Catalytic Ring Opening of Substituted 2-Oxetanones

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Salts or complexes of Pd(II) promote the cleavage of the *C*-alkyl–oxygen bond (1–4 bond) of substituted 2-oxetanones **1** (β-lactones). In aprotic medium, 4-vinylic substituted **1** are isomerized to butadiene carboxylic acids **2** whereas in alcohol the addition of one molecule of solvent takes place. The overall process represents an easy synthetic route to unsaturated ether acids **3** or ether esters **4**. The addition of ligands has a major effect both on the nature of the products formed and on the rate of the reactions. A mechanism involving the formation of unstable η^3 allylic intermediates is proposed to account for the observed results.

The versatility of 2-oxetanones (β-lactones) is considerable and has made them an attractive class of synthetic intermediates[1] as well as a thoroughly investigated family of monomers yielding, under the influence of a wide variety of catalysts, high molecular weight polyesters,[2] some of which are biodegradable.[3]

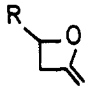
From a mechanistic point of view, the most distinctive feature of these strained cycles is a duality of ring opening; indeed, they can undergo either a classical *C*-acyl–oxygen cleavage or *C*-alkyl–oxygen bond breaking.[4]

The latter type of ring opening has interesting theoretical and synthetic potentialities; we have already reported the catalyzed isomerization of some substituted β-lactones[5] and the goal of this paper is to sum up additional results obtained in this field and to propose a mechanism for the described reactions.

Results

Most of the substituted lactones **1a–i** (Chart I) were synthesized by the addition of ketene to the appropriate aldehyde (see Experimental Section) and the resulting lactones **1** treated with catalytic amounts of group 1B, 6B, and 8 metal complexes.

Chart I. 4-Substituted 2-Oxetanones Submitted to Catalytic Ring-Opening Conditions



1 a-j

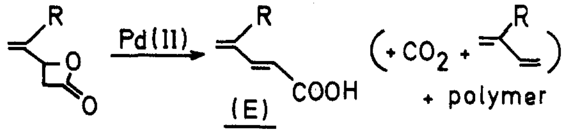
	R		R
a	$-H$	f	$-CH=CH_2$
b	$-CH_3$	g	$-C(CH_3)=CH_2$
c	$-C_2H_5$	h	$-CCl=CH_2$
d	$-CH_2Br$	i	$-C\equiv CH$
e	$-CCl_3$	j	$-CH_2-S-C_{16}H_{33}$

It appeared that, in general, a large majority of the metals used favor polymerization pathways. Carbonyls of Ni, Co, Fe, W, and Cr(0) show no particular activity. However, mostly with some d^6 or d^8 metals such as Ir(III), Rh(III), Pt(II), and Pd(II), monomeric isomerization compounds **2** are obtained with very variable yields but, except for the palladium-catalyzed reactions, the yield of **2** is always poor (below 35%).

The most specific catalysts are Pd(II) derivatives: $PdCl_2$, $Pd(OAc)_2$, and $PdCl_2\cdot 2PhCN$. Although some η^3-allylic species such as η^3-allylpalladium triethyl phosphite chloride (prepared in situ by a 2:1 addition of triethyl phosphite to the dimeric η^3-allyl chloride) also show some catalytic activity, they are in no way superior to the salts, so we concentrate here on the results obtained with the latter in protic and aprotic solvents. Because of its superior activity and solubility, and unless stated otherwise, Pd(II) acetate is used as the standard catalyst throughout this work.

1. Reactions in Aprotic Medium (C_6H_6, $CHCl_3$, CH_2Cl_2 ...). At room temperature, the vinyl lactones **1f** (VPL) and **1g** are isomerized to the corresponding butadiene carboxylic acids **2f** and **2g** (Scheme I) under the influence of catalytic amounts of Pd(II) salts. Molar ratios of Pd(II) to lactones were kept in between 0.01 and 0.05, depending on solubilities.

Scheme I



1f,g 2f,g

The yield of **2** (50–80%) depends on the selected conditions and the reaction rates increase with the solvent polarity. The addition of small amounts of sodium borohydride to the reaction mixture (in benzene or pure, with a ratio of palladium to borohydride varying from 0.1 to 1) did not show any major effects on the reaction rate, as it could be expected to if hydrido complexes were implicated in a slow step of the catalytic process.

Saturated lactones (**1a–e** and **1j**) under the same conditions are slowly polymerized to oligomers seemingly identical with those described by Saegusa,[6] i.e., polyesters with unsaturated acid termini, as shown by ir spectroscopy. On the other hand, **1h** and **1i** are surprisingly stable and have to be heated at 50 °C for several hours to be oligomerized, with almost no unsaturated acid formed. The deactivation of the vinyl group, or its substitution by an acetylenic function, is thus sufficient to prevent any carbon–oxygen bond cleavage. Unsaturated five-membered isomers of **1f**, α- and β-angelica lactones, remain also unaffected under the same catalytic conditions.

