Apiezon L or a fluorosilicone column. A quantitative determination of the volatile products was made by comparing retention times and peak areas of the products with those of series of standard solutions. The results are summarized in Table II.

In control experiments, it was demonstrated that no significant changes in concentration of nitrobenzene or bromobenzene occurred when these compounds were subjected to the reactions cited above.

Reactions of Aryltriphenylstibonium Fluoroborates with Sodium *n*-Butoxide. Clean sodium, 0.002 g-atom, was allowed to react with 7.5 ml of anhydrous *n*-butyl alcohol contained in a glass tube sealed at one end, and the resulting sodium *n*-butoxide solution was cooled in an ice bath. The aryltriphenylsulfonium fluoroborate, 0.001 mol, was added to the solution and the tube sealed. It was placed in an oil bath maintained at about 120° for 188 hr, the tube and its contents being shaken at least once every day. At the end of the reaction period the tube was cooled in an ice bath, opened, and a 5-μl sample subjected to vpc analysis as described previously. The results are summarized in Table II.

A control experiment demonstrated that nitrobenzene was completely destroyed when subjected to the reaction conditions described above for as little as 10 min.

Tri-*m*-chlorophenylstibine. To a solution of 0.1 mol of *m*-chlorophenylmagnesium bromide in 100 ml of ether was added slowly a solution of 7.75 g (0.034 mol) of antimony trichloride in 50 ml of ether. A vigorous reaction occurred, and a steady reflux was maintained during the addition of the antimony trichloride and for 1 hr thereafter. The mixture was cooled and poured into 1000 ml of an ice-cold, saturated, aqueous solution of ammonium chloride. The organic layer was separated from the aqueous layer, and the latter was extracted with ether. The combined organic solution was concentrated to dryness, and the residual oil was induced to crystallize from 95% ethanol. There was obtained 10 g (65%) of tri-*m*-chlorophenylstibine, mp 53–54°.

Anal. Calcd for $C_{18}H_{12}Cl_3Sb$: C, 47.65; H, 2.63; Cl, 23.30. Found: C, 47.46; H, 2.65; Cl, 23.19.

Phenyldi-*p*-tolylstibine. To a Grignard reagent prepared from 0.2 mol of *p*-bromotoluene and 0.2 g-atom of magnesium in 175 ml of ether was added a suspension of 0.1 mol of phenyldichlorostibine[34] in 200 ml of ether over a period of 30 min. The mixture was refluxed for 5 hr, then cooled and added to a mixture of 200 ml of saturated ammonium chloride solution and 200 g of ice. The colorless organic layer was separated from the aqueous layer, which was washed thoroughly with warm benzene. Evaporation of the combined organic layer and benzene wash solution gave a viscous, colorless residue which was induced to crystallize from 95% ethanol to give 12.0 g (33%) of phenyldi-*p*-tolylstibine, mp 71–73°.

Anal. Calcd for $C_{20}H_{19}Sb$: C, 63.0; H, 5.0. Found: C, 62.6; H, 4.8.

Phenyldi-*p*-fluorophenylstibine. Prepared in essentially the same manner as described above for phenyldi-*p*-tolylstibine, the fluoro compound had a mp of 66–67° and was obtained in 52% yield.

Anal. Calcd for $C_{18}H_{13}SbF_2$: C, 55.3; H, 3.3; F, 9.7. Found: C, 55.5; H, 3.4; F, 9.6.

Phenyldi-*p*-anisylstibine. This compound, mp 109–110°, was obtained in 45% yield by the same general procedure as described above.

Anal. Calcd for $C_{20}H_{19}SbO_2$: C, 58.2; H, 4.6. Found: C, 58.1; H, 4.6.

Phenyldi-*p*-chlorophenylstibine. A 56% yield of the compound, mp 82–84°, was obtained.

Anal. Calcd for $C_{18}H_{13}SbCl_2$: C, 51.1; H, 3.1; Cl, 16.8. Found: C, 51.3; H, 3.1; Cl, 17.0.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

(34) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, 72, 3027 (1950).

Oxidation of Organic Compounds with Cerium(IV). X. Oxidation of 1,3,5-Cycloheptatriene[1]

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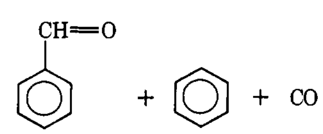
Abstract: The facile oxidation of 1,3,5-cycloheptatriene by 4 equiv of ceric ammonium nitrate in aqueous acetic acid and other solvents is shown to lead to benzaldehyde, benzene, and carbon monoxide. The results of three sets of experiments are presented which strongly support the tropylium ion an an intermediate in this oxidation. Evidence is presented which establishes that the oxygen of the benzaldehyde produced by the ceric ammonium nitrate oxidation of cycloheptatriene in anhydrous acetonitrile comes from the nitrate ion. A mechanism is proposed which is consistent with these and other experimental findings.

