dimethylformamide (4 mL). After the mixture was cooled to -20 °C, oxygen was bubbled through it and 8-acetyl-7,8,9,10-tetrahydro-6,11-dimethoxy-5,12-naphthacenedione (**18**) (150 mg, 2.5 mmol) in dimethylformamide was added. After 1 h, the reaction mixture was acidified with acetic acid and poured into water and the precipitate was collected. The crude residue was chromatographed (SiO_2, 2% CH_3OH–$CHCl_3$) and recrystallized from methanol to give pale yellow needles of 8-acetyl-8-hydroxy-7,8,9,10-tetrahydro-6,11-dimethoxy-5,12-naphthacenedione (**23**) (80 mg, 55%): mp 184–186 °C (lit.[3a] mp 184–186 °C); NMR δ 2.27 (s, 3 H, $COCH_3$), 3.09 (m, 4 H, benzylic), 1.80 (s, 1 H, OH), 3.85 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 7.66–8.27 (m, 4 H, Ar); IR 3510 (OH), 1710 (C=O), 1670 (C=O), 1600 (Ar) cm^{-1}; MS *m/e* 380 (M^+, 18), 362 (21), 337 (100).

8-Acetyl-6,8,11-trihydroxy-7,8,9,10-tetrahydro-5,12-naphthacenedione (24). Method A. Hydroxyketone **23** (38 mg) was dissolved in benzene (25 mL) to which aluminum chloride (67 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 16 h and poured into water. The benzene extract was evaporated. Recrystallization of the residue from methanol afforded red needles of 4-demethoxy-7-deoxydaunomycinone (**24**) (33 mg, 94%): mp 160–162 °C (lit.[3e] mp 160–162 °C); NMR δ 2.40 (s, 3 H, $COCH_3$), 2.99 (m, 4 H, benzylic), 1.96 (m, 2 H, aliphatic), 3.71 (s, 1 H, OH), 7.84 (m, 2 H, Ar), 8.36 (m, 2 H, Ar), 13.54 (s, 2 H, OH); IR 3510 (OH), 1710 (C=O), 1628 (C=O), 1585 (Ar); MS *m/e* 352 (M^+, 17), 334 (18), 309 (100), 291 (25). The synthesized **24** was identical (IR, TLC, MS, mp) with an authentic sample of **24** supplied by Dr. A. S. Kende of the University of Rochester.

Method B. To a mixture of dibromide **15** (430 mg) and TBO (1.5 mL) in DMA (25 mL) was added sodium iodide (2 g). After 1 h at 70 °C, the mixture was poured into aqueous acetic acid and warmed on a steam bath. The resulting red precipitate was extracted into chloroform and chromatographed (SiO_2, $CHCl_3$/$CHCl_3$–EtOAc (5%)) to yield the hydroxy ketone **24** (42.2 mg, 12%), mp 190–193 °C. The mass and NMR spectra of this sample were identical with those of the sample, mp 160 °C, obtained in method A.

The chloroform-insoluble portion was recrystallized from 1,2-dichlorobenzene to yield dimer **25**, mp >300 °C (100 mg).

Reaction of o-Xylylene Dibromide and NPM in the Presence of NaI. A mixture of *o*-xylylene dibromide (0.56 g) and NPM (0.5 g) in DMA (10 mL) at 70 °C was treated with NaI (2 g). Monitoring of aliquots at intervals showed no trace of the expected product by TLC against a comparison sample. Workup of the dark mixture at the end of 5 h gave a dark intractable powder, traces of the diiodide, and NPM.

Acknowledgment. This investigation was supported by Grant CA-24199, awarded by the National Institutes of Health.

Lewis Acid Promoted Decomposition of Unsaturated α-Diazo Ketones. 1. An Efficient Approach to Simple and Annulated Cyclopentenones

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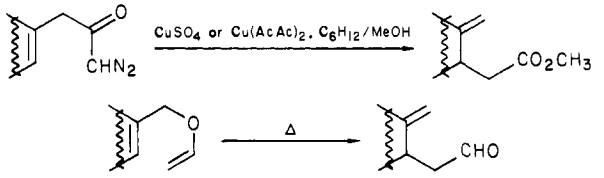
Abstract: The preparation and Lewis acid promoted decomposition of some 24 β,γ- and γ,δ-unsaturated α-diazo ketones are described. The resulting products, summarized in Tables I–III, were found to be simple and annulated cyclopentenone derivatives. In addition, the first examples of polyolefinic cationic cyclization initiated by the α-diazo ketone functionality are described.

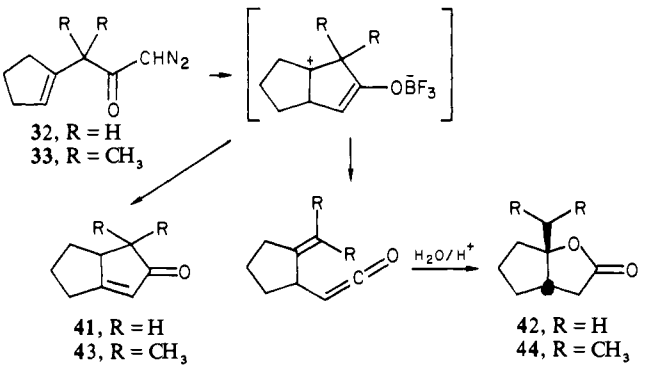
Introduction

During the past several years we have engaged in a systematic study of the chemistry of β,γ-unsaturated diazo ketones. Two principal discoveries have emanated from this effort. First, we observed that β,γ-unsaturated diazo ketones in the presence of a copper catalyst [i.e., $CuSO_4$ or $Cu(AcAc)_2$] efficiently led, via



a novel skeletal rearrangement, to γ,δ-unsaturated acid derivatives.[2,3] This transformation, a synthetic alternative to the Claisen rearrangement of enol vinyl ethers, was termed by us the vinylogous Wolff Rearrangement. Second, we demonstrated that β,γ-unsaturated diazo ketones are synthetically useful precursors of simple[4] and annulated[5] cyclopentenone derivatives, as well as

Scheme I



32, R = H
33, R = CH_3

41, R = H
43, R = CH_3

42, R = H
44, R = CH_3

polycyclic[6] cyclopentanoid systems. That is, the *α-diazo ketone functionality represents an effective initiator of both mono- and polyolefinic cationic cyclization.*

In this, the first of three full accounts of our work in this area, we record the utility of the acid-promoted decomposition of β,-

(1) Camille and Henry Dreyfus Teacher-Scholar, 1978–1983; Recipient of a National Institutes of Health Career Development Award, 1980–1985.
(2) A. B. Smith, III, *J. Chem. Soc., Chem. Commun.*, 695 (1974). Also see J. P. Lokensgard, J. O'Dea, and E. A. Hill, *J. Org. Chem.*, **39**, 3355 (1974).
(3) A. B. Smith, III, B. H. Toder, and S. J. Branca, *J. Am. Chem. Soc.*, **98**, 7456 (1976).
(4) A. B. Smith, III, S. J. Branca, and B. H. Toder, *Tetrahedron Lett.*, 4225 (1975).
(5) A. B. Smith, III, *J. Chem. Soc., Chem. Commun.*, 274 (1975).
(6) A. B. Smith, III, and R. K. Dieter, *J. Org. Chem.*, **42**, 396 (1977).

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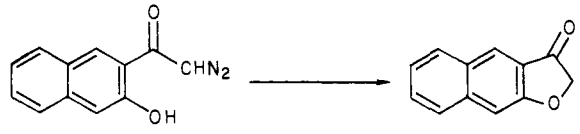
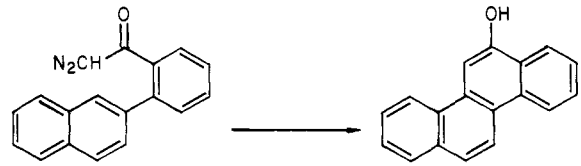
γ-unsaturated diazo ketones for the preparation of simple and annulated cyclopentenones. In addition, we include here the first experiments that suggested that the α-diazo ketone functionality holds potential for the initiation of polyolefinic cyclization. In two subsequent reports we will detail our efforts to exploit the α-diazo ketone functionality as a high-energy initiator of polyene cyclization.

Background

Although it was recognized in 1935 and 1945, respectively, by Eistert[8] and Cook,[9] that α-diazo ketones (e.g., **1** and **2**) possessing

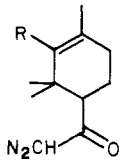


1

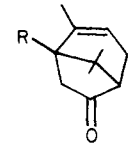


2

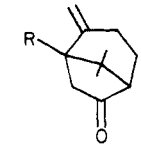
suitably disposed internal nucleophiles (i.e., heteroatom and aryl substituents) undergo facile intramolecular cyclization upon acid-catalyzed decomposition, it was not until 1971 that the first example of intramolecular participation of an isolated olefin in such a cyclization process appeared in the literature. In that year, Erman and Stone[10] reported their elegant strategy for construction of the α-patchoulane class of sesquiterpenes based on the acid-catalyzed cyclization of diazo ketones **3a,b**. In particular,



3a, R = CO_2Et
b, R = H



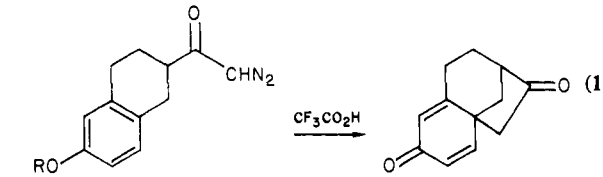
4a, R = CO_2Et (30%)
b, R = H (56%)



5a, R = CO_2Et (3%)
b, R = H (6%)

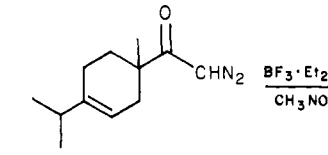
BF_3·Et_2O-induced decomposition of **3a,b** resulted, respectively, in **4a,b** and **5a,b**. The higher yield of cyclized material observed in the case of **3b** was suggested to reflect the greater nucleophilicity of the participating olefin.

Since this pioneering observation, intramolecular cyclization of unsaturated diazo ketones has attracted considerable interest. Most notable has been the extensive efforts of Mander and coworkers[11] at the Australian National University on the acid-induced cyclization of γ,δ-unsaturated diazo ketones. Both the aryl and isolated olefins were exploited as the internal nucleophile. We illustrate below three representative examples (eq 1–3), the latter being the pivotal intermediate in Mander's elegant strategy for construction of the gibberellins.



6a, R = H
b, R = CH_3

(1)[11]



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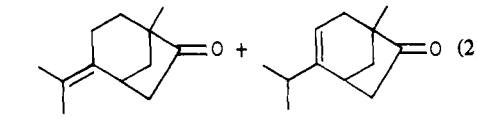
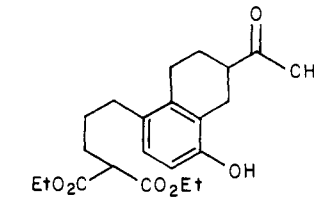


~100% (4:1)

(2)[11]



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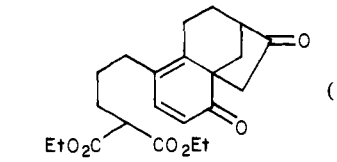
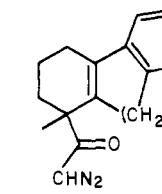


(3)[11]

More recently, Ghatak et al.[12] have taken up this trail. Noteworthy from this laboratory is the synthesis of angularly fused cyclobutanones (i.e., **10**) via the acid-catalyzed decomposition of diazo ketones **9**.



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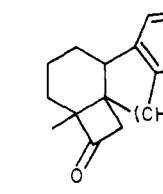


10

Results and Discussion

We initiated work in this area by exploring the acid-promoted decomposition of β,γ-unsaturated diazo ketones **11–13**.[4–6] After an extensive examination of a variety of Lewis acid–solvent couples, guided in large part by the previous efforts of Erman and Mander, we ascertained that the optimal conditions for cyclization consisted of treatment of the diazo ketone with BF_3·Et_2O in freshly distilled nitromethane or methylene chloride at 0 °C (see eq 4–6). In cases where a mixture of α,β- and β,γ-olefinic isomers was anticipated (i.e., eq 5), the reaction mixture was subjected to 10% aqueous HCl at reflux for 30 min in order to generate the more stable α,β-unsaturated ketone.

In our preliminary accounts[4–6] of this area we suggested, as a working hypothesis, that these transformations proceed via initial complexation of the Lewis acid (i.e., BF_3) with the oxygen of the diazo ketone to afford intermediate **A**.[7] Similar suggestions have

(7) For a comprehensive review on the acid-catalyzed decomposition of unsaturated α-diazo ketones see A. B. Smith, III, and R. K. Dieter, Tetrahedron Report, in press.

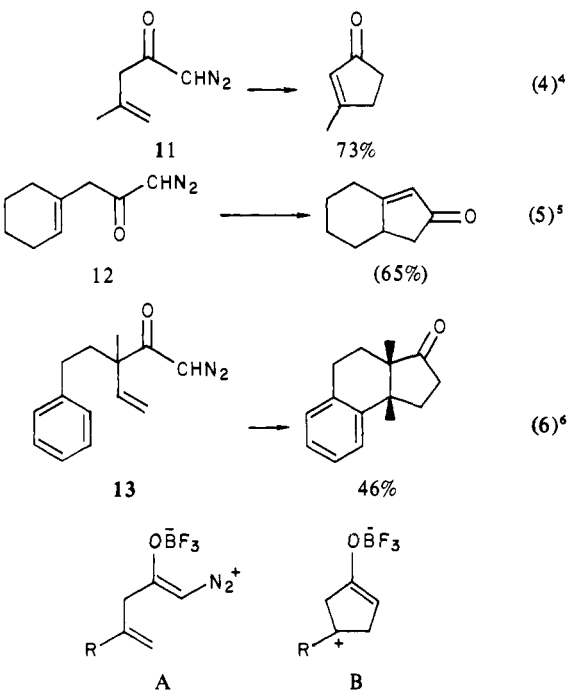
(8) H. Krzikalla and B. Eistert, *J. Prakt. Chem.*, **143**, 50 (1935).