The addition of higher or stoichiometric amounts of metal salts is impossible because of their poor solubility; moreover, side reactions, mostly oligomerizations of **2**, become important when such noncatalytic conditions are used.

With the object of unambiguously checking the position of the migrating hydrogen in the isomerizing cycle, the α,α-dideuterated lactone **1k** has been synthesized from ketene-d_2 and acrolein and submitted to a catalytic ring opening (Scheme II).

The reaction is clean and shows that the migrating atom is a proton α to the carbonyl; H_β in the *non*deuterated acid appears as a doublet of doublet[7] centered at 7.30 ppm (100 MHz) whereas in **2k** the coupling with H_γ (doublet centered at 7,30 ppm, ^3J = 10 Hz) is exclusively observed. Besides, neither is

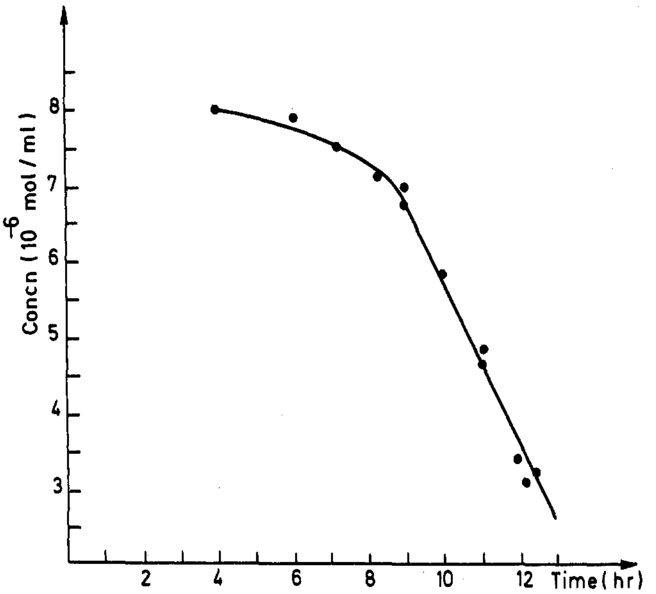
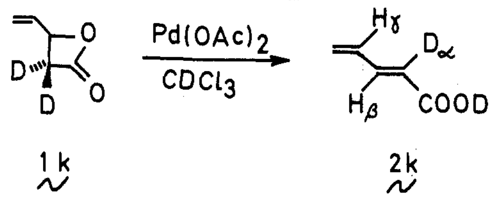


Figure 1. Rate of VPL ring opening as a function of time. Conditions: 25 °C in CH_2Cl_2 with a ratio $Pd(OAc)_2$: VPL 0.02.

Scheme II



H_α (doublet in the protonated molecule, δ 5.91 ppm, $^3J = 15.8$ Hz) nor any acidic proton present. After the addition of a drop of water, the last one shows up at about 11.5 ppm.

No isotopic effect was observed when equimolecular mixtures of **1f** and **1k** were submitted to ring-opening conditions.

2. Effects of Ligands on the Catalysis. The addition of tertiary phosphines or phosphites to the system causes a significant increase in the reaction rate (see kinetics) as well as major changes in the nature of the compounds formed.

For instance, if r represents the molar ratio of the added ligand to $Pd(OAC)_2$, the addition of n-Bu_3P, with $r = 1$, to a methylene chloride solution of VPL leads to an important evolution of CO_2 with formation of polymers (≈50%) whereas polymerization prevails (>80%) when $2 < r < 4$. It is of definite preparative interest that the addition of trimethyl phosphite (TMP) leads to an almost quantitative isomerization into **2f** when $3 < r < 4$; when $r < 3$, the loss of CO_2 remains important (20–50%).

Other ligands (triphenylphosphine, phosphite, or -arsine) gave intermediate results of those described above, although no straightforward correlation appears between basicity or bulkiness of the ligands and the products formed. **2f** and a catalytic amount of triphenyl phosphite do not appreciably react in methylene chloride, as checked by VPC. However, a further addition of palladium acetate to the mixture yields reaction products whose concentration is proportional to the amount of added salt. The relatively high ratio of phosphite to metal is thus probably due to a partial neutralization of the former by the acid formed from the catalyst.

3. Reactions in Protic Solvents. At room temperature in methanol or ethanol, in the presence of a catalytic amount of $PdCl_2$, the ring opening of the unsaturated lactones **1f–i** smoothly takes place with the formation of ether acids **3** (Scheme III). The yield of **3** is above 80%. If the crude mixture of **3** is refluxed for a few hours, a quantitative esterification takes place and the overall process constitutes an easy synthetic route to the polyfunctional molecules **4**.

