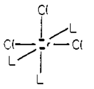
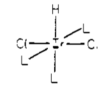
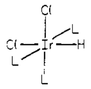
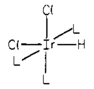
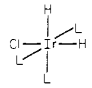
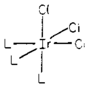
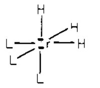
Table I. Iridium–Ligand Bond Lengths (Å) in $L_3H_{3-n}Cl_nIr^{III}$ Complexes [L = PMe_2Ph][a]

	 1[b]	 **2**	 3a	 3b	 4	 **5**	 6[c]
Ir-P (trans to Cl)	2.280 (2)		2.249 (1)	2.234 (1)		2.289 (2)	
Ir-P (trans to P)	[2.366 (2) 2.381 (2)]	2.329 (2)	[2.335 (2) 2.343 (2)]	[2.344 (2) 2.352 (2)]	2.292 (2)		
Ir-P (trans to H)		2.365 (2)			2.331 (2)		2.294 (3)
Ir-Cl (trans to Cl)	2.366 (1)	[2.364 (2) 2.402 (2)]					
Ir-Cl (trans to P)	2.437 (2)		2.453 (2)	2.449 (2)		2.463 (2)	
Ir-Cl (trans to H)			[2.518 (2) 2.492 (2)]	2.503 (2)	2.505 (1)		
Ir-H (trans to Cl)[d]			[1.56 (1) 1.58 (1)]		1.557 (9)		
Ir-H (trans to P)[d]		1.616 (7)			1.603 (8)		

[a] Average values are given where two or more measurements do not differ significantly. Bracketed values refer to notionally equivalent bond lengths which vary as a result of differing inter and/or intramolecular contacts. A discussion of these variations and details of the crystallographic work will be given elsewhere. [b] Results agree, within experimental error, with those reported in ref 1. [c] Results from ref 2. [d] See ref 3.

trans influences of chloride and hydride ligands, both molecules exhibit near identical Ir–P distances. There seems little doubt that the effect is due to the small steric requirement of the hydride ligand;[7] indeed, bond-angle changes at the metal atom, on substituting hydride for chloride, confirm a significant shift of ligands toward the hydride site.[8] However, since the Ir–Cl distances are effectively invariant to hydride substitution, we are certainly not seeing something as simple as first-coordination sphere ligand–ligand repulsion effects.[9] Rather, the determining factor would appear to be a rebalancing of bonding forces and the nonbonding interactions due to anionic ligand/phosphine substituent and phosphine substituent/phosphine substituent contacts.[10]

Separation of the effects of these two nonbonding interaction types is not possible for the present series of complexes. Anionic ligand/phosphine substituent interactions are certainly very important. Thus, observed Pt–P distances in *trans*-$[(P\text{-}i\text{-}Pr_3)_2Cl_2Pt^{II}]$ (**7**), and *trans*-$[(P\text{-}i\text{-}Pr_3)_2HClPt^{II}]$ (**8**), are 2.340 (2) and 2.287 (1) Å,[11] and in *trans*-$[(PPh_3)_2Cl(CH_2CN)Pt^{II}]$ (**9**), and *trans*-$[(PPh_3)_2H(CH_2CN)Pt^{II}]$ (**10**), are 2.309 (3) and 2.274 (4) Å, respectively.[12] Phosphine substituent/phosphine substituent interactions are apparently of similar importance since (a) replacement of monodentate by chelating phosphines (hence reducing the number of substituent/substituent contacts in otherwise similar complexes) is generally accompanied by M–P bond length compression[13] and (b) comparison of the Pt–P distances in $[(PPh_3)_3HPt^{II}][(CF_3CO_2)_2H]$ (**11**), [2.312 (6) Å trans to P][14] with those in **9** [2.309 (3) Å] and **10** [2.274 (4) Å] shows the effects of the substitutions H for Cl and PPh_3 for CH_2CN to be largely self-cancelling.

