted cyclization to the cis-fused tricyclic ketones **5**, **11**, and **15**, in 43–46% yield, respectively. Diazo ketones **3** and **4**, on the other hand, did not afford tricyclic products; instead, benzocycloheptanones **20–22** were obtained in moderate to good yield (ca. 22–59%). The mechanism of the cyclization process is discussed in terms of cationic intermediates. In the case of the diazo ketones **3** and **4**, a marked solvent effect on product distribution provided insight into the nature of the cyclization process.

## Introduction

In the preceding paper<sup>2</sup> we demonstrated that  $\beta,\gamma$ -unsaturated diazo ketones, through agency of Lewis acids, are viable synthons of simple and annulated cyclopentenone derivatives (eq 1). During

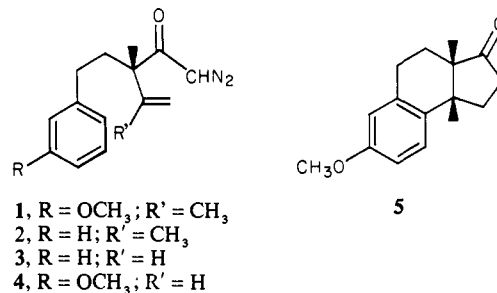


the course of that investigation we uncovered two acyclic diazo ketones which afford bicyclic products (eq 2 and 3), thereby suggesting that the  $\alpha$ -diazo ketone functionality can serve as an initiator of polyene cyclization.<sup>3</sup> Our motivation in exploring these systems was to compete, in an intramolecular case, monocyclization at two different olefinic sites. In the event, however, polyolefinic cyclization predominated.

Our initial success, albeit serendipitous, prompted us to explore in general the feasibility of employing the diazo ketone functionality for the initiation of polyolefinic cationic cyclizations.<sup>3</sup> To the best of our knowledge, unsaturated diazo ketones have not previously been employed in this manner. In fact, recent investigations of biomimetic polyene cyclizations have utilized increasingly stable carbonium ion initiators.<sup>4</sup> We were, therefore, particularly interested in the effect that the highly energetic diazonium ion would have on the cyclization process.

In this, the second detailed account of our work in the area of Lewis acid promoted decomposition of unsaturated diazo ketones, we report that the  $\alpha$ -diazo ketone functionality is indeed an effective initiator for polyene cyclization when employed in conjunction with highly nucleophilic olefins.

At the outset it was anticipated that a systematic modification of substrate structure would provide insight into both the scope and limitations of the  $\alpha$ -diazo ketone functionality in such a cyclization process. To this end we selected diazo ketones 1–4



which would not be expected to become involved in complex structural rearrangements. In addition, diazo ketone **1** appeared ideally suited for our initial study since two of the four possible tricyclic products (**5** and **6**) had been prepared and their stereochemistry rigorously established by Jeger and co-workers.<sup>5</sup>

## Preparative Experiments

The required diazo ketones (1–4) were prepared in nearly quantitative yields from the corresponding  $\beta,\gamma$ -unsaturated acids by sequential treatment with oxalyl chloride and excess diazomethane. The acids **8a–d**, in turn, were obtained by aqueous alkaline hydrolysis of esters **7a–d**. Hydrolysis of these  $\alpha$ -neopentyl esters proved problematic in that prolonged reaction times led to considerable decomposition. Optimal conditions were found (ca. 5% aqueous sodium hydroxide, 95% ethanol, heat at reflux for 14 h) which afforded acids **8a,b** as crystalline solids (mp 73.5–74.5 and 67–68 °C, respectively), while acids **8c,d** were obtained as viscous oils.

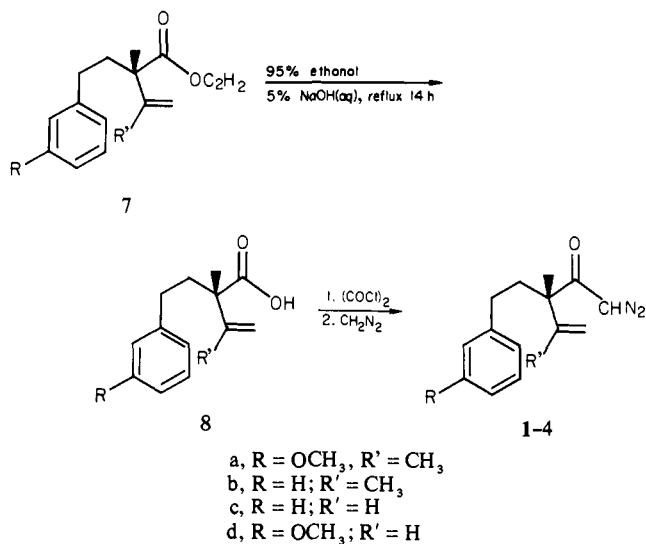
(1) Camille and Henry Dreyfus Teacher Scholar, 1978–1983; National Institutes of Health (National Cancer Institute) Career Development Awardee, 1980–1985.

(2) A. B. Smith, III, B. H. Toder, S. J. Branca, and R. K. Dieter, *J. Am. Chem. Soc.*, preceding paper in this issue.

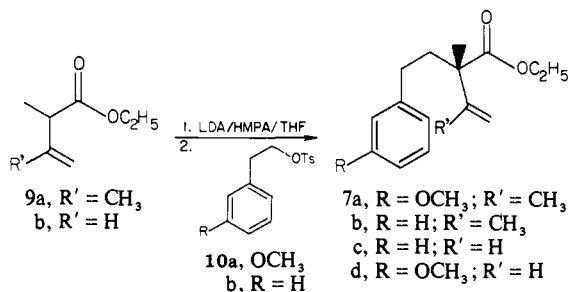
(3) For a preliminary report see A. B. Smith, III, and R. K. Dieter, *J. Org. Chem.*, **42**, 396 (1977).

(4) In a systematic investigation, the Johnson group found the allylic alcohol and acetal functionality to be efficient initiators of cationic polyene cyclizations. To this list must be added the terminal epoxide of Goldsmith and van Tamelen and the cyclopropyl ketone of Stork. These functionalities initiate a stereospecific cyclization process in moderate to excellent yield. For reviews of this general area, see: W. S. Johnson, *Bioorg. Chem.*, **5**, 51 (1976); W. S. Johnson, *Angew. Chem., Int. Ed. Engl.*, **15**, 9 (1976); E. E. Van Tamelen, *Acc. Chem. Res.*, **8**, 152 (1975); K. E. Harding, *Bioorg. Chem.*, **2**, 248 (1973); D. Goldsmith, *Fortschr. Chem. Org. Naturst.*, **29**, 363 (1971); E. E. Van Tamelen, *Acc. Chem. Res.*, **1**, 111 (1968); W. S. Johnson, *ibid.*, **1**, 1 (1968); W. S. Johnson, *Trans. N. Y. Acad. Sci.*, **29**, 1001 (1967).

(5) V. T. Wirthlin, H. Wehrli, and O. Jeger, *Helv. Chim. Acta*, **57**, 351 (1974).



Esters **7a-d** were prepared by alkylation of the requisite ester enolates by employing as base the lithium diisopropylamide-hexamethylphosphoramide complex as described by Rathke<sup>6</sup> and Schlessinger.<sup>7</sup> To this end, alkylation of ethyl 2,3-dimethyl-3-butenate (**9a**) with the tosylate ester of  $\beta$ -(*m*-methoxyphenethyl) alcohol (**10a**) or  $\beta$ -phenethyl alcohol (**10b**) afforded esters **7a** and **7b**, respectively, in 65–70% yield. Similar alkylation of ethyl



2-methyl-2-butenate (**9b**) afforded esters **7d** and **7c** in 52–65% yield. Interestingly, when  $\beta$ -(*m*-methoxyphenethyl) bromide was employed as the alkylating agent elimination predominated.

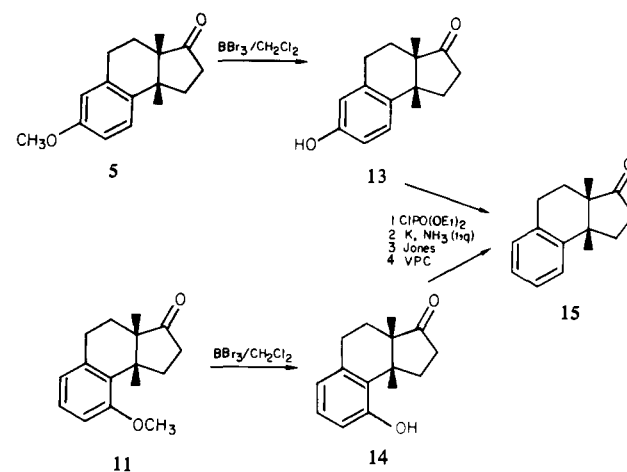
For the record all products obtained from the acid-catalyzed decomposition of unsaturated diazo ketones, as well as all synthetic intermediates (*vide infra*), were fully characterized; for those not discussed in detail here, structural assignment rests on spectroscopic properties and elemental composition data on record in the Experimental Section.

## Results

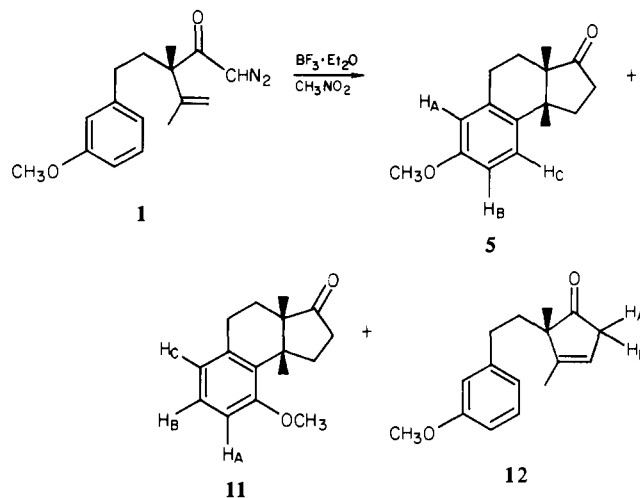
After examination of a variety of Lewis acid and complementary solvent systems, it was ascertained that 1.1 equiv of boron trifluoride etherate in freshly distilled nitromethane at room temperature for 0.5 h constituted the optimal conditions to effect cyclization. Under these conditions, diazo ketone **1** resulted in the immediate and vigorous evolution of nitrogen. Kugelrohr distillation of the reaction mixture gave a 73% yield of volatile material which upon vapor-phase chromatography (VPC) indicated the presence of three major components: **5**, **11**, and **12** in 31%, 12%, and 10% yields, respectively.

