Characterization of Intermediates in the Reaction of Ozone with Di-*tert*-butylacetylene. A Novel Pivaloylating System[1]

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Received April 21, 1981

Reaction of di-*tert*-butylacetylene (**1a**) with ozone in $<$-40 °C aprotic solvents upon warming leads to pivalic anhydride, pivalil, and pivalic acid, with evolution of isobutane, isobutene, carbon dioxide, and carbon monoxide. Spectral and chemical evidence indicated the presence of at least two labile intermediates in the reaction. Ozonolysis of the alkyne in the presence of compounds containing a hydroxyl function led to their pivaloyl derivatives with incorporation of both *tert*-butyl groups, probably via fragmentation of an adduct of ROH to an intermediate carbonyl oxide.

Introduction

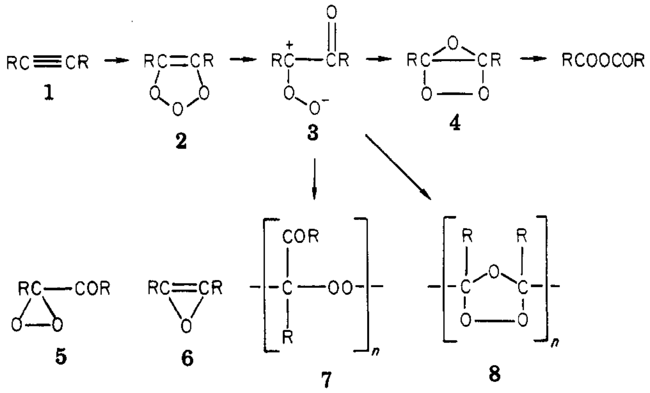
The reactions of ozone with organic compounds is a subject of sustained interest from mechanistic, synthetic, and environmental aspects.[2,3] The classic reaction of ozone with alkenes has received the lion's share of attention and has been the subject of lively controversy over the years.[2] The less-studied reaction of ozone with alkynes usually leads to mixtures of the corresponding dione and anhydride, along with acids resulting from cleavage of the triple bond.[4] These products can be accomodated by modifications[4] of the Criegee mechanism for olefins (Scheme I), although interesting oxygen heterocycles such as **5** and **6** may also play a role in the reactions.

We carried out a study of the ozonolysis of di-*tert*-butylacetylene (**1a**) in anticipation that the bulky alkyls might stabilize reaction intermediates, and with the hope that ozone and a hindered alkyne might lead to **6a** by analogy to the formation of epoxides from ozone and hindered alkenes.[5]

Results

Solutions of **1a** (0.008–1.2 M) in aprotic solvents at −30 to −78 °C exposed to a stream of ozone (<6% in oxygen), followed by removal of the excess ozone with a stream of nitrogen, gave clear, pale yellow solutions whose properties were unchanged even after several days at −78 °C. If the solutions were allowed to warm, an exothermic reaction ensued around 0 °C with vigorous gas evolution. Chromatographic separation of the ozonolysis products revealed pivalil as the major, yellow component (IR, NMR) in all but one case, together with more variable amounts of pivalic acid and its anhydride (Table I, runs 1–13). There was no obvious correlation between yields and solvent properties. Chromatographic analysis of the evolved gases in one case (run 7) showed the presence of carbon dioxide, carbon monoxide, isobutene, and isobutane, whose relative amounts decreased in the order given. These products presumably account for the mass defect in the other runs as well. No oxygen was detected among the evolved gases in run 7.

Scheme I[a]



[a] 1a, R = *t*-Bu.

The yield of pivalil was remarkably unresponsive to changes in initial concentration of **1a** (runs 1–4) or the rate of introduction of ozone (runs 5, 6; 8, 9), although in acetone a decreased yield of anhydride was observed with the shorter reaction time. Crude measurements showed that the absorbance at 360 nm of ozonized 0.21 M **1a** in CDCl$_3$ at −55 °C did not change after warming and recooling to this temperature. We first interpreted this result as indicating that pivalil was formed exclusively during ozonolysis.[1] Since dioxetanes commonly have absorption extending into the visible, we scanned the 330–450-nm region in a more careful study with a vacuum-jacketed cell. The spectrum of the ozonized solution (Figure 1) is distinct from the one taken after warming and suggests that some pivalil is formed during the decomposition of the labile intermediate. Similar results were obtained from 0.06 M **1a** in acetone. The spectra in the latter case indicated that no more than half of the pivalil found after warming was present in the cold solution immediately after ozonolysis.

