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Vinylogous Wolff Rearrangement. 4. General Reaction of β,γ-Unsaturated α'-Diazo Ketones[1]

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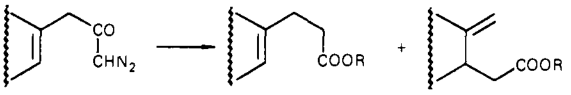
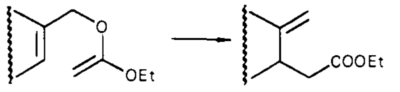
Abstract: The preparation and vinylogous Wolff rearrangement (VWR) of some 21 acyclic and monocyclic β,γ-unsaturated α'-diazo ketones are described. The resulting γ,δ-unsaturated esters are summarized in Tables I–VI. The rearrangement is promoted by $CuSO_4$, $Cu(AcAc)_2$, or $Cu(OTf)_2$ in the presence of various alcohols and is postulated to involve insertion of the diazo carbon into the β,γ-olefinic bond to form a bicyclo[2.1.0]pentanone which in turn undergoes fragmentation to an unsaturated ketene and then capture by the alcohol. Stereochemical observations, in accord with the proposed mechanism, are also presented.

Since the pioneering work of Arndt and Eistert,[3] rendering α-diazo methyl ketones readily accessible, such intermediates have assumed a place of importance in synthetic organic chemistry.[4] Principal among their utility is the Wolff rearrangement,[5] one of two reactions comprising the classic Arndt–Eistert protocol for homologation of carboxylic acids. This procedure, first introduced in the 1930's, has become a general synthetic method.[6] In 1974 however, we reported in a preliminary communication that β,γ-unsaturated diazo ketones not only undergo the normal Wolff rearrangement leading to the homologated acid but also yield, via a novel skeletal rearrangement, an isomeric derivative (eq 1).[1a] The latter transformation, a synthetic alternative to the Johnson ortho ester Claisen rearrangement (eq 2),[7] was termed by us the vinylogous Wolff rearrangement (VWR).

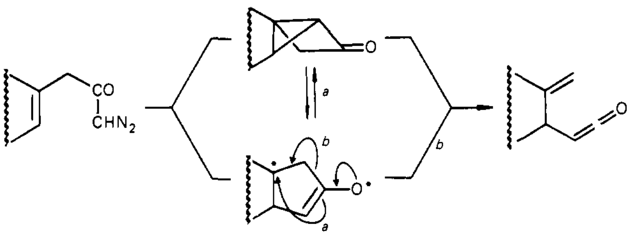


(1)



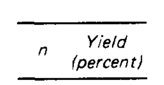
(2)

To account for the vinylogous Wolff product we postulated[1b] initial insertion of the diazocarbon into the β,γ-olefinic bond to form a bicyclo[2.1.0]pentanone derivative. Fragmentation of this intermediate leads to a β,γ-unsaturated ketene which in turn could be captured by available nucleophiles (eq 3). Refinement of this scheme allows the insertion and/or fragmentation process to proceed in a stepwise manner (i.e., a or b) as illustrated in eq. 3.



(3)

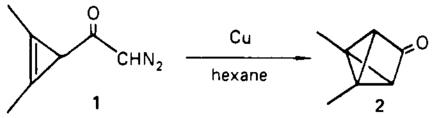
Our initial rationale for postulating the intermediacy of a bicyclopentanone derived from the observations of Stork[8] and Gutsche,[9] that unsaturated alicyclic diazo ketones undergo intramolecular insertion into the olefinic bond upon treatment with copper sulfate. This reaction has found wide applicability in natural product chemistry.[10] The efficiency of the process however is directly related to the number of intervening carbon atoms between the olefin and the diazo ketone functionalities. Best results are obtained where the double bond is γ,δ (i.e., $n = 2$). Interestingly, no simple examples were on record wherein the olefinic bond was β,γ to the carbonyl group (i.e., $n = 1$).



(4)

n	*Yield (percent)*
2	59
3	37
4	3

In fact, prior to our work, the only example of a copper-promoted decomposition of a β,γ-unsaturated diazo ketone was that of Doering and Pomerantz (eq 5).[11] In this case, treatment of diazo ketone **1** with copper powder, at the reflux point of hexane, gave



(5)

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[1] For parts 1–3 and 5 respectively, see: (a) Smith, A. B., III, *J. Chem. Soc., Chem. Commun.* **1974**, 695. (b) Smith, A. B., III; Toder, B. H.; Branca, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 7456. (c) Branca, S. J.; Lock, R.; Smith, A. B., III, *J. Org. Chem.* **1977**, *42*, 3165. (d) Smith, A. B., III; Toder, B. H.; Richmond, R.; Branca, S. J. *J. Am. Chem. Soc.*, following paper in this issue. For a comprehensive review on the Lewis acid promoted decomposition of unsaturated diazo ketones, see: Smith, A. B., III; Dieter, R. K. *Tetrahedron*, **1981**, *37*, 2407 and references cited therein.

[2] Camille and Henry Dreyfus Teacher–Scholar, 1978–1983; recipient of a National Institutes of Health (National Cancer Institute) Career Development Award.

[3] Arndt, F.; Eistert, B.; Partale, W. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 1364. Arndt, F.; Amende, J. *Ibid.* **1928**, *61*, 1122. Arndt, F.; Eistert, B. *Ibid.* **1928**, *61*, 1949. Arndt, F.; Eistert, B. *Chem. Ber.* **1935**, *68B*, 200.

[4] For a comprehensive review of this area see: Dave, V.; Warnhoff, E. W. *Org. React.* **1970**, *18*, 217. Kirmse, W. *Prog. Org. Chem.*, **1964**, *6*, 164. Kirmse, W. "Carbene Chemistry"; Academic Press: New York; 1971. Jones, M., Jr.; Moss, R. A. "Carbenes"; Wiley: New York, 1973. Burke, S. D.; Grieco, P. A. *Org. React.* **1979**, *26*, 361.

[5] Wolff, L. *Justus Liebigs Ann. Chem.* **1912**, *394*, 23.

[6] Eistert, A.; Regitz, M.; Heck, G.; Schwall, H. In "Methoden der Organische Chemie"; Mueller, E., Ed.; Theme: Stuttgart, 1968; Vol. X, Part 4, p 474. Reid, W.; Mengler, H. *Fortschr. Chem. Forsch.* **1965**, *5*, 1. Rodina, L. L.; Korobitsyna, I. K. *Russ. Chem. Rev.* **1967**, *36*, 260. Meier, H.; Zeller, K-P. *Angew. Chem., Int. Ed. Engl.* **1975**, 32.

[7] Johnson, W. S.; Gravestock, M. B.; McCarry, B. E. *J. Am. Chem. Soc.* **1971**, *93*, 4332.

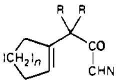
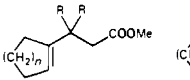
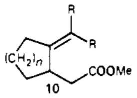
[8] Stork, G.; Ficini, J. *J. Am. Chem. Soc.* **1961**, *83*, 4678.

[9] Fawzi, M. M.; Gutsche, C. D. *J. Org. Chem.* **1966**, *31*, 1390.