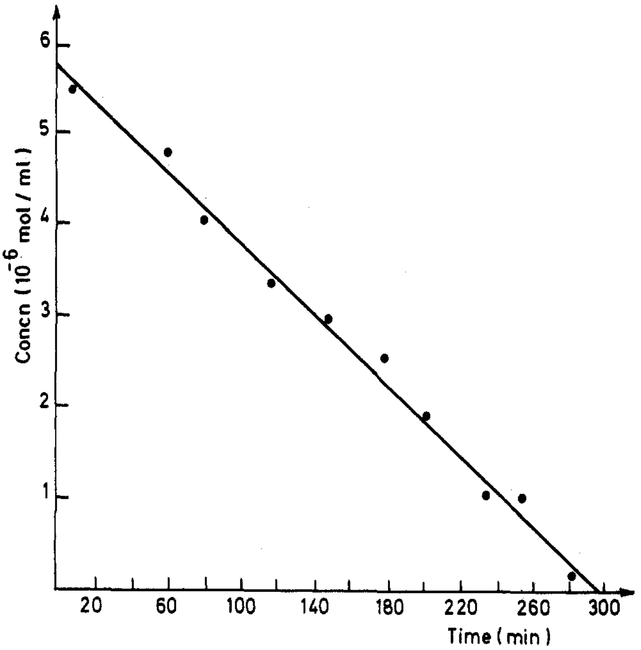
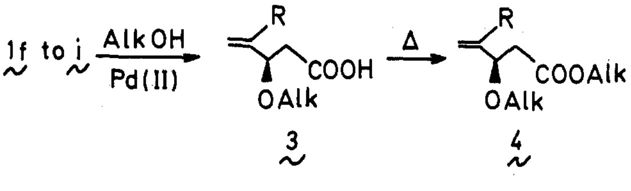


Figure 2. Same as Figure 1 but after addition of trimethyl phosphite (TMP). Conditions: 0 °C in CH_2Cl_2, ratio $Pd(OAc)_2$: VPL 0.02 and TMP: Pd(II) 4.

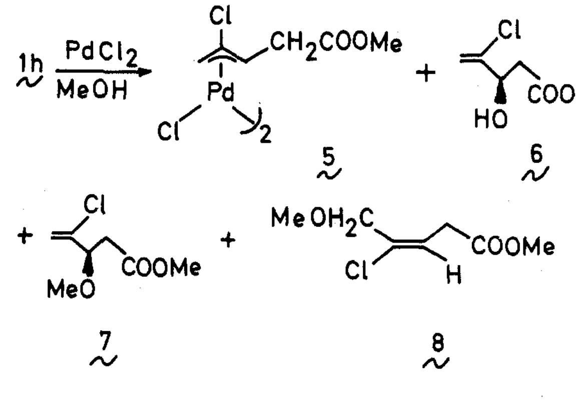
Scheme III



Isolation of the acid **3** renders a further esterification noncatalytic in palladium and a precipitation of Pd(0) is then observed. Thus it seems that metal complexation is different in the crude mixture and in a solution of previously isolated **3**, where a competition between esterification and formation of η^3-allylic species probably occurs. It was checked that under the same catalytic conditions, neither was **3** nor **4** formed when **2f** was reacted with methanol at 25 or at 60 °C. In the latter case, **2f** methyl ester is formed (as identified by comparison with an authentic sample). That allows the ruling out of **2f** as being an intermediate in the formation of **3**.

Deactivation of the vinyl function in **1h** is reflected by a poor reactivity at room temperature and by a competitive ring opening with breaking of either C-alkyl or C-acyl–oxygen bonds and formation of **6** and **7** in about 35 and 45% yields, respectively, at 50 °C (Scheme IV).

Scheme IV



In addition, about half of the metal is recovered as a η^3-allylic species **5**, and an estimated 7–10% of **8** is identified as a product of the reaction.

In the same conditions, no alcohol ester corresponding to **6** is ever observed with **1f** or **1g**; that rules out a possible formation of **6** by a reaction of **1h** with the water resulting from esterification of the acid. It was checked that under the conditions used, **6** was neither transformed into **7** nor was **7** into **8** in an appreciable amount. Moreover, **5** is not a catalyst for the ring opening of β-lactones.

4. Kinetics of the Reaction. The rate of the VPL ring opening in CH_2Cl_2 under the influence of $Pd(OAC)_2$ has been studied at 25 °C with no added ligand (Figure 1), and at 0 °C after the addition of TMP, $r = 4$ (Figure 2). In both experiments the ratio of Pd(II) to VPL was 0.02. An induction period of several hours is observed when the Pd(II) salt alone is used but *not* if any TMP is added to the sample.