We have found that 4 equiv of ceric ammonium nitrate (CAN) in aqueous acetic acid and other solvents smoothly oxidizes 1,3,5-cycloheptatriene (CHT) to a high yield of benzaldehyde, benzene, and carbon monoxide. The reaction is quite facile (a few minutes at 90° in most solvents used), being more rapid in 50% aqueous acetic acid than the oxidation of benzyl alcohol.[2] CHT and substituted cycloheptatrienes[1g] have



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(1) (a) For Part IX, see W. S. Trahanovsky, M. G. Young, and P. M. Nave, *Tetrahedron Lett.*, 2501 (1969). (b) This work was partially supported by Public Health Service Grant No. GM 13799 from the National Institute of General Medical Sciences. The mass spectrometer was purchased with funds from the National Science Foundation Grant GP 1715 and a grant from the Iowa State Alumni Research Foundation. We thank these organizations for their support. (c) Based on work by L. B. Y. and M. D. R. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State University. (d) U. S. Public Health Service Fellow, 1966–1967. (e) National Science Foundation Trainee, 1967–1969. (f) Preliminary Communication: Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., September, 1966, p 52 S. (g) All cycloheptatrienes mentioned in this paper are 1,3,5-cycloheptatrienes.

(2) W. S. Trahanovsky, L. B. Young, and G. L. Brown, *J. Org. Chem.*, 32, 3865 (1967).

Table I. Oxidation of 1,3,5-Cycloheptatriene by Ceric Ammonium Nitrate (CAN)

			Yield,[b] %		
Concn of CAN, *M*[a]	Solvent	Temp, °C	PhCHO	PhH	PhCHO/PhH
0.5	Water	95	64	11	85/15
1.0	Water	25			87/13
0.4	Water + 0.15 *N* KOH	75			86/14
0.5	Water + 0.5 *N* $HClO_4$	95	58	9	87/13
0.5	10% aqueous HOAc	95	46	6	88/12
0.5	50% aqueous HOAc	25	60	14	80/20
0.5	50% aqueous HOAc	30	79	16	83/17
0.5	50% aqueous HOAc	95	72	20	78/22
0.5	50% aqueous HOAc + 0.15 *N* NaOAc	75			78/22
0.5[c]	50% aqueous HOAc + 3 *N* HNO_3	95	46	18	72/28
0.5	80% aqueous HOAc	95	70	21	77/23
0.5	100% HOAc	95	56	21	73/27
0.5	50% aqueous sulfolane	75			83/17
0.5	50% aqueous sulfolane + 3 *N* HNO_3	75			79/21
0.5	100% sulfolane	75	61	15	80/20
0.5[c,d]	100% sulfolane	75	28	16	64/36
0.5[d,e]	50% aqueous MeCN	25	30–50		85/15
0.5	100% MeCN	75	80	18	82/18
0.5[d]	100% MeCN	75	2		
0.5[f]	100% MeCN	75	44		
0.5[g]	100% MeCN	75	85		85/15

[a] All reactions were carried out using 4 equiv of cerium(IV) unless otherwise specified. [b] Yields were determined by glpc using xylene as a standard. Toluene was present to the extent of *ca.* 4% in the CHT. [c] Average of two runs. [d] Two equivalents of oxidant was used. [e] Approximately half of the CHT was recovered. [f] Three equivalents of oxidant was used. [g] Two equivalents of oxidant was added and the reaction was allowed to go to completion, and then 2 more equiv was added.

been oxidized by other oxidants[3–6] and even cerium(IV) under conditions different than ours,[6] but the yields of isolable products were never greater than 40% and usually much lower. The facile oxidation of CHT to a high yield of isolable products by CAN under our conditions makes this reaction particularly attractive to study. A detailed understanding of the mechanism of this reaction should be relevant to the understanding of the mechanisms of the oxidation of unsaturated hydrocarbons in general.

Results

The yields of benzaldehyde and benzene from the oxidation of CHT by CAN under various conditions are summarized in Table I. Benzene and benzaldehyde were identified by gas–liquid partition chromatography (glpc) peak enhancement with authentic samples on several columns and by nuclear magnetic resonance (nmr). The ratio of benzaldehyde to benzene obtained by glpc measurements agreed quite well with those obtained by nmr.

The amount of gas produced from the reaction in 50% aqueous acetic acid corresponded approximately to the production of 1 mol of carbon monoxide for each mol of benzene produced. The gas was identified as carbon monoxide since mass spectral analysis of the gas showed a large peak at *m/e* 28 and it reduced palladium(II) to palladium metal.[7]

CHT was oxidized by 0.5 *M* ceric perchlorate in 50% aqueous acetic acid that contained 3 *M* perchloric acid. A large amount of polymer was formed and only 3% benzaldehyde was produced. Similar results were obtained in 50% aqueous sulfolane.

Oxidation of CHT by potassium permanganate in 15% aqueous acetone, 1 *M* in sulfuric acid, or in water at 25° gave no benzene or benzaldehyde. Oxidation of CHT by chromium trioxide in 80% aqueous acetic acid at 25° gave 34% benzaldehyde and 3% benzene.

