

found that strong acids (HX) will readily add to the complexes $(PPh_3)_2Pt(\text{acetylene})$ to give $(PPh_3)_2PtX_2$,⁵ with the hydrogen transferring to the acetylene to form an olefin. The reaction proceeds with the initial formation of a vinyl complex which may then react further with a second molecule of the acid to give the olefin. Most of our work has been carried out with HCl, but the reaction also proceeds with HBr, picric acid, thioacetic acid, and trifluoroacetic acid,⁶ all of which have been found to give hydrides with $(PPh_3)_4Pt$.⁵

We have found that the reaction with the but-2-yne complex is very rapid with a quantitative conversion to but-2-ene; gas chromatography shows that the isomers are in the thermodynamic ratio of 80% *trans* and 20% *cis*, and that there is no formation of alkane. The diphenylacetylene complex reacts with HCl in $CHCl_3$ solution to give a quantitative yield of *trans*-stilbene, but in benzene solution the yield is only about 60%. *cis*- $(PPh_3)_2PtCl_2$, which is obtained in quantitative yield with the but-2-yne complex and with the diphenylacetylene complex in $CHCl_3$ as solvent, is insoluble in common organic solvents, but the nonvolatile residue from the reaction of the diphenylacetylene complex in benzene as solvent is however partially soluble in $CHCl_3$. The nmr spectrum of this complex in $CDCl_3$ shows a multiplet for the phenyl protons at τ 2.75 and a sharp singlet at τ 3.13. This resonance can be assigned to the protons in the vinyl complex by analogy with other platinum vinyl complexes.^{6,7} When HCl is added to this solution the peak at τ 3.13 disappears and is replaced by a peak at τ 3.01, which is identical in position with the nmr of the olefinic proton in pure stilbene (mp 122°) as prepared by us, and by comparison with the published value.⁸ Final confirmation of the structure of the complex has been obtained by preparing it by the addition of only 1 mol of HCl to the diphenylacetylene complex.⁹ From this reaction the vinyl complex has been obtained pure (*Anal.* Calcd for $C_{50}H_{41}P_2ClPt$: C, 64.20; H, 4.38; Cl, 3.78. Found: C, 64.14; H, 4.29; Cl, 4.01) and shows a band in the ir for the $C=C$ stretch at 1590 cm^{-1} (m) and the nmr peak for the olefinic protons at τ 3.13.

We believe that the mechanism of the reaction is the one shown in Scheme I, which involves the intermediate formation of two platinum hydrides. A study has been made of the replacement reaction of one acetylene coordinated to $(PPh_3)_2Pt$ by a second acetylene, and the mechanism has been considered to follow a scheme where dissociation to $(PPh_3)_2Pt$ occurs initially followed by the reaction of this reactive intermediate with the second acetylene to form the new complex.¹⁰ It is possible that a similar mechanism may occur in this reaction, where the acetylene initially dissociates to give $(PPh_3)_2Pt$ which then oxidatively adds HCl to give the hydride.¹ The free acetylene can then insert into the platinum hydride to give the intermediate vinyl

(5) P. B. Tripathy and D. M. Roundhill, *J. Organometal. Chem.*, in press.

(6) D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, *Chem. Commun.*, 621 (1969).

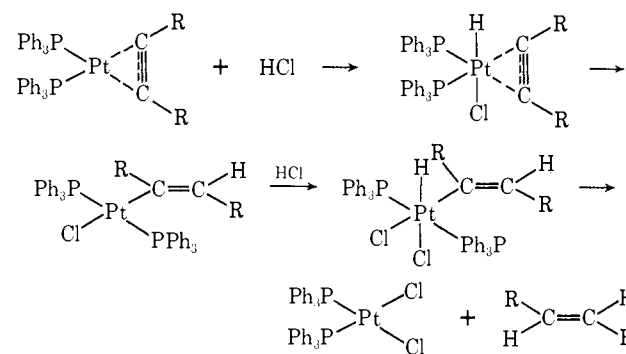
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(9) In ref 6, the preparation of a similar vinyl complex from trifluoroacetic acid has been reported, which can also be prepared from the $(PPh_3)_2Pt(COOCF_3)_2$ and diphenylacetylene.

(10) A. D. Allen and C. D. Cook, *Can. J. Chem.*, 42, 1963 (1964).