Steric modification of metal–phosphine distances is already well established.[7,15,16] We believe it important, however, to draw attention to the *magnitude* of the effect even in complexes with small phosphine ligands. Both in the complexes discussed here and in the cationic species $[(PEt_3)_3XPt^{II}]^+$ (X = Cl, F, H) described in ref 16, the M–P compression due to H for Cl substitution is fairly constant at ca. 0.04 Å. The near equivalence is probably fortuitous, reflecting a balance between phosphine size and number of ligands coordinated. Clearly, however, the frequently made assumption that trans and particularly cis electronic effects on bond lengths are large relative to steric effects in octahedral and square-planar phosphine complexes requires validation.

Registry No. 1, 15664-86-5; **2**, 12099-72-8; **3**, 32914-89-9; **4**, 12099-74-0; **5**, 21919-29-9; **6**, 12099-83-1.

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(7) Tolman, C. A. (*Chem. Rev.* **1977**, *77*, 313) has estimated cone angles of 75° for H, 102° for Cl, and 122° for PMe_2Ph.

(8) Except for the fac-complexes **5** (with mean P–Ir–P angle = 100°) and **6** (with mean P–Ir–P angle = 101°)[2].

(9) Because the variations in Ir–Cl and Ir–P bond lengths with changes in trans ligand are similar it seems unlikely that the Ir–Cl bond is much less easily deformed than the Ir–P bond.

(10) Even though these contacts are not exceptionally short. In **2** the shortest nonbonding contacts to anionic ligands are H···H (2.63 Å), H···Cl (2.77 Å) and in **4** are H···H (2.56 Å) and H···Cl (2.59 Å).

(11) Robertson, G. B.; Tucker, P. A., unpublished results.

(12) Ros, R.; Michelin, R. A.; Belluco, U.; Zanotti, G.; Del Prā, A.; Bombieri, G. *Inorg. Chim. Acta* **1978**, *29*, L 187.

(13) For example, $RhCl(PPh_3)_3$ Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 655] [Rh–P (trans to Cl) 2.214, 2.225 Å, Rh–P (trans to P) 2.304–2.338 Å] and $RhCl(Ph_2PC_3H_6PPhC_3H_6PPh_2)$ [Nappier, T. E.; Meek, D. W.; Kirchener, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4194] [Rh–P (trans to Cl) 2.201 Å, Rh–P (trans to P) 2.288 Å); $RhCl(PPh_3)_2(C_2F_4)$ [Hitchcock, P. B.; McPartlin, E. M.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1969**, 1367] (Rh–P 2.372 Å) and $RhCl(PPh_2C_6H_4CHCHC_6H_4PPh_2)$ [Robertson, G. B.; Tucker, P. A.; Whimp, P. O. *Inorg. Chem.* 1980, *19*, 2307] (Rh–P 2.285 Å); *cis*-$PdCl_2(PMe_2Ph)_2$ [Martin, L. L.; Jacobson, R. A. *Inorg. Chem.* **1971**, *10*, 1795] Pd–P 2.260 Å) and $PdCl_2(PPh_2(CH_2)_nPPh_2)$ [n = 1–3: Steffen, W. L.; Palenik, G. *Inorg. Chem.* **1976**, *15*, 2432] (Pd–P 2.226–2.250 Å).

(14) Caputo, R. E.; Mak, D. K.; Willet, R. D.; Roundhill, S. G. N.; Roundhill, D. M. *Acta Crystallogr., Sect. B* **1977**, *B33*, 215.

(15) Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183.

(16) Mazid, M. A.; Russell, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1737.