Several experiments were carried out in order to determine whether the tropylium ion is an intermediate in the cerium(IV) oxidation of CHT. Some evidence for the tropylium ion as an intermediate comes from oxidations carried out in anhydrous acetonitrile. It was observed that 4 equiv of CAN in anhydrous acetonitrile oxidized CHT to 80% benzaldehyde and 20% benzene. However, it was found that 2 equiv of CAN in anhydrous acetonitrile consumed all the CHT and produced only 2% benzaldehyde (notice that in 50% aqueous acetonitrile, 2 equiv of CAN gave about half the benzaldehyde that 4 equiv produced). In addition, 3 equiv of CAN produced one-half the amount of benzaldehyde produced when 4 equiv was used. The production of a stable species which could be oxidized to benzaldehyde from the oxidation of CHT with 2 equiv of CAN in anhydrous acetonitrile was demonstrated by adding 2 equiv of CAN, allowing the reaction to go to completion (as evidenced by fading of the orange cerium(IV) color to colorless cerium(III) and precipitation of cerium(III) salts), and then adding 2 more equiv of CAN. The net result was that benzaldehyde was produced in the same yield as if all 4 equiv of CAN had been added at once. An obvious possibility is that the intermediate produced in the oxidation of CHT by 2 equiv of CAN in anhydrous acetonitrile was tropylium ion or a closely related species formed *via* a two-electron oxidation of CHT.

The presence of tropylium ion or a closely related species in the reaction mixture from the oxidation of CHT by 2 equiv of CAN in anhydrous acetonitrile was

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(3) G. Merling, *Chem. Ber.*, **24**, 3108 (1891).

(4) E. Buchner, *ibid.*, **29**, 106 (1896).

(5) G. Juppe and A. P. Wolf, *ibid.*, **94**, 2328 (1961).

(6) M. J. S. Dewar, C. R. Ganellin, and R. Pettit, *J. Chem. Soc.*, **55**, (1958).

(7) G. Lund, "Technical Gas-Analysis," Van Nostrand Co., New York, N. Y., 1914, p 238.

confirmed in the following way: the reaction mixture from the oxidation of CHT by 2 equiv of CAN was diluted with water and extracted with ether to remove all ether-soluble materials, aqueous ethanol was added, and the solution was neutralized with solid sodium bicarbonate producing a flocculent precipitate of cerous hydroxide. From this mixture was obtained a 35.3% yield (based on CHT) of ethyl tropyl ether and an additional 15.2% yield of a product containing the 7-oxycycloheptatriene moiety, probably tropyl alcohol or ditropyl ether. Comparison of these yields with those obtained from treatment of tropylium fluoroborate with aqueous ethanol and sodium bicarbonate shows that the amount of tropylium ion present in the CAN–CHT anhydrous acetonitrile reaction mixture was at least 73% based on starting CHT.

Further support for the intermediacy of tropylium ion is that tropylium fluoroborate in 50% aqueous acetonitrile was rapidly oxidized (<5 min at 25°) by 2 equiv of CAN to a 62% yield of benzaldehyde and a 9% yield of benzene which is a benzaldehyde to benzene ratio of 87/13. In addition, ethyl tropyl ether which should give tropylium ion upon protonation was oxidized to benzaldehyde and benzene in the ratio of 86/14.

The most compelling evidence for tropylium ion as an intermediate in the CAN oxidation of CHT is the result of a deuterium-labeling experiment. Cycloheptatriene-7-*d* (CHT-7-*d*) was prepared from the reduction of tropylium fluoroborate by sodium borodeuteride. Mass spectral analysis indicated that the compound was 99.5% monodeuterated and the nmr spectrum of the material indicated that the deuterium was in the 7 position. The deuterated CHT was oxidized by CAN in 80% aqueous acetic acid to benzaldehyde and benzene. By mass spectral analysis 61.4% of the benzaldehyde and 60.6% of the benzene contained one deuterium. The nmr spectrum of the deuterated benzaldehyde showed peaks for the aldehydic, *ortho*, and *meta* and *para* positions with areas 15.97:33.06:50.97. The calculated ratio of these areas assuming random distributions of the deuterium in the d_1 species is 16.67:33.33:50.00. Each of these numbers agrees with the observed values within 4% whereas if complete scrambling had not occurred and all the deuterium was only in the aldehydic, *ortho*, *meta* and *para*, or aromatic positions, the largest differences between the observed and calculated values would be 118%, 28%, 15%, and 14%, respectively. Thus, the precursor of the benzaldehyde must be some species which permits the deuterium to enter all positions randomly, such as tropylium ion.

When the oxidation of CHT was carried out in anhydrous acetonitrile, the products were still benzaldehyde (80% yield) and benzene (18% yield), the same as in aqueous media. The only possible source of the oxygen incorporated into the benzaldehyde is nitrate ion. The possibility that oxygen incorporation into the benzaldehyde occurred during aqueous work-up of the reaction mixture was eliminated by infrared analysis of the anhydrous reaction mixture before work-up, which showed the characteristic absorption band of the carbonyl group. The possibility of incorporation of molecular oxygen into the product was eliminated by showing that benzaldehyde was still a major product when the reaction was carried out under nitrogen in nitrogen-purged acetonitrile. It is conceivable that tropylium ion could be oxidized to benzaldehyde and benzene by nitrate alone, however, cerium(IV) is also necessary for this conversion since heating a solution of tropylium bromide and sodium nitrate gave no benzaldehyde or benzene. If a nitrogen(III) species is produced during the CHT oxidation by CAN, it would be rapidly oxidized since 2 equiv of a 1 *M* CAN solution oxidizes 1 equiv of a 1 *M* sodium nitrite solution as fast as they can be mixed.