Scheme I



complex. Although this second mechanism is possible, we favor the one proposed since we have been unable to readily insert diphenylacetylene into $(PPh_3)_2Pt(H)Cl$ to give the vinyl complex even under the acid conditions prevailing in the reaction. We have not isolated either of the intermediate hydrides but they represent reasonable structures since hydrides of both Pt(II)^{1,2,11} and Pt(IV)^{1,12} have been isolated and characterized in similar systems. With $(PPh_3)_2Pt(CF_3C\equiv CCF_3)$ and excess HCl the product is the vinyl complex $(PPh_3)_2Pt(Cl)[(CF_3)C=C(CF_3)H]$, which is too stable to be decomposed to 1,2-bis(trifluoromethyl)but-2-ene.

Although preliminary data suggest that this method can be used for the preparation of *trans* olefins from acetylenes, further work is in progress to study the scope of the reaction and also to correlate the effect of solvent on the nature of the product.

Acknowledgment. This investigation was supported in part by funds provided by the Graduate School Research Funds, and by Cities Service Oil Co., Cranbury, N. J.

(11) J. C. Bailar and H. Itatini, *J. Amer. Chem. Soc.*, 89, 1592 (1967).

(12) J. H. Nelson, H. B. Jonassen, and D. M. Roundhill, *Inorg. Chem.*, 8, 2591 (1969).

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The Peracid Oxidation of Acetylenes. 1,2-Methyl Migration, Cyclopropane Formation, and Stereoselective 1,5- and 1,6-Transannular Insertion¹

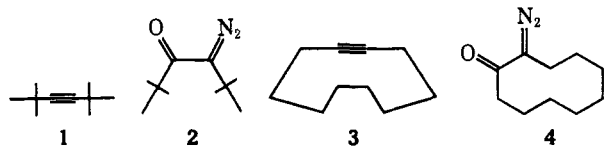
Sir:

Although the peracid oxidation of olefins has been thoroughly studied, relatively little is known concerning the chemistry and mechanism of peracid oxidation in the acetylene series.² We report here the first examples of 1,2-methyl migration, cyclopropane formation, and stereoselective 1,5- and 1,6-transannular insertion in the peracid oxidation of acetylenes. We have investigated the reaction of di-*t*-butylacetylene (1) and cyclodecyne (3) with *m*-chloroperbenzoic acid (MCPBA) and compared the results with those obtained

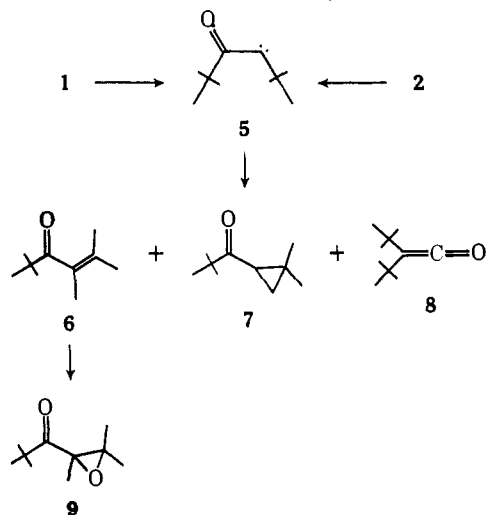
(1) This work was presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 7-12, 1969, Abstracts, ORGN-152.

(2) (a) V. Franzen, *Chem. Ber.*, 88, 717 (1955), and previous papers; (b) R. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, 86, 4866 (1964); (c) J. K. Stille and D. D. Whitehurst, *ibid.*, 86, 4871 (1964).

from the decomposition of the structurally related α -diazoketones **2** and **4**, respectively.³



Treatment of **1** with MCPBA (1:1) in methylene chloride under nitrogen for 72 hr at room temperature followed by aqueous work-up afforded in addition to unreacted **1**, α,β -unsaturated ketone **6**,⁵ epoxy ketone **9**, and cyclopropyl ketone **7**⁶ in a ratio of 21:72:7.^{7,8} Since **9** was shown to be a secondary oxidation product



of **6**, the true ratio of **6** to **7** is 93:7. The thermal decomposition of α -diazoketone **2**⁵ similarly afforded compounds **6** and **7** in a ratio of 94:6.

Reaction of cyclodecyne (**3**)⁹ with MCPBA (1:1) in various solvents afforded as major products *cis*-bicyclo[5.3.0]decan-2-one (**11**),¹⁰ *cis*-bicyclo[4.4.0]decan-

(3) See W. Kirmse, "Carbene Chemistry," Vol. I, Academic Press, New York, N. Y., 1964, Chapter 7.