In both cases (but only after an induction time of about 7 h at 25 °C), the disappearance of the lactone is independent of its concentration in the solution. Such an observation is characteristic of a process with a rate-controlling active catalytic species. Any determination of the reaction order with respect to the metal was hampered by solubility problems. Nevertheless, the above results also show that the reaction is not autocatalytic in the sense that the products formed have little influence on the reaction rate. Furthermore, the initially added **2** (alone, with $PdCl_2$ or as a Pd(II) salt) has no influence on the induction time and thus **2** is not a co-catalyst. After consumption of the initial lactone, isomerization of some freshly added monomer immediately starts again although at a slightly different rate.

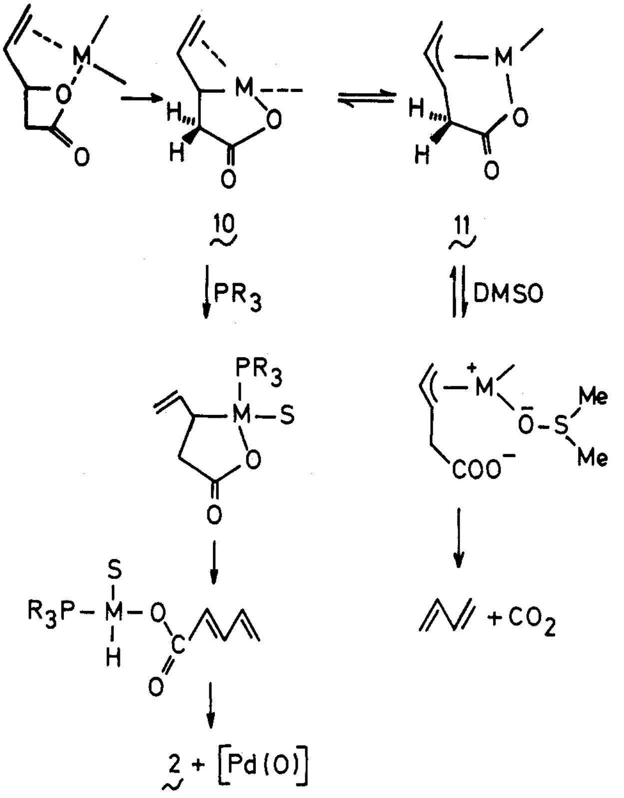
Discussion

The experimental data indicate that we are dealing with a true catalytic process and that an unsaturated vinyl group β to the carbonyl is necessary for its observation. Its replacement by a chain containing an heteroatom susceptible to assist the ring opening[8] such as in **1j** leads to an inert compound as far as our catalytic system is concerned.

On the other hand, it is well known that palladium derivatives form reactive π complexes with olefins.[9] The examination of molecular models of VPL (**1f**) strongly favors a bidentate type of complexation with the endocyclic oxygen acting as the second site of coordination. The complexation of the endocyclic oxygen is also substantiated by the finding that ring opening of β-lactones on aluminum alkoxide catalysts takes place through coordination of the same oxygen to the Lewis acid site.[10] Thus, it is reasonable to propose on the basis of favorable steric factors a bidentate type of complexation of the monomer.

The induction period observed could be explained by a slow reduction of the catalyst by the olefinic lactone to a palladium(0) complex which then reacts with another lactone molecule by oxidative addition to give **10** or **11**. The latter quickly stabilize to either an unsaturated acid **2** or a polymer or loses CO_2, depending upon the experimental conditions (Scheme V).

Scheme V



Examples are known where π-allyls possessing an α activated methylene are easily transformed into conjugated molecules when bases (e.g., amines) are added to the system.[11] Not only does the opening of the lactone cycle ipso facto generate a base (the carboxylate anion) but it does so close to the activated methylene. The abstraction of one hydrogen liberates an acyldiene which obviously, if the reaction is to proceed catalytically, does not effectively compete with the pure lactone for coordination to the metal. We have indeed confirmed that **2f** reacts more slowly than the lactone itself with the catalysts and mostly forms insoluble oligomers after several days.

The proposed mechanism is supported by the stability to our catalysts of the otherwise reactive acetylenic lactone **1i**; the spatial factors for a favorable coordination (bidentate) and the possibility of formation of π-allylic derivatives both lack in this case. The deep red color immediately observed after the addition of the highly reactive 1,5-cyclooctadienenickel(0) to a benzene solution of VPL is also characteristic of a π-allyl path. Although then another reactional pathway (mostly polymerization) is favored over the formation of **2f** ($\approx$10%), it clearly hints that the ability to form such species could be determinant.

