

Table I. Oxidation of $H_nXO_3^{n-3}$ Species by $HCrO_4^-$

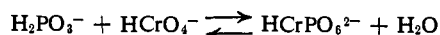
Reductant	Oxidation products	Rate	k	$K_f[H_{n-1}CrXO_6]$	Ref.
$H_2AsO_3^-$	$H_2AsO_4^-$	$\frac{K_f k [Cr(VI)] [H_2AsO_3^-]}{1 + K_f [H_2AsO_3^{2-}]}$	3.5×10^{-4}	22.4	<i>a</i>
$H_2PO_3^-$	$H_2PO_4^-$	No reaction at 25°	...	7.0	<i>b</i>
H_3PO_3	H_3PO_4	$\frac{K_f k [Cr(VI)] (H_3PO_3) [H^+]}{1 + K_f [H_3PO_3]}$	3×10^{-5}	26.0	<i>b</i>
HSO_3^-	$S_2O_6^{2-} + SO_4^{2-}$	$\frac{k K_f [Cr(VI)] [HSO_3^-]^2 [H^+]}{1 + K_f [HSO_3^-]}$	4×10^6	36	<i>c</i>

^a See ref. 1. ^b This work. ^c See ref. 2.

acetate buffer showed striking differences in rates and stoichiometry. HSO_3^- is oxidized half to $S_2O_6^{2-}$ and half to SO_4^{2-} , while $H_2AsO_3^-$ is oxidized exclusively to $H_2AsO_4^-$. The rate constant (not strictly comparable) for oxidation of HSO_3^- is about 10^6 vs. 10^{-4} for oxidation of $H_2AsO_3^-$. Since the structure of arsenite in solution is not certain while that for $H_2PO_3^-$ is known to contain an H-P bond, it seemed interesting to obtain the kinetics and stoichiometry for the reaction of $H_2PO_3^-$ with $HCrO_4^-$ in an acetate buffer for comparison.

The reaction of H_3PO_3 with $HCrO_4^-$ has been studied previously in rather concentrated solutions of $HClO_4$, H_2SO_4 , and HCl containing enough $Cr(VI)$ that $Cr_2O_7^{2-}$ was probably the principle species present.³ No formal rate law was determined.

In acetate buffer no reaction between $HCrO_4^-$ and $H_2PO_3^-$ is observed over a period of several days. At 100° very slow reaction occurs with apparently all the $H_2PO_3^-$ being converted to $H_2PO_4^-$, similar to the oxidation of arsenite. Thus, $S_2O_6^{2-}$ but neither $As_2O_6^{4-}$ nor $P_2O_6^{4-}$ can be produced by acid chromate oxidation of HSO_3^- , $H_2AsO_3^-$, and $H_2PO_3^-$, respectively. The equilibrium



was studied directly by spectrophotometric techniques previously reported.⁴ The results on the three systems are compared in Table I. Apparently the H-P bond in $H_2PO_3^-$ inhibits oxidation of phosphite and limits the product to phosphate using $HCrO_4^-$ as an oxidant.

Oxidation of H_3PO_3 by $HCrO_4^-$ in 1 *M* H^+ is reasonably fast for study. Preliminary results indicate the rate law is

$$\text{rate} = \frac{(H_3PO_3)(Cr(VI))(H^+)(k_1 + k_2[H_3PO_3])}{(1 + K(H_3PO_3))}$$

where k_1 and k_2 are $\sim 10^{-4}$ and $K = [H_2CrPO_6^{2-}]/[H_3PO_3][HCrO_4^-] = 26$. Units are moles per liter and seconds. Chloride ion forms CrO_3Cl^- and inhibits the reaction.

Table I gives the preliminary results of our study showing the striking differences in behavior of HSO_3^- , $H_2PO_3^-$, and $As(III)$ as reducing agents for $HCrO_4^-$ in aqueous solution.

(3) B. Kirson, *Bull. soc. chim. France*, 52 (1948).

