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Ozonation of Acetylenes and Related Compounds in the Presence of Tetracyanoethylene and Pinacolone

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The ozonation of olefins has been a subject of continuing research interest because of its application in degradative and synthetic chemistry.[1,2] Contributions from many laboratories have led to a better understanding of its reaction pathway.[1-3] The ozonation of acetylenes, on the other hand, has received only limited attention.[4-9] The reaction has been suggested to proceed *via* an analogus pathway to the ozonation of olefins.[2,5] Derivatives of carboxylic acids and α-dicarbonyl compounds have been obtained among the reaction products, and α-diketones have been isolated in moderate yields (30–60%) when ozonated acetylenes were reduced immediately with sodium iodide.[5] Contributions from Criegee's laboratory demonstrated that olefins were smoothly cleaved by ozone in the presence of tetracyanoethylene (TCNE) to give carbonyl compounds in good yields (reaction 1).[10] Later work by Story suggested

$$R_1R_2C{=}CR_3R_4 + O_3 + (NC)_2C{=}C(CN)_2 \longrightarrow R_1R_2C{=}O + R_3R_4C{=}O + (NC)_2C(O)C(CN)_2 \quad (1)$$

$$R_1R_2C{=}CR_3R_4 + O_3 + CH_3COC(CH_3)_3 \longrightarrow R_1R_2C(O)CR_3R_4 + CH_3COOC(CH_3)_3 \quad (2)$$

that ozonation of olefins in pinacolone yielded dioxetanes which could give carbonyl compounds upon decomposition (reaction 2).[11] In order to gain more insight into the action of ozone on acetylenes and to devise a more efficient method for the conversion of acetylenes to α-diketones, the ozonation of acetylenes in the presence of TCNE or pinacolone as the *in situ* reducing agents was investigated. In addition, the ozonation of several olefins in the presence of TCNE was also studied.

Experimental Section

Diphenylacetylene, phenylacetylene, TCNE, 9-bromofluorene, and 2-adamantanone were purchased from Aldrich Chemical Co., 5-decyne and 1-phenyl-1-butyne from Farchan Chemical Co., and pinacolone from Chemical Sample Co. They were used as received. Bis(fluorenylidene) was prepared from 9-bromofluorene[12] and bis(adamantylidene) from 2-adamantanone[13] according to known procedures. Silica gel (Woelm) was purchased from the Waters Associates. Solvents used were reagent grade. Melting points given were not corrected.

General Procedure. Ozone (2%) in oxygen was generated in a laboratory ozonator.[14] The flow rate was approximately 200 ml/min. The reaction mixture was kept at low temperature with a Dry Ice–acetone bath. The temperature given was that of the reaction mixture. The ozonation was continued until the solution turned light blue indicating the presence of unreacted ozone. At this point, the reaction was 80–100% complete depending on the acetylene used. Diphenylacetylene was qualitatively less reactive than the other acetylenes. Since acetylenes are less reactive than olefins, unreacted ozone which passed through the solution to turn an aqueous solution of KI to a brown color was not a good indication for the conclusion of this reaction. TCNE epoxide was readily isolable from the reaction mixture owing to its low solubility (56–66%), and no attempt was made to optimize its yield. Also no attempt was made to demonstrate the presence of *tert*-butyl acetate in the ozonation of acetylenes in pinacolone.

Benzil, benzoic acid, 9-fluorenone, 2-adamantanone, and bis(adamantylidene) epoxide[15] were identified by comparison with the respective authentic sample. Phenylglyoxal, bp 73–77° (5 mm), was identified as 2-phenylquinoxaline, mp 74–76° (lit. mp 76–77°),[16] 1-phenylbuta-1,2-dione as its dioxime, mp 207–210° (lit. mp 215–216°),[17] and deca-5,6-dione as its bis(phenylhydrazone), mp 127–129° (lit. mp 127°).[18]

The procedure is illustrated by the ozonization of 1-phenyl-1-butyne below and the results are summarized in Table I.