Tricyclic ketone **5** was readily identified by comparison of its infrared (IR) and nuclear magnetic resonance (NMR) spectra with those previously obtained by Jeger.<sup>5,8</sup> Ketone **11** was new;

## Scheme I



identification was by analysis of its spectroscopic properties after further purification by high-pressure liquid chromatography. In particular, the 220-MHz NMR spectrum displayed the following



absorptions: methyl singlets at  $\delta$  1.00 (3 H) and 1.40 (3 H), a singlet at  $\delta$  3.90 (3 H) for a methoxy substituent, and two triplets in the aromatic region at  $\delta$  6.62 ( $J_{AB} = J_{CB} = 9$  Hz,  $\delta_A$  6.60,  $\delta_C$  6.64, 2 H, H<sub>A</sub> and H<sub>C</sub>) and  $\delta$  7.00 ( $J_{BA} = J_{BC} = 9$  Hz, 1 H, H<sub>B</sub>), integrating for three protons. Although the observed chemical shifts of the tertiary methyl substituents were inconsistent with those reported by Jeger for the *trans* tricyclic ketone **6**,<sup>5</sup> the presence of a cyclopentanone ring (i.e., absorption at 1740 cm<sup>-1</sup> in the infrared spectrum)<sup>9</sup> suggested that complete cyclization had in fact occurred. On this basis and in conjunction with analysis of the splitting pattern in the aromatic region, structure **11** was assigned. That is, the proton (H<sub>B</sub>) at  $\delta$  7.00 displayed two typical ortho couplings each of 9.0 Hz;<sup>10</sup> H<sub>B</sub> is therefore ortho to two protons (H<sub>A</sub> and H<sub>C</sub>). The apparent triplet at  $\delta$  6.62, integrating for two aromatic protons (H<sub>A</sub> and H<sub>C</sub>), can best be understood in terms of the fortuitous overlap of two doublets with identical coupling constants ( $J = 9.0$  Hz).

The structure, including the stereochemistry of **11**, was confirmed by chemical correlation with **5**; that is, both **11** and **5** were converted via a demethylation–dehydroxylation reaction sequence

(9) R. T. Conley, "Infrared Spectroscopy", 2nd ed., Allyn and Bacon, Boston, 1972, pp 101–121; J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, NJ, 1965, p 49–52.

(10) L. M. Jackmann and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, London, 1969, pp 302–303. J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, NJ, 1965, p 99.

(6) M. W. Rathke and D. Sullivan, *Tetrahedron Lett.*, 4249 (1972).

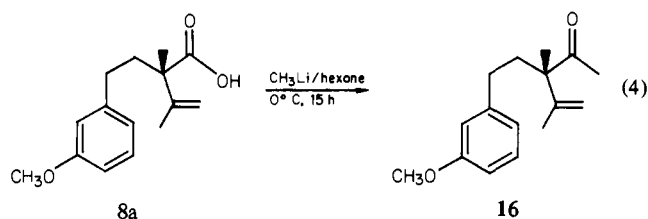
(7) J. L. Herrmann, G. R. Kieczkowski, and R. H. Schlessinger, *Tetrahedron Lett.*, 2433 (1973).

(8) We are grateful to Dr. W. Graf and Professor Oskar Jeger for providing the IR and NMR spectra of authentic **5** and **6**.

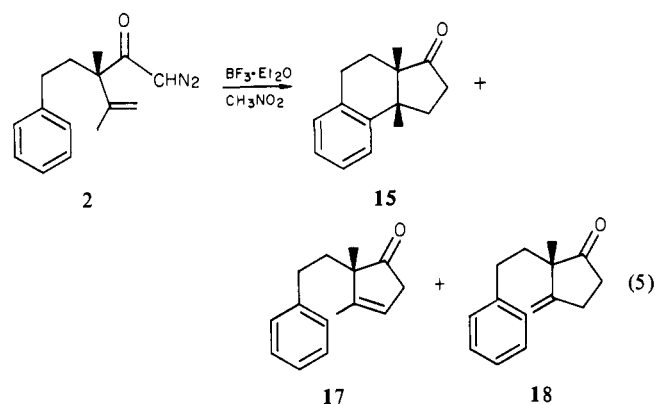
to **15**. To this end, cleavage of the phenolic methyl ethers with boron tribromide<sup>11</sup> led to phenols **13** and **14** (Scheme I) which were subsequently transformed to the corresponding diethyl phosphate esters with diethyl chlorophosphate.<sup>12</sup> Reduction with excess potassium in liquid ammonia, employing ether as a co-solvent according to the method of Rossi and Bunnett,<sup>12</sup> followed by Jones oxidation<sup>13</sup> gave in both cases the same tricyclic ketone (i.e., **15**).

The third component was identified after further purification by thin-layer chromatography (TLC) to be **12** from its spectroscopic properties. Here, the 220-MHz <sup>1</sup>H NMR spectrum displayed singlets at  $\delta$  1.77 (3 H) and 5.75 (1 H) as well as a complex multiplet at  $\delta$  6.50–7.11 integrating for four aromatic protons, while the IR spectrum (CCl<sub>4</sub>) exhibited a strong carbonyl absorption at 1760 cm<sup>-1</sup> consistent with a partially cyclized product containing a  $\beta,\gamma$ -unsaturated cyclopentenone moiety.<sup>9,14</sup>

Interestingly, when methylene chloride was employed as solvent, a small amount (2%) of **16** was formed in addition to **5**, **11**, and **12**. For comparison, an authentic sample of this ketone (**16**) was prepared by treatment of acid **8a** with 2 equiv of methyl lithium in hexane<sup>15</sup> (eq 4).



Turning next to diazo ketone **2**, cyclization under similar conditions afforded a 69% yield of volatile material. Again, vapor-phase chromatography indicated the presence of three components: **15**, **17**, and **18** (eq 5) in 46%, 10%, and 2% yields,

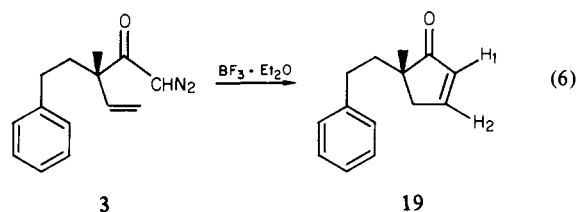


respectively. Tricyclic ketone **15** was identical in all respects with that prepared previously by demethylation-dehydroxylation of tricyclic ketones **5** and **11**. Structures **17** and **18**, on the other hand, were derived from their spectroscopic properties. The 220-MHz NMR spectrum of **17** displayed the following resonances: a tertiary methyl singlet at  $\delta$  1.05 (3 H), a doublet at  $\delta$  1.77 (3 H,  $J = 2$  Hz) for a vinyl methyl group, a broad singlet at  $\delta$  5.77 (1 H) for an olefinic proton, and a multiplet between  $\delta$  6.89 and 7.27 (5 H) for aromatic ring protons. Additional evidence for structure **17** was forthcoming from the infrared spectrum which displayed both a strong carbonyl absorption at 1750 cm<sup>-1</sup>, indicative of an  $\beta,\gamma$ -unsaturated cyclopentenone de-

rivative,<sup>9,14</sup> and a strong C–H bending vibration at 694 cm<sup>-1</sup>, characteristic of a monosubstituted benzene ring.<sup>9</sup>

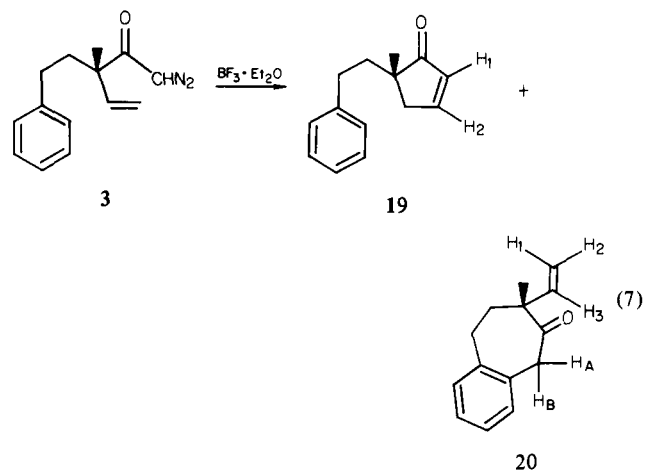
Diagnostic of structure **18** were two broad singlets at  $\delta$  4.95 (1 H) and 5.11 (1 H) in the 220-MHz NMR spectrum, characteristic of a terminal methylene group, as well as a multiplet at  $\delta$  6.97–7.20, integrating for five aromatic protons. The IR spectrum revealed strong absorptions at 1745 and 890 cm<sup>-1</sup>, indicative, respectively, of a cyclopentanone ring and a terminal methylene group.<sup>9</sup>

The third diazo ketone to be explored was **3**. By employment of similar conditions (i.e., boron trifluoride etherate in nitromethane), **3** afforded ketone **19** (eq 6) in moderate yield (22%)



as the only volatile product. The structure of **19** followed immediately from its spectroscopic properties and molecular composition (C<sub>14</sub>H<sub>16</sub>O). The 60-MHz NMR spectrum displayed multiplets at  $\delta$  6.00–6.25 (1 H, H<sub>1</sub>) and  $\delta$  7.25–7.70, (1 H, H<sub>2</sub>) characteristic of a conjugate cyclopentenone, and a broad singlet at  $\delta$  7.14 (5 H) for the aromatic ring protons. Significantly, no resonances for a monosubstituted vinyl group were observed, suggesting that only partial cyclization had occurred. The presence of the  $\alpha,\beta$ -cyclopentenone functionality was confirmed by absorptions at 1710 (s) and 1595 (w) cm<sup>-1</sup>.

In an attempt to obtain tricyclic material from diazo ketone **3**, we explored a number of acid-solvent couples. Unexpectedly, boron trifluoride etherate in dichloromethane led to cycloheptanone **20** (17%) as well as to the previously identified cyclopentenone **19** (11%)<sup>16</sup> (eq 7).



This remarkable solvent effect prompted us to reexamine the decomposition of diazo ketones **1** and **2** in methylene chloride; in both cases the product distribution was essentially unchanged. An explanation for the above solvent effect on both product composition and distribution for diazo ketones **3** and **4** (vide infra) is presented in the Discussion.