(9) J. W. Cook and R. Schoental, *J. Chem. Soc.*, 288, (1945).

(10) W. F. Erman and L. C. Stone, *J. Am. Chem. Soc.*, **93**, 2821 (1971). Also see W. F. Erman and L. C. Stone, *J. Agric. Food Chem.*, **19**, 1093 (1971).

(11) D. J. Beames and L. N. Mander, *Aust. J. Chem.*, **24**, 343 (1971); D. J. Beames, T. R. Klose, and L. N. Mander, *J. Chem. Soc. D*, 773 (1971); D. J. Beames and L. N. Mander, *Aust. J. Chem.*, **27**, 1257 (1974); D. J. Beames, T. R. Klose, and L. N. Mander, *ibid.*, **27**, 1269 (1974); D. W. Johnson and L. N. Mander, *ibid.*, **27**, 1277 (1974); T. R. Klose and L. N. Mander, *ibid.*, **27**, 1287 (1974); D. J. Beames, L. N. Mander, and J. V. Turner, *ibid.*, **27**, 1977 (1974); L. N. Mander, J. V. Turner, and B. G. Coombe, *ibid.*, **27**, 1985 (1974).

(12) U. R. Ghatak and B. Sanyal (nee Maitra), *J. Chem. Soc., Chem. Commun.*, 876 (1974).

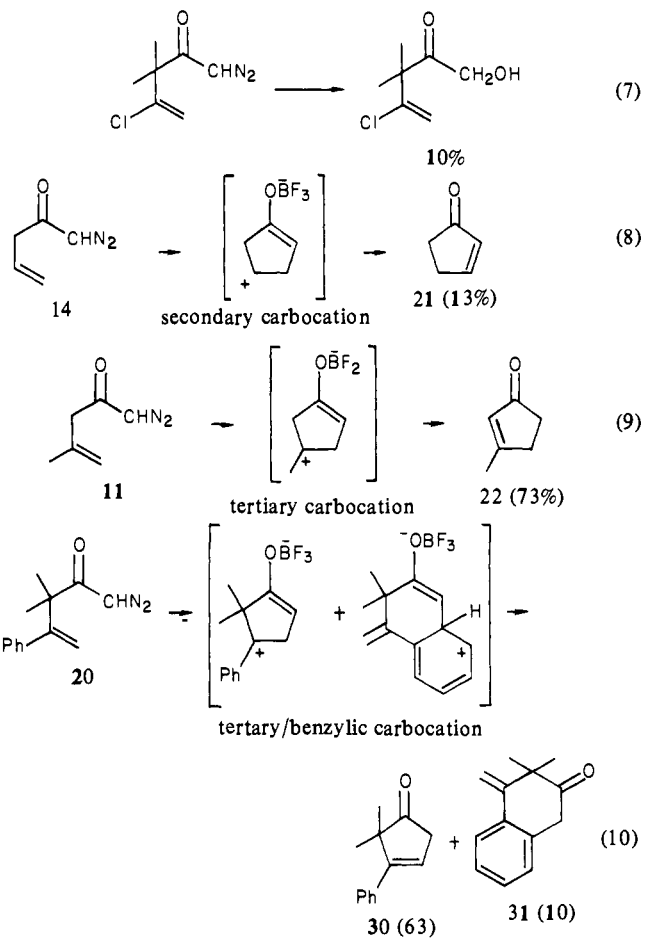


been made by Mander.[11] Subsequent loss of nitrogen and cyclization then leads to a stabilized tertiary carbocation (i.e., B). At present the exact timing of the cyclization process, vis-ā-vis, loss of nitrogen, is unknown. That is, loss of nitrogen could precede σ-bond formation, and/or the π system of the β,γ olefinic bond could participate directly in the displacement of nitrogen. The resultant tertiary carbocation can then either eliminate a proton or if sufficiently long lived as in eq 6 can be captured internally by a neighboring π system. In the former event, treatment with aqueous acid leads to the conjugated cyclopentenone derivative, while in the latter case a polycyclic system is generated.

Encouraged by our initial results, we set out to define the generality and limitations of this approach to simple and annulated cyclopentenone derivatives. To this end we examined a wide variety of structural types. As illustrated in Tables I and II our results demonstrated that both simple and annulated cyclopentenones can be prepared in modest to good yields (e.g., 40–75%) from readily available unsaturated acids. 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.

Let us consider first those diazo ketones which lead to simple cyclopentenone derivatives (see Table I). Significant here is the fact that even the parent β,γ-unsaturated diazo ketone **14** undergoes the cyclization process, albeit in only 13% yield. Presumably the low yield in this case results both from the reduced nucleophilicity of the participating π system and from the reduced stability of the intermediate secondary carbocation. That in fact both the nucleophilicity of the participating π system and the stability of the postulated intermediate carbonium ion are important parameters in the acid-catalyzed cyclization of unsaturated diazo ketones is further supported by the trend of increasing percent cyclization observed with the diazo ketones illustrated in eq 7–10. Similar observations by Johnson and co-workers in the area of polyolefinic cyclization indicate that the weakly nucleophilic terminating group $CHCl{=}CH_2$ fails to participate in polyene cyclizations, while the vinyl and isopropenyl groups are correspondingly more effective.[13]

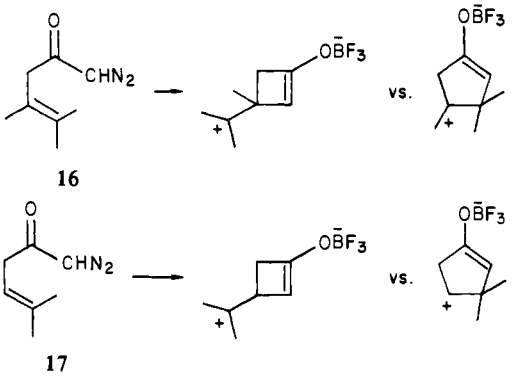
Interestingly, the last diazo ketone in this series (i.e., **20**) also affords a small amount of enone **31**. This result raises several



intriguing questions. First, is there a preferred ring size for acid-induced cyclization of unsaturated diazoketones? Second, what are the relative nucleophilicities of the olefinic partners in these intramolecular alkylations?

To explore the question of ring size, we subjected the diazo ketones illustrated in Table III to the $BF_3{\cdot}Et_2O/CH_2Cl_2$ reaction conditions. In each case the cyclization proceeded; however, the yield of enone decreases monotonically as the site of unsaturation from the diazo carbon increases.[14] Significant here is the fact that these examples were designed such that only the number of intervening methylene groups was altered. That is, the nucleophilicity of the participating olefin as well as the stability of the intermediate carbocation (i.e., tertiary) was identical in each case.

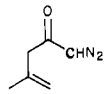
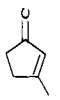
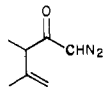
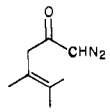
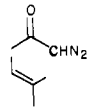
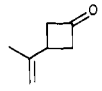
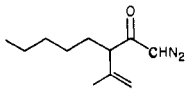
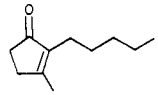
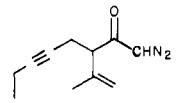
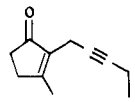
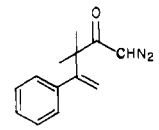
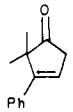
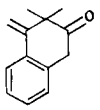
To define further the relative importance of ring size (i.e., entropy effects) vs. stability of the intermediate carbonium ion, we explored the cyclization of diazo ketones **16** and **17**. As illustrated below there are two modes of cyclization available to **16** which result in a tertiary carbonium ion, while in **17** only one closure mode affords a tertiary carbocation.



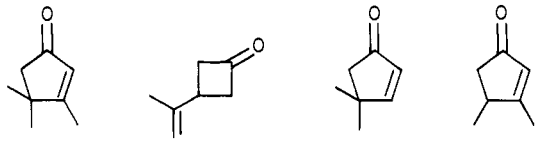
(13) W. S. Johnson and L. A. Bunes, *J. Am. Chem. Soc.*, **98**, 5597 (1976); see ref 5 and references cited therein.

(14) D. J. Beames and L. N. Mander, *Aust. J. Chem.*, **27**, 1257 (1974).

Table I. Acyclic Diazo Ketones → Monocyclic Cyclopentenones

entry	diazo ketone	solvent	product(s) (% yield)
A	 **14**	CH_3NO_2	 **21** (13)
B	 **11**	CH_2Cl_2, CH_3NO_2	 **22** (73) (64)
C	 **15**	CH_3NO_2	 **23** (40)
D	 **16**	CH_2Cl_2	 **24** (77)
	 **17**	CH_2Cl_2	 **25** (31)  **26** (12.2)  **27** (27.7)
F	 **18**	CH_3NO_2	 **28** (65)
G	 **19**	CH_3NO_2	 **29** (40)
H	 **20**	CH_3NO_2	 **30** (63)  **31** (10)

In the event, a single cyclopentenone (**24**) was obtained in 77% yield from **16**, while diazo ketone **17** afforded a three-component mixture (**25**–**27**); the combined yield in the latter case was 71%.



24 **25** **26** **27**

The major product here was identified as cyclobutanone **25** on the basis of infrared bands at 1775 and 890 cm^{-1} in conjunction with resonances in the ^1H (220 MHz) NMR spectrum at δ 1.80 (br s, 3 H), 4.82 (br s, 1 H), and 4.85 (br s, 1 H) characteristic of an isopropenyl substituent. The minor products were identified as cyclopentenones **26** and **27**.

Product formation in both cases would appear to result from a delicate balance between carbonium ion stability and ring strain, with carbonium stability apparently being the overriding factor. For example, diazo ketone **16**, having two modes of ring closure leading to a tertiary carbonium ion, affords the less strained cyclopentenone **24** as the sole product, whereas diazo ketone **17**, having the choice between closure to a four-membered ring bearing an *exocyclic* tertiary carbocation vs. closure to a five-membered ring with an *endocyclic* secondary cation, affords the strained cyclobutanone as the major product. It should also be recognized

Table II. Monocyclic Diazo Ketones → Bicyclic Cyclopentennones

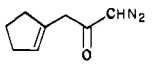
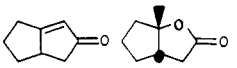
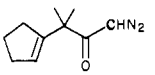
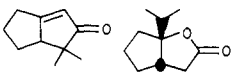
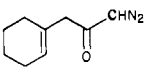
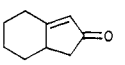
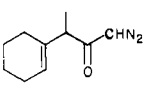
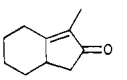
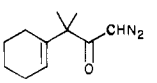
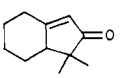
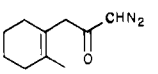
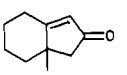
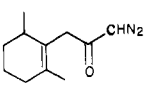
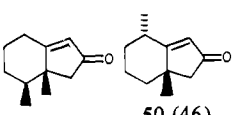
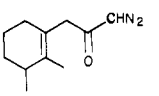
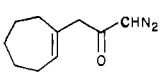
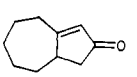
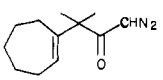
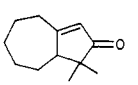
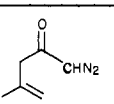
entry	diazo ketone	solvent	product(s) (% yield)
A	 **32**	CH_2Cl_2	 **41** (50) **42** (10)
B	 **33**	CH_2Cl_2	 **43** (41) **44** (30)
C	 **12**	CH_3NO_2	 **45** (50)
D	 **34**	CH_3NO_2	 **46** (63)
E	 **35**	CH_3NO_2	 **47** (65)
F	 **36**	CH_3NO_2	 **48** (57)
G	 **37**	CH_3NO_2	 **49** (8) **50** (46)
H	 **38**	CH_3NO_2	**49** (31.4) **50** (21)
I	 **39**	CH_2Cl_2	 **51** (60.5)
J	 **40**	CH_2Cl_2	 **52** (68)

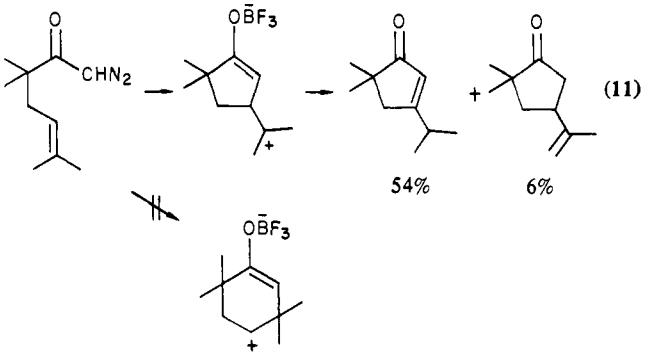
Table III

entry	diazo ketone	site of unsaturation	product (s)	yield, %
A	 **11**	β,γ		73
B	**53**	γ,δ		55
C	**54**	δ,ε	2:1	42

that only the minor cyclopentenone product (i.e., **26**) results via a direct cyclization–proton elimination sequence; the major cyclopentenone derivative arises via a Wagner–Meerwein shift of

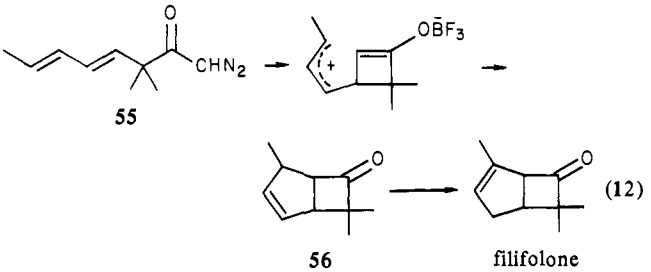
a methyl group to generate a more stable tertiary carbocation which subsequently expels a proton. That cyclopentenones **26** and **27** do not arise via secondary rearrangement of cyclobutanone **25** was demonstrated by subjecting **25** to the reaction conditions.