[10] After the initial observation of Stork and Gutsche, the intramolecular cyclization of unsaturated diazo ketones has found widespread application in the synthesis of theoretically interesting compounds, as well as the synthesis of natural products. See ref 4 for reviews of this area.

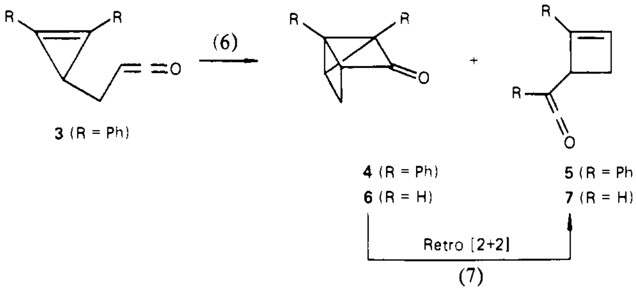
[11] Doering, W. v. E.; Pomerantz, M. *Tetrahedron Lett.* **1964**, 961.

Table I. Preliminary Studies on the Vinylogous Wolff Rearrengement

Diazoketone	*Reaction conditions*	*Product(s) and yield(s) (percent)*	
 8		 9	 10
a, n = 1, R = Me	Ag_2O/MeOH/Δ	58	42
	$CuSO_4$/2% MeOH/Δ	—	85
	$h\nu$/MeOH	92[17]	8[17]
b, n = 2, R = H			
	$CuSO_4$/2% MeOH	—	31
	$h\nu$/MeOH	79	—
c, n = 2, R = Me	Ag_2O/MeOH/Δ	50[1d]	5[1d]
	$CuSO_4$/2% MeOH/Δ	—	67
	$h\nu$/MeOH	95	—
d, n = 3, R = Me	Ag_2O/MeOH	61	28
	$CuSO_4$/2% MeOH/Δ	—	90
	$h\nu$/MeOH	93	7

a highly strained tetracyclic ketone **2**, albeit in extremely poor yield (<1%)! Embodied within the tetracyclic skeleton of **2** is a bicyclo[2.1.0]pentanone system, the intermediate postulated in the vinylogous Wolff rearrangement.[12,13]

Earliest precedent for the proposed fragmentation process of a bicyclo[2.1.0]pentanone can be found in the work of Masamune (eq 6)[14] who observed that the intramolecular [2+2]-cycloaddition of cyclopropenyl ketene **3** affords both the tricyclic adduct **4** and an isomeric ketene **5**. The latter was suggested to arise via cycloreversion of the bicyclo[2.1.0]pentanone system present in **4**. More recently, Bond[15] demonstrated that tricyclo[2.2.0.0^{2,6}]hexan-3-one **6** undergoes facile fragmentation to ketene **7** above 50 °C (eq 7).[16]



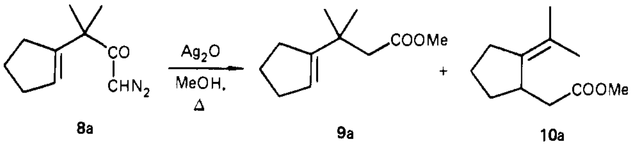
3 (R = Ph)

4 (R = Ph)
6 (R = H)

5 (R = Ph)
7 (R = H)

Preliminary Experiments

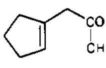
As part of a photochemical problem,[17] we required a convenient preparation of ester **9a**. The latter appeared to be readily available from β,γ-unsaturated diazo ketone **8a** through application of the well-known Wolff rearrangement. In the event however, decomposition of **8a** employing the usual Wolff conditions (Ag_2O, MeOH, Δ) not only led to the expected chain-lengthened ester **9a** (58%) but also led to a substantial amount of an isomeric ester **10a** (42%). Inspection revealed the isomeric ester to be a vinylogue of the normal Wolff product. Similar silver oxide promoted decomposition of closely related β,γ-unsaturated diazo ketones **8b–d** (see Table I) again led to mixtures consisting of the normal chain-lengthened esters **9b–d** and the vinylogous esters **10b–d**. In no example did the yield of the vinylogous Wolff ester exceed that of the normal Wolff product when silver ion was utilized to promote decomposition. In contrast, decomposition of diazo ketones **8a–d** employing a modification of the Stork–Gutsche[8,9] protocol [i.e., $CuSO_4$ in cyclohexane containing 2% (v/v) methanol] afforded only the vinylogous Wolff esters **10a–d**.[1a]



8a 9a 10a

Significant from point of view of our initial objective, irradiation of **8a–d** in methanol afforded the desired chain homologated esters **9a–d**, with only diazo ketone **8a** and **8d** yielding an appreciable amount (ca. 10%) of the vinylogous Wolff esters **10a** and **10d**.[17,18]

Simultaneous with our disclosure of the vinylogous Wolff rearrangement two closely related examples appeared in the literature. Lokensgard,[19] exploring the chemistry of diazo ketone **11**, demonstrated that bis(acetylacetonato)copper(II), a more soluble copper complex than $CuSO_4$, efficiently promoted the vinylogous Wolff rearrangement. Zimmerman,[20] on the other hand, attempted to prepare bicyclo[2.1.0]pentanone **13** via copper-bronze-induced decomposition of diazo ketone **12**. Although **13** was not isolated, evidence suggestive of its existence derived from the observation of a carbonyl infrared band at 1786 cm^{-1} as well as production of vinylogous Wolff ester **14**. The latter was obtained upon treatment of the crude reaction mixture with hot methanol.



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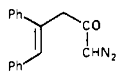

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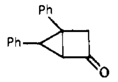
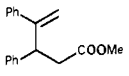
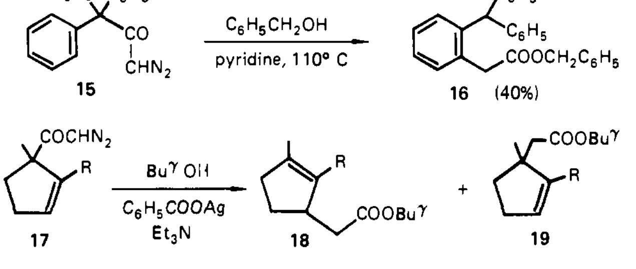


13



14

The only additional literature precedent for the vinylogous Wolff rearrangement is contained in a series of papers by A. L. Wilds and co-workers beginning in the late 1950's. In this work, skeletal rearrangements were observed to take place when (triphenylacetyl)diazomethane (**15**) and closely related analogues were subjected to *thermal* decomposition.[21] Interestingly, only diazo ketones disubstituted on the α-carbon underwent rearrangement. This observation led Wilds to conclude that relief of steric strain



15 16 (40%)

17 18 19

R = 6-Methoxy-2-naphthyl-

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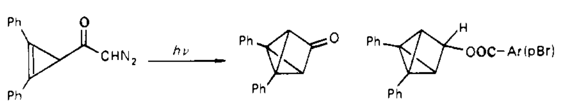
(12) Masamune also prepared this same strained tricyclo[2.1.1.0^{2,5}]pentan-2-one ii, by means of photolysis of β,γ-unsaturated diazo ketone i, the structure of which was demonstrated by means of a single crystal X-ray analysis of a derivative (iii); see Masamune, S. *J. Am. Chem. Soc.* **1964**, *86*, 735. Trotter, J.; Gibbons, C. S.; Natatsuka, N.; Masamune, S. *Ibid.* **1967**, *89*, 2792. For other approaches to the bicyclo[2.1.0]pentanone and closely related systems see: Hanack, M. *Suom. Kemistil.* **1966**, *39*, 93. Lee, T. V.; Roberts, S. M.; Newton, R. F. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1179. Gilbert, J. C.; Luo, T.; Davis, R. E. *Tetrahedron Lett.* **1975**, 2545. Grudzinski, Z.; Roberts, S. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1767.



ii iii

(13) Intervention of the vinylogous Wolff rearrangement may explain the failure of Gutsche[9] and Hudlicky to observe cycloproponation in the Cu(II)-promoted decomposition of β,γ-unsaturated diazo ketones; see Hudlicky, T.; Sheth, H. J. P.; Gee, V.; Barnvos, D. *Tetrahedron Lett.* **1979**, 4889.