Regiospecific Cleavage of Strained Tri- and Tetraquinane β-Diketones via Retro-Claisen Reaction[1]

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Received September 17, 1981

We have been interested for some time[2a-f] in the synthesis of polyquinane ring systems, some of which contain reactive β-di-

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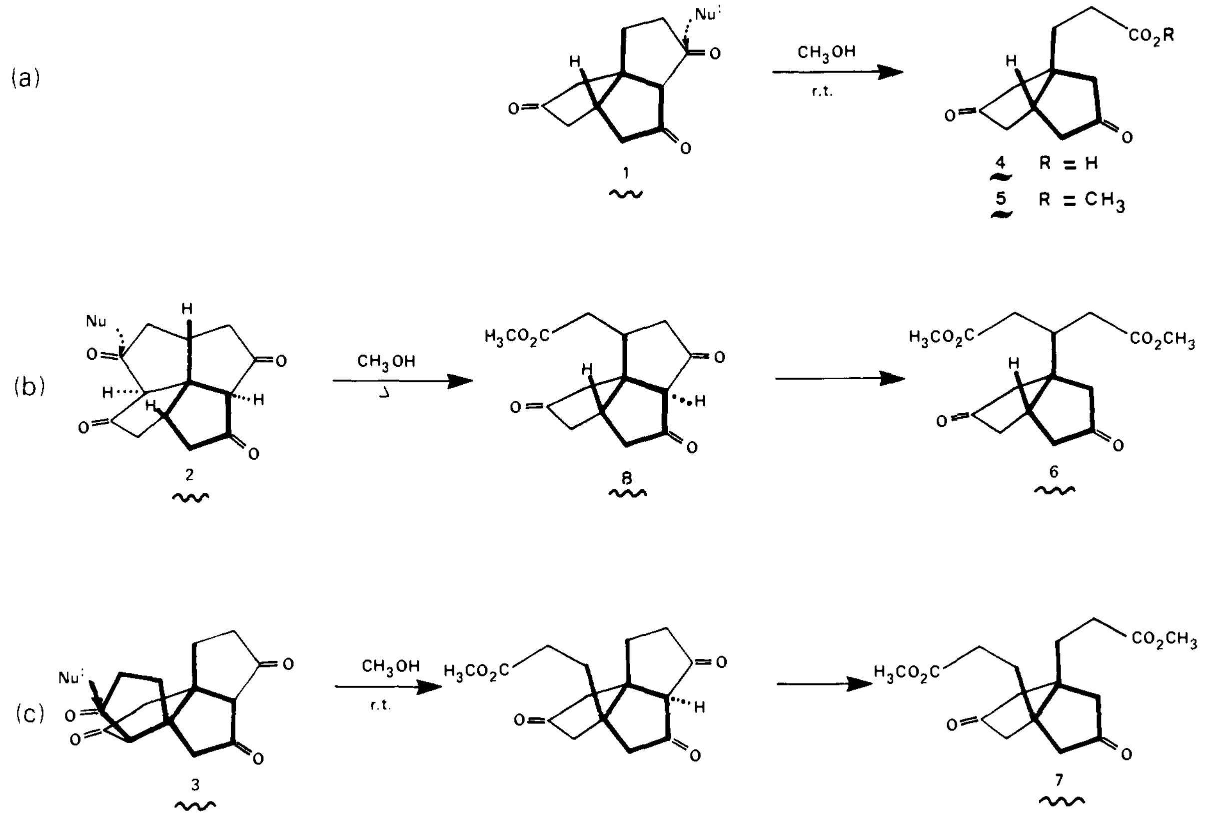
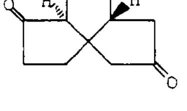
(1) A brief report on part of the subject matter of the present communication has been incorporated into a recent review: Mitschka, R.; Oehldrich, J.; Takahashi, K.; Cook, J. M.; Weiss, U. *Tetrahedron*, in press.