After completion in our laboratory of the above experiment, Lorne and Listrumelle[15] reported the results of a similar competition experiment which demonstrated that closure to a five-membered ring possessing an *exocyclic* tertiary carbonium ion is favored over closure to a six-membered ring bearing an *endocyclic* secondary cation (see eq 11).



(11)

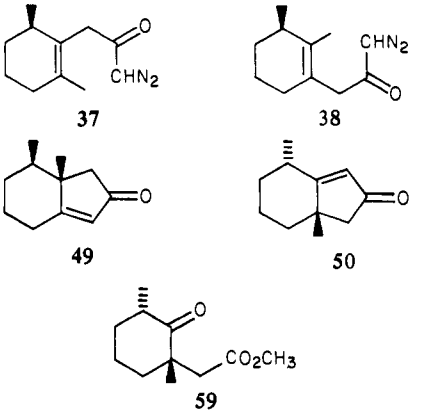
Finally, we note that Hudlicky and Kutchan[16] have exploited the acid-catalyzed cyclization of diazo ketone **55** to cyclobutanone **56** (eq 12) in their synthesis of filifolone. Presumably, this cyclization proceeds via initial closure to a four-membered ring followed by intramolecular capture of the boron enolate.



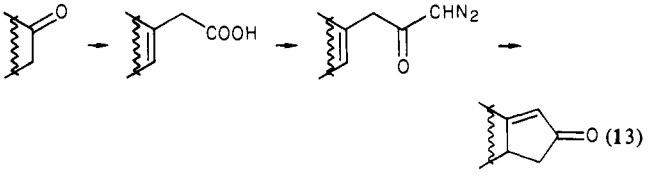
(12)

Having defined the structure–reactivity relationships for the Lewis acid promoted cyclization of simple diazo ketones, we examined next the feasibility of exploiting this transformation as a method for cyclopentenone annulation.[17] Our results, illustrated in Table II, demonstrated that *the Lewis acid catalyzed decomposition of β,γ-unsaturated diazo ketones*, in conjunction with the now numerous approaches to β,γ-unsaturated acid derivatives including the improved Reformatsky sequences[18] and the facile ester alkylation–deconjugation procedure introduced by Rathke[19] and Schlessinger,[20] *is, in fact, a general cyclopentenone annulation strategy*. The overall reaction sequence is illustrated in eq 13.

Chart I



In general, yields of annulated cyclopentenones based on the starting cyclic ketone (i.e., ketone → β,γ-unsaturated diazo ketone → cyclopentenone) were quite good.



(13)

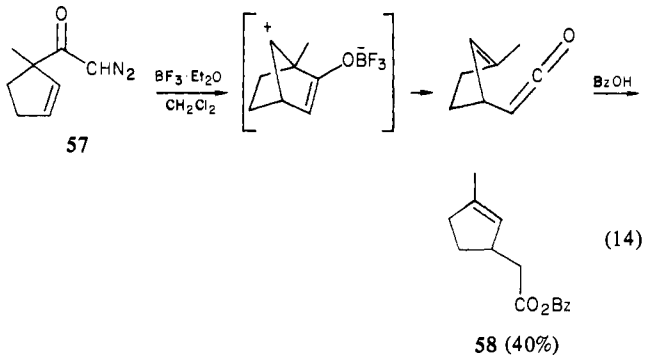
Several additional comments concerning the results in Table II are in order. First, in addition to the expected annulated cyclopentenones **41** and **43**, diazo ketones **32** and **33** afford in low yield bicyclic lactones **42** and **44**, respectively (Scheme I). Initial structural assignments here, based on elemental composition data and observation of a strong band at 1775 cm^{-1}, were confirmed by alternate synthesis (vide infra).

Formation of lactones **42** and **44** is explicable in terms of our overall mechanistic model. In particular, after initial loss of nitrogen and cyclization, the intermediate tertiary carbocation can either eliminate a proton to yield enones **41** and **43** as the major products or, alternatively, can fragment to a ketene. Upon aqueous workup, the ketene is transformed into a γ,δ-unsaturated acid which in turn undergoes lactonization. The driving force for fragmentation presumably results from the strain inherent in the bicyclic [3.3.0]oct-1-ene system. In line with this argument, lactone formation is not observed when the β,γ olefinic bond of the diazo ketone is contained in a six-membered ring. It should be recognized that this overall transformation is an example of an acid-catalyzed vinylogous Wolff rearrangement, a reaction previously observed to take place only upon metal ion catalyzed decomposition of β,γ-unsaturated diazo ketones.[21]

To our knowledge, the only additional example of an *acid*-catalyzed vinylogous Wolff rearrangment occurs upon decomposition of diazo ketone **57**. In this case, treatment of **57** with $BF_3{\cdot}Et_2O$ in methylene chloride for 10 min followed by the usual workup (aqueous $NaHCO_3$) afforded no volatile material.[22] However, treatment of the reaction mixture with 1.2 equiv of benzyl alcohol, after evolution of nitrogen had ceased, led to benzyl ester **58** in 40% yield as the only volatile product (eq 14). As in the previous example, ester **58** presumably arises via fragmentation of a bicycloheptane intermediate to generate a ketene which in this case is captured with benzyl alcohol.

Finally, we draw attention in Table II to diazo ketones **37** and **38** which were specifically designed to examine the stereochemical consequences of the acid-catalyzed cyclization of β,γ-unsaturated diazo ketones. Interestingly, both systems afford the same pair

(15) R. Lorne and G. Linstrumelle, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **282**, 761 (1976).
(16) T. Hudlicky and T. Kutchan, *Tetrahedron Lett.* **21**, 691 (1980).
(17) R. M. Jacobson, R. A. Raths, and J. H. McDonald, *J. Org. Chem.*, **42**, 2545 (1977), and references cited therein; S. A. Monti, F. G. Cowherd, and T. W. McAninch, *ibid.*, **40**, 858 (1975); B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **95**, 289 (1973); P. E. Eaton and R. H. Mueller, *ibid.*, **94**, 1014 (1972); S. Dev, *J. Indian Chem.*, **34**, 169 (1957); J.-M. Conia and M.-L. Leriverend, *Bull. Soc. Chim. Fr.*, 2981 (1970). T. Hiyama, M. Shinoda, and H. Nozaki, *Tetrahedron Lett.*, 771 (1978); Y. Hayakawa, K. Yokoyama, and R. Noyori, *J. Am. Chem. Soc.*, **100**, 1799 (1978); M. E. Jung and J. P. Hudspeth, *ibid.*, **99**, 5509 (1977); P. L. Fuchs, *ibid.*, **96**, 1607 (1974); P. T. Lansbury, *Acc. Chem. Res.*, **5**, 311 (1972); S. Dev, *Chem. Ind. (London)*, 1017 (1954); E. Negishi and H. C. Brown, *Synthesis*, 77, (1974).
(18) M. S. Newman and M. C. Vander Zwan, *J. Org. Chem.*, **39**, 1186 (1974); J. F. Ruppert and J. D. White, *J. Org. Chem.*, **39**, 269 (1974); R. A. Bell, M. B. Gravestock, and V. Y. Taguchi, *Can. J. Chem.*, **50**, 3749 (1972); M. W. Rathke and A. Lindert, *J. Org. Chem.*, **35**, 3966 (1970); J. W. Frankenfeld and J. J. Werner, *J. Org. Chem.*, **34**, 3689 (1969).
(19) M. W. Rathke and D. Sullivan, *Tetrahedron Lett.*, 4249 (1972).
(20) J. L. Herrmann, G. R. Kieczykowski, and R. H. Schlessinger, *Tetrahedron Lett.*, 2433 (1973).
(21) For other examples of the vinylogous Wolff rearrangement see: A. L. Wilds, R. L. Von Trebra, and N. F. Woolsey, *J. Org. Chem.*, **34**, 2401 (1969); H. E. Zimmerman and R. D. Little, *J. Am. Chem. Soc.*, **96**, 4623 (1974).
(22) Presumably the basic workup affords the corresponding carboxylic acid which remained in the aqueous phase.



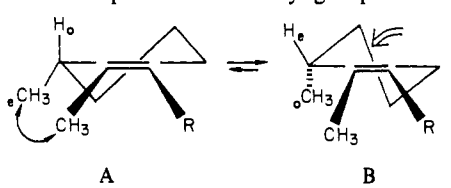
57 (14) 58 (40%)

of bicyclic enones, **49** and **50** (see Chart I). Enone **49** was identical with an authentic sample kindly provided by Professor Evans,[23] while the structure of **50** rests on its conversion to keto ester **59** (a, RuO_4 oxidation; b, CH_2N_2 esterification), the latter previously prepared in our laboratory.[24] Significant here is the fact that the trans isomer of **49** was not observed (ca. <5%).

A reasonable pathway for the formation of **49** and **50** is illustrated in Scheme II. Although in both cases the combined yield of cyclized material was identical within experimental error (ca. 52% and 54%), the ratio of **49** to **50** differed significantly. Thus, while there is a certain kinship of the pathways leading to product formation (i.e., 1,2-methyl migrations), equilibration between intermediates **60** and **61** is apparently not involved.

Concerning the stereochemical outcome, only enone **49** can provide a detailed picture of the reaction coordinate, since enone **50** loses its stereochemical integrity due to a methyl substituent disposed vinylogously α to the carbonyl that under the acidic reaction conditions would be expected to undergo epimerization to the more stable trans isomer. The sole formation (>19:1) of the cis isomer of **49** from both **37** and **38**, on the other hand, demands that the diazo carbon attack the olefinic linkage anti to the secondary methyl group. In the case of **37** this result is quite reminescent of our previous observations on the stereochemical consequences of the vinylogous Wolff rearrangement where, in diazo ketone **37**, approach of the diazo carbon anti to the methyl substituent predominated in a 9:1 ratio.[25] Both observations (i.e., vinylogous Wolff rearrangement and acid-promoted cyclization of diazo ketone) are explicable in terms of a serious $A^{1,3}$ nonbonded interaction between the secondary methyl and the α′-methylene group upon approach of the diazo carbon syn to the secondary methyl.[26]

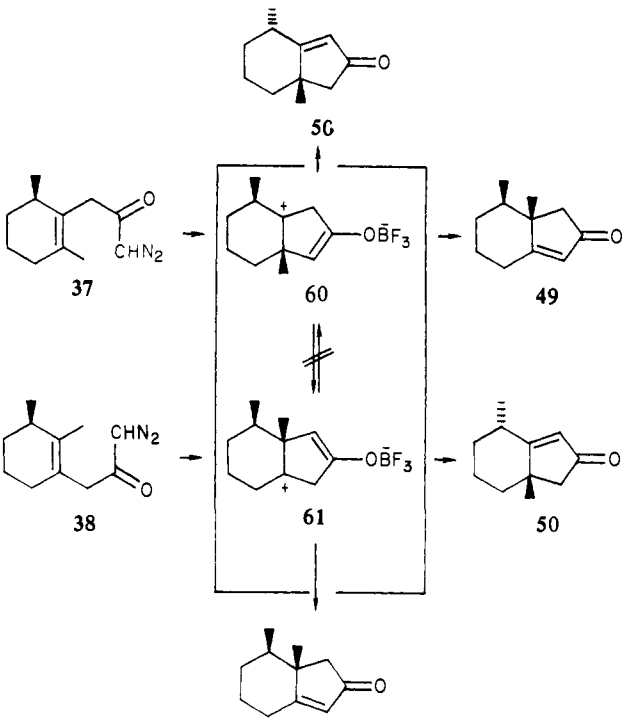
Exclusive formation of cis enone **49** in the case of diazo ketone **38** can be understood in terms of $A^{1,2}$ nonbonded interaction between the vicinal methyl substituents. Consider for the moment, the two interconvertible half-chair conformations of diazo ketone **38**. In A, eclipsing of the pseudoequatorial secondary methyl group with the vinyl methyl destabilizes this conformation relative to conformer B, which possesses the methyl group in the pseudoaxial position. Thus, conformer B would be expected to predominate (eq 15). The pseudoaxial methyl in B, in turn, shields one face of the olefinic bond, thereby forcing approach of the diazo carbon to occur anti to the pseudoaxial methyl group.[27]



(15)

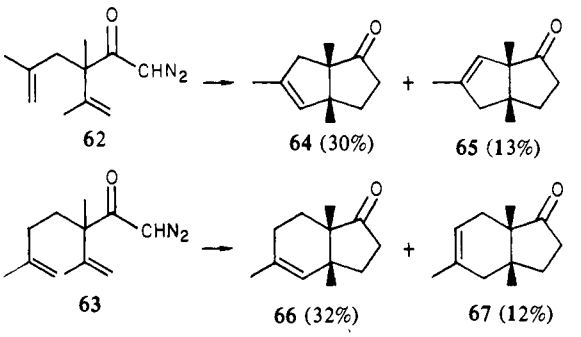
A B

Scheme II



To conclude our study on the acid-promoted cyclization of *simple* unsaturated diazo ketones, we wished to explore, in an intramolecular case, competition between two different olefinic sites. In particular, we hoped to compete participation of a β,γ vs. γ,δ olefin as well as participation of a β,γ vs. δ,ε olefin. For such competition to be valid, of course, the nucleophilicity of both olefinic sites as well as the stability of the intermediate carbocations would have to be identical. Ideal candidates for this study appeared to be the readily available diazo ketones **62** and **63**, the synthesis of which are recorded in the Experimental Section.