The final diazo ketone explored in this study was **4**. Here, cyclization with boron trifluoride etherate in nitromethane afforded three products: **21**–**23** (eq 8) in 11%, 3%, and 24% yields, respectively. The same products were also obtained by utilizing methylene chloride as solvent, but the yields differed markedly, being 45%, 13%, and 11%, respectively. That the products were isomeric follows from their elemental composition data. The structures of bicyclic ketones **21** and **22** were initially suggested on the basis of their high-field NMR data as well as by analogy

(16) Upon closer examination, decomposition of **3** in nitromethane was found to give a small amount (<1%) of cycloheptanone **20**.

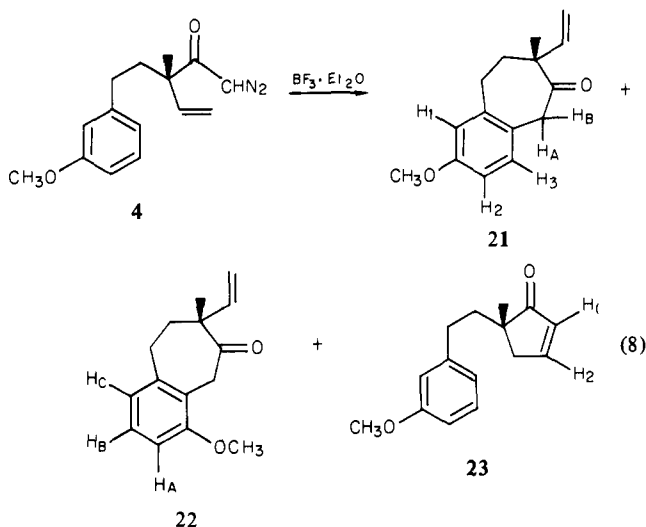
(11) J. F. W. McOmie, M. L. Watts, and D. E. West, *Tetrahedron*, **24**, 2289 (1968).

(12) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 2314 (1973).

(13) Reduction of the ketone also occurred; reoxidation was effected by the method of Jones: A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemlin, *J. Chem. Soc.*, 2548 (1953); C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

(14) P. A. Grieco, *J. Org. Chem.*, **37**, 2363 (1972).

(15) J. C. Dalton and H.-F. Chan, *Tetrahedron Lett.*, 3145 (1973).



with cycloheptanone **20**. In both cases the NMR spectra were quite similar, displaying a tertiary methyl singlet, a multiplet centered at  $\delta$  3.10 for five protons (i.e., overlapping singlet for a methoxy and an AB quartet), an ABC pattern characteristic of a monosubstituted terminal vinyl group, and in the case of **21** and **22** three aromatic protons. The aromatic pattern in **21** could be readily understood in terms of a doublet at  $\delta$  6.55 (d,  $J = 2$  Hz, 1 H) overlapping a doublet of doublets centered at  $\delta$  6.57 (dd,  $J = 2.0, 8$  Hz, 1 H). A second doublet was observed at  $\delta$  7.01 (d,  $J = 8$  Hz, 1 H). This pattern is consistent only with benzocycloheptanone **21**, arising via para closure.

The aromatic protons in **22**, on the other hand, displayed a splitting pattern (see Experimental Section) very reminiscent of that observed for tricyclic ketone **11**, thereby suggesting an ortho mode of ring closure. In both cases (**21** and **22**) the infrared spectrum displayed strong carbonyl absorptions at  $1708\text{ cm}^{-1}$ .<sup>9</sup>

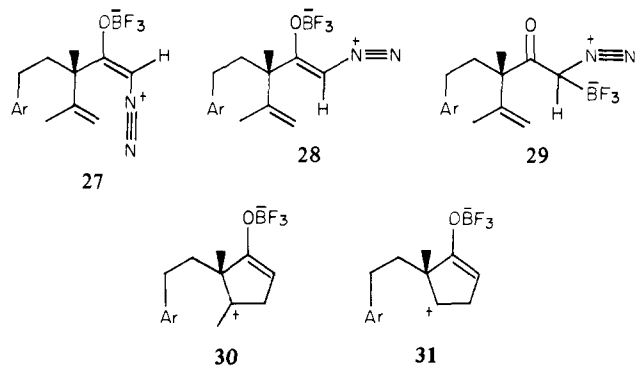
Confirmation of structures **21** and **22** was obtained by chemical correlation. To this end, individual hydrogenation gave the cycloheptanones **24** and **25** (Scheme II), respectively, which in turn were prepared by cyclization of diazo ketone **26** with boron trifluoride etherate in dichloromethane. Diazo ketone **26** was readily available from the corresponding ethyl ester, the latter obtained by hydrogenation of **7d**.

Finally, structure **23** was deduced from the close similarity of its spectral properties to those of **19**.

### Discussion

We begin discussion by noting that diazo ketones **1** and **2** undergo polyolefinic cationic cyclization to give tricyclic ketones **5**, **11**, and **15** in moderate to good yields, while diazo ketones **3** and **4** did not afford tricyclic products; instead, the isomeric benzocycloheptanones **21** and **22** were produced in good yield in the case of diazo ketone **4**. Second, exclusive formation of cis-fused tricyclic products (i.e., **5**, **11**, and **15**) is not unexpected due to the tertiary geometry of the  $\alpha$ -carbon center.

A reasonable reaction pathway for the above cyclizations involves initial complexation of boron trifluoride with the oxygen or carbon atom of the diazo ketone functionality to yield inter-



### Scheme II

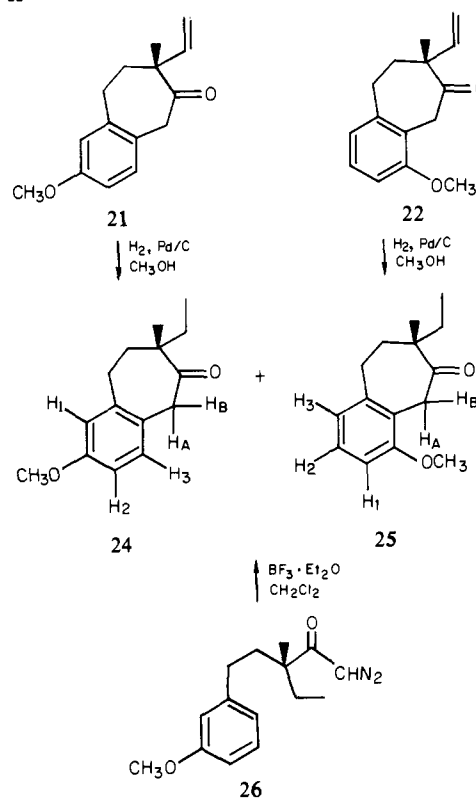


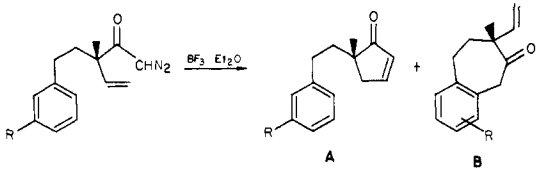
Table I. Product Compositions Obtained from the Decomposition of Diazo Ketones **1** and **2**

R	solvent	% yield		total % $\pi$ participation
		A	B	
H	$\text{CH}_3\text{NO}_2$	12	46	58
$\text{OCH}_3$	$\text{CH}_3\text{NO}_2$	10	43	53

mediates **27**, **28**, and/or **29**; subsequent loss of nitrogen and cyclization then leads in the case of **1** and **2** to a tertiary carbonium ion (**30**). The resultant tertiary carbonium ion is, in most instances, sufficiently long lived to suffer capture by the  $\pi$  system of the aromatic ring before the cation can be removed from the reaction coordinate by proton loss. Support for the stepwise nature of this sequence arises from the boron trifluoride etherate catalyzed decomposition of diazo ketones **3** and **4** in nitromethane, which affords cyclopentenones **19** and **23**, respectively, in moderate yields, as the major products. In this case, initial cyclization leads to a less stable (ca. 11 kcal/mol),<sup>17</sup> short-lived secondary carbonium ion (**31**) which rapidly loses a proton before capture by the aromatic system can take place. Also consistent with a stepwise mechanism is the fact that the yields of tricyclic ketones obtained from diazo ketones **1** and **2** (see Table I) are independent of the nucleophilicity of the aromatic ring. In addition, partially cyclized products have been shown not to be intermediates in the cyclization process leading to tricyclic ketones. That is,  $\beta,\gamma$ -unsaturated cyclopentenone **17** was recovered unchanged in nearly quantitative

(17) J. L. Fry and G. J. Karabatsos in "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Eds., Wiley, New York, 1970, p 523; A. E. Evans, "The Reactions of Organic Halides in Solution", Manchester University Press, Manchester, 1946, p 15.

Table II. Effect of Solvent Medium on the Product Compositions Obtained from the Decomposition of Diazo Ketones 3 and 4



R	Solvent	% yield		total % $\pi$ participation
		A	B	
H	CH <sub>3</sub> NO <sub>2</sub>	22	<1	22
OCH <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub>	24	14	38
H	CH <sub>2</sub> Cl <sub>2</sub>	11	17	28
OCH <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	11-15	58	69-73

yield when treated with boron trifluoride etherate in nitromethane at room temperature for 24 h.

The question of whether nitrogen loss is synchronous with or precedes  $\sigma$ -bond formation is more complex and may well depend upon both the solvent and nature of the participating nucleophile. For example, decomposition of diazo ketones 3 and 4 led to identical products in either dichloromethane or nitromethane; the ratio of products, however, was markedly solvent dependent. This influence of solvent on product distribution offers several mechanistic insights. In particular, it is entirely possible that competing S<sub>N</sub>1 and S<sub>N</sub>2 pathways are responsible for the observed product distributions.

Examination of Table II reveals that the yields of cycloheptanones in either solvent are directly proportional to the nucleophilicity of the aromatic ring. In addition, the distribution of products obtained in dichloromethane reflect the relative nucleophilicities of the competing aryl and olefinic nucleophiles. These observations are a necessary, although not sufficient, requirement for an S<sub>N</sub>2 reaction pathway.<sup>18</sup> Finally, the yields of cycloheptanones are significantly increased by changing the solvent from nitromethane to dichloromethane, suggesting that the latter solvent favors a concerted pathway.