Ozonation of 1-Phenyl-1-butyne (1c). A solution of **1c** (1.3 g, 10 mmol) in 20 ml of ethyl acetate containing an equivalent amount of TCNE (1.28 g, 10 mmol) was kept at −78° with a Dry Ice–acetone bath and treated with ozone until the solution turned a light blue color. After the solution had been warmed up to room temperature, TCNE epoxide was removed by filtration (830 mg, 59%). The filtrate was evaporated and the residue was chromatographed on silica gel (activity II). 1-Phenylbuta-1,2-dione (1.14 g) was isolated in 71% yield.

A solution of **1c** (1.3 g, 10 mmol) in pinacolone (10 ml) was cooled to −45° in a Dry Ice–acetone bath and treated with ozone. After the conclusion of the reaction, the solution was evaporated and the residue was chromatographed over silica gel. Benzoic acid (920 mg) was isolated in 75% yield and a fraction (430 mg) containing about 60% of 1-phenylbuta-1,2-dione (by nmr) was also isolated. Pure 1-phenylbuta-1,2-dione may be isolated from that fraction by vpc on a 10% SF-96 on Chromosorb column (5 ft × 0.25 in., 140°).

In a separate experiment, a solution of **1c** (10 mmol) in 20 ml of pinacolone was ozonated under similar conditions. The crude reaction mixture exhibited ir frequencies at 1780 and 1730 cm^{-1}, indicating the presence of acid anhydrides.[19] The mixture was then treated with aniline (980 mg, 10 mmol) and was allowed to remain at 23° for 1 hr. The whole mixture was then chromatographed on silica gel (activity IV). From this chromatography, an earlier fraction containing 1-phenylbuta-1,2-dione (4%), benzanilide [80 mg, 4%, mp 160–162° (lit. mp 161°)],[20] benzoic acid (290 mg, 24%), and propionanilide [536 mg, 36%, mp 105–106° (lit. mp 103°)][20] were isolated.

Another sample of **1c** was ozonated in an equivolume mixture of pinacolone and ethyl acetate at −78° and 9,10-diphenylethynylanthracene was added to the reaction mixture after the ozonation. Chemiluminescence similar to the fluorescence of the fluorescer added was observed when the solution was warmed to room temperature.

Ozonation of Ethylidenecyclohexane. A solution of ethylidenecyclohexane (550 mg, 5 mmol) in ethyl acetate (20 ml) containing an equivalent amount of TCNE (640 mg, 5 mmol) was ozonated at − 78°. After the reaction, vpc analysis of the mixture (20% Carbowax 20M on Chromosorb P, 15 ft × 0.25 in., 120°) revealed the presence of both acetaldehyde and cyclohexanone. The mixture was distilled at 0.5 mm and −20° to give a distillate which was chemiluminescent upon heating and a residue. TCNE epoxide (370 mg, 51%) was isolated from the residue by washing it with dichloromethane. The distillate was redistilled at 5 mm and −20° to give a nonchemiluminescent distillate which contained acetaldehyde but no cyclohexanone by vpc analysis and a chemiluminescent residue which contained no acetaldehyde but cyclohexanone by vpc analysis.

Discussion

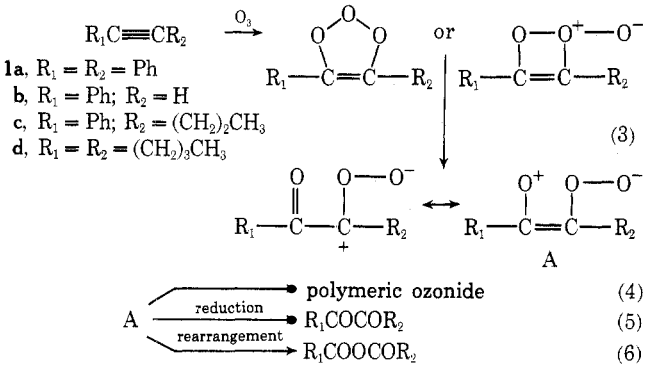
Ozonation of acetylenes has been suggested to proceed *via* the following pathways, and the presence of A as an intermediate is supported by spectroscopic evidence at −40°.[6,9]