While at the outset it was certainly not our intent to explore polyolefinic cyclization,[28] it soon became evident that this was, in fact, the overriding process. Our results are illustrated in eq 16 and 17. Indeed, decomposition of both **62** and **63** with 1.2



(16) (17)

equiv of freshly distilled BF_3·Et_2O in methylene chloride afforded predominantly bicyclic products, the combined yield of bicyclic material being 43–44%.

The structure of each bicyclic ketone, initially assigned on the basis of its spectral properties in conjunction with elemental composition data, was later confirmed by alternate synthesis (see Experimental Section). That the only bicyclic ketones derived from diazo ketones **62** and **63** were, respectively, bicyclooctenones and indenones, when other bicyclic systems are formally possible,

(23) D. A. Evans and C. L. Sims, *Tetrahedron Lett.*, 4691 (1973). We are grateful to Professor Evans for providing us with the NMR spectrum of enone **49**.

(24) S. J. Branca and A. B. Smith, III, *J. Org. Chem.*, **42**, 1026 (1977).

(25) The initial stereochemistry of the ring closure, by analogy with that observed in the Vinylogous Wolff rearrangement, with the same diazo ketones would be expected to lead to *trans*-**49**. See ref 3.

(26) For an excellent review on $A^{1,2}$ and $A^{1,3}$ strain in six-membered rings see F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

(27) F. Johnson and A. Whitehead, *Tetrahedron Lett.*, 3825 (1964); S. K. Malhotra and F. Johnson, *ibid.*, 4027 (1965), and references cited therein.

(28) W. S. Johnson, *Trans. N. Y. Acad. Sci.*, **29**, 1001 (1967), and references cited therein; W. S. Johnson, *Acc. Chem. Res.*, **1**, 1 (1968); W. S. Johnson, *Angew. Chem., Int. Ed. Engl.*, **15**, 9, (1976); W. S. Johnson, *Bioorg. Chem.*, **5**, 51 (1976).

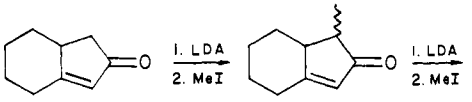
is completely consistent with our previous observations vis-à-vis the facility with which five-, six-, and seven-membered rings are formed in the Lewis acid catalyzed decomposition of monounsaturated diazo ketones.

From the point of view of synthesis, it is significant that *such cyclizations proceed in modest yield without the advent of complex rearrangements* (i.e., hydride shifts, etc.). These observations suggest that β,γ-unsaturated diazo ketones suitably designed hold considerable promise for construction of complex natural products. Our efforts on this front will be forthcoming in due course.

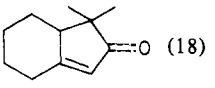
Preparative Experiments

The unsaturated diazo ketones employed in this study were prepared in the usual manner via treatment of the respective acid chlorides with excess diazomethane.[29] The requisite unsaturated acids in turn were available from the corresponding esters which were prepared either by the alkylative deconjugation procedure introduced by Schlessinger[20] and Rathke[19] or by addition of ethyl lithioacetate to appropriate ketones followed by dehydration. In all cases the yields of unsaturated esters were good to excellent.

The previously unknown annulated cyclopentenone **47** was readily available via dialkylation of **45** with methyl iodide, through agency of the kinetically derived enolate[30] (eq 18).

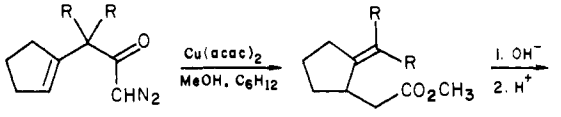


45

 (18)

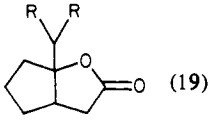
47

Vinylogous Wolff Products. The structures of the vinylogous Wolff products (e.g., lactones **42** and **44** and ester **58**) were secured by alternate synthesis. Here application of the copper-catalyzed vinylogous Wolff rearrangement[23] employing methanol in the case of diazo ketones **32** and **33** and benzyl alcohol for **57** afforded unsaturated esters **68**, **69**, and **58** in 82%, 86%, and 74% yields, respectively (eq 19 20). Benzyl ester **58** was identical in all

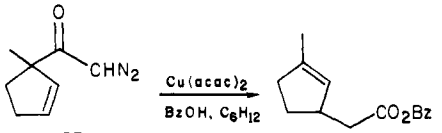


32, R = H
33, R = CH_3

68, R = H
69, R = CH_3

 (19)

42, R = H
44, R = CH_3

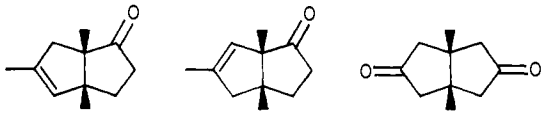


(20)

57 58

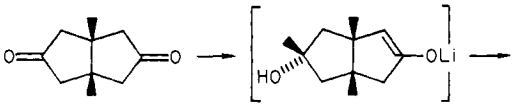
respects with that derived from **57** under the acid-catalyzed conditions, while lactones **42** and **44** were prepared from **68** and **69** via alkaline hydrolysis followed by lactonization employing methanolic HCl. In both cases, a single lactone was obtained, which was identical with the lactone derived under the acidic conditions.

Bicyclooctenones and Indenones. To establish the structure of the previously unknown bicyclic ketones derived via polyolefinic cyclization of diazo ketones **62** and **63**, we undertook their synthesis. Since both diazo ketones afforded two bicyclic systems, believed to differ only in location of unsaturation, we designed our synthetic strategy in each case such that both isomers would be available from a common intermediate. Let us consider first bicyclooctenones **64** and **65**. As starting material, the previously



64 65 70

known, readily available bicyclooctanedione **70**[31] appeared to be ideal in that the carbonyl group in each ring provided the needed functionality (a) to introduce the required vinyl methyl substituent and (b) to effect a 1,2-ketone migration. Toward this end, treatment of **70**, even with excess methyllithium (i.e., 3.3 equiv) afforded monoalcohol **72** in 70% yield (eq 21), contaminated only by starting diketone.



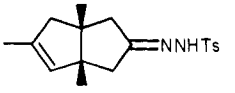
70 71

 (21)

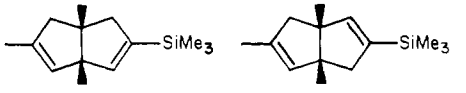
72 73

That diketone **70** undergoes only monoaddition of methyllithium is explicable in terms of enolate formation (e.g., **71**) which serves to protect the second carbonyl group from reaction. Dehydration of the mixture by employing toluenesulfonic acid at the reflux point of benzene then afforded a mixture of the desired ketone **73** and starting material (i.e., **70**), the latter being readily separated by chromatography.

With ketone **73** in hand, a regiodivergent 1,2 ketone migration would then afford both **64** and **65**. To this end, we examined initially the vinylsilane procedure recently introduced by Paquette.[32] Treatment of tosylhydrazone **74** derived from ketone



74



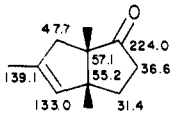
75a, b

73 with *n*-butyl lithium in TMEDA followed by quenching the reaction mixture with trimethylsilyl chloride led to vinyl silanes **75a** and **75b** as a 4:1 mixture (VPC). Progress, however, was thwarted at this point by the highly selective, albeit unwanted, epoxidation of the olefin bearing the methyl substituent. *This observation should serve as a caveat to those attempting the Paquette 1,2 ketone transposition sequence in polyunsaturated systems.*

Frustrated in our initial attempt to convert **73** to **64** and **65**, we turned our attention next to the Trost vinylsulfide procedure.[33]

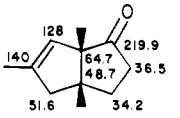
(29) E. L. Eliel, H. Haubenstock, and R. V. Acharya, *J. Am. Chem. Soc.*, **83**, 2351 (1961).
(30) B. H. Toder, S. J. Branca, R. K. Dieter, and A. B. Smith, III, *Synth. Commun.*, **5**, 435 (1975).
(31) U. Weiss and J. M. Edwards, *Tetrahedron Lett.*, 4885 (1968).
(32) W. E. Fristad, T. R. Bailey, and L. A. Paquette, *J. Org. Chem.*, **43**, 1620 (1978).
(33) B. M. Trost, K. Hiroi, and S. Kurozumi, *J. Am. Chem. Soc.*, **97**, 438 (1975).

Chart II



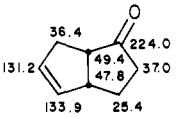
64

[λ_{max} 286 (ϵ 75)]



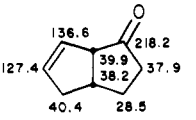
65

[λ_{max} 298 (ϵ 254)]



80

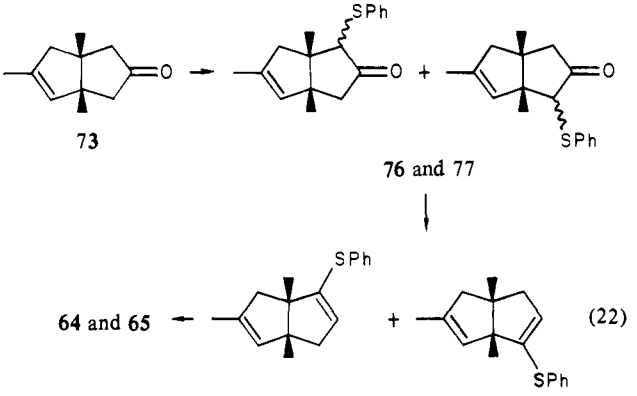
[λ_{max} 293 (ϵ 25)]



81

[λ_{max} 298 (ϵ 89)]

Here alkylation of the lithium enolate derived from ketone **73** with diphenyl sulfide provided a mixture of keto sulfides **76** and **77** in 63% yield (eq 22). After removal of the starting ketone by



(22)

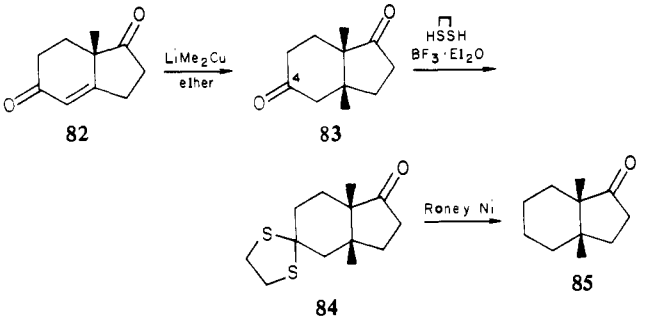
chromatography, reduction of the carbonyl group with sodium borohydride followed by treatment with methanesulfonyl chloride and triethylamine and then with potassium *tert*-butoxide in dimethyl sulfoxide at room temperature for 18 h led in near quantitative yield to vinyl sulfides **78** and **79**. Attempted separation at this point by employing a variety of chromatographic techniques (LC, TLC, and VPC) proved fruitless.

With the knowledge that the desired ketones **64** and **65** were readily separable, the vinyl sulfides **78** and **79** were subjected to hydrolysis by employing mercuric chloride in aqueous acetonitrile. In that event, ketones **64** and **65**, identical in all respects with the ketones obtained by Lewis acid decomposition of **64**, were obtained in 84% yield.

While the above synthetic scheme establishes beyond any question the carbon skeleton of **64** and **65**, the position of the olefinic bond in each was still an open concern. To secure this last point, we examined both the ultraviolet and ^{13}C NMR spectra of each. Since one of the bicyclic ketones was known to be β,γ-unsaturated and the other γ,δ-unsaturated, we could anticipate observing in one an enhanced absorption of the $n \rightarrow \pi^*$ transition. Our results are illustrated in Chart II. For comparison purposes we also list the λ_{max}, extinction coefficients, and ^{13}C NMR spectral data for the two parent ketones (**80**[34,36] and **81**[35,36]). Observation of enhanced absorption in ketone **65** as well as the similarity of the ^{13}C NMR spectra of **64** and **65** with those of the parent systems completes the structural assignments.

Turning next to the synthesis of indenones **66** and **67**, the readily available enone **82**[37] appeared to be an appropriate starting material in that reaction with lithium dimethylcuprate was expected

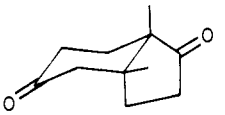
Scheme III



to afford *cis*-**83**[38] (Scheme III). Indeed, the ^1H NMR (60 MHz) spectrum and melting point (163.5–165 °C) were inconsistent with the corresponding data reported by Reusch[39] for the trans isomer of **83**. To secure the stereochemistry of **83**, we carried out a chemical correlation with the previously known *cis*-indenone **84**.[40] Reaction of **83** with ethanedithiol and boron trifluoride etherate[41] afforded ethylene thioketal **85** which in turn gave **84** upon desulfurization with Raney nickel.[42]

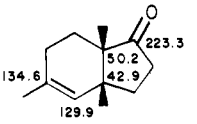
Completion of the carbon skeletons of **66** and **67** requires only introduction of a methyl at C(4) and then a nonregioselective dehydration. To this end treatment of dione **83** with 1.0 equiv of methyllithium and dehydration of the resultant alcohol by employing thionyl chloride and pyridine in ether afforded the desired bicyclic ketones **66** and **67**. The major product, as expected, was the more stable $\Delta^{4,5}$-hexahydroindenone **66**.[43]

It is interesting to note in passing that dione **83** shows a high degree of selectivity in its reaction with ethanedithiol and methyllithium. This chemoselectivity presumably arises from steric hindrance at the cyclopentanone carbonyl.