A possible reaction path involves the formation of tropone and its subsequent rearrangement to benzaldehyde and benzene. The formation of tropone from the oxidation of both CHT and tropylium ion has been reported. Radlick has reported that the selenium dioxide oxidation of CHT leads to tropone in 25% yield.[8] Nozoe, Mukai, Tezuka, and Osaka found that chromium trioxide in pyridine converts CHT to tropone in 30% yield, and tropylium ion to tropone in 40% yield.[9] The possible involvement of tropone in the CAN oxidation of CHT has been eliminated by demonstrating that tropone does not rearrange to benzaldehyde and/or benzene under the reaction conditions.

In an attempt to trap a radical intermediate, CHT was oxidized with 4 equiv of CAN in 80% aqueous acetic acid in the presence of acrylamide, a known radical trap.[10] A considerable quantity of polymer was formed, but benzaldehyde and benzene were produced in the same yield as when the radical trap was absent. The polymerization of the acrylamide must have been initiated by an insignificant side reaction.

Discussion

Oxidation of a cycloheptatriene by cerium(IV) has been reported only for the oxidative decarboxylation of cycloheptatriene-7-carboxylic acid where the product was found to be tropylium ion in 30% yield.[6] The CAN oxidation of CHT under our conditions is unique in that the reaction is facile and leads to a high yield of products. It seems *a priori* rather surprising that a one-electron oxidant such as cerium(IV) should lead to a high yield of products in a system where polymerization should be a facile process.

The formation of benzene from the oxidation of CHT has not previously been reported, although a high yield of benzene has been obtained from oxidation of tropylium ion by hydrogen peroxide as reported by Vol'pin and Kursanov.[11] However, we have found that in addition to the CAN oxidation of CHT, the chromium trioxide oxidation of CHT also leads to benzene as a minor product (3% yield). Possibly benzene is a minor product in other oxidative aromatizations, for example in the chromium trioxide and silver oxide oxidations of tropylium ion.[12]

The results of three sets of experiments strongly support the tropylium ion as an intermediate in the CAN oxidation of CHT. First, ethyl tropyl ether was ob-

[8] P. Radlick, *J. Org. Chem.*, **29**, 960 (1964).

[9] T. Nozoe, T. Mukai, T. Tezuka, and K. Osaka, *Nippon Kagaku Zasshi*, **84**, 662 (1963).

[10] (a) G. Mino, S. Kaizerman, and E. Rasmussen, *J. Amer. Chem. Soc.*, **81**, 1494 (1959); (b) W. S. Trahanovsky, L. H. Young, and M. H. Bierman, *J. Org. Chem.*, **34**, 869 (1969); (c) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **90**, 4755 (1968); (d) W. S. Trahanovsky, P. J. Flash, and L. M. Smith, *ibid.*, **91**, 5068 (1969).

[11] M. E. Vol'pin and D. N. Kursanov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **126**, 397 (1959); (b) M. E. Vol'pin, D. N. Kursanov, and V. G. Dulova, *Tetrahedron*, **8**, 33 (1960).

[12] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **79**, 352 (1957).

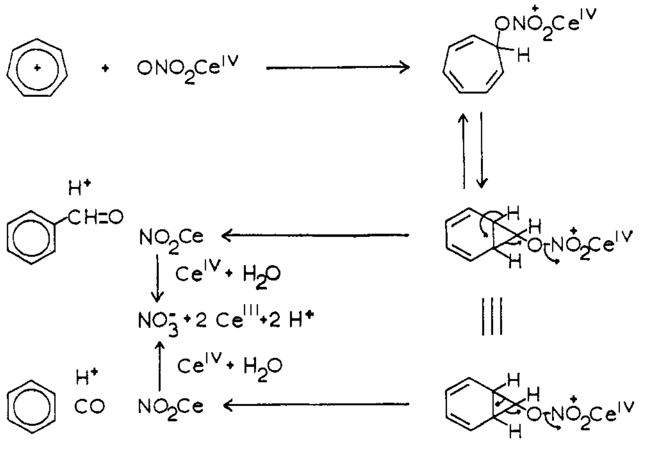
tained by the addition of ethanol and sodium bicarbonate to the mixture produced by oxidation of CHT by 2 equiv of CAN in anhydrous acetonitrile. Second, the benzaldehyde-*d* obtained from the oxidation of CHT-7-*d* had deuterium distributed randomly in all positions. Finally, the ratio of benzaldehyde to benzene obtained from the CAN oxidation of tropylium ion was the same as that obtained from the oxidation of CHT.

The intermediacy of a tropylium ion is further supported by the fact that CAN oxidations of 7-methylcycloheptatriene and a mixture of 1-, 2-, 3-, and 7-methylcycloheptatrienes gave identical product mixtures as would be predicted if methyltropylium ion was formed as an intermediate.[13]

The finding of a tropylium ion intermediate in the CAN oxidation of CHT is similar to the conclusion of Juppe and Wolf[5] that the tropylium ion is an intermediate in the chromium trioxide oxidation of CHT. Their conclusion is based on the fact that the chromium trioxide oxidation of cycloheptatriene-7-^{14}C leads to benzoic acid with six-sevenths of the ^{14}C in the aromatic ring and one-seventh in the carboxyl carbon.