Our results indicate that ozonation of acetylenes in the presence of TCNE yields α-dicarbonyl compounds in good to excellent yields while the ozonation in the presence of pinacolone yields acid anhydrides or acid derivatives as the major products (Table I). At −78°, acetylenic solutions containing TCNE turn yellow instantaneously when ozonated while those containing pinacolone do not. There-

Table I

Unsaturated compd (mmol)	Registry no.	*In situ* reductant	Solvent (volume, ml)	Temp, °C	Products (yield, %)	Registry no.
1a (2)	501-65-5	TCNE (2 mmol) (670-54-2)	EtOAc (15)	−78	Benzil (92)[a]	134-81-6
1a (2)		Pinacolone (10 ml) (75-97-8)		−40 ± 5	Benzil (31), benzoic acid (28)[a]	
1b (10)	536-74-3	TCNE (10 mmol)	EtOAc (20)	−78	PhCOCHO (60,[b] 16[c])	1074-12-0
1b (20)		Pinacolone (20 ml)		−40	PhCOCHO (50,[b] 31[c]), benzoic acid (15)[d]	
1c (10)	4250-81-1	TCNE (10 mmol)	EtOAc (20)	−78	$PhCOCOCH_2CH_3$ (71)[a]	3457-55-4
1c (10)		Pinacolone (10 ml)		−45	$PhCOCOCH_2CH_3$ (16), benzoic acid (75)[a]	
1c (10)		Pinacolone (10 ml)	EtOAc (10)	−78	$PhCOCOCH_2CH_3$ (4), benzoic acid (24), benzanilide (4), propionanilide (36)[e,f]	
1d (10)	1942-46-7	TCNE (10 mmol)	EtOAc (20)	−78	5,6-Decadione (67),[a] *n*-valeric anhydride (12)[g]	5579-73-7[i]
1d (20)		Pinacolone (20 ml)		−40 ± 5	5,6-Decadione (4), *n*-valeric acid (64)[a]	
1d (20)		Pinacolone (20 ml)		−42 ± 3	5,6-Decadione (6), *n*-valeric acid acid (5),[b] *n*-valeric anhydride (65)	
1d (10)		Pinacolone (10 ml)	EtOAc (10)	−78	5,6-Decadione–*n*-valeric anhydride (1:7)[f,g]	
2 (1.0)	746-47-4	TCNE (1 mmol)	EtOAc (20)	−78	Fluorenone (87)[a]	486-25-9
3 (0.5)	30541-56-1	TCNE (0.5 mmol)	EtOAc–CH_2Cl_2 (30, 2:1)	−78	Bis(adamantylidene) epoxide (57)[h]	29186-07-0
3 (1.0)		Pinacolone (70 ml)		−45	Bis(adamantylidene) epoxide (67),[h] 2-adamantanone (15)	

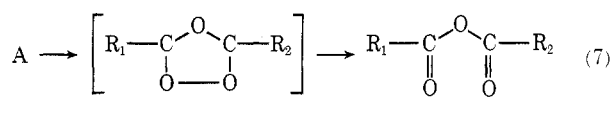
[a] Isolated by chromatography on silica gel (activity II). [b] Estimated from nmr spectrometry. [c] Isolated by distillation at 2 mm. [d] Isolated from the residue of distillation by chromatography on silica gel. [e] Isolated from the aniline-treated reaction mixture by chromatography on silica gel (activity IV). [f] The reaction mixture was chemiluminescent in the presence of 9,10-diphenylethynylanthracene when it was warmed from −78° to 21°. [g] Estimated by vpc on a SF-96 (10%) on Chromosorb P Column at 140°. [h] Isolated by chromatography on Florisil. [i] For 5,6-decadione.