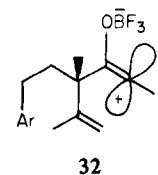
The yields of cyclopentenones (see Table II), however, are independent of the nucleophilicity of the aromatic ring in both solvents. Since the aromatic ring is a competing nucleophile, this observation is consistent with an S<sub>N</sub>1 reaction pathway leading to cyclopentenones 19 and 23. If the energy barrier for cyclization is sufficiently low, a reasonable assumption in view of the observed rapid loss of nitrogen, so that the Curtin-Hammett principle is not applicable, the distribution of products could reflect the relative population of ground-state conformers.<sup>19</sup> Entropy considerations as well as conformational factors should then favor the formation of cyclopentenones rather than cycloheptanones. Experimentally, decomposition of diazo ketones 3 and 4 in nitromethane affords cyclopentenones as the major products, suggesting that nitromethane enhances the S<sub>N</sub>1 pathway.

Collectively, these results suggest that the formation of cyclopentenones and cycloheptanones is occurring by two different reaction pathways involving two distinct nonequilibrating intermediates. Since nitromethane appears to enhance a stepwise pathway and dichloromethane appears to favor a concerted pathway, an attractive explanation would be that one intermediate reacts by an S<sub>N</sub>1 pathway and the second by an S<sub>N</sub>2 pathway. Under these conditions, the product distribution would be a reflection of the relative ratio of the two intermediates which is solvent dependent. Although the nature of these intermediates is currently unknown, two possibilities can be considered.

(18) These observations are also consistent with a two-step process in which nitrogen loss is fast and cyclization occurs in the rate-determining step. Although conceivable in view of the rapid loss of nitrogen, this view does not adequately explain the apparent formation of cyclopentenones and cycloheptanones from diazo ketones 3 and 4 by two different reaction pathways.

(19) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, 1967, pp 28-31.

The first possibility assumes that boron trifluoride complexation occurs on oxygen which, as shown by EHMO calculations,<sup>20</sup> NMR studies,<sup>21</sup> and IR studies,<sup>22</sup> is the most negative site in the diazo ketone functionality. Complexation of BF<sub>3</sub> on oxygen could then give rise to the two geometrical isomers 27 and 28. In a solvent of low dielectric constant such as dichloromethane ( $\epsilon = 8$ ),<sup>23</sup> the cis isomer 28 would, on the basis of charge stabilization, be more favored. It is significant, in this regard, that Kaplan and Meloy<sup>24</sup> have reported that diazo ketones exist as an equilibrium mixture of cis and trans isomers as a result of hindered rotation about the C-C bond. In particular, low-temperature NMR studies revealed that the cis form of alkyl diazo ketones was the preferred isomer. In nitromethane, a solvent of high dielectric constant ( $\epsilon = 40$ ),<sup>23</sup> solvent stabilization of the zwitterionic complex may favor the trans isomer 27. The nitrogen leaving group in the cis isomer (28) is favorably oriented for backside displacement by either the aryl or olefinic  $\pi$  systems. This is not so for the trans isomer, and reaction of 27 must occur by equilibrium to 28 or by an S<sub>N</sub>1 pathway. Reaction of 27 by an S<sub>N</sub>1 pathway would generate a vinyl cation (32); the latter is not unreasonable, considering that



vinyl cations have been generated under solvolytic conditions.<sup>25</sup> Reaction of 28 by an S<sub>N</sub>2 pathway, however, requires displacement of nitrogen at an sp<sup>2</sup> center with concomitant inversion of this center. The lack of precedent for S<sub>N</sub>2 displacement at a vinylic carbon atom makes this pathway unattractive. However, as noted by Miller<sup>26</sup> and Kelsey and Bergman,<sup>27</sup> there are, in principle, no fundamental objections to such a reaction pathway. That is, the extended Hückel molecular orbital calculations of Kelsey and Bergman<sup>27</sup> predicted that an S<sub>N</sub>2 reaction of hydride ion with ethylene is disfavored by 14.5 kcal/mol over that of an S<sub>N</sub>2 reaction of hydride ion with ethane. They therefore suggest that such a process has not been observed because other pathways (i.e., addition-elimination, elimination-addition, and S<sub>N</sub>1) are energetically more favorable. However, they conclude that an S<sub>N</sub>2 displacement at an sp<sup>2</sup> center is not energetically unfavorable in an "absolute sense".

A second possible explanation is that the concerted pathway arises from a carbon-complexed intermediate such as 29, while the stepwise process occurs from an oxygen-complexed species (e.g., 27 and 28). In this case, dichloromethane could conceivably favor the carbon-complexed intermediate 29 where opposite formal charges on nitrogen and boron are closely oriented in space. A

(20) I. G. Csizmadia, S. A. Houlden, O. Merez, and P. Yates, *Tetrahedron*, **25**, 2121 (1969).

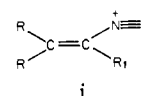
(21) M. Allard, J. Levisalles, and J. M. Sommer, *J. Chem. Soc. D*, 1515 (1969); C. Wentrup and H. Dahn, *Helv. Chim. Acta*, **53**, 1637 (1970).

(22) E. Fahr, *Justus Liebigs Ann. Chem.*, **617**, 11 (1958); E. Fahr, *ibid.*, **638**, 1 (1960); P. Yates, B. L. Shapiro, N. Yoda, and J. Fugger, *J. Am. Chem. Soc.*, **79**, 5756 (1957).

(23) A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, 1972, p 18.

(24) F. Kaplan and G. K. Meloy, *J. Am. Chem. Soc.*, **88**, 950 (1966).

(25) For example, Jones and Miller [*J. Am. Chem. Soc.*, **89**, 1960 (1967)] have shown that acid treatment of triazenes affords the corresponding vinyl diazonium ion i which undergoes loss of nitrogen with formation of a vinyl cation. For reviews in this area see: M. Hanack, *Acc. Chem. Res.*, **3**, 209 (1970); L. R. Subramanian and M. Hanack, *J. Chem. Educ.*, **52**, 80 (1975).



(26) S. I. Miller in *Adv. Phys. Org. Chem.*, **6**, 265 (1968).

(27) D. R. Kelsey and R. G. Bergman, *J. Am. Chem. Soc.*, **93**, 1953 (1971).

highly polar solvent (nitromethane), on the other hand, would favor oxygen complexation.<sup>28</sup>

At present it is not possible to choose between these two mechanistic alternatives since the nature of the intermediates is currently unknown. However, diazo ketones 1–4 in acid medium do not lose nitrogen below  $-20^{\circ}\text{C}$ ; the exciting possibility therefore exists that the nature of the intermediate complexes could be determined. In this regard, low-temperature NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ , or  $^{15}\text{N}$ ) may provide clues as to their nature.

Finally, the distribution of products arising from diazo ketones 1 and 2 is relatively insensitive to solvent influence. In these examples, the more nucleophilic disubstituted olefin with favorable entropic and conformational factors can effectively compete with the aromatic ring in the displacement of nitrogen.

### Summary

In conclusion, this investigation demonstrated that Lewis acid promoted decomposition of  $\alpha$ -diazo ketones can effectively initiate polyolefinic cationic cyclization. The synthetic utility of this approach to polycyclic ketones is readily apparent when one considers alternative approaches to such tricyclic systems. For example, 5 was prepared by Jeger and co-workers<sup>5</sup> in 18 steps from dehydroabiatic acid. Our systematic modification of substrate structure, however, reveals that successful polyene cyclizations require the participation of highly nucleophilic olefins.

### Experimental Section

**Materials and Methods.** Solvents used for the cyclization studies were Mallinckrodt nitromethane and Mallinckrodt analytical reagent grade dichloromethane. Nitromethane was distilled at atmospheric pressure, and dichloromethane was distilled from phosphorus pentoxide prior to use. Tetrahydrofuran was distilled from sodium and benzophenone. Diazomethane was prepared as an ethereal solution from *N,N*-dimethyl-*N,N'*-dinitrosoterephthalamide (Aldrich, 70% in mineral oil). Phenethyl alcohol, *m*-methoxyphenylacetic acid, and diethyl chlorophosphate were obtained from Aldrich. Boron tribromide was obtained from Alfa (Ventron). All vapor-phase chromatography (VPC) was done by using a Varian Aerograph Model 920 with one of the following columns: (A) 6% Carbowax 20M, 20 ft  $\times$   $1/4$  in.; (B) 1.5% OV-101, 5 ft  $\times$   $1/4$  in.; (C) 12.5% OV-101, 10 ft  $\times$   $3/8$  in.; (D) 6% SE-30, 10 ft  $\times$   $3/8$  in. The oven was operated at  $160$ – $230^{\circ}\text{C}$ , and the helium carrier gas flow rate was  $50$ – $100$  mL/min. High-pressure liquid chromatography was done by using a Perkin-Elmer Model 601 on SIL-X-1 with a dichloromethane–hexane (3:2 v/v) solvent system. Precoated alumina GF (Analtech) or silica GF (Analtech) plates were used for thin-layer chromatography (TLC). Plates with  $1000$ – $2000$ - $\mu\text{m}$  thickness were used for preparative separations. Melting points were obtained by using a Thomas-Hoover apparatus and are corrected; boiling points were not corrected. Unless otherwise noted, both IR and NMR spectra were obtained for carbon tetrachloride solutions, the former on a Perkin-Elmer Model 337 spectrophotometer and the later on a Varian Model A-60 (60 MHz) or HR-220 (220 MHz) spectrometer. Chemical shifts are reported as  $\delta$  values in parts per million relative to tetramethylsilane ( $\delta$  0.00). The yields of cyclization products were determined from VPC calibration curves and are based upon the starting acid.

**Alkylation of Ethyl 2,3-Dimethyl-3-butenate (9a) and of Ethyl 2-Methyl-3-butenate (9b).** A solution containing 25 mL of dry tetrahydrofuran and 2.4423 g (24.0 mmol) of freshly distilled diisopropylamine was cooled under nitrogen to  $0$ – $5^{\circ}\text{C}$ , and 9.6 mL (2.5 M in hexane, 24 mmol) of *n*-butyllithium was added. After 15 min the solution was cooled to  $-77^{\circ}\text{C}$ , and 4.6 g (26 mmol) of freshly distilled hexamethylphosphoramide was added. Approximately 30 min later, the appropriate ester (24 mmol) in 5 mL of dry tetrahydrofuran was added dropwise over a period of 30 min. The solution was stirred at  $-77^{\circ}\text{C}$  for an additional 20 min and then warmed to  $0$ – $5^{\circ}\text{C}$ , whereupon the

tosylate ester (22 mmol) of  $\beta$ -phenylethyl alcohol or  $\beta$ -(*m*-methoxyphenyl)ethyl alcohol was added dropwise in 10 mL of dry tetrahydrofuran. The resulting red solution was stirred overnight at room temperature, poured into saturated aqueous ammonium chloride, and extracted with ether. The combined organic phase was washed with saturated aqueous sodium bicarbonate, water, and brine and dried. Removal of solvent in vacuo and distillation gave the following esters as pale yellow oils.