Moreover, the precipitation in some frozen-out samples of a highly unstable black compound which quickly evolves CO_2 upon handling is consistent with a structure such as **10.** Since no isotopic effect was observed, the insertion step with the breaking of the lactone cycle and the formation of **10** is probably rate determining.

The quantitative evolution of CO_2, observed in good coordinating aprotic solvents (DMF, Me_2SO) is explained by a poor solvation of the carboxylate anion, and that promotes reaction through the carboxylate (evolution of CO_2).

Alcohols, which stabilize the developing positive charge when the cycle opens up, predominantly give nucleophilic substitution products (ether acids **3**). The influence of phosphites or phosphines is less clear. They surely compete for coordination, as indicated by the various colorations observed with different ratios of metal to ligands, and significantly reduce the induction time; such an effect has previously been noted.[12] However, the competition for coordination (e.g., between an olefinic bond and the phosphorus atom) should also promote rearrangement through the σ-allyl and/or stabilize some metal hydride intermediate. The formation of allylic cations such as those previously proposed as reactive intermediates in nucleophilic substitutions[13] of η^3-allyl enhances the electrophilic character of the species; that would favor an attack of the carboxylate ion on a methylenic proton[14] and thus cannot be ruled out.

Experimental Section

NMR spectra were recorded on Varian T-60 or HA-100 spectrometers with chemical shifts measured in parts per million (δ) downfield from Me_4Si or HMDS. The abbreviations for multiplicity employed are s = singlet, d = doublet, a = quartet, pt = pseudotriplet, m = multiplet.

Ir spectra were obtained neat (NaCl disks) on Perkin-Elmer 21 or 125 instruments.

VPC were carried out on a Varian 1700 (analytical) or on a Varian 2800 (preparative) instrument equipped with thermal conductivity detectors. The analytical columns used were 6 × 0.25 in., 15% SE-30 on Chromosorb W 30–60 and the preparative columns 16 × 0.75 in., 15% Carbowax on Cellite 30–60.

Boiling points are uncorrected.

Kinetic Runs. The disappearance of the C═O stretching vibration of VPL (1825 cm^{-1}) is plotted against a calibration curve and against the appearance of the absorption of the conjugated acid (1695 cm^{-1}) and of the polyester (1735 cm^{-1}).

Preparation of Lactones. 2-Oxetanone (**1a**) was purchased from Fluka AG and used as such. 4-Bromomethyl-2-oxetanone (**1d**) was prepared according to ref 15. 4-Trichloromethyl-2-oxetanone (**1e**) was prepared according to ref 16. For 4-vinyl-2-oxetanone (**1f**, VPL), see ref 17. For γ-(*n*-hexadecylthio)-β-butyrolactone (**1j**), see ref 9.

The other lactones (**1b**, **1c**, **1g**, **1h**, and **1i**) were prepared by cycloaddition of ketene to the appropriate aldehyde with boron trifluoride etherate as catalyst according to the following general description.

A 2% solution of the catalyst in dry diethyl ether was kept under nitrogen at −20 to −40 °C. Ketene was then bubbled in and the aldehyde added at approximately equimolecular rate via a perfusor.

Every hour, some fresh catalyst was added, usually half the initial amount, and after all the aldehyde was in, the flow of ketene was continued for about 15 min, and finally the solution was flushed with nitrogen. Enough triethylamine to neutralize the catalyst was then slowly introduced into the cooled solution and after removal of the solvent, the mixture quickly distilled under vacuum. A second distillation on toluene 2,4-diisocyanate (drying agent) gave the pure lactone.

4-Methyl-2-oxetanone (1b) from acetaldehyde, 80%: bp 55–57 °C (18 mm); ir (neat) 1828 cm^{-1} (C═O); NMR (neat, 60 MHz, HMDS) δ 1.40, d, 3 H, $^3J = 5.5$ Hz (CH_3); (AB) H_A 2.90, H_B 3.48, $^2J = 16.4$ Hz (CH_2); (X) 4.30–4.80, m, 1 H.

4-Ethyl-2-oxetanone (1c) from propionaldehyde, 75%: bp 53–55 °C (15 mm); ir (neat) 1824 cm^{-1} (CO); NMR (neat, 100 MHz, Me_4Si) δ 1.0, t, 3 H, $^3J = 7.2$ Hz; 1.76, m, 2 H (CH_2); (AB) H_A 3.16, H_B 3.61, $^2J = 16.5$ Hz; (X) 4.50, m, 1 H.