(14) Masamune, S.; Fukumoto, K. *Tetrahedron Lett.* **1965**, 4647.

(15) Ho, C.-Y.; Bond, F. T. *J. Am. Chem. Soc.* **1974**, *96*, 7355. Also see: Bond, F. T.; Ho, C.-Y. *J. Org. Chem.* **1976**, *41*, 1421.

(16) For an additional example of the proposed fragmentation process see: Hart, H.; Shih, E. *J. Org. Chem.* **1976**, *41*, 3377 and references cited therein.

(17) Agosta, W. C.; Smith A. B., III *J. Am. Chem. Soc.* **1973**, *95*, 1961.

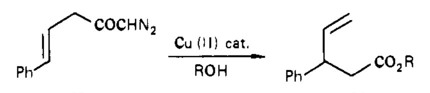
(18) On a number of occasions we have found that the photochemical Wolff rearrangement first introduced by Horner et al. [Horner, L.; Spietschka E.; and Gross, A. *Justus Liebigs Ann. Chem.* **1951**, *576*, 17. See: Horner, L.; Spietschka, E. *Chem. Ber.* **1952**, *85*, 225] is considerably more efficient than the thermal or catalyzed Wolff rearrangement.

(19) Lokensgard, J. P.; O'Dea, J.; Hill, E. A. *J. Org. Chem.* **1974**, *39*, 3355.

(20) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 4623.

(21) Wilds, A. L.; von Trebra, R. L.; Woolsey, N. F. *J. Org. Chem.* **1969**, *34*, 2401 and references cited therein.

Table II

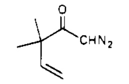
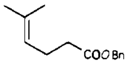
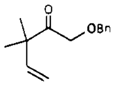
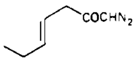
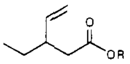
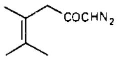
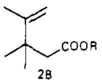


20 21

Cu(II) catalyst	Alcohol	Product (VWR)	Yield of product (percent)
$Cu(AcAc)_2$	MeOH	21a (R = Me)	16
	t-BuOH	21b (R = t-Bu)	19
	BnOH	21c (R = Bn)	59
$Cu(OTf)_2$	t-BuOH	21b (R = t-Bu)	52
	BnOH	21c (R = Bn)	71

Table III

$$\text{Diazo ketone} \xrightarrow[\text{cyclohexane, }\Delta]{\text{Cu(II), ROH}} \text{product(s)}$$

Diazo ketone	Cu(II), ROH	Product(s) and yield(s) (percent)	
 22	$Cu(OTf)_2$, BnOH	 25 (32)	 26 (26)
 23	$Cu(AcAc)_2$, t-BuOH $Cu(AcAc)_2$, MeOH $Cu(OTf)_2$, BnOH	 27	a, R = t-Bu (20) b, R = Me (14) c, R = Bn (52)
 24	$Cu(AcAc)_2$, MeOH $Cu(AcAc)_2$, BnOH $Cu(OTf)_2$, BnOH	 28	a, R = Me (34) b, R = Bn (70) b, R = Bn (78)

at the α-carbon was the principal driving force. In conjunction with this work, Wilds noted an unpublished finding of M. S. Newman[22] wherein the silver benzoate promoted decomposition of diazo ketone **17** gave a 3:1 mixture of the vinylogous Wolff product **18** and the normal Wolff ester **19**.[23]

With this as background, we present here a full account of our work on the vinylogous Wolff rearrangement. We demonstrate that the rearrangement is indeed applicable to a wide range of β,γ-unsaturated diazo ketones. In addition, we define the stereochemical consequences of the vinylogous Wolff rearrangement and the optimal rearrangement protocol. In the following paper we present our observations concerning the mechanism of the vinylogous Wolff rearrangement.[1d]

Table IV

$$\text{Diazoketone} \xrightarrow[\text{cyclohexane, }\Delta]{\text{Cu(II), ROH}} \text{product(s)}$$

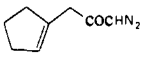
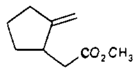
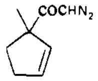
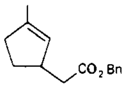
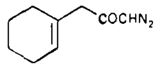
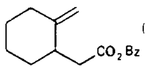
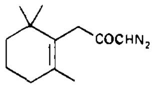
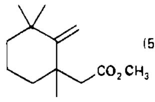
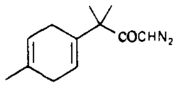
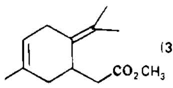
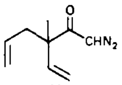
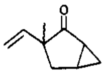
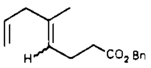
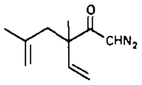
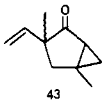
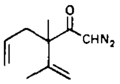
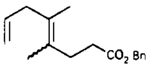
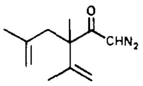
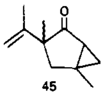
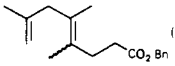
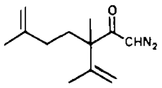
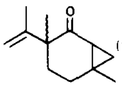
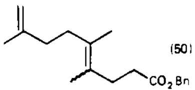
Diazo ketone	Cu (II), alcohol	Product(s) and yield(s) (percent)
 11	$Cu(AcAc)_2$, MeOH	 32 (48)
 29	$Cu(OTf)_2$, BnOH $Cu(AcAc)_2$, BnOH	 33 (56) (74)
 8b	$Cu(OTf)_2$, BnOH	 10 (63)
 30[1c]	$Cu(AcAc)_2$, MeOH	 34[1c] (56)
 31	$CuSO_4$, MeOH	 35 (34)

Table V

$$\text{Diazoketone} \xrightarrow{Cu(OTf)_2\text{, BnOH, cyclohexane, }\Delta} \text{product(s)}$$

Diazoketone	Product(s)[a] and yield(s) (percent)	
 36	 41 (51)	 42 (23)
 37	 43 (53)	
 38		 44 (66)
 39	 45 (23)	 46 (51)
 40	 47 (17)	 48 (50)

[a] All products are 1:1 diasteriomeric or cis-trans mixtures.