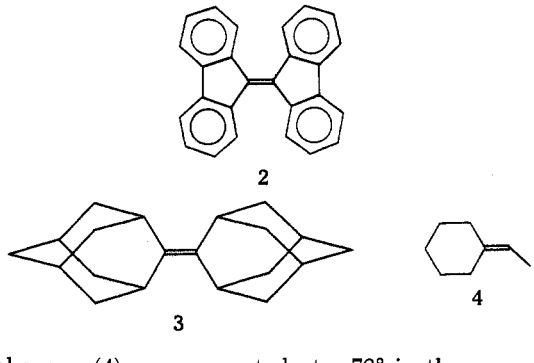
fore, TCNE is a much more effective *in situ* reducing agent of the ozonation intermediate, most probably A, to α-dicarbonyl compounds than pinacolone. Since α-dicarbonyl compounds are frequently formed in low yields in the absence of added reducing agents,[4,5] it is probable that unsaturated compounds, including acetylenes themselves, may function as *in situ* reducing agents of ozonation intermediates from acetylenes.

Among the acetylenes studied, arylacetylenes gave higher yields of α-dicarbonyl compounds than alkynes. Intermediates A from arylacetylenes are stabilized by delocalization of the positive charge into the aryl group, while those from alkynes cannot be. Such a stabilization will cause A from arylacetylenes to undergo the rearrangement to acid anhydride more slowly (reaction 6) but will have little effect on the rate of reduction (reaction 5). Therefore, the results may be attributed to a more favorable competition of the reduction of A over the rearrangement.

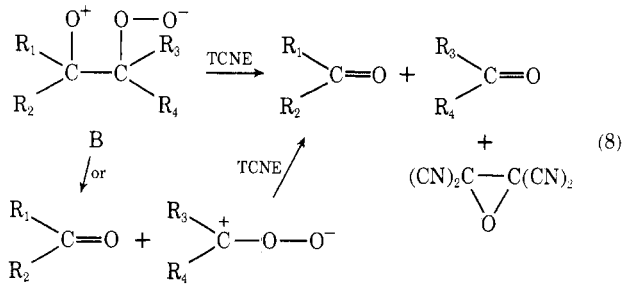
In order to detect the possible presence of energy-rich intermediates in the ozonation of acetylenes, a small amount of 9,10-diphenylethynylanthracene, a fluorescer, was added to the ozonated solution of **1c** in pinacolone–ethyl acetate at −78°. The mixture was quickly warmed to room temperature in a dark room; a weak but observable chemiluminescence was detected. The chemiluminescence was visually similar to the fluorescence of the fluorescer but was too weak to be analyzed spectroscopically. Although the exact significance of such an observation is difficult to evaluate, the possible role of a metastable trioxabicyclo[2.1.1]pentane intermediate from the decay of A cannot be excluded (reaction 7).



Since pinacolone has been suggested as a reagent for the conversion of ozonides to dioxetanes,[11] we examined the possible application of TCNE in this reaction. Bis(fluorenylidene) (**2**), bis(adamantylidene) (**3**), and ethylidenecyclohexane (**4**) were ozonated at −78° in the presence of TCNE, since their corresponding dioxetanes may exhibit



unusual stability or have been well characterized.[21-23] The major product isolated from 2 was fluorenone and that from 3 was the corresponding epoxide. The results indicate that dioxetanes were not formed in appreciable amounts in these two reactions. The formation of epoxide from hindered olefins has been noted before,[24] and 3 is apparently another such case. 3,3-Pentamethylene-4-methyl-1,2-dioxetane, the dioxetane derived from 4, is known to be quite stable at −20° but will decompose with chemiluminescence at higher temperatures.[24] After 4 was ozonated in the presence of TCNE at −78°, the reaction mixture was quickly fractionated at −20°. Acetaldehyde and cyclohexanone, the expected decomposition products of the dioxetane, were isolated in separate fractions of the distillate, indicating that the dioxetane was not the intermediate in the formation of products. Therefore, carbonyl compounds formed in the ozonation of olefins in the presence of TCNE may be derived from the reduction of zwitterion intermediate B during the ozonation (reaction 8).