Ozonized solutions of **1a** were virtually inert to nucleophilic reducing agents, except for a curious diversion to some trimethylpyruvic acid (runs 24–26) at the expense of pivalic anhydride. Sodium iodide did react with an intermediate at low temperatures to give additional pivalil

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[1] Presented in part at the Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 24–29, 1980. This work was supported in part at Battelle–Columbus Laboratories by the U.S. Army Research Office under Grant No. DAAG29-78-C-0001.

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0022-3263/81/1946-3997$01.25/0

Table I. Product Distribution from Di-*tert*-butylacetylene and Ozone

					mol/mol 1a of			
run	T, °C	solvent, column	added reagent	$[1]_{t=0}$, M	t-Bu-CO_2H	$(t$-Bu-$CO)_2$	$(t$-Bu-$CO)_2O$	other
1	−55	$CFCl_3$, A		0.03	0.17	0.29	0.10	
2	−55	$CFCl_3$, A		1.16	0.20	0.32	0.11	
3	−55	acetone, B		0.077	0.40	0.33	0.26	
4	−55	acetone, A		0.34	0.28	0.32	0.28	
5	−55	acetone, B		0.0083[a]		0.35	0.34	
6	−55	acetone, B		0.0083[b]		0.35	0.20	
7	−55	$CDCl_3$, A		0.32	0.22	0.44	0.19	CO_2, CO, i-C_4H_8, i-C_4H_{10}
8	−55	$CDCl_3$		0.17		0.44		
9	−55	$CDCl_3$		0.17		0.44[c]		
10	−78	n-hexane, A		0.37	0.02	0.32	0.12	
11	−78	EtOAc, A		0.28	0.17	0.41	0.16	
12	−45	pyridine, A		0.26		0.32	0.07	
13	−78	CH_2Cl_2, A		0.24	0.19	0.49	0.12	
14	−78	MeOH, A		0.25	0.11	0	0	1.42 t-BuCOOMe
15	−78	EtOH, A		0.21	0.15	0	0	1.22 t-BuCOOEt
16	−78	i-PrOH, A		0.24	0.25	0.22	0.24	0.22 t-BuCOOPr-i
17	−78	$CDCl_3$, A	4 equiv of t-BuCOOH	0.25		0.13	0.95	
18	−78	MeOH, A	1 equiv of TCNE	0.27	0.10	0	0	1.82 t-BuCOOMe
19	−78	MeOH, A	1 equiv of TCNE[d]	0.24	0.10	0	0	1.46 t-BuCOOMe
20	−78	EtOAc, A	1 equiv of TCNE	0.23	0.04	0.73	0.14	
21	−78	EtOAc, A	1 equiv of TCNE[d]	0.25	0.14	0.40	0.14	
22	−78	acetone, A	5 equiv of TCNE	0.21		0.81	0.09	
23	−55	$CDCl_3$, A	2 equiv of Ph_2S[e]	0.29	0.23	0.45	0.13	
24	−55	$CDCl_3$, A	2 equiv of Ph_3P[d]	0.48	0.22	0.45	0.06	0.04 t-BuCOCOOH
25	−78	CH_2Cl_2, A	5 equiv of Ph_3P[d]	0.33	0.19	0.45	0.07	0.05 t-BuCOCOOH
26	−55	$CDCl_3$, A	5 equiv of n-Bu_3P[e]	0.24	0.33	0.49	0.14	ca. 0.05 t-BuCOCOOH
27	−95	MeOH, B	2 equiv of NaI[f]	0.072		0.26	0	
28	−55	$CDCl_3$, A	2 equiv of NaI[f]	0.26	0.46	0.47	0.004	
29	−78	acetone, A	2 equiv of NaI[f]	0.25	0.50	0.52	0	
30	−55	acetone	0.26 equiv of $Cu(OAc)_2$[d,g]	0.77		0.29	0.19	