Results and Discussion

Conditions, Scope, and Limitations of the Vinylogous Wolff Rearrangement. At the outset, we sought the optimal reaction protocol by exploring various copper(II) salt–alcohol couples. Our studies, as those of Lokensgard,[19] demonstrated that copper sulfate was in fact inferior to $Cu(AcAc)_2$. We therefore selected $Cu(AcAc)_2$ and $Cu(OTf)_2$[24] as the principal copper salts[25] to screen with various alcohols. The alcohols included methanol, *tert*-butyl alcohol, and benzyl alcohol. The results of a typical series of

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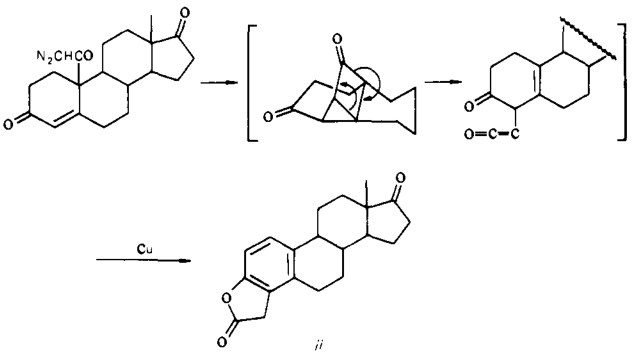
(22) Wilds, A. L.; Van der Berghe, J.; Winestock, C. H.; von Trebra, R. L.; Woolsey, N. F. *J. Am. Chem. Soc.* **1962**, *84*, 1503 (see ref 7).

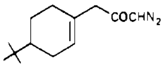
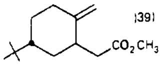
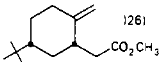
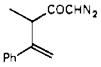
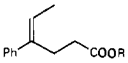
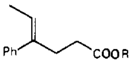
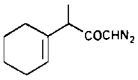
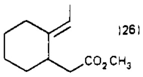
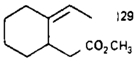
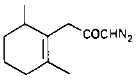
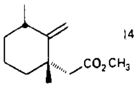
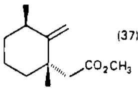
(23) Mateus and Ceronado recently reported what appears to be a further example of the vinylogous Wolff rearrangement. Specifically, heating diazo ketone i at reflux in cyclohexane containing copper afforded lactone ii. The rearrangement was suggested to proceed through a bicyclopentanone intermediate; fragmentation followed by intramolecular capture and aromatization thus led to ii; see: Mateus, J. L.; Ceronado, V. M. *Rev. Latinoam. Quim.* **1975**, *6*, 72.



(24) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843.

(25) In two cases copper(I) triflate was found to be inferior to copper(II) triflate in the promotion of the vinylogous Wolff rearrangement.

Table VI. Stereochemical Consequences of the Vinylogous Wolff Rearrangement

Diazo ketone	Cu (II), alcohol	Product(s) and yield(s) (percent)	
 49	Cu(AcAc)$_2$, MeOH	 (39) 53	 (26) 54
 50	Cu(AcAc)$_2$, MeOH Cu(AcAc)$_2$, BnOH Cu(OTf)$_2$, BnOH	 55 a, R = Me (14) b, R = Bn (13) b, R = Bn (13)	 56 a, R = Me (25) b, R = Bn (45) b, R = Bn (53)
 51	Cu(AcAc)$_2$, MeOH	 (26) 57	 (29) 58
 52[1h]	Cu(AcAc)$_2$, MeOH	 (4) 59[1h]	 (37) 60[1h]

experiments are illustrated in Table II.

Interestingly, when Cu(AcAc)$_2$ was employed with either methanol or *tert*-butyl alcohol the yield of the vinylogous Wolff ester was at best modest. However when benzyl alcohol was employed a dramatic increase in the efficiency of the process was noted. Furthermore it was found that Cu(OTf)$_2$ was much more effective than Cu(AcAc)$_2$. For example, the yield of the vinylogous Wolff ester employing Cu(OTf)$_2$ and *tert*-butyl alcohol was almost threefold that of Cu(AcAc)$_2$ and *tert*-butyl alcohol. Best results however were obtained with Cu(OTf)$_2$ and benzyl alcohol.[26]

With an effective protocol in hand, we turned to define the generality of the process. Twenty-one acyclic and monocyclic β,γ-unsaturated diazo ketones were explored. The results are depicted in Tables I–VI. Several comments concerning these observations are in order. First, the vinylogous Wolff rearrangement is indeed a general process, proceeding in good to excellent yield depending upon the structure of the specific substrate. Central here is the degree of substitution of the β,γ-olefinic bond, the overall order of reactivity being tetra > tri > di > monosubstituted. Acyclic and monocyclic systems proceed with equal facility. Interestingly, highest yields were obtained when the α-carbon was disubstituted. This is the same observation as obtained by Wilds in the thermal decomposition of (triphenylacetyl)diazomethane **15**.[21]

Second, the results listed in Table III corroborate the fact that the Cu(OTf)$_2$–benzyl alcohol couple is the optimal reaction system to promote the vinylogous Wolff rearrangement.

Third, a potential competitive process available to β,γ-unsaturated diazo ketones is illustrated with diazo ketone **22** (Table III), a system possessing a monosubstituted olefinic bond. In this case both the vinylogous Wolff ester **25** and an isomeric α-benzyloxy ketone **26** are obtained as a 1:1 mixture. Presumably the benzyloxy ketone arises via copper(II)-promoted insertion of the diazo carbon into the O–H bond of benzyl alcohol. Such a process is well-known when saturated alkyl diazo ketones are subjected to copper(II)-promoted decomposition.[27] That insertion into the O–H bond competes in this case with the vinylogous Wolff process is a reflection of the general observation that electron-poor olefins do not undergo efficient cyclopropanation.[28]

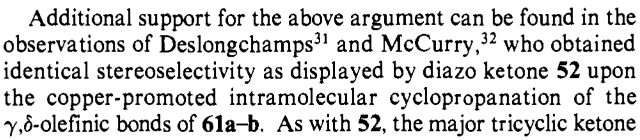
Finally, in experiments designed to compete the vinylogous Wolff reaction (i.e., insertion into the β,γ bond) vs. γ,δ-cyclopropanation (see Table V), the degree of substitution of the olefinic bond dramatically influenced the overall course of the reaction.[29] That is, with the exception of diazo ketone **40**, products arising from the vinylogous Wolff rearrangement predominate when the β,γ-olefin is equally or favorably substituted compared to the $\gamma'\delta'$-double bond. This trend is also observed when a β,γ-olefin competes against a δ',ϵ'-olefin. With respect to diazo ketone **40**, wherein both olefins are disubstituted, decomposition affords (as predicted) a 3:1 mixture respectively of vinylogous Wolff esters **48** and bicyclic ketone **47**, the overall yield being 67%.

Stereochemical Consequences of the Vinylogous Wolff Rearrangement.[1b] Having demonstrated that the vinylogous Wolff rearrangement is widely applicable, and thereby held promise as a general synthetic method, we examined the stereochemical consequences of the process. Four diazo ketones, **49–52** (see Table VI), were selected to define the response of both the insertion and the fragmentation steps of the rearrangement to steric bias.