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Bromination of 2-Phenyl-2-methallylindan-1,3-dione

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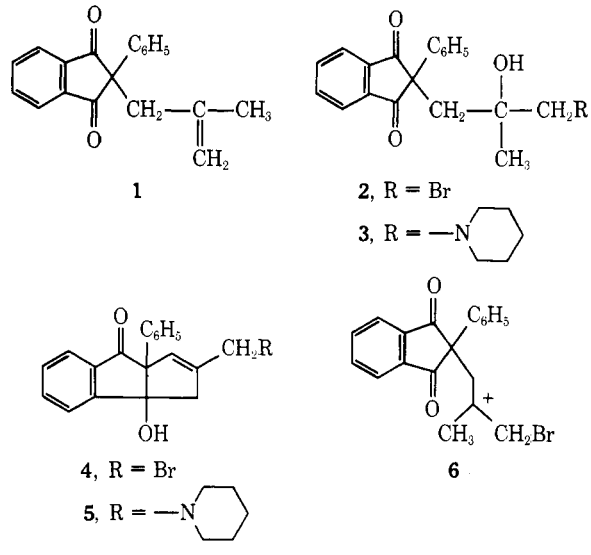
Aren, Zitsmanis, and Valter[1] have claimed that the bromination of 2-phenyl-2-methallylindan-1,3-dione (1) in glacial acetic acid produces the tricyclic primary bromide 4 and that displacement of the bromine in 4 by piperidine gives the tricyclic amine 5. Their structure proof was based upon incomplete elemental analyses, integrated carbonyl absorption in the infrared, and ultraviolet spectra.

We have repeated their experiments and find that the correct structures of the bromination product of 1 and its piperidine displacement product are 2 and 3, respectively.



Our results differ from those reported[1] in the following respects. (1) The correct molecular formulas of 2 and 3 were established by mass spectrum and complete elemental analysis; the difference of a molecule of water from the earlier structures 4 and 5 would not be evident from the incomplete analyses previously reported. (2) The nmr spectra of the products are inconsistent with structures 4 and 5 because the aliphatic regions show only methylene and methyl protons and no vinyl or allylic protons. The exocyclic NCH_2 group in 3 appears as an AB quartet in the nmr, indicating nonequivalence of the two protons.[2] Models indicate that hydrogen bonding between the piperidine nitrogen and the tertiary hydroxyl group would be possible. (3) The presence of the CH_2Br group in 2 is established by its nmr position,[3] by the loss of CH_2Br in the mass spectrum, and by a strong band at 1250 cm^{-1} in the infrared.[4] The formation of product 2 can be accounted for through the intermediacy of carbonium ion 6 during bromination, and the displacement with piperidine to form 3 probably involves the assistance of the hydroxyl group in 2.

Experimental Section[5]

2-Phenyl-2-methallylindan-1,3-dione (1) was prepared according to the literature[1,6] in 82% yield after recrystallization from EtOH: mp 97–98°; ν_{max} ($CHCl_3$) 1740, 1705, and 1240 cm^{-1}; λ_{max} 342 nm (ϵ 166), 302 (630), and 225 (46,500); ^1H nmr δ 8.08–7.68 (m, C_6H_4), 7.55–7.12 (m, C_6H_5), 4.67 (s, vinyl CH_2), 3.03 (s, allylic CH_2), and 1.52 ppm (s, CH_3); mass spectrum *m/e* 276 (M^+), 261 [$(M - CH_3)^+$], 233 [$(M - C_3H_7)^+$ and $(M - CH_3 -$