[a] Flow adjusted to give end point in 4 min. [b] End point in 5 s. [c] Flow rate as for run 8, ozonizer voltage reduced from 118 to 70 V. [d] Reagent dissolved in solvent, added after ozonolysis and N_2 flush. [e] As footnote *d*, but added neat. [f] Reagent in small volume *i*-PrOH containing 5% HOAc. [g] In 1.4 mL of saturated MeOH.

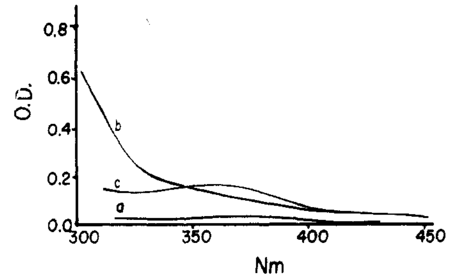

Figure 1. Spectra at −24 ± 4 °C of di-*tert*-butylacetylene: (a) 0.058 M in $CHCl_3$, (b) after partial ozonolysis of the solution, and (c) after warming the ozonized solution to 25 °C and recooling. The final concentration of pivalil was 0.0062 M.

and pivalic acid (runs 28, 29).

Transition-metal compounds are powerful catalysts for the decomposition of 1,2-dioxetanes into two carbonyl fragments.[6] We allowed an ozonized solution of **1a** in acetone to warm in the presence of cupric acetate in the hope of diverting structure **4a** into additional amounts of pivalic anhydride. There was no significant difference in the yield of anhydride from this run (30), however.

Tetracyanoethylene, which can act as an oxygen atom acceptor from carbonyl oxides such as **3**,[4e] had no effect on the product distribution if added after ozonolysis of **1a** but enhanced the yield of pivalil when it was present in solution during the reaction (runs 21, 22).

In contrast to the behavior in aprotic solvents, ozonolysis of **1a** at low temperatures in methanol or ethanol gave *colorless* solutions, which upon warming evolved some gas and showed the unprecedented conversion of *both* alkyl

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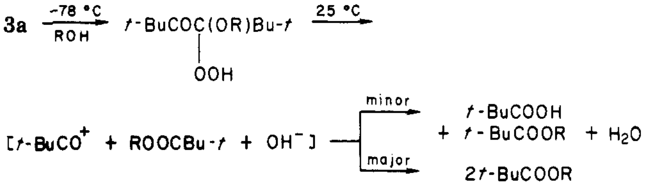
groups into pivalic esters (runs 14, 15). Methyl pivalate was formed only if methanol was present during ozonolysis of the alkyne and not if added subsequent to ozonolysis. The ester yield was further enhanced if TCNE were present during the reaction (run 18). In 2-propanol a superposition of protic and aprotic products distributions was observed (run 16). Pivalic acid itself, added to the reaction mixture before ozonolysis, could be trapped and converted into additional pivalic anhydride (run 17).

In order to study the intermediates in the reaction with hydroxylic solvents, we ozonized **1a** in methanol-d_4 at −78 °C and examined the ^{1}H NMR spectrum at −70 °C. The spectrum differed markedly from the low-temperature spectra of reaction mixtures in $CDCl_3$, which showed incompletely resolved signals in the aliphatic region, and displayed two sharp singlets from products of about equal intensity at δ 1.20 and 0.96, with a shoulder at δ 1.06. After the mixture was warmed to 25 °C, the spectrum (at −70 °C) showed only an enhanced singlet at δ 1.19 ($(CH_3)_3C$-CO). Addition of sodium iodide to the cold solution before warmup led to pivalil in 26% yield (run 27), which indicated that the alkyne framework was still intact in the intermediate we observed at −70 °C. In earlier studies Bailey, Chang, and Kwie showed that ozonolysis of unhindered alkynes in alcohols led to compounds in which the alcohol had added in a formal sense to carbonyl oxide **3**, and that these hydroperoxide adducts decomposed on heating to give equimolar amounts of acid and ester.[7] An analogous mechanism, with the added feature of a fragmentation of the intermediate, can account for our results.