The proposed mechanism implies that the stereochemical outcome of the rearrangement will be determined by the initial bond formation step in the case of diazo ketones **49** and **52**, whereas substrates **50** and **51** should also respond to the fragmentation step. Furthermore, examination of molecular models reveals that in the case of **49** approach by the diazo carbon to the β,γ-olefin from either side is sterically unencumbered, while one of the two possible reaction conformations for diazo ketones **50–52** appears to lead to considerable nonbonded interaction (e.g., allylic $A^{1,3}$ strain[30]) between the methyl substituent on the ring and the methylene carbon of the diazo ketone chain in **52**. Such nonbonded interactions should lead to a preferred conformation, and thereby significantly affect selectivity in the initial insertion reactions of **50–52** as compared to **49**.

Our results, given in Table VI, are quite consistent with the above stereochemical conjectures. For example, while all four diazo ketones afforded diastereomeric mixtures when subjected to the VWR conditions, diazo ketones **49–51** reacted with little or no selectivity to give the vinylogous Wolff esters **53–58**, whereas diazo ketone **52** gave esters **59** and **60** with high stereoselectivity (9:1). Thus, the initial insertion step seems to be stereoselective, responding to the presence (as in **52**) or absence (as in **49**) of stereochemical bias; the fragmentation step, on the other hand, would appear to proceed with loss of any selectivity derived from the initial addition to the to the β,γ-olefinic bond. The latter is exemplified by comparison of the results for diazo ketones **50** and **51** with **52**.

Additional support for the above argument can be found in the observations of Deslongchamps[31] and McCurry,[32] who obtained identical stereoselectivity as displayed by diazo ketone **52** upon the copper-promoted intramolecular cyclopropanation of the γ,δ-olefinic bonds of **61a–b**. As with **52**, the major tricyclic ketone (**62**) results from insertion trans to the secondary methyl substituent.



61 62 9 : 1 63

(a) R = H; P. M. McCurry, Jr., Ref. 32.

(b) R = OCH$_2$CH$_2$O; P. Deslongchamps *et al.*, Ref. 31

Preparative Experiments

β,γ-Unsaturated Diazo Ketones. The unsaturated diazo ketones employed in this study were prepared in the usual manner via treatment of the respective acid chlorides with excess diazomethane.[4] The requisite acids in turn were available from the corresponding esters which were prepared either by the alkyla-

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(26) Recently, Doyle and Trudell observed a pronounced solvent effect in the reaction of β,γ-unsaturated diazo ketones with Cu(OTf)$_2$. In particular, treatment of diazo ketone **8b** with Cu(OTf)$_2$ in *nitromethane* affords exclusively Δ^3-hydrindan-2-one [private communication from Professor Doyle (Hope College)]. For leading references on the Lewis acid promoted decomposition of unsaturated diazo ketones see ref 1. In our hands, treatment of **8b** with the Cu(OTf)$_2$–benzyl alcohol couple *in cyclohexane* affords **10b** in 63% yield, see Table IV.

(27) Yates, P. *J. Am. Chem. Soc.* **1952**, *74*, 5376.

(28) For leading references see: W. Kirmse "Carbene Chemistry"; Academic Press: New York, 1971; pp 338–343.

(29) The stereochemistries of the bicyclo[3.1.0]hexanones and bicyclo[4.1.0]heptanones were not determined.

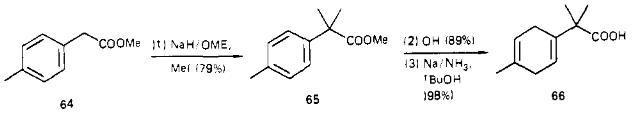
(30) Johnson, F.; Malhotra, S. K. *J. Am. Chem. Soc.* **1965**, *87*, 5492.

(31) Mongrain, M.; Lafontaine, J.; Belanger, A.; Deslongchamps, P. *Can. J. Chem.* **1970**, *48*, 3273.

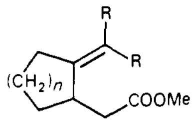
(32) McCurry, P. M., Jr. *Tetrahedron Lett.* **1971**, 1845.

tive–deconjugative procedure introduced by Schlessinger[33] and Rathke[34] or by addition of ethyl lithioacetate[35] or ethyl diethylphosphonoacetate[36] to appropriate ketones followed by dehydration and/or deconjugation. In all cases the yields of unsaturated esters and diazo ketones were good to excellent.

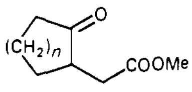
The previously unknown acid **66** was readily available via dialkylation of *p*-tolylacetic acid methyl ester **64** with methyl iodide, followed by basic hydrolysis and Birch reduction[37] of the resultant carboxylic acid. The yield for the three-step process was 69%.



Vinylogous Wolff Products. Early in our investigation the carbon skeletons of three vinylogous Wolff esters, were established rigorously by chemical correlation. Toward this end, ruthenium tetroxide–sodium metaperiodate oxidation[38] of **10a**,**b**,**d** afforded keto ester **67a**,**b**,**d**. Authentic samples of the latter were then



10 a, *n* = 1, R = Me
b, *n* = 2, R = H

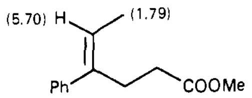


67 a, *n* = 1
b, *n* = 2

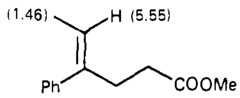
prepared by known methods (see Experimental Section for details). All remaining vinylogous Wolff products, as well as all synthetic intermediates (vide infra), were fully characterized; for those not discussed in detail here, structural assignments derive from the spectroscopic properties and elemental composition data on record in the Experimental Section.

Stereochemical Assignments. The structural and stereochemical assignments for the diastereomeric esters obtained from diazo ketones **49**–**52** were secured through a combination of spectroscopic and chemical methods. Simplest in this regard proved to be esters **53** and **54**, which were known compounds.[39] Their identities were established by direct comparisons with authentic spectra kindly provided by Professor Trost.[40]

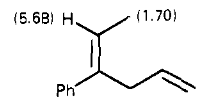
Disposition of the vinyl methyl substituents in the isomeric pairs that derive from diazo ketones **50** and **51** were based on NMR studies. In the case of **55** and **56**, we employed the well-known empirical observation that a vinyl proton resonance cis to an aromatic nucleus is deshielded relative to that for the trans hydrogen, while signals resulting from allylic hydrogens (in our case the methyl group) are shielded relative to that for the trans allylic hydrogens.[41] For comparison purposes we provide here the available chemical shift data for the closely related olefins **68** and **69**.[42]



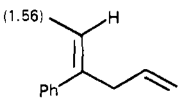
55



56

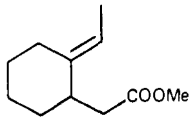


68



69

To establish the orientation of the methyl substituents in esters **57** and **58**, we carried out an NMR lanthanide-shift experiment.[43]



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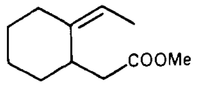
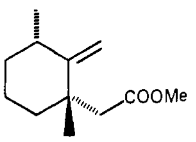


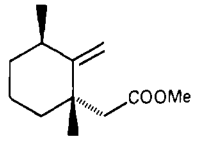
58

When equimolar solutions of **57** and **58** were progressively doped with the lanthanide-shift reagent Eu(fod)$_3$, the olefinic methyl resonance of the *Z* isomer (**58**, δ 1.58) underwent a greater downfield shift relative to the methyl resonance of the *E* isomer (**57**, δ 1.57). Conversely, the olefinic resonance (δ 5.10) of **57** experienced a larger deshielding effect compared to the same signal of the *Z* isomer (i.e., δ 5.12).