In the results section, evidence is presented which clearly establishes that the oxygen of the benzaldehyde produced by the CAN oxidation of CHT in anhydrous acetonitrile comes from the nitrate ion. Since the ratio of benzaldehyde to benzene and total yield of products are very nearly the same in solvents ranging from anhydrous to entirely aqueous (see Table I) the involvement of nitrate ion in all these reactions seems likely. Additional support for nitrate involvement is given by the low yield (3.2%) of benzaldehyde obtained from the oxidation of CHT by ceric perchlorate in perchloric acid. In Scheme I a mechanism is proposed for the conversion of tropylium ion to benzaldehyde and benzene by CAN. This mechanism is in accord with the above results plus the inability of sodium nitrate to convert tropylium ion to benzaldehyde and benzene, which means that cerium(IV) must be involved in this step, the results that eliminate tropone as an intermediate, and the fact that cerium(IV) rapidly oxidizes nitrite to nitrate. The symbol "ONO_2Ce^{IV}" is used to represent a nitrated cerium(IV) species. Only one nitrate ligand is depicted but no doubt others are present. The nitrate is probably a bidentate ligand.[14] The norcaradiene form is drawn for convenience, but is not necessary since a similar mechanism involving a cycloheptatriene structure can be drawn. The route of formation of benzaldehyde from the norcaradiene intermediate is similar to that proposed by Doering and Knox for the formation of benzaldehyde in the chromium(VI) oxidation of tropylium ion.[12] The species "NO_2Ce" can be considered to be a nitrite ion and cerium(IV) or a nitrogen dioxide molecule and cerium(III) (or, in fact, some other combination of oxidation states which adds up to seven). In any case, oxidation of this species by another cerium(IV) gives two cerium(III) species and a nitrogen(V) species. In aqueous media, the nitrogen(V) species is no doubt nitrate but in the anhydrous media, a nitrogen(V) oxide such as dinitrogen pentoxide, N_2O_5, might be formed.

Scheme I



A significant point is that the mechanism proposed in Scheme I involves at least in part the oxidation of the substrate by a ligand, followed by oxidation of the reduced ligand by the metal-ion oxidant. This type of scheme may occur in other oxidations by CAN and may account for the fact that CAN often behaves like a two-electron oxidant[2,15] and has brought about more successful reactions with organic compounds than any other cerium(IV) salt.

An experimental result which is quite striking is the solvent independence of the benzaldehyde to benzene ratio. From the data in Table I it is seen that this ratio varies from 73/27 to 88/12 in water, aqueous acetic acid, anhydrous acetic acid, anhydrous sulfolane, and anhydrous acetonitrile using 4 equiv of cerium(IV). Since the basicities of these solvents differ considerably, it is unlikely that the bases needed to bring about the proton removals shown in Scheme I are solvent molecules either free or as ligands of cerium. A possible explanation for this solvent independent ratio is that the bases needed to bring about the proton removals shown in Scheme I are nitrate ligands on the cerium which is bound to the substrate. Cyclic transition states involving ligands of a metal have been proposed for other oxidations,[16] such as the oxidation of alcohols to ketones by chromium(VI); however, experimental support for such transition states has been lacking.

Experimental Section

Methods and Materials. Reagents and solvents were obtained from commercial sources and used without further purification. Equipment[17] and the method of preparing standardized CAN solutions[2] have been previously described. Glpc analyses were carried out using a 6 ft × $^1/_4$ in. column packed with 20% QF-1 on Chromosorb P (30/60 mesh) at 80–200° or a 5 ft × $^1/_4$ in. column packed with 20% Apiezon L on Chromosorb P (60/80 mesh) at 100–225°. A 6 ft × $^1/_4$ in. column packed with 20% Carbowax 20M on Chromosorb P (60/80 mesh) at 75° was used for the analysis of toluene in cycloheptatriene.

CHT was either Shell technical grade (91–92% pure) or Aldrich (96% pure) and was used unpurified or after distillation, bp 114–116° (1 atm) (lit.[3] bp 117° (749 mm)). The absence of benzene

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(13) W. S. Trahanovsky, M. D. Robbins, L. Van Roekel, and L. B. Young, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn, April 1969, ORGN 68.

(14) L. B. Young and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **91**, 5060 (1969).

(15) L. B. Young and W. S. Trahanovsky, *J. Org. Chem.*, **32**, 2349 (1967).

(16) K. B. Wiberg, Ed., "Oxidations in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965.

(17) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

as an impurity was shown by glpc and nmr. The major impurity was toluene.

Tropylium fluoroborate was prepared using the method of Conrow[18] or Dauben.[19] Ethyl tropyl ether was obtained from tropylium fluoroborate using the method of Conrow,[20] bp 64° (8.5 mm) (lit.[20] bp 62° (8 mm)).