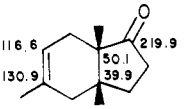


83

Assignment of the position of the olefinic bond in **66** and **67** derives both from analysis of carbon NMR data and from chemical degradation. First, the ^{13}C NMR spectrum of **66** displays



66



67

two olefinic resonances at δ 134.6 (s) and 129.9 (d) whereas **67** displays resonances δ 130.9 (s) and 116.6 (d). The multiplicities displayed in the single-frequency off-resonance decoupled spectrum allowed assignment of the quaternary and methine olefinic carbons. On the basis of substituent effects[44] (i.e., the methine olefinic carbon in **66** is α to a quaternary center), the methine olefinic carbon in **66** should experience a downfield shift relative to that of **67**. That this is indeed the case ($\Delta\delta$ = 13.3 ppm) allows assignment of the position of olefinic bond in **66** and **67**.

Additional evidence for the above assignments was provided by chemical degradation. Specifically, ozonolysis of **66** afforded

(34) J. K. Crandall and L.-H. Chang, *J. Org. Chem.*, *32*, 532 (1967).
(35) L. A. Paquette, O. Cox, M. Oku, and R. P. Henzel, *J. Am. Chem. Soc.*, **96**, 4892 (1974), and references cited therein.
(36) J. K. Whitesell and R. S. Matthews, *J. Org. Chem.*, **42**, 3878 (1977).
(37) Z. G. Hajos and D. R. Parrish, *J. Org. Chem.*, **39**, 1612 (1974). Also see C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2022 (1959).
(38) J. A. Marshall, W. I. Fanta, and H. Roebke, *J. Org. Chem.*, **31**, 1016 (1966).
(39) Professor W. H. Reusch, Michigan State University, personal communication, 1977.
(40) Private communication from Professor William Reusch; see ref 5.
(41) K. H. Baggaley, S. G. Brooks, J. Green, and B. T. Redman, *J. Chem. Soc. C*, 2671 (1971).
(42) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, 1967, p 729.
(43) L. Velluz, J. Valls, and G. Nominé, *Angew Chem., Int. Ed. Engl.*, **4**, 181 (1965), and references cited therein.
(44) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, 1972, Chapter 3.

an aldehyde which displayed a singlet at δ 9.70 in the ^1H (60 MHz) NMR spectrum while **67** afforded an aldehyde which exhibited a triplet at δ 9.75 (J = 1.0 Hz). Unfortunately, the instability of these aldehydes precluded rigorous purification and thereby full characterization.

Experimental Section

Materials and Methods. All VPC separations were accomplished on a Varian Aerograph Model 920 employing one of the following columns: A, 25% Carbowax 20M 10 ft × 0.375 in.; B, 6% Carbowax 20M, 50 ft × 0.25 in.; C, 25% QF-I, 50 ft × 0.25 in.; D, 25% SE-30, 50 ft × 0.25 in.; E, 25% QF-I, 10 ft × 0.375 in.; F, 25% DEGS, 10 ft × 0.375 in.; G, 12% OV-101, 10 ft × 0.375 in. The column oven was operated at 150–190 °C, and the helium carrier gas flow rate was 100–120 mL/min. Compounds purified by VPC were obtained as colorless liquids. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are corrected. Boiling points are uncorrected. Solutions were dried over $MgSO_4$ unless specified otherwise. IR and NMR spectra were obtained for CCl_4 solutions, the former on a Perkin-Elmer Model 337 spectrophotometer and the latter on Varian A-60 (60 MHz) and HR-220 (220 MHz) spectrometers. Carbon-13 spectra were obtained in $CDCl_3$ on a JEOL PS-100 spectrometer. The internal standard for both ^1H and ^{13}C NMR spectroscopy was Me_4Si. Photochemical experiments were carried out with a Hanovia Model L mercury lamp (no. 679A-360) in a quartz immersion well with Pyrex 7740 as a filter. All liquid reagents and solvents were distilled prior to use; the following drying agents were employed: CaH for $BF_3{\cdot}Et_2O$ and HMPA; P_2O_5 for CH_2Cl_2; sodium–benzophenone for THF and Et_2O; $CaSO_4$ for CH_3NO_2.

General Procedure A. Alkylation of Esters and Ketones. A solution of 10 mL of THF and 11 mmol of diisopropylamine was cooled to 0 °C under a N_2 atmosphere. An 11-mmol sample of *n*-BuLi (2.1 M) was added via syringe. After 15 min, the pale yellow solution was cooled to −78 °C whereupon 11 mmol of hexamethylphosphoramide was added. After 1 h, 10 mmol of the reactant ester or ketone dissolved in 5 mL of THF was added dropwise. After an additional hour at −78 °C, 11 mmol of the alkylating agent was introduced. The reaction mixture was maintained at −78 °C for 1 h followed by warming to room temperature over the course of 1 h. The reaction mixture was then poured into 25 mL of saturated aqueous NH_4Cl and extracted with ether. The combined organic material was washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$, and brine and dried. Removal of the solvent in vacuo and distillation afforded the desired alkylated product.

General Procedure B. Addition of Ethyl Lithioacetate to Ketones. To a solution containing 50 mL of dry THF and 55 mmol of freshly distilled diisopropylamine, cooled under N_2 to 0 °C, was added 55 mmol of *n*-BuLi (2.1 M). After 15 min the pale yellow mixture was cooled to −78 °C, and 50 mmol of freshly distilled ethyl acetate was added. After 30 min a solution of 50 mmol of the appropriate ketone in 20 mL of THF was added. The resulting solution was stirred for 1 h at −78 °C and then for 2 h at room temperature. The reaction mixture was then poured into saturated aqueous NH_4Cl and extracted with Et_2O; the combined organic material was washed with H_2O, and brine and dried. Removal of the solvent in vacuo followed by distillation afforded the desired β-hydroxy ester.

General Procedure C. Dehydration of Alcohols. A solution of the appropriate alcohol (5 mmol), pyridine (790 mg, 2 equiv), and 10 mL of anhydrous Et_2O at 0 °C under N_2 was treated with thionyl chloride (1 equiv, 360 μL). After being stirred for 2 h at 0 °C, the resulting solution was washed with 10% aqueous HCl and H_2O and dried. Removal of the solvent in vacuo and distillation afforded the desired unsaturated compound.

General Procedure D. Preparation of Carboxylic Acids from the Corresponding Esters. A solution consisting of 10 mmol of the appropriate pure ester, 10 mL of 5% NaOH, and 10 mL of 95% ethanol was deoxygenated with N_2 and then heated at reflux under N_2 for 2 h. After cooling, the reaction mixture was extracted with Et_2O, and the aqueous phase was acidified with 10% HCl and then reextracted with ether. The combined organic material from the acidic aqueous phase was washed with brine and dried. Removal of the solvent in vacuo, and distillation when appropriate, afforded the desired carboxylic acid (85–95%) which was shown to be >95% pure by NMR.

General Procedure E. Preparation of Diazo Ketones. Acyl chlorides were prepared by treating the respective carboxylic acid with either 2 equiv of $SOCl_2$ or 1.2 equiv of oxalyl chloride and allowing the mixture to stir for 4 h. Excess thionyl chloride or oxalyl chloride was removed in vacuo and the residue distilled. The purified acyl chloride (88–95%) was dissolved in 10 mL of Et_2O and was added dropwise by pipet to an excess (>3 equiv) of distilled ethereal diazomethane (from Diazald) cooled in an ice bath. The reaction mixture was allowed to warm to room temperature overnight. Excess diazomethane and solvent were removed by evaporation on a steam bath and then in vacuo. The diazo ketones thus prepared showed strong absorption at 2100 and 1650 cm^{-1} in their IR spectra (other carbonyl absorptions were absent) and were used in subsequent steps without further purification.

General Procedure F. Boron Trifluoride Catalyzed Decomposition of Diazo Ketones in CH_3NO_2. A solution consisting of 1.0 mmol of the appropriate diazo ketone and 50 mL of freshly distilled CH_3NO_2 was treated under N_2 at 0 °C with $BF_3{\cdot}Et_2O$ (ca. 1.2 equiv). After 30 min, during which the color of the reaction mixture turned from yellow to deep orange, 10 mL of 10% aqueous HCl was added and the resultant mixture heated at reflux for 1 h. The reaction mixture was then added to saturated aqueous $NaHCO_3$ and extracted with ethyl acetate. The combined organic material was then washed with H_2O and brine and dried. Removal of the solvent in vacuo afforded the product mixture.

General Procedure G. Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketones in CH_2Cl_2. A solution consisting of 1 mmol of the appropriate diazo ketone and 100 mL of freshly distilled CH_2Cl_2 was treated at 0 °C under N_2 with 1.2 mmol of $BF_3{\cdot}Et_2O$. Over a period of 2 h, the color of the reaction mixture turned from yellow to deep orange. The reaction mixture was then washed with saturated aqueous $NaHCO_3$, water, and brine and dried. Removal of the solvent in vacuo afford the product mixture.

Preparation of Ethyl 2-(2′-Propenyl)heptanoate. Ethyl 3,3-dimethyl acrylate (10 mmol, 1.28 g) was alkylated with 1-bromopentane according to general procedure A. Distillation of the residue [82-84 °C (2 mmHg)] afforded 1.86 g (94%) of the desired ester. An analytical sample obtained by VPC on column A possessed the following spectral data: IR 3080 (w), 3000 (s), 2850 (s), 1735 (s), 1650 (w), 895 (s) cm^{-1}; NMR (60 MHz) δ 0.95–1.75 (m, 17 H), 2.85 (q, J = 7 Hz, 1 H), 4.19 (q, J = 7 Hz, 2 H), 4.83 (s, 2 H).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.70; H, 11.17.

Preparation of Ethyl 2-(2′-Propenyl)-4-heptynoate. Ethyl 3,3-dimethyl acrylate (10 mmol, 1.28 g) was alkylated with 1-bromo-2-pentyne[45] according to general procedure A. Distillation of the residue [92–95 °C (1 mm)] afforded 1.65 g (85%) of ethyl 2-(2′-propenyl)-4-heptynoate. An analytical sample obtained by VPC on column A possessed the following spectral characteristics: IR 3000 (w), 2980 (s), 2945 (s), 2920 (s), 1740 (s), 1650 (m), 895 (s); NMR (60 MHz) δ 0.86–1.35 (m, 6 H), 1.77 (s, 3 H), 1.82–2.64 (m, 4 H), 3.03 (q, J = 6 Hz, 1 H), 4.13 (q, J = 6 Hz, 2 H), 4.88 (s, 2 H).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.24; H, 9.28.

Preparation of Ethyl 2,4-Dimethyl-2-(2′-propenyl)-4-pentenoate. Ethyl 3,3-dimethylacrylate (1.28 g, 10 mmol) was alkylated with MeI according to general procedure A. Distillation of the residue [45–46 °C (1 mm)][46] afforded 1.31 g (92%) of ethyl 2,3-dimethyl-3-butenoate which had the following spectral characteristics: IR 3075 (w), 2950 (s), 1740 (s), 1650 (w), 895 (s) cm^{-1}; NMR (60 MHz) δ 1.08–1.43 (m, 6 H), 1.72 (s, 3 H), 3.05 (q, J = 7 Hz, 1 H), 4.07 (q, J = 7 Hz, 2 H), 4.81 (s, 2 H).

This ester (2.1 g, 14.8 mmol) was alkylated with methallyl bromide according to general procedure A. Distillation [71–73 °C (2 mm)] afforded 2.66 g (94%) of the desired ester. An analytical sample obtained by VPC on column A had the following spectral characteristics: IR 3075 (w), 2980 (s), 2820 (s), 1735 (s), 1645 (m), 895 (s) cm^{-1}; NMR (60 MHz) δ 1.20 (s, t, J = 7 Hz, 6 H), 1.65 (s, 3 H), 1.70 (s, 3 H), 2.48 (dd, J = 10 and 14 Hz, 2 H), 4.05 (q, J = 7 Hz, 2 H), 4.63–4.88 (m, 4 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.23; H, 10.27.

Preparation of Ethyl 2,5-Dimethyl-2-(2′-propenyl)-5-hexenoate. Ethyl 2,3-dimethyl-3-butenoate (13.49 g, 95 mmol) was alkylated with the tosylate derived from 3-methyl-3-propen-1-ol according to general procedure A. Distillation [74–78 °C (1.8 mm)] afforded 13.31 g (76%) of the desired ester. An analytical sample obtained by VPC on column A gave analytically pure ester which had the following spectral characteristics: IR 3090 (w), 3075 (s), 2938 (s), 1725 (s), 1640 (m), 895 (s), 888 (s) cm^{-1}; NMR (60 MHz) δ 1.23 (t, J = 7 Hz, 3 H), 1.25 (s, 3 H), 1.70 (d, J = 1 Hz, 6 H), 1.82 (br s, 4 H), 4.11 (q, J = 7 Hz, 2 H), 4.66 (br s, 2 H), 4.84 (br s, 2 H).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.27; H, 10.55.

Preparation of Ethyl 2,2-Dimethyl-3-phenyl-3-butenoate. Methyl β-cinnamate (1.90 g, 10 mmol) was alkylated with methyl iodide as described in general procedure A. Distillation [79–82 °C (0.4 mm)] af-

(45) A. A. Kraevskii, I. K. Sarycheva, and N. A. Preobrazhenskii, *Zh. Obshch. Khim.*, **33**, 1831 (1963).