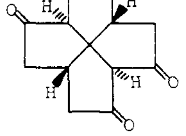
0002-7863/82/1504-0318$01.25/0

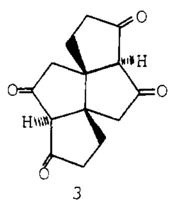
Scheme I



ketone functionality. The three substances of this type which are of interest for the present discussion are tricyclo[6.3.0.0^{1,5}]undecane-3,6,9-trione[2c] (**1**), tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane-2,6,8,12-tetraone (stauranetetraone)[2c] (**2**), and tetracyclo[6.6.0.0^{1,5}.0^{8,12}]tetradecane-2,7,9,14-tetraone (**3**).[2f]


1


2


3

During earlier work directed toward the preparation of **1**,[2c] it was observed that this compound was converted regiospecifically into the monoacid **4** on treatment with aqueous base; none of the spirocyclic regioisomer[2g] was obtained during the fission of the β-diketone group present in **1**. When the analogous experiment was carried out with sodium methoxide in methanol, or even with methanol alone, only regioisomer **5** was formed by retro-Claisen reaction. The analogous regiospecificity was also observed when **2** or **3** were treated with methanol; again, exclusive formation of the regioisomers **6** and **7**, respectively, took place.

The relative rates of ring opening were found to follow a definite pattern: 1 > 3 > 2.[1] It was of particular interest that stauranetetraone (**2**) underwent this retro-Claisen reaction at a rate markedly slower than either **1** or **3**, although comparison of both IR spectra[1] and Dreiding models indicated that **2** should be more strained than **1** or **3**.

To explore the differences in reactivity of these molecules in more detail, single crystals of **2** and **3** were subjected to X-ray analysis. General details of bond lengths, bond angles, and torsion angles will be presented in ref 1.

Neither compound is required to have symmetry in the crystal, and although both possess approximate twofold axes, stauranetetraone (**2**) does not possess the C_{2v} symmetry of the chemical formula.[2c] As far as molecular dimensions are concerned, the two molecules are remarkably similar, and strain is not particularly manifested in bond lengths or angles. If anything, the less reactive and apparently more symmetrical compound **2** shows more strain in that some of the bonds to carbon atoms with four heavy atom substituents are longer, and there is some evidence of torsional strain (Figure 1) caused by a definite relative flattening of all the five-membered rings when compared with **3**. For completeness, full crystallographic details for the two structures were submitted to the referees and are available as supplementary material. For the purposes of this paper, we are concerned with the approach of a nucleophile to a carbonyl carbon atom. The geometric details of such a reaction are discussed in detail in ref 3a. In essence, the nucleophile approaches along a trajectory such that the geometrical arrangement necessary for the bonds to be formed is attained. The approach is along a path at approximately the tetrahedral angle to the carbonyl bond and bisects the angle between the other two bonds. The distortion of the angle at the carbonyl carbon atom as the nucleophile approaches is discussed in ref 3b, but for the present purpose, this aspect probably need not be considered. A bicyclo[3.3.0]octane moiety possesses a concave and a convex side, and the trajectory of the nucleophile is considerably more hindered on the concave side.

The X-ray data agree with deductions from models that, apart from minor effects due to different conformations of the five-membered rings, all of the rings of stauranetetraone (**2**) have a very similar situation in that each can be regarded as part of two