**Ethyl 4-(*m*-Methoxyphenyl)-2-methyl-2-(2'-propenyl)butyrate (7a).** Distillation afforded 7a in 70.5% yield: bp  $125$ – $135^{\circ}\text{C}$  (0.3 mmHg); IR 3100 (w), 2985 (s), 2960 (s), 2942 (m), 1730 (vs), 1645 (m), 1601 (s), 1595 (s), 1490 (s), 1455 (s), 1380 (s), 1260 (s), 1230 (s), 1153 (s), 1108 (s), 894 (s), 687 (s)  $\text{cm}^{-1}$ ; NMR (60 MHz)  $\delta$  1.26 (t,  $J = 7$  Hz, 3 H), 1.33 (s, 3 H), 1.74 (d,  $J = 1$  Hz, 3 H), 1.85–2.25 (m, 2 H), 2.30–2.70 (m, 2 H), 3.73 (s, 3 H), 4.13 (q,  $J = 7$  Hz, 2 H), 4.88 (br s, 2 H), 6.50–6.86 (m, 3 H), 6.93–7.33 (m, 1 H).

Anal. Calcd for  $\text{C}_{17}\text{H}_{24}\text{O}_3$ : C, 73.88; H, 8.75. Found: C, 73.92; H, 8.68.

**Ethyl 2-Methyl-4-phenyl-2-(2'-propenyl)butyrate (7b).** Distillation afforded 7b in 65.5% yield: bp  $105$ – $110^{\circ}\text{C}$  (0.7 mmHg); IR 3100 (w), 3075 (m), 3040 (s), 2990 (vs), 1730 (vs), 1650 (m), 1615 (w), 1508 (w), 1460 (s), 1390 (s), 1232 (s), 1110 (s), 1028 (s), 895 (s), 692 (s)  $\text{cm}^{-1}$ ; NMR (60 MHz)  $\delta$  1.25 (t,  $J = 7.2$  Hz, 3 H), 1.33 (s, 3 H), 1.74 (d,  $J = 1$  Hz, 3 H), 1.85–2.68 (m, 4 H), 4.13 (q,  $J = 7.2$  Hz, 2 H), 4.88 (br s, 2 H), 7.14 (br s, 5 H).

Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_2$ : C, 78.01; H, 9.00. Found: C, 77.99; H, 9.05.

**Ethyl 2-Methyl-4-phenyl-2-vinylbutyrate (7c).** Distillation afforded 7c in 64.5% yield: bp  $125$ – $129^{\circ}\text{C}$  (2.8 mmHg); IR 3090 (m), 3070 (m), 3030 (m), 2980 (s), 1730 (vs), 1635 (m), 1601 (m), 1495 (m), 1455 (m), 1415 (m), 1375 (m), 1250 (m), 1180 (s), 1110 (s), 1028 (m), 1000 (w), 918 (s), 695 (s)  $\text{cm}^{-1}$ ; NMR (60 MHz)  $\delta$  1.25 (t,  $J = 7$  Hz, 3 H), 1.30 (s, 3 H), 1.70–2.16 (m, 2 H), 2.28–2.75 (m, 2 H), 4.12 (q,  $J = 7$  Hz, 2 H), an ABC pattern [5.08 (dd,  $J_{AC} = 18.5$  Hz,  $J_{AB} = 1$  Hz, 1 H), 5.10 (dd,  $J_{BC} = 9.5$  Hz,  $J_{BA} = 1$  Hz, 1 H), 6.08 (dd,  $J_{CA} = 18.5$  Hz,  $J_{CB} = 9.5$  Hz, 1 H)], 7.13 (br s, 5 H).

Anal. Calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_2$ : C, 77.55; H, 8.68. Found: C, 77.55; H, 8.81.

**Ethyl 2-Methyl-4-(*m*-methoxyphenyl)-2-vinylbutyrate (7d).** Distillation afforded 7d in 52% yield: bp  $120$ – $126^{\circ}\text{C}$  (0.4 mmHg); IR 3080 (m), 3050 (w), 2980 (s), 2950 (s), 2935 (s), 1725 (s), 1595 (s), 1580 (s), 1451 (s), 1268 (s), 1170 (s), 1160 (s), 1112 (s), 1050 (s), 998 (m), 918 (s), 690 (s)  $\text{cm}^{-1}$ ; NMR (60 MHz)  $\delta$  1.25 (t,  $J = 7$  Hz, 3 H), 1.29 (s, 3 H), 1.68–2.16 (m, 2 H), 2.25–2.70 (m, 2 H), 3.76 (s, 3 H), 4.15 (q,  $J = 7$  Hz, 2 H), an ABC pattern [5.06 (dd,  $J_{AC} = 18$  Hz,  $J_{AB} = 1$  Hz, 1 H), 5.10 (dd,  $J_{BC} = 10$  Hz,  $J_{BA} = 1$  Hz, 1 H), 6.12 (dd,  $J_{CA} = 18$  Hz,  $J_{CB} = 10$  Hz, 1 H)], 6.52–7.35 (m, 4 H).

Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_3$ : C, 73.25; H, 8.45. Found: C, 73.06; H, 8.47.

**Hydrolysis of Esters 7a–d.** The  $\alpha$ -disubstituted esters were difficult to hydrolyze since prolonged heating under the strongly alkaline conditions led to decomposition. Partial hydrolysis and recycling of unreacted ester proved effective. Nitrogen was bubbled through a solution of 4 g of ester in 35 mL of 95% ethanol for 15 min, and this was then mixed with 25 mL of similarly degassed 5% aqueous sodium hydroxide. The mixture was heated at reflux under nitrogen for 14 h, cooled to room temperature, poured into 20 mL of water, and washed three times with ether. The ether washings were extracted two times with 5% sodium hydroxide, and the aqueous phases were combined. The ether washings were washed with water and brine and dried. Removal of solvent in vacuo yielded unreacted ester which was recycled. The aqueous phase was acidified with 10% aqueous hydrochloric acid and extracted three times with 25 mL of ether. The ether extracts were washed with water and brine and dried. Removal of solvent in vacuo gave the following crude acids.

**4-(*m*-Methoxyphenyl)-2-methyl-2-(2'-propenyl)butyric Acid (8a).** Recrystallization from hexane gave pure 8a: mp  $73.4$ – $74.4^{\circ}\text{C}$ ; IR 3400–2400 (vbr, s), 2950 (s), 1700 (s), 1645 (w), 1601 (m), 1595 (m), 1490 (w), 1455 (m), 1400 (m), 1380 (m), 1264 (s), 1157 (m), 1050 (m), 900 (m), 688 (m)  $\text{cm}^{-1}$ ; NMR (60 MHz)  $\delta$  1.42 (s, 3 H), 1.85 (d,  $J = 1$  Hz, 3 H), 1.80–2.25 (m, 2 H), 2.30–2.83 (m, 2 H), 3.75 (s, 3 H), 5.00 (br s, 2 H), 6.50–6.83 (m, 3 H), 6.96–7.33 (m, 1 H), 11.58 (br s, 1 H).

Anal. Calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_3$ : C, 72.55; H, 8.12. Found: C, 72.29; H, 8.08.

**2-Methyl-4-phenyl-2-(2'-propenyl)butyric Acid (8b).** Recrystallization from hexane gave pure 8b: mp  $67$ – $68^{\circ}\text{C}$ ; IR 3500–2500 (vbr, s), 3080 (w), 3060 (w), 3025 (w), 1700 (vs), 1640 (m), 1455 (m), 1400 (m), 1280 (m), 900 (s), 695 (s)  $\text{cm}^{-1}$ ; NMR (60 MHz)  $\delta$  1.40 (s, 3 H), 1.83 (d,  $J = 0.75$  Hz, 3 H), 1.68–2.78 (m, 4 H), 4.98 (br s, 2 H), 7.13 (s, 5 H), 11.28 (s, 1 H).

(28) Recently, Brown et al. [*J. Hooz*, J. N. Bridson, J. G. Calzada, H. C. Brown, M. Midland, and A. B. Levy, *J. Org. Chem.*, **38**, 2574 (1973)] proposed that the alkylation of  $\alpha$ -diazo carbonyl compounds with trialkyl boranes involves complexation of the alkyl borane on carbon, followed by alkyl migration with concomitant displacement of nitrogen and finally rearrangement of boron to oxygen. A similar mechanistic pathway can be envisioned for the  $\text{BF}_3$  etherate promoted cyclization of olefinic and aromatic  $\alpha$ -diazo ketones. Here the assumption is made that only the carbon–boron-complexed species undergoes competing  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  cyclization processes. This view would also account for the observed solvent effects. While this mechanistic alternative was considered both by us and by a referee, it should be noted that this mechanism requires both the equilibration between carbon- and oxygen-complexed intermediates and the existence of a common intermediate.

Anal. Calcd for  $C_{14}H_{18}O_2$ : C, 77.03; H, 8.31. Found: C, 76.19; H, 8.20.

**2-Methyl-4-phenyl-2-vinylbutyric Acid (8c).** Acid **8c** was obtained as a viscous oil: IR 3525 (br, w), 3450–2250 (vbr, s), 3090 (m), 3070 (m), 3030 (m), 1700 (vs), 1455 (m), 1400 (m), 1070 (m), 1030 (m), 998 (m), 920 (s), 693 (s)  $cm^{-1}$ ; NMR (60 MHz)  $\delta$  1.36 (s, 3 H), 1.78–2.22 (m, 2 H), 2.37–2.80 (m, 2 H), an ABC pattern [5.14 (dd,  $J_{AC} = 10.5$  Hz,  $J_{AB} = 1$  Hz, 1 H), 5.15 (dd,  $J_{BC} = 18$  Hz,  $J_{BA} = 1$  Hz, 1 H), 6.10 (dd,  $J_{CB} = 18$  Hz,  $J_{CA} = 10.5$  Hz, 1 H)], 7.13 (s, 5 H), 11.92 (s, 1 H); mass spectrum,  $m/e$  204.1149 ( $M^+$ , calcd for  $C_{13}H_{16}O_2$  204.1149).