(46) R. C. Huston and G. L. Goerner, *J. Am. Chem. Soc.*, **68**, 2504 (1946).

forded 1.87 g (92%) of ethyl 2-methyl-3-phenyl-3-butenoate. An analytical sample obtained by VPC on column A gave analytically pure ester which had the following spectral data: IR 3060 (w), 2980 (s), 2945 (m), 1727 (s), 1630 (w), 905 (s), 695 (s) cm^{-1}; NMR (60 MHz) δ 1.13 (t, J = 7 Hz, 3 H), 1.31 (d, J = 7 Hz, 3 H), 3.56 (q, J = 7 Hz, 1 H), 4.04 (q, J = 7 Hz, 2 H), 5.17 (s, 1 H), 5.27 (s, 1 H), 7.07–7.50 (m, 5 H).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.43; H, 7.96.

A sample of monoalkylated ester (1.84 g, 9.0 mmol) was alkylated with methyl iodide as described in general procedure A. Distillation [87–90 °C (0.4 mm)] afforded 1.82 g (92%) of a single compound identified as ethyl 2,2-dimethyl-3-phenyl-3-butenoate. An analytical sample obtained by preparative VPC on column A displayed the following spectral data: IR 3080 (m), 3060 (m), 2965 (s), 2930 (s), 2900 (m), 1720 (s), 1630 (m), 910 (s), 698 (s) cm^{-1}; NMR (60 MHz) δ 1.13 (t, J = 7 Hz, 3 H), 1.32 (s, 6 H), 4.03 (q, J = 7 Hz, 2 H), 5.05 (d, J = 1 Hz, 1 H), 5.22 (d, J = 1 Hz), 7.13 (br s, 5 H).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.11; H, 8.23.

Preparation of Ethyl 2,6-Dimethyl-1-cyclohexeneacetate. 2,6-Dimethylcyclohexanone (5.42 g, 43 mmol) was treated with ethyl lithioacetate according to general procedure B to afford upon distillation [115–120 °C (4 mm)] 8.42 g (92%) of a diastereomeric mixture of hydroxy ester as a colorless oil: IR 3490 (m, br), 2960 (s), 2930 (s), 1725 (s, br) cm^{-1}. The hydroxy ester (18.4 g, 86 mmol) was dehydrated according to general procedure C. Distillation [82–87 °C (1.6 mm)] afforded 15.2 g (90%) of the desired ester as a colorless oil. An analytical sample obtained by VPC on column E possessed the following spectral data: IR 2970 (s), 2940 (s), 2870 (s), 1740 (s) cm^{-1}; NMR (60 MHz) δ 1.00, 1.25 (d, t, J = 7 Hz, J = 7 Hz, 6 H), 1.43–2.50, 1.63 (m, s, 10 H), 2.97 (s, 2 H), 4.10 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.28; H, 10.16.

Preparation of Ethyl 2,3-Dimethyl-1-cyclohexeneacetate. A solution of 2,3-dimethylcyclohexanone (6.3 g, 50 mmol) in THF was treated with ethyl lithioacetate as described in general procedure B to yield upon distillation [95–97 °C (1.2 mm)] 7.24 g (68%) of a hydroxy ester as a diastereomeric mixture: IR 3530 (m), 2950 (s), 1735 (s) cm^{-1}. The hydroxy ester (7.06 g, 33 mmol) was dehydrated as described in general procedure C. Distillation [87–89 °C (1 mm)] provided 5.17 g (76%) of a mixture of two β,γ-unsaturated esters. The desired ester, which was the major component (70% by VPC), was isolated by preparative VPC on column D. An analytical sample displayed the following spectroscopic properties: IR 2970 (m), 2940 (s), 2865 (m), 1740 (s) cm^{-1}; NMR (220 MHz) δ 1.05 (d, J = 8 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 1.35–1.83, 1.67 (m, s, 6 H), 1.93–2.27 (m, 4 H), 2.93 (s, 2 H), 4.08 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.25; H, 9.98.

Preparation of Ethyl 1-Methyl-2-cyclopentenecarboxylate. The desired ester was prepared from 2-(carboethoxy)cyclopentanone by the procedure described by Fuchs.[47] An analytical sample obtained by VPC on column A had the following spectroscopic properties: IR 2985 (s), 2945 (s), 1730 (s) cm^{-1}; NMR (220 MHz) δ 1.23 (s, t, J = 7 Hz, 6 H), 1.55–1.71 (m, 1 H), 2.30–2.47 (m, 3 H), 4.05 (q, J = 7 Hz, 2 H), 5.61 (m, 1 H), 5.68 (m, 1 H).

Preparation of 3-Methyl-3-butenoic Acid. A solution of 3-methyl-3-buten-1-ol (3.244 g, 37.7 mmol) in 250 mL of acetone was cooled to 0 °C and then treated with 20 mL (1.4 equiv, 2.67 M) of Jones reagent. After being stirred at 0 °C for 1 h, the mixture was washed with 5% aqueous NaOH. The aqueous phase separated, acidified (dilute HCl), and extracted with Et_2O. The organic phase was washed with H_2O and brine and dried. Concentration of the filtrate in vacuo followed by distillation [67–70 °C (10 mm)] afforded 3.24 g (86%) of 3-methyl-3-butenoic acid having the following spectral characteristics: IR 3550–2300 (s, br), 1705 (s), 1650 (m), 900 (s) cm^{-1}; NMR (60 MHz) δ 1.85 (br s, 3 H), 3.03 (br s, 2 H), 4.95 (br s, 2 H), 11.67 (br s, 1 H). A sample of 3-methyl-3-butenoic acid was esterified with diazomethane. An analytical sample, which was obtained by preparative VPC on column A, had spectral data in total agreement with literature values.[48]

Preparation of 4-Methyl-4-pentenoic Acid. A solution of 450 mg (4.6 mmol) of 4-methyl-4-penten-1-ol (Chemical Samples) in 25 mL of acetone was cooled to 0 °C and then treated with 2.5 mL (1.5 equiv, 2.67 M) of Jones reagent. After being stirred at 0 °C for 1 h, the mixture was washed with 5% aqueous NaOH. The aqueous phase was separated, acidified (dilute HCl), and extracted with Et_2O. The organic phase was washed with H_2O and brine and dried. Concentration of the filtrate in vacuo followed by distillation [80–85 °C (10 mm)] afforded 428 mg (84%) of 4-methyl-4-pentenoic acid having the following spectral characteristics: IR 3700–2300 (s, br), 1700 (s), 890 (s) cm^{-1}; NMR (60 MHz) δ 1.73 (br s, 3 H), 2.00–2.70 (m, 4 H), 4.68 (br s, 2 H), 11.10 (br s, 1 H).

Preparation of 5-Methyl-5-hexenoic Acid. Diazo ketone **53** (2.81 g, 20.3 mmol) which was prepared from 4-methyl-4-pentenoic acid, as described in general procedure E, was added to freshly distilled MeOH, and the mixture was degassed and photolyzed for 90 min under N_2. The solution was concentrated under reduced pressure to about 10 mL whereupon 15 mL of 5% NaOH was added and the mixture heated at reflux for 2 h under N_2. The solution was washed with Et_2O, separated, and acidified (dilute HCl). Extraction with Et_2O, drying, and concentration of the filtrate afforded upon distillation [80–85 °C (10 mm)] 1.80 g (71% from **53**) of the desired acid[49] which had the following spectral characteristics: IR 3500–2500 (s, br), 1700 (s), 1645 (w), 885 (s) cm^{-1}; NMR (60 MHz) δ 1.27–2.35 (m, 9 H), 4.63 (br s, 2 H), 10.63 (br s, 1 H).

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 14. Diazo ketone **14** prepared in 90% yield from vinylacetic acid was decomposed according to general procedure F. Product analysis on column A indicated a complex mixture of components from which cyclopentenone **21** (13%) was isolated by preparative VPC and shown to be identical in all respects (IR, NMR, VPC retention time) with an authentic sample.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 11. Diazo ketone **11** prepared in 86% yield from the appropriate acid was decomposed according to general procedure G. Product analysis on column A gave a single product identified as 3-methyl cyclopentenone **22**, (73%). An analytical sample obtained by preparative VPC displayed spectroscopic properties which are in good agreement with literature values:[50] IR 3080 (w), 2980 (m), 2925 (m), 2865 (m), 2845 (m), 1705 (s), 1630 (w), 835 (s) cm^{-1}; NMR (60 MHz) δ 2.08 (br s, 3 H), 2.13–2.70 (m, 4 H), 5.82 (q, J = 1.5 Hz, 1 H). When diazo ketone **11** was decomposed according to general procedure F, the yield was 64%.

Boron Trifluoride Etherate Decomposition of Diazo Ketone 15. Diazo ketone **15**, which was prepared in 81% yield from the appropriate acid, was decomposed according to general procedure F. Product analysis on column A gave a single product identified as 2,3-dimethylcyclopentenone (**23**, 40%). An analytical sample obtained by preparative VPC gave pure **23** which possessed spectral data identical with those reported by Agosta and Smith.[51]

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 17. Diazo ketone **17** prepared in 86% from 4-methyl-3-pentenoic acid[52] was decomposed according to general procedure G. Product analysis on column C indicated the presence of a mixture of three components, **25–27**, in 31%, 12.2%, and 27.7% yields, respectively. Analytical samples of each were obtained by preparative VPC. The first was 4,4-dimethyl-2-cyclopentenone (**26**): IR 3030 (w), 2955 (s), 2925 (m), 2865 (w), 1710 (s) cm^{-1}; NMR (220 MHz) δ 1.23 (s, 6 H), 2.17 (s, 2 H), 5.89 (d, J = 6 Hz, 1 H), 7.34 (d, J = 6 Hz, 1 H).

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.14; H, 9.26.

The second was 3,4-dimethyl-2-cyclopentenone (**27**):[53] IR 3035 (w), 2960 (m), 2930 (m), 2915 (m), 1720 (s) cm^{-1}; NMR (220 MHz) δ 1.16 (d, J = 7 Hz, 3 H), 1.87 (dd, J = 2, 18 Hz, 1 H), 2.07 (s, 3 H), 2.50 (dd, J = 6, 18 Hz, 1 H), 2.76 (t, J = 6 Hz, 1 H), 5.75 (br s, 1 H).

The third was 3-(2′-propenyl)cyclobutanone (**25**): IR 3080 (w), 2975 (m), 2925 (m), 1790 (s), 890 (s) cm^{-1}; NMR (220 MHz) δ 1.80 (br s, 3 H), 2.86–3.20 (m, 5 H), 4.82 (br s, 1 H), 4.58 (br s, 1 H).

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.14; H, 9.26.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 16. Diazo ketone **16**, prepared in 94% yield from 3,4-dimethyl-3-pentenoic acid,[54] was decomposed according to general procedure F. Product analysis on column B gave a single product identified as 3,4,4-trimethyl-2-cyclopentenone (**24**, 77%). An analytical sample obtained by preparative VPC displayed spectroscopic properties which were in good accord with literature data:[53] IR 2960 (m), 1710 (s), 1680 (s), 1615 (m), 840 (m) cm^{-1}; NMR (220 MHz) δ 1.17 (s, 6 H) 2.00 (d, J = 2 Hz, 3 H), 2.15 (s, 2 H), 5.65 (m, 1 H).

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(47) C. A. Bunnell and P. L. Fuchs, *J. Am. Chem. Soc.*, **99**, 5184 (1977).
(48) Y.-S. Cheng and E. Von Rudloff, *Photochemistry*, **9**, 2517 (1970).
(49) H. Lehmkuhl, D. Reinehr, S. Schomburg, D. Henneberg, H. Damen, and G. Schroth, *Justus Liebigs Ann. Chem.*, 103 (1975).
(50) H. N. A. Al-Jallo and E. S. Waight, *J. Chem. Soc. B*, 73 (1966).
(51) W. C. Agosta and A. B. Smith, III, *J. Am. Chem. Soc.*, **93**, 5513 (1971); see ref 8. We are grateful to Professor Agosta for providing us with the authentic spectra of 2,3-dimethyl cyclopentenone.
(52) J. Klein, *Isr. J. Chem.*, **1**, 385 (1963).
(53) J.-M. Conia and M.-L. Leriverend, *Bull. Soc. Chim. Fr.*, 2981 (1970).
(54) M. A. Schexnayder and P. S. Engel, *J. Am. Chem. Soc.*, **97**, 4825 (1975).

18. Diazo ketone **18** prepared in 54% from the appropriate acid was decomposed according to general procedure F. Product analysis on column A gave a single product identified as dihydrojasmone (**28**, 65%). An analytical sample obtained by preparative VPC gave pure **28**, which possessed spectral data (IR and NMR) which were identical in all respects with those of an authentic sample[55] of dihydrojasmone.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 19. Diazo ketone **19** prepared from the appropriate acid was decomposed according to general procedure G. Product analysis on column A gave a single product identified as dehydrojasmone (**29**, 40%). An analytical sample obtained by preparative VPC had the following spectral characteristics: IR 2975 (m), 2915 (m), 1705 (s), 1650 (s) cm^{-1}; NMR (60 MHz) δ 0.92–1.25 (m, 4 H), 1.70–2.67 (m, 8 H), 2.98 (s, 2 H).

The 2,4-dinitrophenylhydrazone was prepared and recrystallized from methanol; mp 165–166 °C (lit.[56] mp 166 °C).

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 20. Diazo ketone **20** prepared in 91% yield from the appropriate acid was decomposed according to general procedure F. Product analysis on column A indicated a 6.3:1 mixture of two components in 73% yield. An analytical sample of each was obtained by preparative VPC. The first fraction was identified as 2,2-dimethyl-3-phenyl-3-cyclopentenone (**30**, mp 58–60 °C) and had the following spectral properties: IR 3055 (w), 3030 (w), 2970 (s), 2930 (m), 1745 (s), 694 (s) cm^{-1}; NMR (60 MHz) δ 1.20 (s, 6 H), 2.98 (d, J = 2.5 Hz, 2 H), 6.11 (t, J = 2.5 Hz, 1 H), 7.27 (br s, 5 H).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.65; H, 7.87.