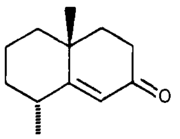
Finally to establish the stereochemical disposition of the 1,3-dimethyl substituents in esters **59** and **60**, a chemical correlation with the known enone **70** was carried out. The results of this study have been described elsewhere.[1b]



59



60



70

Experimental Section[44]

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 nitrogen atmosphere. *n*-Butyllithium (2.1 M, 11 mmol) was added via syringe. After 15 min the pale yellow solution was cooled to −78 °C whereupon 11 mmol of HMPA 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 a period of 1 h. The reaction mixture was then poured into 25 mL of saturated aqueous NH$_4$Cl and extracted with 3 × 50 mL of Et$_2$O. The combined organic extracts were washed with 10% aqueous HCl, saturated aqueous NaHCO$_3$, 5% aqueous sodium thiosulfate, and brine and dried. Removal of the solvent in vacuo and distillation afforded the desired alkylated product.

General Procedure B: Preparation of Carboxylic Acids from the Corresponding Esters. A solution consisting of 10 mmol of the appropriate ester and 10 mL each of 5% aqueous NaOH and 95% ethanol was

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[33] Herrmann, J. L.; Kieczykowski, G. R.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2433.

[34] Rathke, M. W.; Sullivan, D. *Tetrahedron Lett.* **1972**, 4249.

[35] Rathke, M. W. *J. Am. Chem. Soc.* **1970**, *92*, 3222.

[36] Wadsworth, W. S., Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733. For a review see: Wadsworth, W. S., Jr. *Org. React.* **1977**, *25*, 73.

[37] Marshall, J. A.; Wuts, P. G. M. *J. Org. Chem.* **1977**, *42*, 1794.

[38] For leading references on ruthenium tetroxide oxidations see: Smith, A. B., III; Scarborough, R. M. *Synth. Commun.* **1980**, *10*, 205. Carlsen, P. H. J.; Katsaki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936.

[39] Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1975**, *97*, 2534.

[40] We are grateful to Professor Trost for supplying these data.

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[44] **Materials and Methods.** Separations were accomplished on a Varian Aerograph Model 920 employing one of the following columns: A, 25% Carbowax 20 M, 10 ft × 0.375 in.; B, 5% Carbowax 20 M, 50 ft × 0.25 in.; C, 6% SE-30, 10 ft × 0.375 in.; D, 25% DEGS, 10 ft × 0.375 in.; E, 6% Carbowax 20 M, 10 ft × 0.375 in.; F, 10% GF-1, 10 ft × 0.25 in.; the column oven was operated at 150–190 °C and the helium carrier gas flow rate was 100–120 mL/min. All yields are determined by VPC calibration methods unless otherwise noted. Melting points were corrected; boiling points were uncorrected. Solutions were dried over MgSO$_4$. IR spectra were obtained for CCl$_4$ solutions. Photochemical experiments were carried out with a Hanovia Model L mercury lamp. No. 679A-360 in a quartz immersion well with use of Pyrex 7740 as a filter.

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deoxygenated with N_2 and then heated at reflux under a nitrogen atmosphere for 2 h. After cooling, the reaction mixture was extracted with 3 × 25 mL of Et_2O and the aqueous phase acidified with 10% aqueous HCl and then extracted with 3 × 25 mL of Et_2O. The combined organic extracts obtained from the acidic aqueous phase were washed with brine and dried. Removal of the solvent in vacuo, and distillation when appropriate, afforded the desired carboxylic acid.

General Procedure C: Preparation of Diazo Ketones. Acyl chlorides were prepared by treating the respective carboxylic acid, dissolved in benzene, with either 2 equiv of $SOCl_2$ or 1.2 equiv of oxalyl chloride and allowing the mixture to stir for 4 h. Benzene and excess thionyl chloride or oxalyl chloride were removed in vacuo and the residue distilled. The purified acyl chloride was dissolved in 10 mL of Et_2O and added dropwise by pipette to an excess (3 equiv) of freshly distilled ethereal diazomethane (from Diazald, Aldrich) while stirring in an ice bath. The reaction mixture was allowed to stand at room temperature overnight. Excess diazomethane and Et_2O 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 the subsequent step without further purification.

General Procedure D: Copper(II)-Catalyzed Decomposition of Diazo Ketones. A solution consisting of 1.0 mmol of the appropriate diazo ketone, 1.2 mmol of a designated alcohol (methanol, *tert*-butyl alcohol, benzyl alcohol) and 50 mL of freshly distilled cyclohexane was treated under a nitrogen atmosphere with 10 mol % of a designated Cu(II) species [$CuSO_4$, copper(II) acetylacetonate [$Cu(AcAc)_2$], or copper(II) triflate [$Cu(OTf)_2$]].[24] The reaction mixture was heated at reflux for 4 h. Upon cooling, the contents were washed with 50 mL of 10% aqueous HCl and brine and dried. Removal of the solvent in vacuo afforded the product mixture.

General Procedure E: Silver(I) Oxide Catalyzed Decomposition of Diazo Ketones. A solution consisting of 1.0 mmol of the appropriate diazo ketone and 500 mg of Ag_2O (Fisher) was heated at reflux in 50 mL of anhydrous methanol for 3 h. The reaction mixture was then added to an ice-water mixture and extracted with ether. The combined extracts were then dried. Removal of the solvent in vacuo afforded the product mixture.

General Procedure F: Photochemically Induced Decomposition of Diazo Ketones. A solution consisting of 1.0 mmol of the appropriate diazo ketone in 70 mL anhydrous methanol was degassed with nitrogen for 15 min and then irradiated for 2.5 h under nitrogen and through Pyrex with the standard Hanovia 450-W Hg arc (No. 679A-36). The reaction mixture was then added to H_2O and extracted with ether. The combined extracts were washed with water and brine and dried. Removal of the solvent in vacuo afforded the product mixture.

Silver(I) Oxide Catalyzed Decomposition of 1-(1′-Diazo-3′,3′-dimethyl-2′-oxoprop-3′-yl)cyclopentene (8a). Diazo ketone **8a**, prepared from 1.64 g of the corresponding acid chloride as described in general procedure C, was decomposed with Ag_2O in methanol as described in general procedure E. Product analysis on column E indicated the presence of two components. An analytical sample of each was obtained by preparative VPC. The first fraction was methyl ester **9a** (58%) identical in all respects with that prepared by Agosta and Smith.[17]

The second fraction was methyl ester **10a** (42%) identical in all respects with that isolated from the Cu(II)-catalyzed decomposition of **8a**.