**4-(*m*-Methoxyphenyl)-2-methyl-2-vinylbutyric Acid (8d).** Acid **8d** was obtained as a viscous oil: IR 3450–2300 (vbr, s), 3090 (m), 2950 (s), 1700 (vs), 1600 (s), 1590 (s), 1490 (m), 1465 (s), 1440 (m), 1418 (m), 1265 (vs), 1168 (m), 1158 (s), 1055 (s), 1045 (s), 995 (w), 920 (s), 690 (s)  $cm^{-1}$ ; NMR (60 MHz)  $\delta$  1.35 (s, 3 H), 1.67–2.17 (m, 2 H), 2.32–2.78 (m, 2 H), 3.70 (s, 3 H), an ABC pattern [5.14 (dd,  $J_{AB} = 1.1$  Hz,  $J_{AC} = 10$  Hz, 1 H), 5.15 (dd,  $J_{BA} = 1.1$  Hz,  $J_{BC} = 18$  Hz, 1 H), 6.12 (dd,  $J_{CA} = 10$  Hz,  $J_{CB} = 18$  Hz, 1 H)], 6.48–6.82 (m, 3 H), 6.93–7.30 (m, 1 H), 11.87 (br s, 1 H).

**Preparation of Diazo Ketones.** To a solution containing 1.0 g of acid in 10 mL of benzene was added 1.2 equiv of oxalyl chloride. The solution was stirred at room temperature for 5 h and then concentrated in vacuo to give a quantitative yield of acid chloride, IR 1780–1800 (s)  $cm^{-1}$ . The acid chloride was dissolved in 10 mL of dry ether and added dropwise to a rapidly stirring ethereal solution of diazomethane (3.5 equiv) which was then allowed to stand overnight at room temperature. Excess diazomethane was removed by gentle heating on a steam bath, and the ether solution was dried and filtered through a pad of magnesium sulfate. Removal of solvent in vacuo afforded the diazo ketone [IR 2100 (vs)  $cm^{-1}$ ] in quantitative yield which was used without further purification.

**Ethyl 2-Ethyl-4-(*m*-methoxyphenyl)-2-methylbutyrate.** To 307.5 mg of **8d** in 3 mL of absolute methanol was added 18.5 mg of palladium (10%) absorbed on carbon, and the solution was stirred under 1 atm of hydrogen until hydrogen uptake had ceased. The solution was filtered, poured into ether, washed with water and brine and dried. Removal of solvent in vacuo afforded 319.2 mg (100%) of product. Purification on column A gave pure ester: IR 2970 (s), 2930 (s), 2830 (w), 1720 (vs), 1600 (s), 1585 (s), 1485 (m), 1455 (s), 1382 (m), 1267 (s), 1175 (s), 1045 (s), 690 (s)  $cm^{-1}$ ; NMR (60 MHz)  $\delta$  0.85 (t,  $J = 7$  Hz, 3 H), 1.14 (s, 3 H), 1.26 (t,  $J = 7$  Hz, 3 H), 1.40–2.17 (m, 4 H), 2.20–2.70 (m, 2 H), 3.72 (s, 3 H), 4.11 (q,  $J = 7$  Hz, 2 H), 6.48–6.85 (m, 3 H), 6.93–7.32 (m, 1 H).

Anal. Calcd for  $C_{16}H_{24}O_3$ : C, 72.69; H, 9.15. Found: C, 72.55; H, 9.14.

The ester was hydrolyzed, as described above, to the acid [IR 3400–2400 (vbr, s)  $cm^{-1}$ ] which was converted to diazo ketone [IR 2100 (vs)  $cm^{-1}$ ] **26**.

**Decomposition of 1-Diazo-5-(*m*-methoxyphenyl)-3-methyl-3-(2'-propenyl)-2-pentanone (1).** To a solution of 2.44 g (9.0 mmol) of diazo ketone **1** in 50 mL of nitromethane cooled to 0–5 °C under nitrogen was added in one addition 1.35 mL (1.56 g, 11 mmol) of boron trifluoride etherate. The solution immediately turned dark, and after a few seconds the vigorous evolution of nitrogen was observed. The solution was stirred at 0–5 °C for 30 min, poured into saturated aqueous sodium bicarbonate, and extracted with ethyl acetate. The extracts were washed four times with saturated aqueous sodium bicarbonate, water, and brine and dried. Removal of solvent in vacuo gave 2.09 g (100%) of crude material which yielded 1.57 g (73%) of volatile material upon Kugelrohr distillation [bp 160–180 °C (0.30 mmHg)]. Preliminary VPC purification on column A gave three fractions.

Fraction A gave, after final purification on column A, pure 2,3-dimethyl-2-(*m*-methoxyphenethyl)-3-cyclopentenone **12**: 10% yield; IR 3060 (w), 3010 (w), 2975 (s), 2950 (s), 1760 (vs), 1610 (s), 1595 (s), 1502 (s), 1475 (m), 1465 (m), 1450 (m), 1265 (s), 1158 (s), 1050 (s), 695 (m)  $cm^{-1}$ ; NMR (220 MHz)  $\delta$  1.04 (s, 3 H), 1.47–2.05 (m, 2 H), 1.77 (s, 3 H), 2.05–2.32 (m, 2 H), 2.73 (center AB q,  $J_{AB} = 23$  Hz,  $\Delta\nu_{AB} = 20.59$  Hz,  $\delta_A$  2.68,  $\delta_B$  2.78, 2 H,  $H_A$  and  $H_B$ ), 3.75 (s, 3 H), 5.75 (s, 1 H), 6.50–6.88 (m, 3 H), 6.68–7.11 (m, 1 H); mass spectrum,  $m/e$  244.1419 ( $M^+$ , calcd for  $C_{16}H_{20}O_2$  244.1462).

Fraction B gave, after high-pressure LC purification (SIL-X-1), dichloromethane-hexane, 3:2 v/v), pure *cis*-3a,9b-dimethyl-1,2,3a,4,5,9b-hexahydro-9-methoxy-3*H*-benz[e]inden-3-one (**11**): 12% yield; IR 3070 (w), 2980 (s), 2940 (s), 1740 (vs), 1601 (s), 1585 (s), 1470 (s), 1465 (s), 1445 (s), 1385 (m), 1255 (s), 1100 (s), 1068 (m), 1050 (s)  $cm^{-1}$ ; NMR (220 MHz)  $\delta$  1.00 (s, 3 H), 1.32–1.52 (m, 1 H), 1.40 (s, 3 H), 1.70–2.20 (m, 4 H), 2.55–2.82 (m, 3 H), 3.90 (s, 3 H), 6.62 (apparent t,  $J_{AB} = J_{CB} = 9$  Hz, 2 H,  $H_A$  and  $H_C$ ), 7.00 (t,  $J_{BA} = J_{BC} = 9$  Hz, 1 H,  $H_B$ ); mass spectrum,  $m/e$  244.1471 ( $M^+$ , calcd for  $C_{16}H_{20}O_2$  244.1462).

Fraction C gave pure *cis*-3a,9b-dimethyl-1,2,3a,4,5,9b-hexahydro-7-methoxy-3*H*-benz[e]inden-3-one (**5**): 31% yield; IR 3035 (w), 2975 (s),

2940 (s), 1735 (s), 1615 (s), 1501 (s), 1475 (s), 1415 (m), 1285 (s), 1269 (s), 1257 (s), 1240 (s), 1033 (s)  $cm^{-1}$ ; NMR (60 MHz)  $\delta$  0.97 (s, 3 H), 1.27 (s, 3 H), 1.37–2.38 (m, 6 H), 2.47–2.83 (t,  $J = 6$  Hz, 2 H), 3.70 (s, 3 H), 6.44 (d,  $J_{AB} = 2.5$  Hz, 1 H,  $H_A$ ), 6.67 (dd,  $J_{BA} = 2.5$  Hz,  $J_{BC} = 9$  Hz, 1 H,  $H_B$ ), 7.24 (d,  $J_{CB} = 9$  Hz, 1 H,  $H_C$ ) [lit.<sup>5</sup> IR 1738, 1612, 1503, 1479; NMR  $\delta$  1.05 (s, 3 H), 1.32 (s, 3 H), 3.82 (s, 3 H), 6.60 (d,  $J = 2.5$  Hz, 1 H), 6.82 (d,  $J = 8$  Hz, 1 H), 7.40 (d,  $J = 8$  Hz, 1 H)].

**Decomposition of 1-Diazo-3-methyl-5-phenyl-3-(2'-propenyl)-2-pentanone (2).** Similar decomposition of 3.28 g (13.6 mmol) of diazo ketone **2** yielded 2.96 g (100%) of crude material which gave 2.01 g (69%) of volatile material upon Kugelrohr distillation [bp 150–180 °C (0.15 mmHg)]. Preliminary VPC purification on column A gave three fractions.

Fraction A gave, after final VPC purification on column A, pure 2,3-dimethyl-2-phenethyl-3-cyclopenten-1-one (**17**): 10% yield; IR 3085 (w), 3065 (w), 3029 (m), 2970 (s), 2937 (s), 1750 (s), 1601 (w), 1497 (w), 1448 (m), 1194 (m), 1004 (m), 694 (s)  $cm^{-1}$ ; NMR (220 MHz)  $\delta$  1.05 (s, 3 H), 1.48–1.91 (m, 1 H), 1.77 (d,  $J = 2$  Hz, 3 H), 1.80–2.04 (m, 1 H), 2.14–2.56 (m, 2 H), 2.59–2.93 (m, 2 H), 5.77 (br s, 1 H), 6.98–7.27 (m, 5 H); mass spectrum,  $m/e$  214.1369 ( $M^+$ , average value obtained from several spectra; calcd for  $C_{15}H_{18}O$  214.1357).

Fraction B gave, after TLC purification on alumina (benzene) and final VPC purification column B, pure 2-methyl-3-methylene-2-phenethylcyclopentan-1-one **18**: 2% yield; IR 3070 (w), 3025 (w), 2965 (m), 2930 (m), 1745 (vs), 1655 (s), 1600 (w), 1495 (w), 1450 (m), 1405 (w), 890 (s), 690 (s)  $cm^{-1}$ ; NMR (220 MHz)  $\delta$  1.11 (s, 3 H), 1.45–1.89 (m, 2 H), 2.14–2.56 (m, 4 H), 2.59–2.73 (m, 2 H), 4.95 (s, 1 H), 5.11 (s, 1 H), 6.96–7.27 (m, 5 H); mass spectrum,  $m/e$  214.1361 ( $M^+$ , calcd for  $C_{15}H_{18}O$  214.1357).