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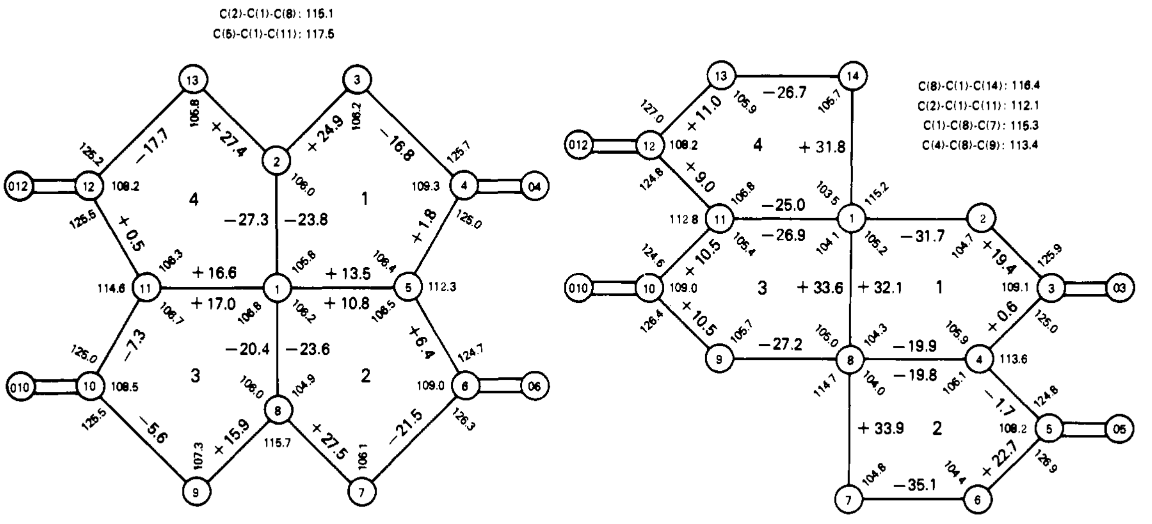
(2) (a) Weiss, U.; Edwards, J. M. *Tetrahedron Lett.* **1968**, 4885. (b) Yang, S.; Cook, J. M. *J. Org. Chem.* **1976**, *41*, 1903. (c) Oehldrich, J.; Cook, J. M.; Weiss, U. *Tetrahedron Lett.* **1976**, 4549. (d) Weber, R. W.; Cook, J. M. *Can. J. Chem.* **1978**, *56*, 189. (e) Mitschka, R.; Weiss, U.; Cook, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 3973. (f) Gawish, A.; Mitschka, R.; Weiss, U.; Cook, J. M. *Tetrahedron Lett.* **1981**, *22*, 211. (g) At no time were any of the spirocyclic regioisomers isolated from reaction of **1**, **2**, or **3** with methanol. These would have arisen from attack on the concave side of either **1**, **3**, or **8** by the nucleophile followed by fission of the β-diketone bond (see ref 1 for details).

(3) (a) Bürgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563. (b) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 738.



	1	2	3	4
Φm	25.7	27.8	20.4	28.8
Δ	27.5	8.9	5.0	33.8

2

	1	2	3	4
Φm	33.5	36.3	33.5	31.9
Δ	34.5	30.4	0.2	4.2

3

Figure 1. Torsion angles, bond angles, and conformational parameters for **2** and **3**. Comparison of the data for **2** and **3** indicates the very close similarity of all the various classes of bond lengths and angles. The parameters ϕ_m (maximum torsion angle) and Δ (pseudo rotation angle) follow: Altona, C.; Geise, H. J.; Romers, C. *Tetrahedron* **1968**, *24*, 13. Δ would be zero for an ideal half-chair conformation and 36° for an ideal envelope. The flattening of the rings and possible concomitant torsional strain is clearly indicated by the lower ϕ_m values for **2**. The dihedral angles between a π orbital on a carbonyl carbon atom and the diketone bond β to the atom, e.g., atom 4 and bond 5–6 in **2**, are as follows. **2**: Atoms 4, 6, 10, 12; 33°, 39°, 42°, 36°; **3**: atoms 3, 5, 10, 12; 35°, 36°, 42°, 28°.

bicyclooctane moieties. The result of the unique geometry of **2** is that the face of a carbonyl group on the convex side of one bicyclooctane unit is also concave to a second [3.3.0] system. In the less symmetrical tetraone **3**, there are three bicyclooctane moieties, and two of the rings are present only in one such unit, while the other two rings are shared. Consequently in tetraone **3**, there are two β-diketone carbonyl groups open to attack from a free convex face of the molecule. Pictured in Figure 2 are two stereopairs to illustrate the situation. While the approach of a nucleophile is not completely unhindered in **3**, the trajectory is considerably more open than that in stauranetetraone (**2**), especially if rigorous adherence to a bisecting path is not required. Deviation from the preferred trajectory would not improve the situation in **2**.