4-Isopropenyl-2-oxetanone (1g) from methacrolein, 70%: bp 36–38 °C (3 mm); ir (neat) 1825 (CO), 1660 cm^{-1} (C═C); NMR (neat, 100 MHz, Me_4Si) δ 1.77, weakly coupled d, 3 H; (AB) H_A 3.24, H_B 3.66, $^2J = 16.5$ Hz; (X) 4.9 pt, 1 H, $J = 5.5$ Hz; 5.0–5.2, 2 H, olefinic protons, $J = 1.2$ Hz (═CH_2).

4-(α-Chlorovinyl)-2-oxetanone (1h) from α-chloroacrolein, 45%: bp 53–56 °C (5 mm); ir (neat) 1845 (CO) and 1624 cm^{-1} (C═C); NMR (neat, 60 MHz, HMDS) δ (AB) 3.5, 2 H, $^2J = 16.2$ Hz (CH_2); (X) 5.0, pt, 1 H, $J = 5.0$ Hz; 5.46–5.62, $^2J = 2.4$ Hz (═CH_2).

4-Ethynyl-2-oxetanone (1i) from propynal was prepared according to ref 18.

The catalyst was not destroyed by the addition of triethylamine, which leads to an almost explosive polymerization of the monomer, but instead, after removal of the solvent, the cooled reaction mixture was quickly washed twice with cold water, dried on Drierite, and distilled: bp 34–36 °C (3 mm); 40%; ir (neat) 3330 (≡CH), 2145 (C≡C), and 1830 cm^{-1} (CO); NMR ($CDCl_3$, 100 MHz, HMDS) δ 2.97, d, 1 H, $^3J = 2.0$ Hz (≡CH); (AB) 3.71, $H_A = 3.54$, $H_B = 3.87$, $^2J = 16.7$ Hz; (X) 5.0–5.14, m, 1 H. Irradiation on the acetylenic proton gives the pure H_x system, four sharp lines.

4-Vinyl-2-oxetanone-*3-d*$_2$ (1k). The deuterated ketene was prepared by cracking of acetone-d_6. By comparison with its nondeuterated analogue, the complete disappearance of the CH_2 AB system is observed whereas CH X appears as a large doublet at 4.84 ppm, $^3J = 6.5$ Hz. The vinylic part of the molecule remains unchanged.

Catalysis. The reactions were performed under a nitrogen atmosphere; the solvents used were dried and kept under an inert atmosphere to ensure reproducible results, although no major differences were observed when no such precautions were taken. The lactones were added to the catalyst solution through a septum (catalytic ratio of 0.01–0.05) and the reaction followed as described, by VPC, ir, and NMR.

Ring-Opening Catalysis of 1. The conditions used for the isomerization of **1f** are typical.

A. With the Palladium Salt Alone (No TMP Added). $Pd(OAc)_2$ (15 mg) was added to a solution of 1 ml of VPL in 2 ml of methylene chloride. The mixture was stirred overnight at room temperature under a nitrogen atmosphere, and after complete disappearance of the lactone (ir), the solvent was removed under vacuum and the residue extracted three times with 5 ml of hot pentane or hexane. Upon cooling, needles of **2** precipitate, isolated yield 50%. The acid can be further sublimed under vacuum for analytical purpose, mp 72 °C, NMR as described in ref 17.

B. With Trimethyl Phosphite–Pd(OAc)$_2$, *r* = 3.5. The overall procedure is the same as described above; 28 μl of TMP was added to the lactone solution through a septum and after 0.5 h, the solution worked up as described, isolated yield 80–90%.

(*E*)-3-Methyl-1,3-butadiene-1-carboxylic Acid (2g): NMR ($CDCl_3$, 100 MHz, Me_4Si) δ 12.50, s, 1 H (COOH); 1.90, t, 3 H, $^4J = 2.2$ Hz (CH_3); 5.40, m, 2 H (═CH_2); 7.45, d, 1 H, $^3J = 15.8$ Hz (H_2); 5.89, d, 1 H, $^3J = 15.8$ Hz (H_1).

3-Ethoxy-4-pentenoic Acid (3f), R = H; Alk = C$_2$H$_5$. See ref 5.

3-Methoxy-4-pentenoic Acid Methyl Ester (4f, R = H; Alk = CH$_3$), bp 68–70 °C (15 mm), 85%.

Anal. Calcd for $C_7H_{12}O_3$: C, 58.33; H, 8.33. Found: C, 58.2; H, 8.2.

Ir (neat) 1747 (CO_2CH_3) and 1645 cm^{-1} (C═C); NMR ($CDCl_3$, 60 MHz, HMDS) δ 3.60, s, 3 H ($COOCH_3$); 3.80, s, 3 H (OCH_3); 2.5, 2 H, $^2J = 12.5$ Hz (CH_2AB); 3.78–4.13, m, 1 H (CH X); 5.06–6.0, m, 2 H (═CH_2 ABC).