Fraction C gave pure *cis*-3a,9b-dimethyl-1,2,3a,4,5,9b-hexahydro-3*H*-benz[e]inden-3-one (**15**): 46% yield; IR 3070 (m), 3025 (m), 2970 (vs), 2940 (vs), 2880 (s), 2860 (m), 1737 (vs), 1495 (m), 1475 (s), 1450 (s), 1415 (m), 1485 (m), 1475 (m), 1300 (m), 1280 (m), 1270 (m), 1250 (m), 1163 (m), 1110 (m), 1078 (m), 1068 (m), 1042 (m), 1048 (m), 972 (m), 721 (m)  $cm^{-1}$ ; NMR (220 MHz)  $\delta$  1.02 (s, 3 H), 1.34 (s, 3 H), 1.39–1.59 (m, 1 H), 1.85–2.32 (m, 5 H), 2.59–2.72 (m, 2 H), 6.89–7.25 (m, 3 H), 7.32 (d,  $J = 8$  Hz, 1 H); NMR (60 MHz)  $\delta$  0.98 (s, 3 H), 1.30 (s, 3 H), 1.42–2.45 (m, 6 H), 2.53–2.83 (m, 6 H), 6.83–7.50 (m, 4 H).

Anal. Calcd for  $C_{15}H_{18}O$ : C, 84.07; H, 8.47. Found: C, 83.72; H, 8.57.

**Decomposition of 1-Diazo-3-methyl-5-phenyl-3-vinyl-2-pentanone (3).** To a solution of 1.2721 g (5.48 mmol) of diazo ketone **3** in 500 mL of dichloromethane cooled to 0–5 °C under nitrogen was added in one addition 1.47 mL (1.70 g, 12 mmol) of boron trifluoride etherate. The solution immediately turned dark, and after a few seconds the vigorous evolution of nitrogen was observed. The solution was stirred at 0–5 °C for 30 min and then poured into brine. The organic phase was washed two times with saturated aqueous sodium bicarbonate, water, and brine and dried. Removal of solvent in vacuo gave 1.17 g (100%) of crude material which gave 0.7863 g (72%) of volatile material upon Kugelrohr distillation [bp 130–170 °C (0.50 mmHg)]. Preliminary VPC purification on column A gave two fractions.

Fraction one gave, after TLC purification on silica (hexane-ether, 1:1 v/v) and final VPC purification on column A, pure 7-methyl-6,7,8,9-tetrahydro-7-vinyl-5*H*-benzocyclohepten-6-one (**20**): 17% yield; mp 49–50 °C; IR 3075 (m), 3025 (m), 2978 (s), 2930 (s), 2855 (m), 1710 (vs), 1635 (m), 1495 (m), 1458 (m), 1420 (m), 1380 (m), 1282 (s), 1210 (m), 1055 (s), 990 (w), 920 (s)  $cm^{-1}$ ; NMR (220 MHz)  $\delta$  1.11 (s, 3 H), 1.66 (dd,  $J_1 = 11$  Hz,  $J_2 = 14$  Hz, 1 H), 2.12 (dd,  $J_1 = 8$  Hz,  $J_2 = 14$  Hz, 1 H), 2.73 (dd,  $J_1 = 8$  Hz,  $J_2 = 15$  Hz, 1 H), 3.13 (dd,  $J_1 = 11$  Hz,  $J_2 = 15$  Hz, 1 H), 3.70 (center of AB q,  $J_{AB} = 11$  Hz,  $\Delta\nu_{AB} = 195.8$  Hz,  $\delta_A$  3.25,  $\delta_B$  4.15, 2 H,  $H_A$  and  $H_B$ ), an ABC pattern [5.04 (d,  $J_{13} = 17$  Hz, 1 H,  $H_1$ ), 5.17 (d,  $J_{23} = 11$  Hz, 1 H,  $H_2$ ), 6.01 (dd,  $J_{32} = 11$  Hz,  $J_{31} = 17$  Hz, 1 H,  $H_3$ ), 6.82–7.11 (m, 4 H)].

Anal. Calcd for  $C_{14}H_{16}O$ : C, 83.96; H, 8.05. Found: C, 83.87; H, 8.05.

Fraction two gave, after TLC purification on alumina (benzene), pure 5-methyl-5-phenethyl-2-cyclopenten-1-one (**19**): 11% yield; IR 3090 (w), 3068 (w), 3040 (w), 2965 (m), 2930 (m), 1710 (s), 1590 (w), 1490 (w), 1460 (w), 1430 (w), 1370 (w), 1340 (w), 1195 (m), 695 (m)  $cm^{-1}$ ; NMR (220 MHz)  $\delta$  1.09 (s, 3 H), 1.54–1.93 (m, 2 H), 2.16–2.62 (m, 3 H), 2.62–2.77 (m, 1 H), 6.05–6.20 (m, 1 H), 6.95–7.26 (m, 5 H), 7.50–7.65 (m, 1 H); NMR (60 MHz)  $\delta$  1.08 (s, 3 H), 1.50–1.92 (m, 2 H), 2.08–2.70 (m, 4 H), 6.00–6.25 (m, 1 H,  $H_1$ ), 7.14 (br s, 5 H), 7.25–7.70 (m, 1 H,  $H_2$ ); mass spectrum,  $m/e$  200.1200 ( $M^+$ , calcd for  $C_{14}H_{16}O$  200.1200).

**Decomposition of 1-Diazo-5-(*m*-methoxyphenyl)-3-methyl-3-vinyl-2-pentanone (4).** Decomposition of 1.71 g (5.93 mmol) of diazo ketone **4**, as described above, gave 1.0591 g (77.5%) of volatile material upon Kugelrohr distillation [bp 150–200 °C (1.2 mmHg)]. Preliminary VPC



purification on column A gave three fractions.

Fraction A gave, after TLC purification on alumina (benzene) and final VPC purification on column B, pure 4-methoxy-7-methyl-6,7,8,9-tetrahydro-7-vinyl-5*H*-benzocyclohepten-6-one (**22**): 13% yield; IR 3085 (w), 3000 (m), 2930 (s), 2840 (m), 1708 (vs), 1630 (w), 1600 (m), 1538 (s), 1465 (vs), 1445 (s), 1325 (m), 1268 (vs), 1080 (s), 988 (w), 955 (m), 918 (s), 710 (m)  $\text{cm}^{-1}$ ; NMR (220 MHz)  $\delta$  1.10 (s, 3 H), 1.67 (dd,  $J_1 = 11$  Hz,  $J_2 = 14$  Hz, 1 H), 2.12 (dd,  $J_1 = 9$  Hz,  $J_2 = 14$  Hz, 1 H), 2.70 (dd,  $J_1 = 9$  Hz,  $J_2 = 15$  Hz, 1 H), 3.05 (dd,  $J_1 = 11$  Hz,  $J_2 = 15$  Hz, 1 H), 3.08 (m, s plus overlapping AB q, 5 H), an ABC pattern [5.06 (d,  $J_{AC} = 18$  Hz, 1 H), 5.17 (d,  $J_{BC} = 11$  Hz, 1 H), 6.01 (dd,  $J_{CA} = 18$  Hz,  $J_{CB} = 11$  Hz, 1 H)], 6.60 (apparent t,  $J_{AB} = J_{CB} = 8.2$  Hz, 2 H,  $H_A$  and  $H_C$ ), 6.96 (t,  $J_{BC} = J_{BA} = 8.2$  Hz, 1 H,  $H_B$ ); mass spectrum,  $m/e$  230.1358 ( $M^+$ ,  $\Delta = 23$  ppm, calcd for  $C_{15}H_{18}O_2$  230.1306).

Fraction B gave, after final purification on column B, pure 2-methoxy-7-methyl-6,7,8,9-tetrahydro-7-vinyl-5*H*-benzocyclohepten-6-one (**21**): 45% yield; mp 76–78 °C; IR 3090 (w), 3030 (w), 3000 (m), 2925 (m), 2930 (s), 2860 (m), 2840 (m), 1710 (vs), 1610 (s), 1588 (m), 1550 (s), 1455 (s), 1437 (s), 1370 (m), 1315 (m), 1325 (m), 1272 (vs), 1042 (s), 988 (w), 920 (s)  $\text{cm}^{-1}$ ; NMR (220 MHz)  $\delta$  1.11 (s, 3 H), 1.67 (dd,  $J_1 = 11$  Hz,  $J_2 = 14$  Hz, 1 H), 2.14 (dd,  $J_1 = 8$  Hz,  $J_2 = 14$  Hz, 1 H), 2.67 (dd,  $J_1 = 8$  Hz,  $J_2 = 15$  Hz, 1 H), 3.11 (dd,  $J_1 = 11$  Hz,  $J_2 = 15$  Hz, 1 H), 3.64 (center of AB q,  $J_{AB} = 11$  Hz,  $\Delta\nu_{AB} = 162.85$  Hz,  $\delta_A$  3.27,  $\delta_B$  4.01, 2 H,  $H_A$  and  $H_B$ ), 3.72 (s, 3 H), an ABC pattern [5.09 (d,  $J_{AC} = 16$  Hz, 1 H), 5.20 (d,  $J_{BC} = 11$  Hz, 1 H), 6.05 (dd,  $J_{CA} = 16$  Hz,  $J_{CB} = 11$  Hz, 1 H)], 6.55 (d,  $J_{12} = 2$  Hz, 1 H,  $H_1$ ), 6.57 (dd,  $J_{21} = 2$  Hz,  $J_{23} = 8$  Hz, 1 H,  $H_2$ ), 7.01 (d,  $J_{32} = 8$  Hz, 1 H,  $H_3$ ).

Anal. Calcd for  $C_{15}H_{18}O_2$ : C, 78.23; H, 7.88. Found: C, 77.92; H, 7.84.

Fraction C gave, after TLC purification on alumina (benzene) and final VPC purification on column B, pure 5-(*m*-methoxyphenethyl)-5-methyl-2-cyclopenten-1-one (**23**): 11% yield; IR 3060 (w), 3000 (w), 2960 (s), 2925 (s), 2865 (m), 2840 (m), 1710 (vs), 1600 (s), 1590 (s), 1490 (m), 1458 (m), 1440 (m), 1340 (m), 1265 (s), 1168 (m), 1158 (s), 1110 (m), 1072 (m), 1050 (s), 695 (m), 683 (m)  $\text{cm}^{-1}$ ; NMR (220 MHz)  $\delta$  1.09 (s, 3 H), 1.50–1.87 (m, 2 H), 2.14–2.57 (m, 3 H), 2.66 (d,  $J = 18$  Hz, B part of AB q, 1 H), 3.72 (s, 3 H), 6.08 (d,  $J_{12} = 4$  Hz, 1 H,  $H_1$ ), 6.39–6.75 (m, 3 H), 7.03 (apparent t,  $J = 8$  Hz, 1 H), 7.53 (d,  $J_{21} = 4$  Hz, 1 H,  $H_2$ ).