(4) G. F. Hennion and T. F. Banigan, Jr., *J. Amer. Chem. Soc.*, **68**, 1202 (1946); W. H. Puterbaugh and M. S. Newman, *ibid.*, **81**, 1611 (1959).

(5) M. S. Newman and A. Arkell, *J. Org. Chem.*, **24**, 385 (1959). We are grateful to Professor M. S. Newman for sending us the infrared spectrum of **6**.

(6) J. K. Crandall and L. C. Lin, *J. Amer. Chem. Soc.*, **89**, 4526 (1967). We thank Professor J. K. Crandall for providing us with an authentic sample of **7**.

(7) Pivalil and di-*t*-butyl ketone were also identified as very minor products (<1% each by vpc). The latter compound undoubtedly arises from oxidation of di-*t*-butylketene (**8**), a Wolff rearrangement product.

(8) The identification of all compounds was effected by spectral and vpc comparison with authentic samples. Analytical work was accomplished satisfactorily with a 0.125 in. \times 15 ft column packed with 15% Carbowax 20M-Chromosorb W DMCS acid-washed 100-120 mesh; a 0.25 in. \times 10 ft column packed with 15% Carbowax 20M-Chromosorb W DMCS acid-washed 80-100 mesh was used for preparative work.

(9) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucusy, Jr., *J. Amer. Chem. Soc.*, **74**, 3636 (1952); V. Prelog, H. Schenker, and H. H. Gunt-hard, *Helv. Chim. Acta*, **35**, 1598 (1952).

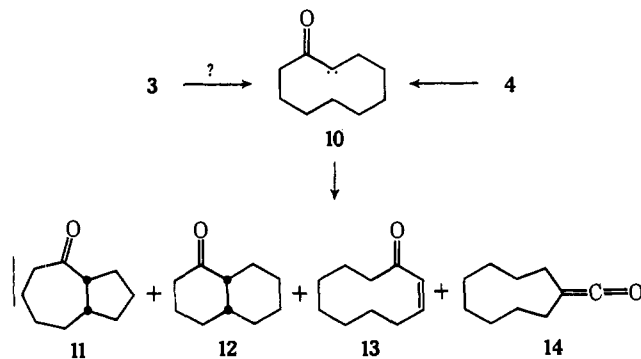
(10) A. C. Cope and G. Holzman, *J. Amer. Chem. Soc.*, **72**, 3062 (1950); H. L. Goering, A. C. Olson, and H. H. Espy, *ibid.*, **78**, 5371 (1956). We are grateful to Professor H. L. Goering for sending us an authentic sample of the 2,4-dinitrophenylhydrazone of **11**.

(11) C. D. Gutsche and H. H. Peter, *ibid.*, **77**, 5971 (1955).

(12) R. G. Carlson and J. H. Bateman, *J. Org. Chem.*, **32**, 1608 (1967). We are grateful to Professor R. G. Carlson for providing us with spectral data and an authentic sample of **13**.

(13) Cyclononanone was also identified as a very minor product (<1% by vpc) and probably arises from oxidation of the intermediate ketene **14**.

(14) All analytical work was performed with a 0.02 in. \times 50 ft SCOT Carbowax 20M capillary column.

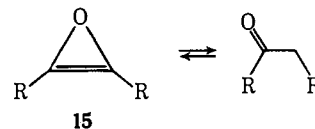


2-one (*cis*- α -decalone) (**12**),¹¹ and *cis*-2-cyclodecenone (**13**).¹²⁻¹⁴ Thermal decomposition of 2-diazocyclodecanone (**4**)¹⁵ under various conditions similarly yielded products **11**, **12**, and **13**, but in remarkably different distribution.¹⁶ The results are summarized in Table I.