Silver(I) Oxide Catalyzed Decomposition of 1-(1′-Diazo-3′,3′-dimethyl-2-oxoprop-3′yl)cycloheptene (8d). Diazo ketone **8d**, prepared from 200 mg of acid chloride according to general procedure C, was decomposed with Ag_2O (150 mg) in 100 mL of methanol. Product analysis on column A indicated the presence of two components. An analytical sample of each was obtained by preparative VPC. The first fraction was **9d** (61%): IR 3070 (w), 2980 (m), 2955 (m), 2930 (s), 2855 (m), 1745 (s), 1455 (m), 14455 (m), 1245 (m), 1215 (m), 1135 (m), 1112 (m), 1030 (m), 850 (m), 715 (w); NMR (60 MHz) δ 1.08 (s, 6 H), 1.10–2.35, 2.30 (m, s, 12 H), 3.53 (s, 3 H), 5.62 (bt, $J = 7$ Hz, 1 H).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.28; H, 10.44.

The second fraction was methyl ester **10d** (28%) identical in all respects with that obtained from the $Cu(AcAc)_2$–methanol decomposition of **8d**.

Photochemically Induced Decomposition of 1-(1′-Diazo-3′,3′-dimethyl-2′-oxoprop-3′-yl)cyclopentene (8a). Diazo ketone **8a** (206 mg, 1.16 mmol) prepared from α,α-dimethyl-1-cyclopentene-1-acetic acid[47] as described in general procedure C was irradiated in methanol for 2 h as described in general procedure F. Product analysis on column C indicated the presence of two components. Pure samples of each were obtained by preparative VPC. The first fraction was methyl ester **9a** (92%) identical in all respects with that prepared by Agosta and Smith.[17]

The second fraction was methyl ester **10a** (8%) identical in all respects with that derived from the Cu(II)-catalyzed decomposition of **8a**.

Photochemically Induced Decomposition of 1-(1′-Diazo-2′-oxoprop-3′-yl)cyclohexene (8b). Diazo ketone **8b**, prepared from 199 mg of the corresponding acid chloride according to general procedure C, was irradiated for 2.5 h in 70 mL of methanol as described in general procedure F. Product analysis on column A indicated one component. An analytical sample of **9b** (79%), obtained by preparative VPC, possessed the following spectral properties: IR 3040 (w), 3010 (m), 2940 (s), 2870 (m), 2840 (m), 1740 (s), 1440 (m), 1170 (s), 620 (m); NMR (60 MHz) δ 1.40–2.36 (m, 12 H), 3.58 (s, 3 H), 5.38 (bm, 1 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.45; H, 9.73.

Photochemically Induced Decompositon of 1-(1′-Diazo-3′,3′-dimethyl-2′-oxopropyl-3′-yl)cyclohexene (8c). Diazo ketone **8c**, prepared from 181 mg of the corresponding acid chloride according to general procedure C, was irradiated for 2.5 h in 70 mL of methanol according to general procedure F. Product analysis on column A indicated one component. A pure sample was obtained by preparative VPC and determined to be **9c** (95%) by spectral comparison to that obtained via the Ag_2O decomposition of **8c**.

Photochemically Induced Decomposition of 1-(Diazo-3′,3′-dimethyl-2-oxoprop-3′-yl)cycloheptene (8d). Diazo ketone **8d**, prepared from 181 mg of the corresponding acid chloride as described in general procedure C, was irradiated in 70 mL of methanol for 2 h as described in general procedure F. Product analysis on column A indicated two components. A pure sample of each was obtained by preparative VPC. The first was methyl ester **9d** (93%), identical with that obtained in the Ag_2O decomposition of **8d**.

The second fraction was methyl ester **10d** (7%) identical with that obtained in the Cu(II)–methanol decomposition of **8d**.

Copper(II)-Catalyzed Decomposition of 1-(1′-Diazo-3′,3′-dimethyl-2′-oxoprop-3′-yl)cyclopentene (8a). Diazo ketone **8a** (402 mg, 2.26 mmol), prepared in 90% yield from α,α-dimethyl-1-cyclopentene-1-acetic acid[48] as described in general procedure C, was decomposed with $Cu(AcAc)_2$ and MeOH according to general procedure D. Product analysis on column A indicated the presence of only one component. An analytical sample obtained by preparative VPC was determined to be ester **10a** (85%), which had the following properties: IR 2980 (s), 2945 (s), 1735 (s) cm^{-1}; NMR (60 MHz) δ 1.37–1.83, 1.58, 1.63 (m, s, s, 10 H), 2.00–2.42 (m, 4 H), 2.75–3.25 (m, 1 H), 3.57 (s, 3 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.48; H, 9.95. Found: C, 72.53; H, 9.90.

Copper(II)-Catalyzed Decomposition of 1-(1′-Diazo-2′-oxoprop-3′-yl)cyclohexene (8b). Diazo ketone **8b** (744 mg, 4.54 mmol), prepared in 89% yield from 1-cyclohexene-1-acetic acid[49] as described in general procedure C, was decomposed with $Cu(OTf)_2$ and benzyl alcohol as described in general procedure D. Product analysis on column E indicated the presence of only one component. An analytical sample obtained by preparative VPC was determined to be ester **10** (i.e., benzyl ester) (63%), which possessed the following spectral data: IR 3075 (w), 3040 (w), 2935 (s), 2855 (m), 1735 (s), 1645 (w), 895 (s), 695 (s) cm^{-1}; NMR (60 MHz) δ 0.93–2.85 (m, 11 H), 4.50–4.60 (m, 2 H), 5.02 (s, 2 H), 7.22 (s, 5 H).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.87; H, 8.30.

Copper(II)-Catalyzed Decomposition of 1-(1′-Diazo-3′,3′-dimethyl-2′-oxoprop-3′-yl)cyclohexene (8c). Diazo ketone **8c** (261 mg, 1.36 mmol), prepared in 92% from α,α-dimethyl-1-cyclohexene-1-acetic acid,[50] was decomposed with $CuSO_4$ and MeOH as described in general procedure D. Product analysis on column A indicated the presence of only one compound. An analytical sample obtained by preparative VPC was determined to be methyl ester **10c** (67%), which possessed the following spectral characteristics: IR 2915 (s), 2855 (s), 1735 (s), 1440 (s), 1165 (s) cm^{-1}; NMR (60 MHz) δ 1.07–2.78 (m, 16 H), 3.03–3.25 (m, 1 H), 3.57 (s, 3 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.53; H, 10.31.

Copper(II)-Catalyzed Decomposition of 1-(1′-Diazo-3′,3′-dimethyl-2-oxoprop-3′-yl)cycloheptene (8d). Diazo ketone **8d** (171 mg, 0.83 mmol), prepared in 89% yield from α,α-dimethyl-1-cycloheptene-1-acetic acid,[50] was decomposed with $Cu(AcAc)_2$ and MeOH as described in general procedure D. Product analysis on column A indicated the presence of only one component. An analytical sample obtained by preparative VPC was determined to be methyl ester **10d** (90%), which possessed the fol-

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lowing spectral characteristics: IR 2985 (s), 2955 (s), 1735 (s) cm^{-1}; NMR (60 MHz) δ 0.92–2.62, 1.67 (m, s, 19 H), 3.58 (s, 3 H).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.24; H, 10.60.