In summary then **2** can be considered to be made up of two *cis*-bicyclo[3.3.0]octane-3,7-dione units in such a fashion that each one of its four cyclopentanone rings is part of the convex face of one bicyclooctanedione unit and the concave face of another one at right angles to the unit. As a consequence, every possible attack by a nucleophile must of necessity occur at the concave face of one of the bicyclooctane dione units, i.e., in a manner which is sterically unfavorable, although not impossible. In contrast, the two more reactive compounds, **1** and **3**, both possess cyclopentanone rings (one or two of them, respectively) which are part of one bicyclooctanedione system; as a result, unobstructed approach to the convex face of this system is possible (see Scheme I).

These observations at once account for the greater reactivity of **1** and **3** and the greater resistance of **2** to nucleophilic attack. In addition, they also explain the regiospecificity of this attack in all three compounds. Attack of, e.g., methanol on the exposed convex face of **1**, with the required approach vector of 109.3°,[3] necessarily yields the observed product **5**; the situation in the case of **3** is perfectly analogous (Scheme I). Formation, from **1**, of the alternative spirocyclic isomer[2g] would have to involve attack upon the concave side of a bicyclooctanedione unit.

The less facile attack on **2** can only yield **8**, derived from the same ring system as **1**, and hence likely to undergo rapid cleavage in the same manner as **1**, producing the observed compound. The postulated intermediate **8** was not observed; this is understandable, since its further conversion into **6** must be much faster than its formation from **2**.

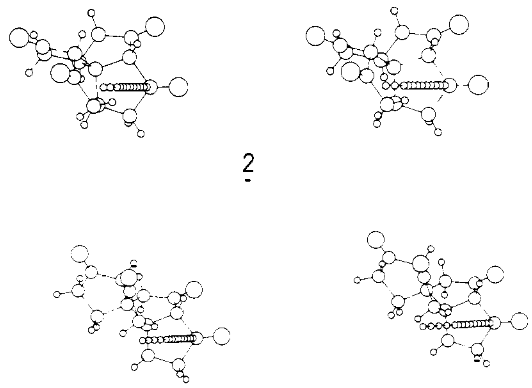


Figure 2. Approach of a nucleophile to a carbonyl group in molecules **2** and **3**. The molecule is projected onto the plane of a carbonyl group and is seen from the convex side of a bicyclooctane in each case. The trajectory of the nucleophile is represented by the small balls, which are 0.5 Å apart near the carbonyl carbon atom and later 1.0 Å apart.

We conclude, therefore, that both the decreased rate of ring opening of **2** vs. those of **1** and **3** and the complete regiospecificity of these retro-Claisen reactions rest solely on the ready steric accessibility of the convex side of the constituent bicyclooctanedione units and the difficulty of approach to their concave faces.

The diminished reactivity of **2** as compared to those of **1** and **3** is important for further research in this field. Both Dauben[4] and Eaton[5] have shown recently that β-diketone units in similar

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[4] Dauben, W. G.; Walker, J. M. *J. Org. Chem.* **1981**, *46*, 1103.

J. Am. Chem. Soc. 1982, 104, 321-323

systems can be manipulated without substantial cleavage. Consequently, it appears **2**, under suitably chosen conditions, might serve as a precursor for molecules quoted[6] as possible progenitors for structures which contain a planar tetracoordinate carbon atom. Studies toward this goal are presently being pursued in our laboratory and will be reported in due course.

Acknowledgment. We (Han, Takahashi, and Cook) wish to thank the National Science Foundation (CHE-7910302) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support. We wish to thank Gail Boviall for technical assistance.

Supplementary Material Available: Tables of final anisotropic thermal parameters and structure factor amplitudes as well as ORTEP drawings of **2** and **3** (28 pages). Ordering information is given on any current masthead page.

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(5) Eaton, P. E.; Mueller, R. H.; Carlson, G. R.; Cullison, D. A.; Cooper, G. F.; Chou, T. C.; Krebs, E.-P. *J. Am. Chem. Soc.* **1977**, *99*, 2757.