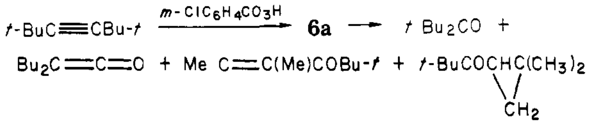
$$\mathbf{3a} \xrightarrow[\text{ROH}]{-78\ ^\circ\text{C}} t\text{-BuCO}\underset{\substack{|\\ \text{OOH}}}{\text{C}}\text{(OR)Bu-}t \xrightarrow{25\ ^\circ\text{C}}$$

$$[t\text{-BuCO}^+ + \text{ROOCBu-}t + \text{OH}^-] \begin{cases} \xrightarrow{\text{minor}} t\text{-BuCOOH} + t\text{-BuCOOR} + H_2O \\ \xrightarrow[\text{major}]{} 2t\text{-BuCOOR} \end{cases}$$

R = Me, Et, *i*-Pr, or *t*-BuCO

Discussion

Ciabattoni and co-workers[8] have proposed the intermediacy of **6a** in the reaction of di-*tert*-butylacetylene and *m*-chloroperbenzoic acid. The compound rearranges by way of the α-keto carbene tautomer to give the products shown in eq 1.

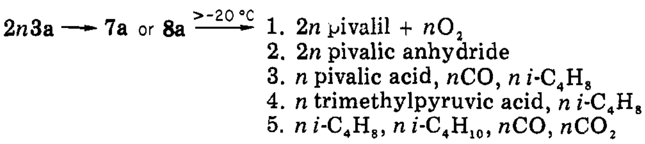


$$t\text{-BuC}{\equiv}\text{CBu-}t \xrightarrow{m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}} \mathbf{6a} \longrightarrow t\ \text{Bu}_2\text{CO} + \text{Bu}_2\text{C}{=}\text{C}{=}\text{O} + \text{Me C}{=}\text{C(Me)COBu-}t + t\text{-BuCOCH}\underset{\text{CH}_2}{\diagdown\!\diagup}\text{C(CH}_3)_2 \quad (1)$$

The olefinic product shown in eq 1 and di-*tert*-butylketene would themselves be expected to undergo further transformations in the presence of ozone.[9] None of these above products or their anticipated transformation products were observed in our reaction mixtures, although only di-*tert*-butylketone was available for the direct comparison of its retention time with those of the reaction products. Formation of these products in our reactions would also be dependent on a faster rate of rearrangement of the keto carbene compared with its further oxidation by ozone or oxygen.

Jackson and Hull[4] preferred structure **4** (R = Ph) for one of the low-temperature intermediates from reacting ozone with diphenylacetylene. The shape and approximate extinction coefficient of the visible tail of our intermediate (Figure 1) are in fact very similar to the spectra reported for several dioxetanes.[10] On the other hand, the behavior of nucleophiles and cupric ion with the intermediate does not support such a structure (or structure **5a**) in our case. One might ascribe a lack of reactivity in **4a** to steric effects, for which there is precedent in the reductive attack[11] on peroxide bonds by Cr^{2+} and S_H2 displacement at oxygen[12] and sulfur[13] by radicals, but comparatively unhindered, face-centered transition states have been advocated for the dioxetane reactions which inspired our attempts.[6b] We did not observe the chemiluminescence[4e,4f] on warming ozonized **1a** that often accompanies the thermolysis of dioxetanes, but the excited state behavior of pivalic anhydride is not known, so that this observation likewise has only qualitative significance.