(4) G. P. Haight, Jr., D. Richardson, and N. Coburn, *Inorg. Chem.*, 3, 1777 (1964).

Acknowledgment. This work was supported by the Swarthmore College Faculty Research Funds.

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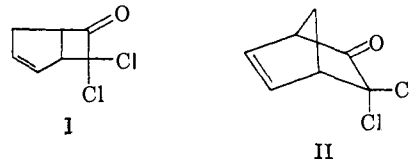
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A New Tropolone Synthesis via Dichloroketene

Sir:

Since Staudinger's unsuccessful attempt to prepare dichloroketene in 1913 by the thermal decomposition of mixed dichloromalonic anhydrides¹ the literature has been void of further references. In connection with a study of reactive chlorine compounds obtainable from basic chlorocarbon materials we investigated an alternate synthesis based on the dehydrochlorination of dichloroacetyl chloride. Although products from the low-temperature reaction were generally polymeric, we were successful in obtaining simple cycloadducts when generating dichloroketene *in situ* in the presence of reactive olefins. Of particular interest to this report is the 1:1 adduct readily obtained with cyclopentadiene which proved to be an immediate precursor of tropolone.²

In a typical cycloaddition experiment, a tenfold excess of cyclopentadiene over dichloroacetyl chloride in dry *n*-hexane was treated with a hexane solution of triethylamine at 0–5°. Removal of the solid hydrochloride and distillation at reduced pressure afforded an adduct $C_7H_8OCl_2$ in 70–75% yield. The liquid product (b.p. 38° (0.25 mm.), n_D^{20} 1.5163, g.l.p.c. purity 99+%) showed a single carbonyl band at 1806 cm^{-1} and olefinic unsaturation at 1609 cm^{-1} . Its proton resonance spectrum exhibited a complex multiplet centered at τ 4.1 relative to tetramethylsilane.



(1) H. Staudinger, E. Anthes, and H. Schneider, *Ber.*, 46, 3541 (1913).

(2) An ingenious three-step tropolone synthesis reported by J. J. Drysdale, W. W. Gilbert, and K. K. Schneider (*J. Am. Chem. Soc.*, 80, 3672 (1958)) involves cycloadducts of tetrafluoroethylene and cyclopentadiene. A cumbersome pyrolytic step at 700–750° and 5 mm. is required to convert the adducts to an isomeric mixture of tetrafluoroheptadienes prior to hydrolysis to tropolone.

(3) Elemental analyses of all compounds reported were satisfactory.