Table I. Product Ratios from the Oxidation of Cyclodecyne and the Decomposition of 2-Diazocyclodecanone

Reactants	Conditions	Product ratios, %		
		11	12	13
3 , MCPBA	CH ₂ Cl ₂ , room temp, 2 hr	67	12	21
3 , MCPBA	C ₆ H ₆ , reflux, 2 hr	61	12	27
4	C ₆ H ₆ , reflux, 24 hr	9	5	86
4	Diglyme, reflux, 2 hr	5	3	92
4	Vpc, injection port, 170°	18	12	70

The similarity of product distribution from the reactions of di-*t*-butylacetylene (**1**) and α -diazoketone **2** is consistent with the intervention of α -ketocarbene **5** as a common intermediate. However, the product distribution in the cyclodecyne (**3**) case is vastly different from that in the 2-diazocyclodecanone (**4**) case and suggests the absence of a common intermediate. It can be seen in Table I that **3** affords primarily 1,5- and 1,6-transannular insertion products **11** and **12**, respectively, whereas **4** affords primarily 1,2-insertion product **13**.¹⁷ Oxirenes **15** may be intermediates in the peracid oxidation of acetylenes and precursors to α -ketocarbenes.^{2,18,19} It is conceivable that in the



cyclodecyne case the derived oxirene may be the intermediate leading to products **11** and **12** via a concerted transannular reaction.^{2,17} Since this oxirene would have fewer degrees of freedom than ketocarbene **10** derived from diazoketone **4**, the predominance of **11**

(15) A. T. Blomquist and F. W. Schlaefer, *J. Amer. Chem. Soc.*, **83**, 4547 (1961); M. Regitz and J. Rüter, *Chem. Ber.*, **102**, 3877 (1969).

(16) Variable yields of cyclononanone were also observed. See C. D. Gutsche and J. W. Baum, *J. Amer. Chem. Soc.*, **90**, 5862 (1968), and references cited therein.

(17) For a review of transannular carbene reactions in medium-sized rings see A. C. Cope, M. M. Martin, and M. A. McKevey, *Quart. Rev. Chem. Soc.*, **20**, 119 (1966).

(18) Oxirenes may possess antiaromatic properties. See R. Breslow, *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968), and previous publications cited therein.

(19) The absence of an oxirene intermediate was demonstrated in the solution photolysis and thermolysis of ¹⁴C-labeled azibenzil: V. Franzen, *Justus Liebigs Ann. Chem.*, **614**, 31 (1958). On the other hand, the intervention of oxirenes has been established in the gas-phase photolysis of two ¹³C-labeled α -diazoketones: I. G. Csizmadia, J. Font, and O. P. Strausz, *J. Amer. Chem. Soc.*, **90**, 7360 (1968).

and **12** in the cycloalkyne case may reflect a smaller negative entropy of activation for transannular insertion relative to the same reaction of **10**. Alternatively, since the conformations of cycloalkyne and diazoketone are obviously different, we may be observing the reactions of two conformationally different ketocarbenes with an entropy factor favoring transannular insertion in the former case. (This would assume of course that subsequent reaction is faster than conformational changes.) Studies are currently in progress to further elucidate the mechanistic implications of these observations.

(20) National Defense Education Act Trainee, 1969–1970.

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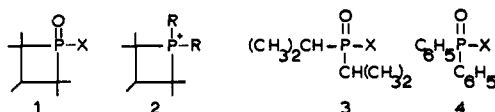
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Inhibition of Rate of Displacement at Phosphorus Due to Angle Strain in a Four-Membered Ring. A Tool to Distinguish Mechanism¹

Sir:

The angle strain present at phosphorus in small rings is known to produce large accelerations in rates of displacement at phosphorus.² These results are important evidence for displacement through a pentacoordinate intermediate in which pseudorotation is possible. We now report two cases in which the same structural effect results in a very large inhibition in rate of displacement at phosphorus. The contrasting effects enable discrimination between associative displacement through a pentacoordinate intermediate and an SN₂-like direct displacement mechanism.

There has recently been great interest in the four-membered ring (**1**) which is readily available.³ This ring system has a twofold effect. (1) The four α -methyl groups provide considerable steric hindrance. (2) The C–P–C angle is approximately 83°. This provides a considerable driving force for formation of pentacoordinate intermediates in which strain can be released.² These effects appear in the esters **1** (X = OCH₃, OC₂H₅) which undergo alkaline hydrolysis with displacement at phosphorus⁴ at a rate which is com-



parable to much less hindered phosphinates^{4,5} and 10⁵ faster than the similarly substituted (but probably

(1) (a) Research supported by Grants GP-8142 and GP-13453 from the National Science Foundation and by Grant AM-12743 from the National Institutes of Health. (b) Some of the results on which this communication is based are found in the Ph.D. Theses of Robert D. Cook (1967) and Paul S. Ossip (1968), University of California, Los Angeles, Calif.