Scheme II



$$2n\mathbf{3a} \longrightarrow \mathbf{7a} \text{ or } \mathbf{8a} \xrightarrow{>-20\ ^\circ\text{C}} \begin{array}{l} 1.\ 2n \text{ pivalil} + nO_2 \\ 2.\ 2n \text{ pivalic anhydride} \\ 3.\ n \text{ pivalic acid}, n\text{CO}, n\ i\text{-}C_4H_8 \\ 4.\ n \text{ trimethylpyruvic acid}, n\ i\text{-}C_4H_8 \\ 5.\ n\ i\text{-}C_4H_8, n\ i\text{-}C_4H_{10}, n\text{CO}, n\text{CO}_2 \end{array}$$

The presence of structures **2a** and **3a** in cold solutions of ozonized **1a** are more easily ruled out because we could not alter the product distributions with TCNE[4e] or with alcohols after the ozonolysis was completed.

Of the remaining structures in Scheme I, the carbonyl oxide oligomer **7a** or ozonide oligomer **8a** may be a viable alternative, though we must then invoke steric hindrance as a major factor to explain their inertness toward sulfides and phosphines. The extended tail in the visible spectrum of the low-temperature intermediate may result from a strained conformation of the OO bond.[14] We may then account for products by the stoichiometric modes of fragmentation shown in Scheme II.

DeMore and Lin[4d] proposed that a polymer from ozone and 2-butyne was responsible for the ultimate reaction products, which included biacetyl and acetic anhydride. It is, however, difficult to rationalize the kinetic instability of these compounds with the relative stability of known tetrasubstituted tetroxanes (**7**, $n = 2$) and simple ozonides. For instance, the benzophenone oxide dimer[15] decomposes at about 200 °C and the one from pinocolone oxide melts above 120 °C.[16] Perhaps oligomers **7a** or **8a** contain thermally labile end groups such as trioxides.

There is, of course, precedent for the direct formation of tetroxanes and two carbonyl compounds on interaction of two carbonyl oxides.[15] There must be other ways to generate pivalil, however, since the oxygen required according to reaction 1 in Scheme II was not detected during the warmup of cold, ozonized **1a**. A reversible dissociation of **7a** to **3a** is also ruled out for the same reasons that exclude **2a** and **3a** as the stable product at low temperatures.

Conclusion

The *tert*-butyl groups in **1a** do not confer any extraordinary stability on the intermediates in its reaction with

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ozone. Except for a novel pathway in participating solvents, the features of the reaction are similar to the reactions of simpler alkynes with ozone. The mechanistic details of the reaction in nonparticipating solvents could not be established unequivocally. The thermal lability of a yellow intermediate in the reaction contrasts greatly with its stability toward nucleophilic attack.

Experimental Section

Di-*tert*-butylacetylene (Chemsamco), methyl pivalate, pivalic acid, and pivalic anhydride (Aldrich) were >99% pure by gas chromatography and were used as received. Pivalil was collected from several reaction mixtures by preparative gas chromatography or by ordinary chromatography on alumina by elution with $CHCl_3$. The yellow liquid showed ϵ 20.4 at 360 nm in $CHCl_3$ at 25 °C, but the extinction coefficient decreased at lower temperatures. Solvents were reagent or spectroscopic grade. Dichloromethane was dried over molecular sieve (Linde 4A) before use. Ozone was produced from a Welsbach Model 14 ozonizer from oxygen at 7-8 psi and passed into solutions in Pyrex test tubes or (in later runs) in 10 × 100 mm Kimble tubes which could be sealed with a plastic screw cap. The solutions were cooled in dry ice/acetone (-78 °C) or liquid nitrogen/solvent baths.

The analysis of the evolved gases (run 13) was accomplished by ozonizing the sample in a tube with a ground glass joint and an adapter with a stopcock, so that the sample could be degassed by cooling to -196 °C and thawing to -78 °C. After degassing, the evacuated tube was closed off with the stopcock and allowed to warm to 25 °C, and the gases above the solution were admitted to a mass spectrometer (Consolidated Electrodynamics Corp. Model 21-620) and gas chromatograph (Hewlett Packard Model 800 equipped with FID and an 8 ft × $^1/_8$ in Porapak Q column) for analysis.