Cycloheptatriene-7-d_1. A solution of 0.6 g (14 mmol) of sodium borodeuteride in 25 ml of 1.5 *M* sodium hydroxide was covered with 25 ml of pentane. A quantity of 6 g (34 mmol) of tropylium fluoroborate was added slowly in portions and the mixture was stirred for 15 min. The pentane layer was separated, washed with 25 ml of water, dried ($MgSO_4$), and the pentane was removed by distillation. The residue weighed 2.11 g (70%) and was found to be 0.5% d_0 and 99.5% d_1 by mass spectral analysis; nmr (CCl_4) δ 6.3 (m, 2), 5.9 (m, 2), 5.1 (t, 2), and 2.0 (t of t, 1).

Oxidation of CHT by CAN. 1. In Aqueous Acetic Acid. To a weighed quantity of *ca.* 400 mg (4 mmol) of CHT was added enough acetic acid or aqueous acetic acid, 1 *M* aqueous CAN solution, and the appropriate acid, base, or salt to give a solution with the desired percentage of acetic acid, a 4:1 molar ratio of cerium(IV) to CHT, and the desired concentration of acid, base, or salt. The resulting mixture was heated and stirred on a hot plate until the orange cerium(IV) color faded to a yellow or light yellow.

Glpc Analysis. A quantity of *ca.* 200 mg of standard, xylene, was accurately weighed into the reaction flask and the mixture was added to water and extracted with ether. The ether layer was washed with 1.5 *N* potassium hydroxide and dried ($MgSO_4$). Glpc analysis of the ether extract gave relative areas of standard, benzene, benzaldehyde, and unreacted starting material and toluene.[21] The yields of the products were calculated by correcting the measured glpc peak areas for differences in relative extraction ratios and thermal conductivities. These corrections were determined by preparing an identical cerium(IV) solution except for the absence of CHT and reducing the solution with *ca.* 10 drops of acetone. Into this solution were weighed benzene, benzaldehyde, and the standard. The solution was then extracted and analyzed by glpc.

2. In Water. The oxidation and glpc analyses were carried out as they were in aqueous acetic acid except that the ether extract was washed with potassium hydroxide only when perchloric or nitric acid had been added to the reaction mixture. In some cases the reaction mixtures were analyzed by nmr instead of glpc.

Nmr Analysis. After the oxidation, the cooled reaction mixture was extracted with carbon tetrachloride. The carbon tetrachloride solution was submitted to nmr analysis and integrated areas of the aldehydic and the benzene proton signals gave the benzaldehyde to benzene ratio.

3. In Anhydrous Acetic Acid. To a weighed quantity of 4 mmol of CHT dissolved in 32 ml of acetic acid was added 16 mmol of CAN. The mixture was heated and stirred for 30 min at which time the solution was yellow and the solid was white. The mixture was analyzed by glpc as described for the aqueous acetic acid runs.

4. In 50% Aqueous Sulfolane. To a weighed quantity of 2 mmol of CHT was added equal amounts of sulfolane and a 1 *M* CAN solution or a 1 *M* CAN solution 6 *M* in nitric acid to give a 4:1 molar ratio of cerium(IV) to CHT. The solution was heated for 6–12 min during which time the solution turned pale yellow. The solution was cooled, poured into 30 ml of saturated sodium chloride solution, and extracted with 15 ml of ether. The ether layer was dried ($MgSO_4$) and analyzed by glpc as described for the aqueous acetic acid runs.

5. In Anhydrous Sulfolane. The oxidation was carried out as in anhydrous acetic acid except that the mixture was heated and stirred for 4 hr during which time the solid CAN dissolved to give a homogeneous solution. The solution was cooled, a quantity of xylene, the standard, was added, the solution was poured into a saturated sodium chloride solution, and the mixture was extracted with ether. The ether layer was dried ($MgSO_4$) and analyzed by glpc as described for the aqueous acetic acid runs. For the runs that had a 2:1 cerium(IV) to CHT molar ratio, only half as much CAN was used.

6. In 50% Aqueous Acetonitrile. To 0.3917 g (3.88 mmol) of CHT in 7.8 ml acetonitrile was added 7.8 ml (7.8 mmol) of 1 *M* CAN solution. The orange cerium(IV) color faded immediately to a cloudy pale yellow. The solution warmed up slightly and two layers formed. The mixture was stirred for 2 min, 100 μl of xylene was added, and the mixture was added to 25 ml of water and extracted with 15 ml of ether. The ether layer was dried ($MgSO_4$) and analyzed by glpc with no corrections for extractions or thermal conductivity differences being made. The glpc peak for benzene was difficult to integrate accurately since it came on the tail of the acetonitrile peak.

7. In Anhydrous Acetonitrile. To a weighed quantity of 2 mmol of CHT was added enough acetonitrile to give a solution 0.125 *M* in CHT. To this solution was added 8 mmol of CAN. The mixture was heated and stirred for 8 min at which time the solid was white and the solution was orange.[22] The mixture was analyzed by glpc as described for the aqueous acetic acid runs. For the runs that had a 3:1 or 2:1 cerium(IV) to CHT molar ratio, only three-fourths or one-half as much CAN was used.