(2) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(3) (a) J. J. McBride, E. Jungermann, J. F. Killheffer, and R. J. Clutter, *J. Org. Chem.*, **27**, 1833 (1962). (b) The structure has been confirmed by determination of the crystal structure: D. D. Swank and C. N. Caughlan, *Chem. Commun.*, 1051 (1968); M. Haque and C. N. Caughlan, *ibid.*, 1228 (1968).

(4) P. Haake, R. D. Cook, W. Schwarz, and D. R. McCoy, *Tetrahedron Lett.*, 5251 (1968).

(5) P. Haake, C. E. Diebert, and R. S. Marmor, *ibid.*, 5247 (1968).

more hindered) di-*t*-butylphosphinate.⁶ Retention of configuration in displacement by hydroxide on phosphonium ions (**2**) has been observed.^{7,8}

We have observed inhibition of rates of displacement at phosphorus in the acid-catalyzed hydrolysis of phosphinamides and in the solvolysis of acid chlorides. The acid-catalyzed hydrolysis of **1**, **3**, and **4** [X = N(CH₃)₂] were studied in 20% dioxane–H₂O.⁹ The progress of the reaction was monitored by the decrease in intensity of the N(CH₃)₂ doublet in the nmr spectra. The relative second-order rate constants ($v = k[\text{H}^+][\text{amide}]$) at 30° for those phosphinamides were $k(\mathbf{1}):k(\mathbf{3}):k(\mathbf{4}) = 1.5 \times 10^{-3}:1:3.8 \times 10^2$. Yet the ethyl ester of **1** undergoes alkaline hydrolysis at about the same rate as esters of **4**^{4,5} and considerably faster than the ethyl ester of **3**.⁶

We have also studied the solvolysis of acid chlorides. Rates were measured in CF₃CO₂H and in 41% aqueous acetone. In these two solvents *t*-butyl chloride solvolyzes at nearly identical rates, so they are solvents of approximately equal ionizing power but vastly different in nucleophilicity.¹⁰ The relative rates for the acid chlorides of **1** and **3** are: $k(41\% \text{ acetone-water})/k(\text{CH}_3\text{CO}_2\text{H}) = 2000$ for **3** (X = Cl) but only 10 for **1** (X = Cl). The transition state for solvolysis of **1** therefore has considerable dissociative character. However, in both chlorides the transition state for hydrolysis appears to involve some nucleophilic participation by water. The four-membered ring chloride (**1**, X = Cl) hydrolyzes 6.5×10^4 times more slowly than **3** (X = Cl) in 41% aqueous acetone—a large rate effect in the same direction as observed in the acid-catalyzed hydrolysis of amides.

The amide hydrolysis has been shown to proceed by an A₂ mechanism involving nucleophilic attack by water on the N-protonated amide.⁹ Therefore, in both the chloride and amide reactions there is nucleophilic attack by water on phosphorus species with very labile bonds: P–Cl and P–N⁺R₃, respectively. The rate inhibition due to the four-membered ring indicates increased strain in the transition state; this requires that the preferred geometry has entering and leaving groups colinear with the phosphorus atom. A reasonable conclusion is that in these reactions direct displacements, similar to SN₂ reactions, are involved.

The problem of intermediates in displacement at phosphorus has often been in a confused state. The transition states for all but a few reactions at phosphorus¹¹ appear to have considerable associative character. Since phosphorus is known to form many stable pentacoordinate compounds,¹² transition states in associative reactions would be expected to be stabilized to at least a small extent by pentacoordinate character and intermediates generally may be involved.

(6) W. Hawes and S. Trippett, *Chem. Commun.*, 577 (1968). The four-membered ring should cause the α -methyl groups to shield phosphorus considerably less in **1** than in di-*t*-butylphosphinates.

(7) W. Hawes and S. Trippett, *ibid.*, 295 (1968).

(8) K. E. DeBruin, G. Zon K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7027 (1969).

(9) P. Haake and T. Koizumi, unpublished results. The solvent isotope effect, entropy of activation, substituent effects, and relative rates to carboxylic amides strongly support an A₂ mechanism involving nucleophilic attack by water on the N-protonated amides.

(10) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956).

(11) P. Haake, P. S. Ossip, and D. A. Tyssee, unpublished results.

(12) E. L. Muetterties and R. A. Schunn, *Quart. Rev. Chem. Soc.*, **20**, 245 (1966).