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Registry No. 8a, 54445-53-3; **8a** (acid), 16642-54-9; **8a** (acid chloride), 71647-57-9; **8b**, 54495-73-7; **8b** (acid), 18294-87-6; **8b** (acid chloride), 84189-13-9; **8c**, 54445-52-2; **8c** (acid), 16642-55-0; **8c** (acid chloride), 90173-13-0; **8d**, 56268-19-0; **8d** (acid), 16642-56-1; **8d** (acid chloride), 90173-12-9; **9a**, 38142-79-9; **9b**, 54445-57-7; **9c**, 54445-59-9; **9d**, 90172-84-2; **10a**, 54445-56-6; **10b**, 54445-54-4; **10c**, 54445-55-5; **10d**, 90172-85-3; **11**, 5261-30-3; **11** (acid), 21622-08-2; **20**, 90172-76-2; **20** (acid), 2243-53-0; **21a**, 90172-86-4; **21b**, 90172-87-5; **21c**, 90172-88-6; **22**, 57690-97-8; **22** (acid), 10276-09-2; **22** (ethyl ester), 58544-20-0; **23**, 90172-77-3; **23** (acid), 1577-18-0; **24**, 76803-37-7; **24** (acid), 14472-55-0; **25**, 90172-89-7; **26**, 90172-90-0; **27a**, 90172-91-1; **27b**, 90172-92-2; **27c**, 90172-93-3; **28a**, 90172-94-4; **28b**, 90172-95-5; **29**, 76803-43-5; **29** (acid), 68317-77-1; **30**, 62861-92-1; **31**, 90172-78-4; **32**, 52358-09-5; **33**, 76803-53-7; **34**, 90172-96-6; **35**, 90172-97-7; **36**, 90172-79-5; **36** (acid), 90173-18-5; **36** (ethyl ester), 90173-19-6; **37**, 90172-80-9; **37** (acid), 90173-20-9; **37** (methyl ester), 66052-38-8; **38**, 90172-81-9; **38** (acid), 90173-21-0; **38** (ethyl ester), 64861-91-2; **39**, 76803-44-6; **39** (acid), 90173-22-1; **40**, 90172-82-0; **40** (acid), 90173-23-2; **41** (isomer 1), 90172-98-8; **41** (isomer 2), 90173-24-3; (*E*)-**42**, 90172-99-9; (*Z*)-**42**, 90173-25-4; **43** (isomer 1), 90173-00-5; **43** (isomer 2), 90243-13-3; (*E*)-**44**, 90173-01-6; (*Z*)-**44**, 90173-26-5; **45** (isomer 1), 90173-02-7; **45** (isomer 2), 90243-14-4; (*E*)-**46**, 90173-03-8; (*Z*)-**46**, 90173-27-6; **47** (isomer 1), 90173-04-9; **47** (isomer 2), 90173-28-7; (*E*)-**48**, 90173-05-0; (*Z*)-**48**, 90173-29-8; **49**, 61346-63-2; **49** (acid), 90173-16-3; **49** (ethyl ester), 54281-01-5; $\Delta^{\alpha,1}$-**49** (ethyl ester), 13733-50-1; **50**, 90172-83-1; **50** (acid), 90173-14-1; **50** (ethyl ester), 25289-62-7; **50** (alcohol), 90173-15-2; **51**, 61346-64-3; **51** (acid), 2205-24-5; **52**, 61140-39-4; **53**, 67463-12-1; **54**, 67463-13-2; **55a**, 90173-06-1; **55b**, 90173-07-2; **56a**, 90173-08-3; **56b**, 90173-09-4; **57**, 90173-10-7; **58**, 90173-11-8; **59**, 61140-29-2; **60**, 61140-28-1; **64**, 23786-13-2; **65**, 68682-48-4; **65** (acid), 20430-18-6; **66**, 90173-17-4; **67a**, 4934-95-6; **67b**, 13672-64-5; **67c**, 75032-18-7; MeOH, 67-56-1; BnOH, 100-51-6; *t*-BuOH, 75-65-0; $CuSO_4$, 7758-98-7; $Cu(AcAc)_2$, 13395-16-9; $Cu(OTf)_2$, 34946-82-2; Ag_2O, 20667-12-3; ethyl tiglate, 5837-78-5; ethyl β-methylcinnamate, 945-93-7; allyl bromide, 106-95-6; methyl tiglate, 6622-76-0; 1-chloro-2-methyl-2-propene, 563-47-3; ethyl 2,3-dimethyl-3-butenoate, 14387-99-6; 2-carboethoxycyclopentanone, 611-10-9; ethyl bromoacetate, 105-36-2; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; 1-(1-cyclohexen-1-yl)pyrrolidine, 1125-99-1; 1-(1-cyclohepten-1-yl)pyrrolidine, 14092-11-6.

Supplementary Material Available: All spectral characterization data, elemental composition data, and experimental procedures for the diazo ketones, their precursor acids, and the derived vinylogous Wolff and other products listed in Tables III–VI are available as supplementary material (14 pages). Ordering information is given on any current masthead page.

Vinylogous Wolff Rearrangement. 5. Mechanistic Studies

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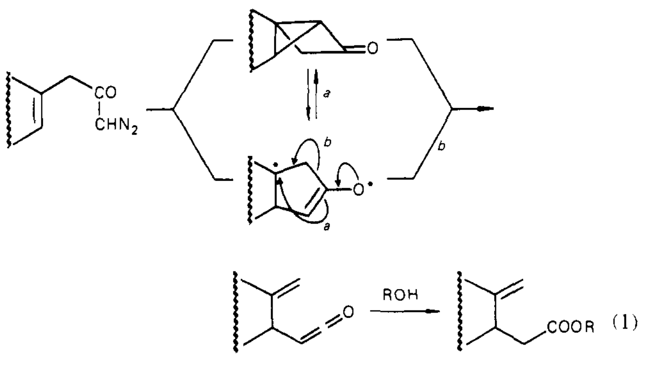
Abstract: A detailed study of the vinylogous Wolff rearrangement (VWR), a general transformation involving skeletal rearrangement of β,γ-unsaturated diazo ketones, is described. Evidence is presented which suggests that the skeletal rearrangement involves initial insertion of the diazo carbon into the β,γ-olefinic bond. The resultant bicyclo[2.1.0]pentan-2-one then undergoes fragmentation to a β,γ-unsaturated ketene which in turn is captured by available nucleophiles (e.g., alcohol) to afford the observed γ,δ-unsaturated ester.

In the preceding paper[2] of this issue we demonstrated that β,γ-unsaturated diazo ketones, through agency of either silver(I) or copper(II) salt–alcohol couples, undergo a novel transformation termed the vinylogous Wolff rearrangement (VWR) to afford γ,δ-unsaturated esters (eq 1). To account for this transformation we postulated[3] initial silver or copper ion induced insertion of the diazo carbon into the β,γ-olefinic bond to yield a bicyclo[2.1.0]pentanone and/or zwitterionic species. Subsequent thermal or metal ion induced fragmentation followed by capture of the resultant β,γ-unsaturated ketene by alcohol would then afford the observed vinylogous Wolff ester (eq 1). Refinement of this scheme allows the insertion and/or fragmentation to proceed in either a concerted or stepwise fashion. In no case employing silver ion to promote the decomposition did the yield of vinylogous Wolff ester exceed that of the normal Wolff product.[2] Copper(II) salts, on the other hand, in general afforded only the vinylogous Wolff esters.[2]



Vinylogous Wolff Rearrangement

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

[2] Smith, A. B., III; Toder, B. H.; Branca, S. J. *J. Am. Chem. Soc.*, preceding paper in this issue.

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