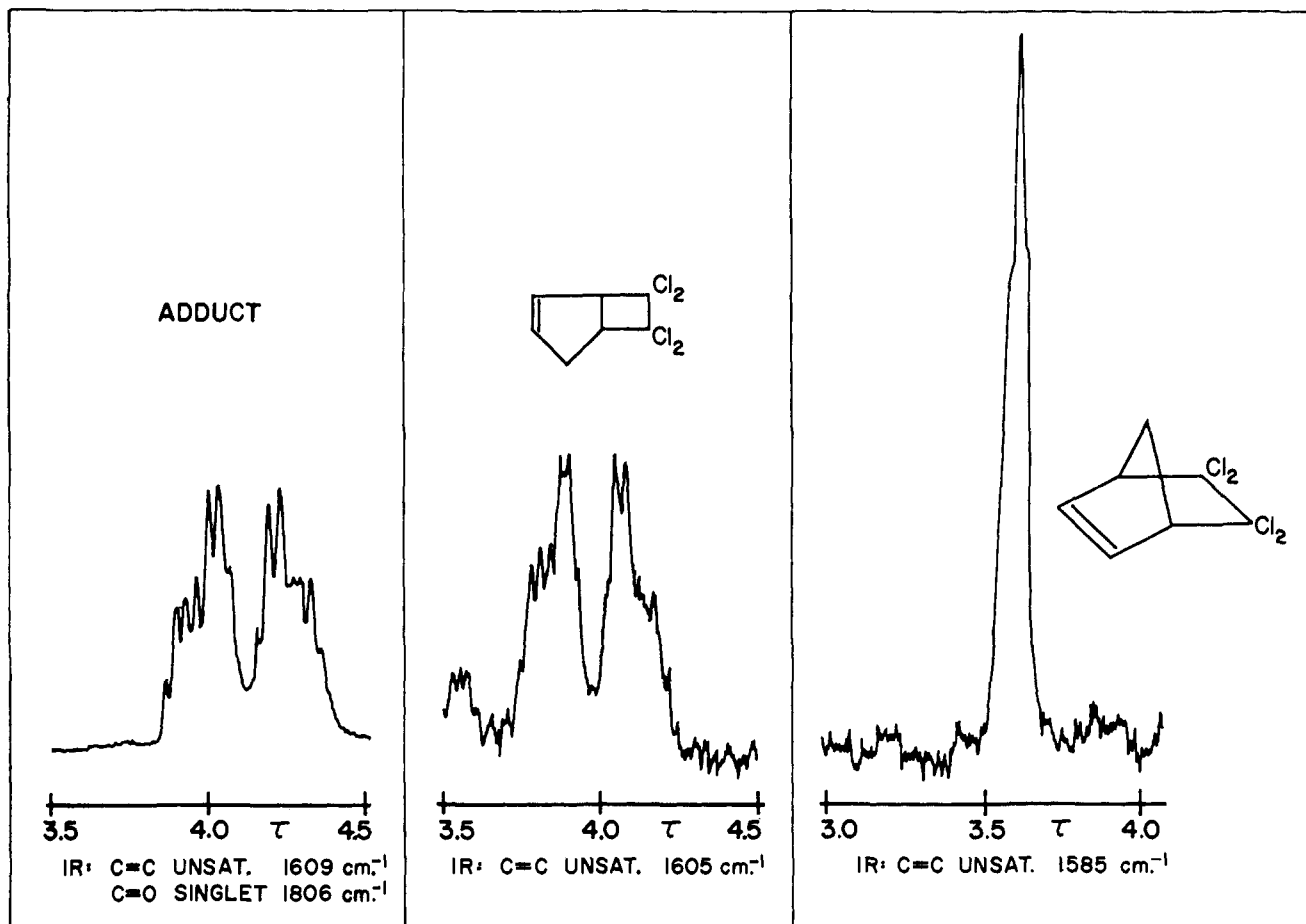


Figure 1. N.m.r. and infrared comparison in the unsaturated region (see ref. 5).

Structure I was assigned to the adduct in preference to Diels-Alder adduct II on the basis of (a) the frequency of the carbonyl absorption,⁴ (b) the n.m.r. and infrared spectra in the unsaturation region⁵ (Figure 1), and (c) the correspondence to the structures of known ketene-diene adducts.⁶ The location of the double bond was assigned in accord with the proposed mechanism of cycloadditions in terms of diradical stabilities.^{7,8}

Conversion of I to tropolone was best accomplished by hydrolysis with acetate in aqueous acetic acid. Refluxing of I (17.7 g.) for 16 hr. in 300 ml. of acetic acid containing 25.0 g. of potassium hydroxide and 10.0 ml. of water was followed by the addition of copper sulfate solution and neutralization with solid sodium

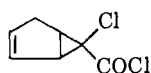
(4) D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946); F. V. Brutcher, Jr., T. Roberts, S. J. Barr, and N. Pearson, *J. Am. Chem. Soc.*, **78**, 1507 (1956).

(5) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 619 (1964); N. J. Turro and P. D. Bartlett, *J. Org. Chem.*, **30**, 1849 (1965). Double bond frequencies for a number of cycloadducts derived from cyclopentadiene and halogenated ethylenes were generally found to fall near 1603 cm^{-1} for the cyclopentenes (1,2 adducts) and near 1585 cm^{-1} for the norbornenes (1,4 adducts) (N. J. Turro, private communication).