Anal. Calcd for  $C_{15}H_{18}O_2$ : C, 78.23; H, 7.88. Found: C, 78.25; H, 7.76.

**Decomposition of 1-Diazo-3-ethyl-5-(*m*-methoxyphenyl)-3-methyl-2-pentanone (**26**).** Similar decomposition of 299.7 mg (0.884 mmol) of diazo ketone **26** gave 189.4 mg (93%) of crude material. VPC purification on column A gave two fractions.

Fraction one gave pure 7-ethyl-4-methoxy-7-methyl-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-6-one (**25**): IR 3070 (w), 2965 (vs), 2930 (vs), 2837 (m), 1702 (vs), 1585 (s), 1463 (vs), 1440 (s), 1380 (m), 1355 (m), 1333 (m), 1265 (vs), 1160 (m), 1092 (vs), 1005 (m), 950 (m)  $\text{cm}^{-1}$ ; NMR (220 MHz)  $\delta$  0.85 (t,  $J = 7.5$  Hz, 3 H), 1.03 (s, 3 H), 1.20–2.14 (m, 4 H), 2.76 (dd,  $J_1 = 9$  Hz,  $J_2 = 15$  Hz, 1 H), 3.05 (dd,  $J_1 = 11$  Hz,  $J_2 = 15$  Hz, 1 H), 3.80 (center of AB q,  $J_{AB} = 12$  Hz,  $\Delta\nu_{AB} = 14.73$  Hz,  $\delta_A$  3.77,  $\delta_B$  3.83, 2 H,  $H_A$  and  $H_B$ ), 3.86 (s, 3 H), 6.70 (apparent t,  $J_{12} = J_{32} = 8$  Hz, 2 H,  $H_1$  and  $H_3$ ), 7.06 (t,  $J_{21} = J_{23} = 8$  Hz, 1 H,  $H_2$ ).

Anal. Calcd for  $C_{15}H_{20}O_2$ : C, 77.55; H, 8.68. Found: C, 77.21; H, 8.62.

Fraction two gave pure 7-ethyl-2-methoxy-7-methyl-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-6-one (**24**): mp 91.7–92.7 °C; IR 3065 (w), 2965 (vs), 2930 (vs), 2845 (m), 1700 (vs), 1610 (s), 1585 (m), 1490 (s), 1455 (s), 1430 (s), 1378 (m), 1355 (m), 1322 (m), 1295 (m), 1265 (vs), 1218 (m), 1190 (m), 1158 (m), 1130 (m), 1110 (m), 1100 (m), 1065 (m), 1040 (s), 865 (m)  $\text{cm}^{-1}$ ; NMR (220 MHz)  $\delta$  0.83 (t,  $J = 7.5$  Hz, 3 H), 1.00 (s, 3 H), 1.27–1.50 (m, 1 H), 1.52–1.73 (m, 1 H), 1.73–2.09 (m, 2 H), 2.69 (dd,  $J_1 = 9$  Hz,  $J_2 = 15$  Hz, 1 H), 3.01 (dd,  $J_1 = 11$  Hz,  $J_2 = 15$  Hz, 1 H), 3.56 (center of AB q,  $J_{AB} = 11$  Hz,  $\Delta\nu_{AB} = 125$  Hz,  $\delta_A$  3.28,  $\delta_B$  3.84, 2 H,  $H_A$  and  $H_B$ ), 3.69 (s, 3 H), 6.53 (d,  $J_{12} = 2$  Hz, 1 H,  $H_1$ ), 6.55 (dd,  $J_{21} = 2$  Hz,  $J_{23} = 8$  Hz, 1 H,  $H_2$ ), 6.95 (d,  $J_{32} = 8$  Hz, 1 H,  $H_3$ ).

Anal. Calcd for  $C_{15}H_{20}O_2$ : C, 77.55; H, 8.68. Found: C, 77.42; H, 8.55.

**5-(*m*-Methoxyphenyl)-3-methyl-3-(2'-propenyl)-2-pentanone (**16**).** To a solution of 332.0 mg (1.34 mmol) of acid **8a** in 20 mL of hexane cooled to 0–5 °C under nitrogen was added 2 mL of methyl lithium (1.8 M in ether, 3.6 mmol) dropwise. After completion of the addition, the solution was warmed to room temperature and stirred overnight. The solution was added dropwise to a rapidly stirring, ice-saturated, aqueous ammonium chloride solution and then extracted three times with ether. The ether extracts were washed with saturated aqueous ammonium chloride, water, and brine and dried. Removal of solvent in vacuo gave 222.6 mg

of crude material which was purified on column D, affording pure methyl ketone **16**: IR 3100 (w), 2962 (s), 2842 (m), 1717 (vs), 1645 (m), 1610 (s), 1595 (s), 1498 (s), 1475 (s), 1465 (s), 1445 (s), 1390 (m), 1365 (m), 1265 (s), 1160 (m), 1158 (s), 1100 (m), 1050 (m), 900 (m)  $\text{cm}^{-1}$ ; NMR (220 MHz)  $\delta$  1.27 (s, 3 H), 1.66 (s, 3 H), 1.70–1.95 (m, 2 H), 2.00 (s, 3 H), 2.20–2.40 (m, 2 H), 4.97 (s, 1 H), 5.01 (s, 1 H), 3.76 (s, 3 H), 6.55–6.70 (m, 3 H), 7.00–7.14 (m, 1 H); mass spectrum,  $m/e$  246.1633 ( $M^+$ , calcd for  $C_{16}H_{22}O_2$  246.1619).

***cis*-3a,9b-Dimethyl-1,2,3a,4,5,9b-hexahydro-7-hydroxy-3*H*-benz[e]-inden-3-one (**13**).** To a solution of 36.9 mg (0.15 mmol) of methyl ether **5** in 2 mL of dichloromethane under nitrogen was added 30.3  $\mu\text{L}$  (80.32 mg, 0.32 mmol) of boron tribromide. The solution was stirred at room temperature for 15 h, poured into water, extracted with ether, and washed with water. The phenol was extracted from the organic phase with 5% aqueous sodium hydroxide, and the aqueous phase was acidified with 10% aqueous hydrochloric acid and extracted with ether. The ether extracts were washed with water and brine and dried. Removal of solvent in vacuo gave 32.8 mg (95.5%) of pure phenol **13**: IR 3610 (m), 3370 (vbr, s) 3025 (w), 2965 (s), 2930 (s), 1725 (s), 1610 (m), 1500 (m), 1445 (m), 1270 (m), 1240 (m), 1160 (m), 1075 (m); NMR (60 MHz)  $\delta$  0.98 (s, 3 H), 1.25 (s, 3 H), 1.13–2.30 (m, 7 H), 2.33–2.83 (m, 2 H), 6.00–6.78 (m, 2 H), 7.20 (d,  $J = 8.6$  Hz, 1 H); mass spectrum,  $m/e$  230.1284 ( $M^+$ , calcd for  $C_{15}H_{18}O_2$  230.1306).

**Demethoxylation of *cis*-3a,9b-Dimethyl-1,2,3a,4,5,9b-hexahydro-7-hydroxy-3*H*-benz[e]inden-3-one (**13**).** The procedure of Rossi and Bunnett<sup>12</sup> was employed. To a solution of 32.4 mg (0.14 mmol) of phenol **13** and 334 mg (2 mmol) of diethyl chlorophosphate in 3 mL of toluene cooled to 0–5 °C was added dropwise 0.75 mL (0.94 mmol) of 15% aqueous sodium hydroxide. The solution was stirred for 2 h at room temperature, diluted with ether, washed with water and brine and dried. Removal of solvent in vacuo gave 51.4 mg of crude material (no O–H absorption in the infrared spectrum).

Into a solution of the phosphate ester in 2 mL of dry ether was condensed 5 mL of liquid ammonia. Potassium metal was added in small pieces until the blue color persisted. The solution was stirred for 15 min at reflux and then quenched by addition of solid ammonium chloride. The ammonia was evaporated and the residue dissolved in ether, washed with water and brine and dried. Removal of the solvent in vacuo gave 19.8 mg of crude alcohol.

To a solution of the crude alcohol in 3 mL of acetone cooled to 0–5 °C was added dropwise 150  $\mu\text{L}$  of 2.6 M Jones reagent. The solution was stirred at 0–5 °C for 30 min, filtered, and extracted with ether. The organic phase was washed with water and brine and dried. Removal of solvent in vacuo afforded 22.7 mg of crude material. Purification on column A gave a pure compound identical with **15** by comparison of IR and NMR (220 MHz) spectra and VPC retention time.

**Demethoxylation of *cis*-3a,9b-Dimethyl-1,2,3a,4,5,9b-hexahydro-9-methoxy-3*H*-benz[e]inden-3-one (**11**).** A 34.9-mg (0.15 mmol) sample of methyl ether **11** was demethylated as described above for **5**, and the resulting phenolic hydroxyl group was reductively removed as described above for **13**. Preparative VPC on column A gave a pure product identical with **15** by comparison of IR and NMR (220 MHz) spectra and VPC retention time.

**Hydrogenation of 2-Methoxy-7-methyl-6,7,8,9-tetrahydro-7-vinyl-5*H*-benzocyclohepten-6-one (**21**).** To 45.2 mg of **21** in 2 mL of absolute methanol was added 9.8 mg of palladium adsorbed on carbon, and the solution was stirred under 1 atm of hydrogen until hydrogen uptake had ceased. The solution was filtered, poured into ether, washed with water and brine and dried. Removal of solvent in vacuo afforded 47.8 mg of crude material. Purification by TLC on alumina (benzene) gave a pure product identical with **24** by comparison of IR and NMR (220 MHz) spectra.

**Hydrogenation of 4-Methoxy-7-methyl-6,7,8,9-tetrahydro-7-vinyl-5*H*-benzocyclohepten-6-one (**22**).** An 11.8-mg (0.051 mmol) sample of **22** was hydrogenated as described above to yield 14.4 mg of crude material. Purification by TLC on alumina (benzene) gave a pure product identical with **25** by comparison of IR and NMR (220 MHz) spectra.

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