Gas chromatography-mass spectroscopy of some of the reaction mixtures was carried out with a Finnigan Model 4000 with an INCOS data system, on a 6 ft × 2 mm i.d. column packed with 3% OV-17 on Gas Chrom Q (120 mesh). With the "gentle" donor CH_5^+-NH_4^+ in the CIMS mode, we were able to see the P + 1 ions for all of the *tert*-butyl derivatives in this work, which undergo extensive fragmentation with EIMS. For routine analysis, we used a Varian Model 1700 TC gas chromatograph and a $^1/_4$ in. × 6 ft column packed with 10% OV-1 on Chromosorb W (column A) or a Hewlett-Packard Model 5700A FID instrument with a $^1/_8$ in. × 10 ft column packed with 10% SP2100 on 100/120 Supelcoport (column B), with mesitylene or hexamethylethane as internal standards. The ^1H NMR spectra were measured with a Varian CFT-20 instrument with internal Me_4Si as a reference (δ 0).

The Pyrex jacketed cell for low-temperature spectral measurements was made as a constant-temperature cell by Mr. Kenneth Tracewell (Chemsamco) from an outer tube $1^5/_{16}$ in. × $3^3/_4$ in. with two inner 10/30 ground glass inlet tubes. The cell was held in place with short pieces of Tygon tubing, which joined the inlet tubes to two copper tubes that were anchored into holes drilled through the sample compartment of a Cary Model 14 spectrometer. The jacket was evacuated with an oil pump. The inner cell compartment was a squared piece of tubing with o.d. $^1/_2$ in. Cold samples were introduced into the cells by syringe through a serum cap. The temperature of the solution was monitored with a copper-constantan thermocouple enclosed in a glass tube and inserted through the serum cap. The thermocouple was calibrated with ice/water and with chloroform slush (-63.5 °C), and the output was displayed continuously on a strip chart recorder. The spectral range in Figure 1 was scanned in about 25 s, during which the temperature change of the solution was less than about 3 °C.

Acknowledgment. We thank Mr. Bruce Hidy, Mr. Robert Iden, and Mr. Thomas Householder of Battelle Laboratories for spectral measurements, and Dr. John R. Nixon for assistance with the NMR spectrometer.

Registry No. **1a**, 17530-24-4; ozone, 10028-15-6.

Peroxomonophosphoric Acid Oxidation. 7.[1] Studies of the Kinetics and Substituent Effect in the Oxidation of Aniline

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Received April 2, 1981

The kinetics of the oxidation of aniline and 12 substituted anilines by peroxomonophosphoric acid (PMPA) have been measured. The reactions are first order in PMPA and first order in amine. The rate laws are given in eq 10 and 13. The unprotonated amine is the reactive species. Correlation of log rates with σ, σ^+, σ^-, and ΔpK_a yielded values of ρ (-1.37), ρ^+ (-1.31); ρ^- (-1.38), and β (0.58), respectively. The values suggest an electron-deficient reaction center, and the Brønsted coefficient, β, indicates considerable bond formation in the transition state. All the ortho substituents provide steric retardation for the formation of the transition state. Oxidation of aniline gives azobenzene, azoxybenzene, *p*-aminophenol, and *p*-benzoquinone routed through the reactive intermediate phenylhydroxylamine. The individual reactivities of various ionized PMPA species with the amine have been estimated.

There have been extensive studies in the oxidation of aniline by peroxo acids like perbenzoic acid,[2] peracetic acid,[3-5] Caro's acid,[6] and trifluoroperacetic acid,[7] and a general picture of the mechanism is now available. A S_N2 intermediate is formed by nucleophilic attack of the amine lone pair on the electrophilic peroxo oxygen which decomposes to phenylhydroxylamine in a rate-limiting step. Further oxidation leads to nitroso- and eventually to nitrobenzene (eq 1).

$$ArNH_2 \rightarrow ArNHOH \rightarrow ArNO \rightarrow ArNO_2 \qquad (1)$$

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