(6) See, for example, A. T. Blomquist and J. Kwiatek, *J. Am. Chem. Soc.*, **73**, 2098 (1951), and also ref. 7, pp. 26 and 48.

(7) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 11 (1962).

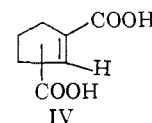
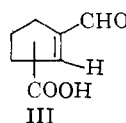
(8) A further structure



suggested by referee 1 appears unlikely, particularly in view of the lack of any appreciable reaction between the adduct and alcoholic silver nitrate at room temperature.

carbonate. Extraction with methylene chloride yielded the crude copper complex of tropolone which was crystallized from chloroform containing a little *n*-hexane. The yield of deeply colored green needles (m.p. 320° dec.) was 52%. Tropolone (m.p. 50–51°) could be liberated quantitatively from the copper complex by treatment with hydrogen sulfide in chloroform followed by crystallization from *n*-hexane.⁹

The hydrolysis of I with aqueous sodium carbonate (or bicarbonate) at 75° proceeded readily, judging by the disappearance of the organic phase and formation of chloride. However, tropolone yields were disappointingly low (1–5%). In addition to much polymeric material a new product was isolated (m.p. 92–94°, yield 15–20%) whose elemental analysis was in agreement with the composition formula $\text{C}_7\text{H}_5\text{O}_3$ (*Anal. Found*: neutr. equiv., 140). The n.m.r. spectrum (CDCl_3 , TMS) showed sharp singlets at τ -1.0 and 0.2 (one proton each), a quasisinglet at τ 2.9 with some two-cycle splitting (one proton), a deformed triplet at τ 6.2 (one proton), and a complex multiplet centered at τ 7.5 (four protons). Structure III was tentatively assigned based on this evidence. Oxidation of III



(9) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **73**, 836, (1951).

with silver oxide yielded dibasic acid IV (m.p. 181–183°. *Anal.* Calcd.: neutr. equiv., 78. Found: 79) with similar n.m.r. spectrum (D_3CCOCD_3 , TMS) save for a downfield singlet at $\tau -0.3$ accounting for the two carboxyl protons and for the missing aldehyde proton signal. The melting point of IV failed to agree with that of any of the reported¹⁰ dicarboxylic acids of cyclopentene. Rigorous structure proof is being undertaken in view of possible further carbon skeleton rearrangements.

Acknowledgment. We are indebted to Professor Paul Bartlett for suggesting this tropolone synthesis and for discussions during its course.

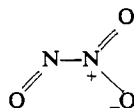
(10) A. Hassel and C. K. Ingold, *J. Chem. Soc.*, 1465 (1926); B. L. Nandi, *J. Indian Chem. Soc.*, 11, 277 (1934); S. Fujise, H. Uda, T. Ishikawa, H. Obaia, and A. Fujino, *Nippon Kagaku Zasshi*, 81, 1871 (1960); P. C. Guha and D. K. Sankaran, *Ber.*, 70, 2109 (1937).

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The Microwave Spectrum of Dinitrogen Trioxide

Sir:

Pure dinitrogen trioxide cannot be isolated in the gas phase since it exists in equilibrium with its dissociation products NO and NO_2 .¹ Infrared² and chemical evidence³ have supported the planar structure with a long N–N bond



At low temperature and pressures, we have observed the microwave spectrum of four isotopic species of N_2O_3 which support the planar model and from which the N–N bond is determined to be $1.85 \pm 0.03 \text{ \AA}$.

The spectra were produced at about 0.1 mm. by mixing NO and NO_2 – N_2O_4 at about equal pressure in an absorption cell cooled to -78° . The spectra could not be observed at room temperature. Equilibrium calculations^{1,4} gave pressures for N_2O_3 of about 1×10^{-3} mm. at -78° and about 1×10^{-6} mm. at room temperature, which correlate with this observed temperature dependence of the intensity. The ratio of observed intensity (roughly 10^{-7} – 10^{-8} cm.^{-1}) to calculated intensity (10^{-5} cm.^{-1}) indicated that the N_2O_3 was about 0.1–1% of the total mixture, which also agrees with equilibrium calculations.