For the run which involved the addition of 4 equiv of CAN in two batches, a quantity of 2.2482 (4.0 mmol) of CAN was added to 0.202 g (2.0 mmol) of CHT in 8 ml of acetonitrile. The mixture was heated and stirred for 5 min at which time the solid was white and liquid orange. To this mixture was added 8 ml of acetonitrile and 2.248 g (4.0 mmol) of CAN and the mixture was heated and stirred for another 35 min at which time the solid was white and the liquid orange. The mixture was analyzed as described for the runs in aqueous acetic acid except that the extraction and thermal conductivity corrections were obtained from the control run used for 4 equiv of CAN in anhydrous acetonitrile.

In one run, 11 mmol of CHT in the presence of 44 mmol of CAN in anhydrous acetonitrile was heated and stirred for 2 hr. The solid was removed by filtration and an infrared spectrum of the liquid in a 0.5 mm polyethylene cell showed absorption at 1700 cm^{-1}, characteristic of benzaldehyde. Moreover, a portion of the acetonitrile solution was injected directly into a glpc and a peak which was enhanced by an authentic sample of benzaldehyde was observed. Thus, benzaldehyde must be a primary product and is not formed during aqueous work-up.

One run was carried out under nitrogen using a nitrogen-purged reaction mixture. A known quantity of toluene was added to the reaction mixture and direct analysis of the reaction mixture by glpc showed that 50% benzaldehyde (identified by glpc peak enhancement) was produced. Thus, the oxygen of the benzaldehyde cannot come from oxygen present during the reaction.

Determination of Carbon Monoxide. The gas evolved from the oxidation of CHT by 4 equiv of CAN in 50% aqueous acetic acid was collected and shown to have a mass of 28 by analysis by mass spectrometry. When the gas was placed above a palladium(II) solution, after 45 min palladium metal was floating on the surface of the solution as would be expected if the gas was carbon monoxide.[7]

The volume of gas evolved from the oxidation of 5 mmol of CHT by CAN in 50% aqueous acetic acid was measured and found to be 18.7 ml at 748 mm at 25°. Correction of this volume for the amount of gas produced in a control experiment with no CHT present, for the water vapor pressure, and to STP gives 0.73 mmol (15%) of carbon monoxide.

Oxidation of CHT in the Presence of Acrylamide. To a solution of 7.00 g (12.7 mmol) of CAN and 6.4 g of acrylamide in 13 ml of water was added 0.294 g (3.18 mmol) of CHT in 51 ml of acetic acid. The solution was heated at 90° for 30 min. Upon cooling, a mass of polymer completely filled the reaction vessel. A quantity of 30 ml of saturated sodium chloride solution was added and the mixture was extracted with 100 ml of a 50:50 mixture of pentane–methylene chloride. The organic phase was washed with water and saturated sodium bicarbonate and dried ($MgSO_4$), and the pentane and methylene chloride were distilled. Nmr analysis showed the benzaldehyde to benzene ratio to be 84:16. A quantity of 0.0459 g of xylene (standard) was added to the product mixture and analysis by glpc showed that the yield of benzaldehyde was 81%.

Isolation of Ethyl Tropyl Ether from the Oxidation of CHT by 2 Equiv of CAN in Anhydrous Acetonitrile. To a solution of 28.3 g (50.0 mmol) of CAN in 100 ml of acetonitrile at 30° was added dropwise with stirring 2.52 g (27 mmol) of CHT. Immediate reaction ensued upon addition of the CHT with precipitation of a white solid. When addition of the CHT was complete, the mixture was stirred for a few minutes and then added to 500 ml of water and extracted three times with ether. A quantity of 250 ml of absolute

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[18] K. Conrow, *Org. Syn.*, **43**, 101 (1963).

[19] H. J. Dauben, Jr., L. R. Honnen, and K. N. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

[20] K. Conrow, *J. Amer. Chem. Soc.*, **83**, 2343 (1961).

[21] CHT and toluene had the same glpc retention times under the conditions used for analysis.

[22] Additional heating up to 1.75 hr produced no visible change in the reaction mixture.

ethanol was added and solid sodium bicarbonate was added portionwise with stirring until the evolution of carbon dioxide ceased. The cerium salts which precipitated during the addition of sodium bicarbonate were filtered and the filtrate was extracted four times with ether. The ether layer was washed two times with water, dried ($MgSO_4$), and the ether was removed by distillation. A quantity of 100 μl of toluene (standard) was added to the yellow-orange liquid residue which was then analyzed by nmr. The nmr spectrum was nearly identical with that of authentic ethyl tropyl ether and toluene with no evidence of ethanol or diethyl ether. Integration of the appropriate peaks showed that 35.2% of an ethoxy moiety and 50.4% of a 7-oxycycloheptatriene moiety was produced (yields based on CHT). The ethoxy moiety must be part of the tropyl ethyl ether, while the extra 7-oxy-CHT moiety (15.2%) may be due to either ditropyl ether or tropyl alcohol. Support for the presence of tropyl alcohol is lent by the observation that the product formed a small second layer, probably water, on standing, possibly from the known reaction of two molecules of tropyl alcohol to form one molecule of ditropyl ether and one of water.