3-Methoxy-4-methyl-4-pentenoic Acid Methyl Ester (4g, R = CH$_3$): ir (neat) 1742 (COOMe) and 1650 cm^{-1} (C═C); NMR, see **4f** except for the olefinic part, 1.60, d, 3 H, $J = 1$ Hz (═C–CH_3); 4.91, m, 2 H (═CH_2).

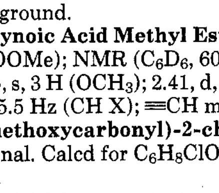
3-Methoxy-4-chloro-4-pentenoic Acid Methyl Ester (7). Anal. Calcd for $C_7H_{11}ClO_3$: C, 47.05; H, 6.16. Found: C, 47.1; H, 6.3.

Ir (neat) 1632 (C═C) and 1743 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$, 60 MHz, HMDS) δ 3.58, s, 3 H ($COOCH_3$); 3.20, s, 3 H (OCH_3); 2.56, 2 H, $^3J = 6.5$ Hz (isochronous protons) (CH_2 A_2); 4.13, pt, 1 H (CH X); 5.3–5.5, m, 2 H (═CH_2).

3-Hydroxy-4-chloro-4-pentenoic Acid Methyl Ester (6). Anal. Calcd for $C_6H_9O_3Cl$: C, 43.77; H, 5.47. Found: C, 43.5; H, 5.2.

Ir (neat) 3500 (OH), 1740 ($COOCH_3$), and 1640 cm^{-1} (C═C); NMR ($CDCl_3$, 60 MHz, Me_4Si) δ 3.63, s, 3 H ($COOCH_3$); 4.20, s, 1 H (disappears after addition of D_2O) (OH); 2.63, 2 H, $^2J = 16.0$ Hz (CH_2 AB); 4.45–4.70, m, 1 H (CH X); 5.51–5.21, m, 2 H (═CH_2).

4-Chloro-5-methoxy-3-pentenoic Acid Methyl Ester (8): bp 68–72 °C (1 mm), purified by GLC; ir (neat) 1740 (CO_2Me) and 1665 cm^{-1} (C═C); mass spectrum (70 eV) *m/e* 178–180, 143 (M − Cl) base peak, 147 (M − OMe), 119 (M − CO_2Me), 118 [M − CH_2═C(OH)OMe], 105–107 (M − CH_2 − COOMe); NMR (C_6D_6, 100 MHz, HMDS) δ 3.25, s, 3 H ($COOCH_3$); 2.95, s, 3 H (OCH_3); 5.85, t of t, $^3J = 6.8$, $^4J = 1.1$ Hz (H_1); 3.00, d of t, $^3J = 6.8$, $^5J = 1.75$ Hz (H_2, H_3); 3.64, m, 2 H ($H_{4,5}$). The stereochemistry at the double bond is proposed on mechanistic ground.



3-Methoxy-4-pentynoic Acid Methyl Ester (4i): ir (neat) 2300 (C≡C) 1750 cm^{-1} (COOMe); NMR (C_6D_6, 60 MHz, HMDS) δ 3.22, s, 3 H ($COOCH_3$); 2.95, s, 3 H (OCH_3); 2.41, d, 2 H, $^3J = 5.5$ Hz (CH_2 A_2); 3.68, t, 1 H, $^3J = 5.5$ Hz (CH X); ≡CH masked by the OMe.

Bis(1-methylenemethoxycarbonyl)-2-chloro-η^3-allylpalladium Chloride (5). Anal. Calcd for $C_6H_8ClO_2Pd$: C, 24.88; H, 2.76. Found: C, 25.1; H, 3.0.

Ir (KBr) 1731 cm^{-1} ($COOCH_3$), no double bond; NMR (C_6D_6, 100 MHz, Me_4Si) δ 3.74, s, 3 H ($COOCH_3$); 2.86, d, 2 H, $^3J = 6.74$ Hz (CH_2); 2.87, d, 1 H, $^2J = 2.93$ Hz (H anti); 4.07, t, 1 H, $^3J = 6.74$ Hz (H anti); 4.20, d, 1 H, $^2J = 2.93$ Hz (H syn).

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Registry No.—**1b**, 3068-88-0; **1c**, 15890-55-8; **1f**, 7379-74-0; **1g**, 43084-06-6; **1h**, 59092-50-1; **1i**, 59092-51-2; **2g**, 4941-92-8; **4f**, 59092-52-3; **4g**, 59092-53-4; **4i**, 59092-54-5; **5**, 59109-99-8; **6**, 59092-55-6; **7**, 59092-56-7; **8**, 59092-57-8; ketene, 463-51-4; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6; methacrolein, 78-85-3; α-chloracrolein, 683-51-2; propynal, 624-67-9.