The second fraction was identified as 3,4-dihydro-3,3-dimethyl-4-methylene-2(1*H*)-naphthalenone **31** which possessed the following spectral data: IR 3095 (w), 3070 (w), 3020 (w), 2975 (s), 2930 (m), 1715 (s), 1625 (m), 900 (s); NMR (60 MHz) δ 1.24 (s, 6 H), 3.56 (s, 2 H), 5.19 (s, 1 H), 5.38 (s, 1 H), 6.92–7.60 (m, 4 H).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.71; H, 7.66.

Boron Trifluoride Catalyzed Decomposition of Diazo Ketone 32. Diazo ketone **32** prepared from the appropriate acid[57] was decomposed according to general procedure F. Product analysis indicated a 5:1 mixture (60%) of two components. Analytical samples obtained by preparative VPC on column A afforded pure **41** and **42**. The first was enone **41**: IR 3170 (w), 2960 (s), 2920 (s), 2870 (m), 1700 (s, br), 1635 (s) cm^{-1}; NMR (60 MHz) δ 0.70–1.62 (m, 1 H), 1.63–3.20 (m, 8 H), 5.77 (m, 1 H).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.5; H, 8.26.

The second was lactone **42**,[58] IR 2970 (m), 2940 (s), 2875 (m), 1775 (s) cm^{-1}; NMR (60 MHz) δ 1.46 (s, 3 H), 1.50–2.95 (m, 9 H).

Boron Trifluoride Catalyzed Decomposition of Diazo Ketone 33. Diazo ketone **33**, which was prepared in 92% yield from the appropriate acid,[58] was decomposed according to general procedure F. Product analysis indicated the presence of two components which were identified as **43** and **44** in 51% and 30% yields, respectively. Analytical samples of each were obtained by preparative VPC. The first was **43**: IR 2970 (s), 2940 (s), 2875 (s), 1705 (s), 1640 (s) cm^{-1}; NMR (60 MHz) δ 0.88 (s, 3 H), 1.09 (s, 3 H), 1.20–2.93 (m, 7 H), 5.74 (br s, 1 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.94; H, 9.53.

The second was **44**: IR 2975 (s), 2955 (s), 2940 (s), 2900 (s), 2890 (m), 1775 (s) cm^{-1}; NMR (220 MHz) δ 0.98 (d, J = 6 Hz, 3 H), 1.01 (d, J = 6 Hz, 3 H), 1.50–2.06 (m, 7 H), 2.13 (dd, J = 3, 18 Hz, 1 H), 2.48–2.82 (m, 2 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.19; H, 9.62.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 12. Diazo ketone **12**, prepared in 83% yield from cyclohexeneacetic acid,[60] was decomposed according to general procedure F. Product analysis on column A gave a single product identified as Δ^3-hydrinden-2-one (**45**, 50%). An analytical sample obtained by preparative VPC gave pure **45** which possessed spectral data in accordance with literature data:[61] IR 2940 (s), 2855 (w), 1710 (s), 1625 (s) cm^{-1}; NMR (60 MHz) δ 0.90–3.30 (m, 11 H), 5.72 (s, 1 H).

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 34. Diazo ketone **34** prepared from the appropriate acid[62] in 87% yield was decomposed according to general procedure F. Product analysis on column A indicated a single product identified as 3-methyl-Δ^3-hydrinden-2-one (**46**, 63%). An analytical sample obtained by preparative VPC possessed the following spectral characteristics: IR 2940 (s), 2910 (s), 1700 (s), 1655 (s) cm^{-1}; NMR (60 MHz) δ 1.00–3.03, 1.62 (m, s).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.83; H, 9.42.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 35. Diazo ketone **35** prepared in 92% from the appropriate acid[62] was decomposed according to general procedure F. Product analysis on column A gave a single product identified as 1,1-dimethyl-Δ^3-hydrinden-2-one (**47**, 65%). An analytical sample obtained by preparative VPC had the following spectral characteristics: IR 2950 (s), 2830 (m), 1710 (s), 1640 (m) cm^{-1}; NMR (60 MHz) δ 0.83–3.08, 0.88, 1.02 (m, s, s, 15 H), 5.67 (br s, 1 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.35; H, 9.95.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 36. Diazo ketone **36** prepared from the appropriate acid[63] was decomposed according to general procedure F. Product analysis on column A indicated a single major component which was identified as 7a-methyl-Δ^3-hydrinden-2-one (**48**, 57%). An analytical sample obtained by preparative VPC possessed the following spectroscopic properties which were identical with those reported for this compound by Djerassi:[64] IR 2940 (s), 2820 (m), 1715 (s), 1630 (s) cm^{-1}; NMR (220 MHz) δ 1.28 (s, 3 H) 1.34–2.73 (m, 10 H), 5.88 (s, 1 H).

Boron Trifluoride Etherate Decomposition of Diazo Ketone 37. Diazo ketone **37**, which was prepared in 93% from the appropriate acid, was decomposed according to general procedure F. Product analysis on column B indicated two components which were identified as **50** and **49** in 46% and 8% yields, respectively. Analytical samples of each were obtained by preparative VPC. The first was **50**: IR 3075 (w), 2970 (s), 2940 (s), 2875 (m), 1710 (s), 1620 (s); NMR (60 MHz) δ 0.83–2.18, 1.15, 1.23, 2.12 (m, d, s, s, J = 6 Hz, 14 H), 2.18–2.73 (m, 1 H), 5.65 (d, J = 1.5 Hz, 1 H); mass spectrum, calcd for $C_{11}H_{16}O$ m/e 164.1200 (M^+), found m/e 164.1201.

The second was **49** which possessed spectral data which were identical with the corresponding spectral data for this enone provided by Evans:[23] IR 3075 (w), 2960 (s), 2940 (s), 2860 (s), 1695 (s, br), 1625 (s) cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 0.96 (distorted d, 3 H), 1.09 (s, 3 H), 1.20–2.70, 2.22 (m, s, 9 H), 5.77 (distorted d, 1 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.49; H, 9.87.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 38. Diazo ketone **38** prepared in 85% yield from the appropriate acid was decomposed according to general procedure F. Product analysis on column D indicated a 40:60 mixture of ketones **49** and **50** (52.4%). Analytical samples of each obtained by preparative VPC gave pure **49** and **50**. Both compounds were identical in all respects (IR, NMR, VPC retention time) with those obtained by the decomposition of diazo ketone **37**.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 39. Diazo ketone **39** prepared in quantitative yield from the corresponding acid[65] was decomposed according to general procedure G. Product analysis on column A indicated a single product identified as ketone **51** (60.5%). An analytical sample obtained by preparative VPC possessed the following spectral characteristics: IR 2920 (s), 2850 (m), 1700 (s), 1600 (s) cm^{-1}; NMR (220 MHz) δ 1.18–1.48 (m, 4 H), 1.48–2.02 (m, 5 H), 2.55 (dd, J = 8 Hz, J' = 18 Hz, 1 H) 2.69 (m, 2 H), 2.89 (m, 1 H), 5.73 (s, 1 H).

The semicarbazone was prepared and recrystallized from ethanol; mp 198–199.5 °C (lit.[66] mp 198–200 °C).

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 40. Diazo ketone **40**, prepared in quantitative yield from α,α-dimethylcycloheptenoic acid,[62] was decomposed according to general procedure G. Product analysis on column A gave a single product identified as ketone **52** (68%). An analytical sample obtained by preparative VPC gave pure **52** which has the following spectral characteristics: IR 3060 (w), 2970 (m), 2930 (s), 2860 (m), 1710 (s), 1625 (m) cm^{-1}; NMR (60 MHz) δ 0.87 (s, 3 H), 1.00 (s, 3 H), 1.10–2.93 (m, 11 H), 5.73 (br s, 1 H).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.75; H, 10.23.

(55) We are grateful to International Flavors and Fragrances for a generous sample of dihydrojasmone.
(56) K. Shishido, Y. Kawashima, and C. Ishida, *Perfum. Essen. Oil Rec.*, **57**, 364 (1966).
(57) P. S. Engel, M. A. Schexnayder, *J. Am. Chem. Soc.*, **97**, 145 (1975).
(58) J. Ficini and A. Maujean, *Bull. Soc. Chim. Fr.*, 4392 (1972).
(59) P. B. Talukdar and P. Bagchi, *J. Org. Chem.*, **20**, 25 (1955).
(60) J. Klein, *J. Org. Chem.*, **23**, 1209 (1958).
(61) R. M. Jacobson, R. A. Raths, and J. H. McDonald, *J. Org. Chem.*, **42**, 2545 (1977).
(62) F. Korte, J. Falbe, and A. Zschocke, *Tetrahedron*, **6**, 201 (1959).
(63) C.-K. Chuang, Y.-L. Tien, and C.-M. Ma, *Chem. Ber.*, **69**, 1494 (1936).
(64) J. Karliner, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 580 (1965).
(65) W. Herz and L. A. Glick, *J. Org. Chem.*, **28**, 2970 (1963).
(66) P. C. Dutta, *J. Indian Chem. Soc.*, **34**, 761 (1957).

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 53. Diazo ketone **53**, prepared from the appropriate acid, was decomposed according to general procedure G. Product analysis on column B indicated a single major component which was identified as 4-methyl-3-cyclohexenone (55%). An analytical sample obtained by preparative VPC displayed spectral data consistent with those assigned by Corey:[67] IR 2960 (s), 2925 (s), 2910 (s), 1710 (s) cm^{-1}; NMR (60 MHz) δ 1.77 (br s, 3 H), 2.27–2.46 (m, 4 H), 2.73 (br s, 2 H), 5.41 (br s, 1 H).

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 54. Diazo ketone **54** prepared from the appropriate acid was decomposed according to general procedure G. Product analysis on column B indicated two components which were identified as 4-methyl-4-cycloheptenone and 4-methyl-3-cycloheptenone as a 1:2 mixture (42%). Analytical samples of each were obtained by preparative VPC. The first was 4-methyl-4-cycloheptenone:[68] IR 2975 (s), 2940 (s), 1705 (s) cm^{-1}; NMR (220 MHz) δ 1.74 (br s, 3 H), 2.02–2.36 (m, 4 H), 2.36–2.61 (m, 4 H), 5.53 (m, 1 H).

The second was 4-methyl-3-cycloheptenone:[68] IR 2985 (s), 2940 (s), 1710 (s) cm^{-1}; NMR (220 MHz) δ 1.72 (br s, 3 H), 1.84–2.05 (m, 2 H), 2.17–2.37 (m, 2 H), 2.37–2.65 (m, 2 H), 3.03 (d, J = 6 Hz, 2 H), 5.27 (d, J = 4 Hz, 1 H).

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 57. Diazo ketone **57** prepared in 93% yield from the appropriate acid was decomposed according to general procedure G. After nitrogen evolution had ceased, about 10 min after the addition of $BF_3{\cdot}Et_2O$, 1.2 equiv of benzyl alcohol was added. Product analysis on column B indicated a single major component which was identified as **58** (40%). An analytical sample obtained by preparative VPC gave pure **58** which possessed the following spectral data: IR 2985 (s), 2955 (s), 1735 (s) cm^{-1}; NMR (220 MHz) δ 1.39–1.57 (m 1 H), 1.70 (s, 3 H), 2.05–2.39 (m, 5 H), 3.27 (br s, 1 H), 5.05 (s, 2 H), 5.20 (s, 1 H), 7.27 (s, 5 H); mass spectrum, calcd for $C_{15}H_{18}O_2$ (M^+) m/e 230.1306, found m/e 230.1284.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 62. Diazo ketone **62**, prepared in 89% from the appropriate acid, was decomposed according to general procedure G. Product analysis on column B indicated the presence of a mixture of three components in 30%, 10%, and 13% yields, respectively. Analytical samples of each were obtained by preparative VPC. The first was **64**: IR 3030 (w), 2955 (s), 2930 (s), 2865 (s), 1740 (s), cm^{-1}; NMR (220 MHz) δ 0.91 (s, 3 H), 1.02 (s, 3 H), 1.50–1.79, 1.64 (m, s, 4 H) 1.80–2.26 (m, 4 H), 2.35–2.45 (m, 1 H), 5.02 (s, 1 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.45; H, 9.67.

The second was tentatively assigned to be either 2.4-dimethyl-2-isopropenyl-3-cyclohexenone or 4,6-dimethyl-4-isopropenyl-3-cyclohexenone on the basis of the following properties: IR 3085 (w), 2965 (s), 2935 (s), 2920 (s), 2860 (m), 1715 (s), 895 (s) cm^{-1}; NMR (220 MHz) δ 1.13 (s, 3 H), 1.64 (s, 3 H), 1.79 (s, 3 H), 2.09–2.21 (m, 1 H), 2.29–2.41 (m, 2 H), 2.63–2.75 (m, 1 H), 4.88 (m, 2 H), 5.26 (s, 1 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.35; H, 9.71.

The third was **65**: IR 3050 (w), 2970 (s), 2940 (m), 2910 (m), 2875 (m), 2845 (m), 1740 (s) cm^{-1}; NMR (220 MHz) δ 0.93 (s, 3 H), 1.07 (s, 3 H), 1.60–1.85, 1.68 (m, s, 5 H) 2.04–2.33 (m, 4 H), 5.01 (s, 1 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.64; H, 10.04.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 63. Diazo ketone **63**, prepared in 90% from the appropriate acid, was decomposed according to general procedure G. Product analysis on column B indicated a mixture of *cis*-2,3,3a,6,7,7a-hexahydro-3a,5,7a-trimethyl-1*H*-inden-1-one (**66**, 32%) and *cis*-2,3,3a,4,7,7a-hexahydro-3a,5,7a-trimethyl-1*H*-inden-1-one (**67**, 12%). Analytical samples for each were obtained by preparative VPC. The first was **66**: IR 3040 (w), 3008 (w), 2965 (s), 2932 (s), 2915 (s), 2873 (s), 1733 (s) cm^{-1}; NMR (220 MHz) δ 0.85 (s, 3 H), 1.01 (s, 3 H), 1.20–1.40 (m, 1 H), 1.57–1.94 (m, 8 H), 2.02–2.16 (m, 2 H), 5.05 (s, 1 H).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.60; H, 10.18.