In order to determine the yield of tropyl ethyl ether expected from the above experiment if 100% of a tropylium ion species had been produced by the oxidation of CHT with 2 equiv of CAN, tropylium fluoroborate was added to aqueous ethanol and the mixture was worked up and analyzed by nmr as described above. Yields of 53.6% of ethoxy moiety (*i.e.*, the ethyl tropyl ether) and 69% of 7-oxycycloheptatriene moiety was obtained. Thus, the amount of 7-oxycycloheptatriene moiety obtained from the ethanol treatment of the product of oxidation of CHT with 2 equiv of CAN was 73% (50.4/69 × 100) of the theoretical yield.

Oxidation of Tropylium Fluoroborate by CAN. A quantity of 1.0 g (5.7 mmol) of tropylium fluoroborate in 10 ml of acetonitrile was added dropwise over a period of 5 min to 10 ml (12 mmol) of a 1.2 *M* CAN solution. After *ca.* 5 min a finely divided precipitate began to form and a gas evolved. Stirring was continued for 15 min and 90.2 mg (0.75 mmol) of mesitylene was added. The mixture was diluted with water and extracted with ether. The ether extracts were washed twice with water, dried ($MgSO_4$), and the ether was removed by distillation. Analysis by nmr ($CDCl_3$): δ 9.9 (s, $C_6H_5C\mathit{HO}$, 39.7 integration units), 7.5 (m, $C_6\mathit{H}_6$ and $C_6\mathit{H}_5$-CHO, 232 integration units), and 6.75 (s, $C_6\mathit{H}_3(CH_3)_3$, 25 integration units).

Oxidation of Ethyl Tropyl Ether by CAN. A quantity of 2 mmol of ethyl tropyl ether was oxidized by 4 mmol of CAN in 50% aqueous acetic acid and was worked up and analyzed by glpc as described for the oxidation of CHT in aqueous acetic acid.

Oxidation of CHT by Ceric Perchlorate. To 0.190 g (2.1 mmol) of CHT in 16.2 ml of acetic acid was added 16.2 ml (8.1 mmol) of 0.496 *M* ceric perchlorate in 6 *M* perchloric acid. The solution was heated on a steam bath for 5 min, cooled, poured into 100 ml of saturated sodium chloride and extracted with ether. The ether solution was analyzed by glpc as described for the CAN oxidation of CHT in aqueous acetic acid. In a similar fashion, the reaction was carried out in 50% aqueous sulfolane and total yield of benzaldehyde and benzene was <10%.

Oxidation of CHT by Permanganate. 1. Acidic Medium. To 0.92 g (10 mmol) of CHT in 7 ml of acetone and 2 ml of 4 *M* sulfuric acid was added 1.58 g (10 mmol) of potassium permanganate in 39 ml of 2 *M* sulfuric acid. There was an immediate exothermic reaction. After 4 hr, the mixture was extracted with carbon tetrachloride and nmr analysis showed the absence of benzene and benzaldehyde.

2. Neutral Medium. To 10 mmol of CHT was added 10 mmol of potassium permanganate in 15 ml of water. After stirring at room temperature for 40 min, the reaction mixture was filtered and extracted with carbon tetrachloride and analysis by nmr showed the absence of benzene and benzaldehyde and the presence of CHT.

Oxidation of CHT by Chromium(VI). A quantity of 0.376 g (4.0 mmol) of CHT was weighed into a flask containing 0.82 g (8 mmol) of chromium trioxide dissolved in 11 ml of acetic acid and 3 ml of water. Heat was evolved immediately and the solution turned dark. After 42 hr at room temperature, the solution was worked and analyzed by glpc as described for the CAN oxidation of CHT in aqueous acetic acid.

Stability of Tropone to Cerium(III) Solutions. To a solution of 16.4 ml (16.0 mmol) of 0.974 *M* CAN and 16.4 ml of acetic acid was added 13 drops of 95% ethanol and the solution was heated until colorless. This solution was added to 0.3 g of tropone[23] and the resulting solution was heated on a steam bath for 12 min. A routine work-up and analysis by glpc showed that no benzene or benzaldehyde had been produced.

Reaction of Tropylium Fluoroborate with Sodium Nitrate. A 50% aqueous acetic acid solution, 0.5 *M* in sodium nitrate and 0.5 *M* in tropylium fluoroborate, was allowed to react at 90° for 20 min. Glpc analysis of the ether extract of the reaction mixture showed no benzaldehyde or benzene.

Oxidation of Nitrite by CAN. After 25 ml of a 1 *M* CAN solution had been added to 25 ml of a 1 *M* sodium nitrite solution at 25°, the solution was clear and colorless. This condition persisted until a total of 50.0 ml of the CAN solution had been added. Upon the addition of more CAN solution, the orange cerium(IV) color persisted.

Oxidation of CHT-7-d_1 by 4 Equiv of CAN in 80% Aqueous Acetic Acid. A quantity of 0.794 g of CHT-7-d_1 was oxidized as described above for the undeuterated CHT. The benzene and benzaldehyde were separated and collected by glpc. The percentage of d_0 and d_1 species was determined by mass spectral analysis and the position of the deuterium in the benzaldehyde was determined by analysis of its nmr spectrum.

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[23] We thank Professor T. H. Kinstle and P. Carpenter for the tropone which was prepared by the method of Radlick.[8]