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Heterocyclic *N*-Oxides as Synthetic Intermediates. 4. Reaction of Benzyne with 1,3,4-Oxadiazin-6-one 4-Oxides and Related Compounds[1]

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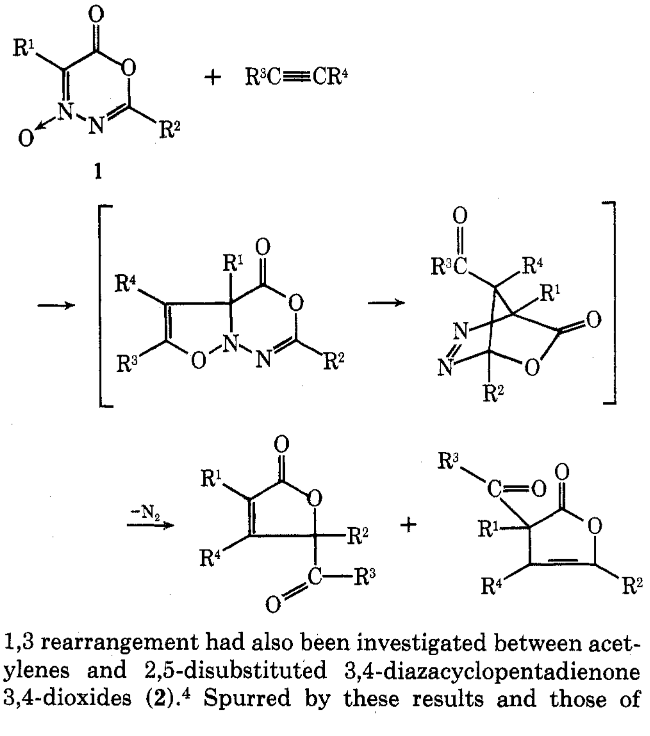
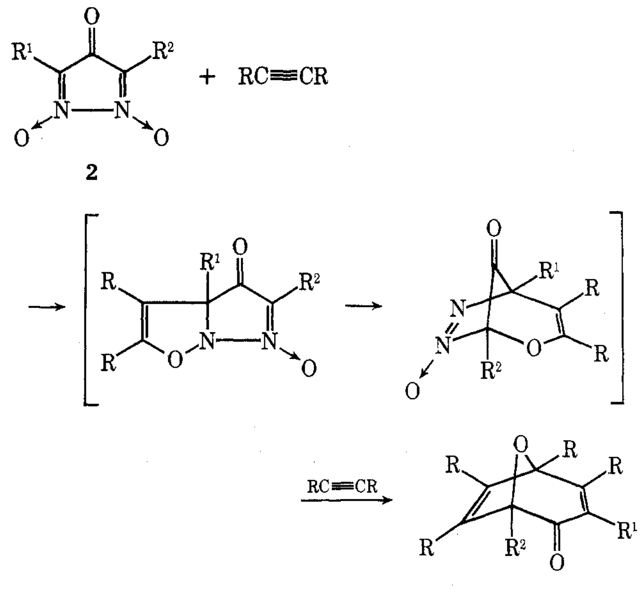
Benzyne, generated from benzenediazonium 2-carboxylate, condenses with 1,3,4-oxadiazin-6-one 4-oxides (**1**) to yield mixtures of substituted benzofurans (**3**) and acylbenzofuranones (**4**). A side product of this reaction, a diaryl homophthalic anhydride (**5**), apparently results from trapping of the benzyne precursor by an intermediate from the primary reaction. A mechanism to rationalize these products is presented and is substantiated in part by isolation of a 1:1 adduct (**10**) from benzyne and 2-methyl-5-phenyl-3,4-diazacyclopentadienone 3,4-dioxide.

It has been shown recently that 1,3,4-oxadiazin-6-one 4-oxides (**1**) react with a variety of acetylenes to produce acylbutenolides.[3] It was proposed that this transformation resulted from a hetero-Cope (3,3) rearrangement within a first-formed 1,3-cycloadduct. A related reaction involving a 1,3 rearrangement had also been investigated between acetylenes and 2,5-disubstituted 3,4-diazacyclopentadienone 3,4-dioxides (**2**).[4] Spurred by these results and those of Abramovitch and co-workers concerning the reactions of other heterocyclic *N*-oxides with benzyne,[5] we now have examined the reactions of this reactive "acetylene" with these two novel heterocyclic systems.


1


2

The oxadiazinone reactions proved to be complex and three main products could be isolated and identified when that heterocycle was heated with benzenediazonium 2-carboxylate as the benzyne precursor. In addition a fourth product was sometimes detected but has not been positively identified. (See Experimental Section.)