The second was **67**: IR 3050 (w), 3028 (w), 2970 (s), 2932 (s), 2879 (s), 1740 (s) cm^{-1}; NMR (220 MHz) δ 0.86 (s, 3 H), 0.92 (s, 3 H), 1.43–1.41 (m, 8 H), 1.00–2.40 (m, 3 H), 5.23 (s, 1 H).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.76; H, 10.25.

Preparation of *cis*-Hexahydro-6a-methyl-2*H*-cyclopenta[*b*]furan-2-one (42). Ester **68**[2] (58.2 mg, 0.38 mmol) is hydrolyzed to the corresponding acid according to general procedure C. Removal of the solvent in vacuo afforded 50.5 mg (95%) of the acid. Without further purification, 50 mg (0.36 mmol) of the acid was dissolved in 5 mL of MeOH and 5 mL of 1 N HCl and heated at reflux for 60 min. The resulting mixture was poured into brine and extracted with Et_2O. The combined organic material was washed with 5% aqueous $NaHCO_3$ and brine and dried. Removal of the solvent in vacuo afforded 34 mg of product. Product analysis on column C indicated a single component which was identified as **42**.

Preparation of *cis*-Hexahydro-6a-isopropyl-2*H*-cyclopenta[*b*]furan-2-one (44). Ester **69**[2] (82.3 mg, 0.45 mmol) was hydrolyzed to give 71.8 mg (95%) of the corresponding acid according to general procedure C. Without purification, 71 mg (0.42 mmol) of the acid was dissolved in 5 mL MeOH and 5 mL aqueous 1 N HCl and heated at reflux for 60 min. The resulting mixture was poured into brine and extracted with Et_2O. The combined organic material was washed with 5% aqueous $NaHCO_3$ and brine and dried. Removal of the solvent afforded 57.2 mg. Product analysis on column C indicated a single component which was identified as **44**.

Preparation of *trans*-Methyl 1,3-Dimethyl-2-oxocyclohexaneacetate (59). A mixture consisting of 150 mg of $RuO_2{\cdot}xH_2O$ (soluble form), 3.5 g of $NaIO_4$, 20 mL of H_2O, and 45 mL of acetone was stirred at 0 °C for 60 min whereupon the acetone layer had assumed a deep yellow (RuO_4) coloration. A solution of 300 mg (1.82 mmol) of enone **50** in 15 mL acetone was then added, and the resulting mixture was stirred at room temperature for 10 h. The reaction mixture was quenched by addition of 1 mL of 2-propanol and filtered. The filtrate was extracted with CH_2Cl_2. The combined organic material was washed with brine and dried. Removal of the solvent in vacuo gave 259 mg (77%) of the corresponding keto acid: IR 3500–2600 (s, br), 1710 (s, br) cm^{-1}.

A solution consisting of 250 mg (1.37 mmol) of this acid in 25 mL anhydrous ether was added dropwise to a chilled, stirred, ethereal solution of CH_2N_2. The resulting solution was allowed to stand at room temperature for 50 min, concentrated to a volume of 50 mL (steam bath), and dried. Removal of the solvent in vacuo gave 262 mg (97%) of keto ester. An analytical sample obtained by VPC on column C was identical (NMR, IR, VPC retention data) with an authentic sample of this keto ester prepared previously in this laboratory.[24]

Preparation of 1,1-Dimethyl-Δ³-hydrinden-2-one (47). Δ³-Hydrinden-2-one **45** (680 mg, 5.0 mmol) was alkylated with methyl iodide as described in general procedure A. Distillation [78–80 °C (1 mm)] afforded 687 mg (92%) of 1-methyl-Δ³-hydrinden-2-one which had the following spectral characteristics: IR 2980 (s), 2920 (s), 1710 (s), 1640 (s) cm^{-1}; NMR (60 MHz) δ 0.88–3.09, 0.90, (m, d, J = 7 Hz, 13 H), 5.65 (br s, 1 H).

The ketone (682 mg, 4.55 mmol) was further alkylated with methyl iodide as described by general procedure A. Distillation afforded 704 mg (93%) of **46** which had identical spectral properties with those of the compound isolated from the decomposition of diazo ketone **34**.

Preparation of Benzyl 3-Methyl-2-cyclopentene-1-acetate (58). Diazo ketone **57** (75 mg 5 mmol) was dissolved in 100 mL of cyclohexane to which were added 567 mg (1.05 equiv) of benzyl alcohol and 20 mg of $Cu(acac)_2$. The mixture was heated at reflux for 4 h under N_2. Upon cooling, the contents of the flask were washed with 10% HCl and brine and dried. The solvent was removed in vacuo. Product analysis on column A indicated a single product identified as **58** (74%, VPC). An analytical sample obtained by preparative VPC possessed spectroscopic properties identical in all respects with those of the product obtained by the decomposition of diazo ketone **57** with $BF_3{\cdot}Et_2O$ and benzyl alcohol.

Preparation of 1,5,7-Trimethyl-*cis*-6-bicyclo[3.3.0]octen-2-one (73). A solution of diketone **70**[31] (1.66 g, 10 mmol) in 150 mL Et_2O was treated at 0 °C under N_2 with MeLi (20 mL, 1.6 M, 3.3 equiv). The resulting suspension was stirred for 2 h at 0 °C, washed with saturated aqueous NH_4Cl, and dried. Removal of the solvent in vacuo yielded 1.70 g of both starting material and a hydroxylic material. The crude mixture, 20 mL of benzene, and 100 mg of TsOH were heated at reflux for 3 h by using a Dean–Stark water separator. The resulting solution was cooled, washed with saturated aqueous $NaHCO_3$, and dried. Removal of the solvent in vacuo followed by distillation [56–58 °C (1 mm)] afforded 784 mg (48% from **70**) of ketone **73** the balance being **70**. An analytical sample obtained by VPC on column A had the following spectral characteristics: IR 3040 (w), 2970 (s), 2020 (s), 2875 (m), 2845 (m), 1740 (s) cm^{-1}; NMR (60 MHz) δ 1.00 (s, 3 H), 1.07 (s, 3 H), 1.67 (s, 3 H), 2.00–2.33 (m, 6 H), 5.12 (br s, 1 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.33; H, 9.61.

Preparation of 1,5,7-Trimethyl-2-(thiophenyl)-*cis*-2,6-bicyclo[3.3.0]-octadiene (78) and 1,5,7-Trimethyl-4-(thiophenyl)-*cis*-3,6-bicyclo-[3.3.0]octadiene (79). Ketone **73** (500 mg, 3 mmol) was alkylated with PhSSPh according to general procedure A. Removal of the solvent in

(67) E. J. Corey and D. S. Watt, *J. Am. Chem. Soc.*, **95**, 2303 (1973).
(68) W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, **34**, 2512 (1969).

vacuo provided 1.85 g of material. Preparative TLC using 13% ethyl acetate–hexane yielded 512 mg (63%) of a mixture of keto sulfides **76** and **77**: IR 3075 (w), 3040 (w), 2975 (s), 2920 (s), 2875 (s), 2845 (s), 1745 (s), 680 (s), cm^{-1}.

A solution of keto sulfides **76** and **77** (512 mg, 1.9 mmol), $NaBH_4$ (100 mg, 1.3 equiv), and 15 mL of 2-propanol was allowed to stir overnight. The resulting solution was washed with H_2O and extracted with Et_2O. The combined Et_2O extracts were dried, and the solvent was removed in vacuo to afford 501.5 mg (95%) of hydroxy sulfides upon distillation [(100–102 °C (0.5 mm)]: IR 3650–3300 (s, br), 3085 (w), 3070 (w), 3040 (w), 2965 (s), 2920 (s), 2875 (m), 2795 (m), 1445 (m), 680 (m) cm^{-1}.

The hydroxy sulfides were converted into the corresponding mesylates as described by Crossland.[69] A solution of the hydroxy sulfides (501.4 mg, 1.38 mmol) Et_3N (308 μL, 1.05 equiv and 10 mL of CH_2Cl_2 was treated at 0 °C with mesyl chloride (160 μL, 1.05 equiv). After being stirred for 15 min, the resulting solution was poured into ice–H_2O, washed with cold 10% aqueous HCl, saturated aqueous $NaHCO_3$, and brine, and dried. Removal of the solvent in vacuo afforded 592 mg (95%) of mesylates: IR 3040 (w), 2960 (s), 2930 (m), 2910 (s), 2865 (m), 2845 (m), 1440 (m), 1370 (s), 1345 (s), 1180 (s), 680 (m) cm^{-1}.

A solution of 10 mL of Me_2SO, *t*-BuOK (81 mg, 0.72 mmol), and the mesylates (212 mg, 0.6 mmol) was allowed to stir overnight under N_2. The resulting mixture was poured into 10% aqueous HCl and extracted with Et_2O. The combined Et_2O extracts were washed with brine and dried. Concentration of the solvent in vacuo afforded 140 mg (91%) of vinyl sulfides **78** and **79**: IR 3080 (w), 3070 (w), 3035 (w), 2975 (s), 2920 (s), 2875 (s), 2845 (s), 1170 (s), 680 (m) cm^{-1}; mass spectrum, calcd for $C_{17}H_{20}S$ (M^+) *m/e* 256.1286, found *m/e* 256.1284.

Preparation of 1,5,7-Trimethyl-*cis*-6-bicyclo[3.3.0]octen-2-one (64) and 1,5,7-Trimethyl-*cis*-6-bicyclo[3.3.0]octen-4-one (65). A solution of 140 mg (0.55 mmol) of vinyl sulfides **78** and **79**, 100 mL of CH_3CN, and $HgCl_2$ (497 mg, 1.1 equiv) was heated at reflux for 24 h under N_2. The resulting solution was cooled, filtered, washed with H_2O, and extracted with Et_2O. The combined organic material was washed with brine and dried. Removal of the solvent in vacuo afforded a clear oil. Product analysis on column B indicated two fractions in a 1:11 ratio. The first fraction (7%, VPC) was identical in all respects (IR, NMR, VPC retention time) with **64**. The second fraction (77%, VPC) was identical in all respects (IR, NMR, VPC retention time) with **65**.

Preparation of 3a,6,7,7a-Tetrahydro-*cis*-3a,7a-dimethyl-1,5(4*H*)-indandione (83). To a suspension of 1.18 g (6.23 mmol) of copper iodide in 30 mL of dry ether cooled to 0 °C was added 9.25 mL (1.3 M in ether, 12.0 mmol) of methyllithium dropwise. The solution became bright yellow ($CuCH_3$), faded, and finally became completely clear and colorless upon addition of the second equivalent of methyllithium. The solution was stirred at 0 °C for 10 min, and 330.4 mg (2.01 mmol) of 7,7a-dihydro-7a-methyl-1,5(4*H*)-indandione (**82**)[29] in 5 mL of dry ether was added dropwise. Stirring was continued for 1 h at 0 °C, and the resulting milky white suspension was added dropwise to a rapidly stirring solution of saturated aqueous ammonium chloride. The aqueous phase was extracted with ether, and the combined ether extracts were washed with saturated aqueous ammonium chloride and brine and dried. Removal of solvent in vacuo and distillation [120–140 °C (0.2 mmol)] afforded 298.2 mg (83%) of dione **83**. TLC purification on silica (hexane–ether, 1:1 v/v) and final purification on column D gave an analytically pure dione: mp 163.5–165 °C; IR 2970 (s), 2875 (m), 1735 (vs), 1720 (vs), cm^{-1}; NMR (60 MHz) δ 0.98 (s, 3 H), 1.00 (s, 3 H), 1.45–1.97 (m, 3 H), 2.00–2.55 (m, 7 H).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30, H, 8.95. Found: C, 73.23; H, 8.82.

Preparation of *cis*-2,3,3a,6,7,7a-Hexahydro-3a,5,7a-trimethyl-1*H*-inden-1-one (66) and *cis*-2,3,3a,4,7,7a-Hexahydro-3a,5,7a-trimethyl-1*H*-inden-1-one (67). To a solution of 322.8 mg (1.80 mmol) of dione **83** in 15 mL of dry ether cooled to −77 °C was added 1.39 mL (1.3 M in ether, 1.80 mmol) of methyllithium. A white salt immediately came out of solution, and the mixture was stirred at −78 °C for 30 min, poured into saturated aqueous ammonium chloride, and extracted with ether. The ether extracts were washed with saturated aqueous ammonium chloride, water, and brine and dried. Removal of solvent in vacuo gave 337.7 mg (95%) of an alcohol [IR 3620 (m), 3475 (br, m), 1735 (s) cm^{-1}] which was used without further purification. The alcohol (337.7 mg) was dehydrated according to general procedure C. Product analysis on column B indicated two fractions in 47% and 41% yields, respectively. An analytical sample of each fraction was obtained. The first fraction gave a product identical with **66** by comparison (IR, NMR, VPC retention time). The second fraction gave a product identical with **67** by comparison (IR, NMR, VPC retention time).

Acknowledgment. It is a pleasure to acknowledge the support of this investigation by the National Institutes of Health through Grant No. GM-24680, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by Research Corp. In addition, we thank Mr. S. T. Bella of the Rockefeller University for the microanalysis and the Middle Atlantic Regional NMR Facility (NIH No. RR 542) at the University of Pennsylvania where the 220- and 360-MHz spectra were recorded.

(69) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).