(6) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992. Hoffmann, R. *Pure Appl. Chem.* **1971**, *28*, 181. Keese, R.; Pfenninger, A.; Roesle, A. *Helv. Chim. Acta* **1979**, *62*, 326. Böhm, M. C.; Gleiter, R.; Schang, P. *Tetrahedron Lett.* **1979**, 2575. ten Hoeve, W.; Wynberg, H. *J. Org. Chem.* **1980**, *45*, 2930. Wiberg, K. B.; Olli, L. K.; Golembeski, N.; Adams, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 7467.

Alkynolate Anions via a New Rearrangement: The Carbon Analogue of the Hofmann Reaction[1]

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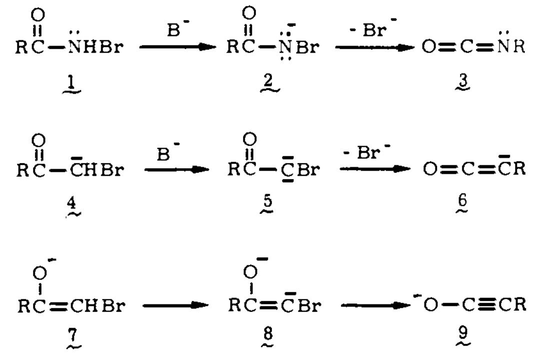
Received September 25, 1981

Herein we report the first examples of a previously unknown reaction, the carbon analogue of the Hofmann rearrangement. The classical Hofmann reaction[2] involves deprotonation of an *N*-bromoamide (**1** → **2**) followed by migration of a group to nitrogen with loss of bromide to form an isocyanate (**2** → **3**). The new reaction described herein is formally isoelectronic with that process; i.e., an α-bromoketone enolate is deprotonated (**4** → **5**) and rearranges with loss of bromide to afford a ketene anion (**5** → **6**). Resonance structures **7**–**9** emphasize the enolate nature of the α-keto dianion intermediate **8** and the alkynolate nature of the product anion **9**. While simple haloenolate monoanions such as **4** are stable and not prone to loss of halide,[3] α-halo-α-keto dianions (**5**) possess a much greater charge density on carbon which should facilitate loss of bromide. Our results presented below indicate this is indeed the case; rearrangement of **5** to **6** does occur, and in fact, rapidly even at −78 °C.

Primary bromoenolate **10**, on treatment with *tert*-butyllithium in ether (−78 °C; then 0 °C) cleanly undergoes metal–halogen exchange to afford the expected α-keto dianion **11**.[4] Addition of cyclohexanone (1.4 equiv, −78 °C, 10 min) followed by quenching with dilute acid affords aldol product **12** in 88% yield. When this same sequence is carried out in tetrahydrofuran (THF) rather than ether, however, the yield of **12** drops to 70% and a new product, spiro-β-lactone **16**, is obtained in 12% yield. Formation of **16** is consistent with deprotonation of **10** (in competition with metal–halogen exchange), leading to alkynolate anion **14** via rearrangement of dianion **13**. Preparation of **14** by a different method has been reported by Schöllkopf[5] as well as reaction of

Scheme I



Scheme II

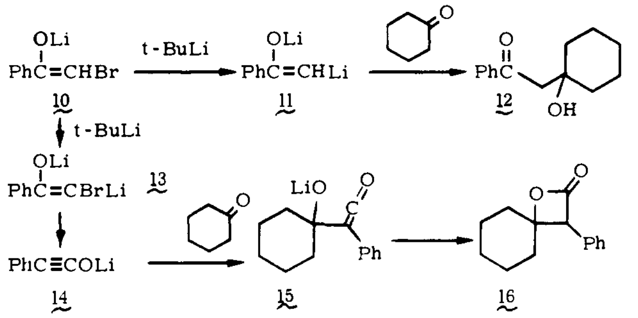
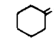
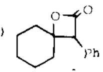
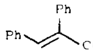
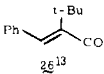


Table I[a]

Entry	Starting Enolate[a]			Product	Yield[b]
1	$\mathrm{Ph\overset{OLi}{C}{=}CHCl}$ **17**	$\xrightarrow[-78°\to RT]{n\text{-BuLi},^{c}\ THF}$	$\xrightarrow{HCl,\ H_2O}$	$PhCH_2CO_2H$	(67%)
2	**17**	"	 (1.3 eq) −78°	 **16**[5]	(43%)
3	**17**	$\xrightarrow[-35°;\ RT^{d}]{t\text{-BuLi},\ THF}$	$\xrightarrow[-78°\to RT]{MeOH}$	$PhCH_2CO_2Me$ **18**	(57%)
4	**17**	"	$\xrightarrow[-78°\to RT]{PhCHO\ (1\ eq)}$	 **19**[7]	(85%)
5	$\mathrm{Ph\overset{OLi}{C}{=}CBr_2}$ **20**	$\xrightarrow[-78°\to RT]{t\text{-BuLi},\ THF}$	$\xrightarrow[-78°\to RT]{PhCHO\ (2\ eq)}$	**19**	(76%)
6	**20**	"	$\xrightarrow[-78°\to RT]{PhCH_2OH\ (3\ eq)}$	$PhCH_2CO_2CH_2Ph$ **21**[19]	(50%)
7	$\mathrm{t\text{-}Bu\overset{OLi}{C}{=}CHCl}$ **22**	$\xrightarrow[-78°\to RT]{t\text{-BuLi},\ THF}$ N. R.	$\xrightarrow{ClSiMe_3}$	$\mathrm{t\text{-}Bu\overset{OSiMe_3}{C}{=}CHCl}$ **23**[13]	
8	$\mathrm{t\text{-}Bu\overset{OLi}{C}{=}CBr_2}$ **24**	$\xrightarrow[-78°\to RT]{t\text{-BuLi},\ THF}$	$\xrightarrow[-78°\to RT]{PhCH_2OH\ (5\ eq)}$	$t\text{-}BuCH_2CO_2CH_2Ph$ **25**[20]	(72%)
9	**24**	"	$\xrightarrow[-78°\to RT]{PhCHO\ (2.4\ eq)}$	 **26**[13]	(75%)[e]

[a] Starting enolates were prepared as noted: 17,[6] 20,[8] 22,[11] 24.[12] [b] Isolated yields based on precursors of starting enolates. [c] Reactions involving *n*-butyllithium were difficult to reproduce; see text. [d] Reaction mixture was warmed briefly to room temperature before quenching to destroy excess *tert*-butyllithium. [e] Single isomer; stereochemistry as shown.

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(1) This work was presented in part at the 1981 Joint Central–Great Lakes Regional ACS Meeting at Dayton, OH, May 21, 1981, and at the I.I.T. Kilpatrick Symposium on Carbenes, Carbenoids, and Cyclopropanes in Organic Synthesis in Chicago, IL, June 2, 1981.

(2) Wallis, E. S.; Lane, J. F. *Org. React.* **1946**, *3*, 267.

(3) (a) In our previous work with haloenolates,[4a,9] we have never observed loss of halide; (b) unsuccessful attempts to induce α-ketocarbene formation from α-chloroenolate anions have been reported by: House, H. O.; Fischer, W. F; Gall, M.; McLaughlin, T. E; Peet, N. P. *J. Org. Chem.* **1971**, *36*, 3429.

(4) (a) Kowalski, C. J.; O'Dowd, M. L.; Burke, M. C.; Fields, K. W. *J. Am. Chem. Soc.* **1980**, *102*, 5411. (b) The bromoenolate **10** was prepared from the corresponding bromoenol acetate and methyllithium at 0 °C.

(5) Hoppe, I.; Schöllkopf, U. *Liebigs Ann. Chem.* **1979**, 219.

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