When $^{14}NO_2$ was mixed with 97%–enriched ^{15}NO , absorption lines from three additional species were observed in relative intensity approximately equal to the normal isotopic species. Since the reaction $^{15}NO + ^{14}NO_2 \rightleftharpoons ^{14}NO + ^{15}NO_2$ is known,⁵ the presence of four isotopic species shows that the absorbing species contains two nonequivalent nitrogen atoms.

Several of the observed transitions, assigned by the Stark effect and frequency fit, are listed in Table I.

- (1) I. R. Beattie, *Progr. Inorg. Chem.*, 5, 1 (1960).
- (2) J. P. Devlin and I. C. Hisatsune, *Spectrochim. Acta*, 17, 218 (1961).
- (3) C. K. Ingold and E. H. Ingold, *Nature*, 159, 743 (1947).
- (4) I. C. Hisatsune, *J. Phys. Chem.*, 65, 2249 (1961).
- (5) E. Leifer, *J. Chem. Phys.*, 8, 301 (1940).

Table I. Microwave Spectrum of N_2O_3 (Mc./sec.)^a

Transition	Observed	Calculated
$O^{14}N^{14}NO_2$		
$2_{02} \rightarrow 3_{03}$	21750.30	21750.30
$2_{12} \rightarrow 3_{13}$	20469.14	20469.17
$2_{11} \rightarrow 3_{12}$	23684.06	23684.10
$2_{21} \rightarrow 3_{22}$	22138.32	22138.35
$2_{20} \rightarrow 3_{21}$	22525.94	22526.40
$O^{15}N^{14}NO_2$		
$2_{02} \rightarrow 3_{03}$	21532.19	21532.16
$2_{12} \rightarrow 3_{13}$	20262.25	20262.25
$2_{11} \rightarrow 3_{12}$	23454.32	23454.31
$3_{03} \rightarrow 4_{04}$	28289.72	28290.06
$3_{12} \rightarrow 4_{13}$	31143.56	31143.82
$O^{14}N^{15}NO_2$		
$2_{02} \rightarrow 3_{03}$	21692.38	21692.34
$2_{12} \rightarrow 3_{13}$	20416.07	20416.06
$2_{11} \rightarrow 3_{12}$	23613.07	23613.04
$3_{03} \rightarrow 4_{04}$	28507.34	28507.89
$3_{12} \rightarrow 4_{13}$	31356.87	31357.26
$O^{15}N^{15}NO_2$		
$2_{02} \rightarrow 3_{03}$	21472.78	21472.77
$2_{12} \rightarrow 3_{13}$	20208.04	20208.08
$2_{11} \rightarrow 3_{12}$	23381.64	23381.65
$3_{03} \rightarrow 4_{04}$	28215.30	28215.69
$3_{12} \rightarrow 4_{13}$	31048.14	31048.65

^a Obtained with a conventional Stark modulated spectrometer. Frequencies are reproducible to ± 0.2 – 0.3 Mc./sec.

Table II. Rotational Constants (Mc./sec.) and Moments of Inertia (a.m.u. \AA^2) for N_2O_3 ^a

	$O^{14}N^{14}NO_2$	$O^{15}N^{14}NO_2$	$O^{14}N^{15}NO_2$	$O^{15}N^{15}NO_2$
<i>A</i>	12,453	12,296	12,458	12,295
<i>B</i>	4,226.49	4,186.29	4,213.00	4,172.49
<i>C</i>	3,152.96	3,120.37	3,145.49	3,112.77
<i>I_a</i>	40.60	41.11	40.58	41.12
<i>I_b</i>	119.6101	120.7587	119.9931	121.1581
<i>I_c</i>	160.3354	162.0100	160.7161	162.4055
Δ	0.13	0.14	0.14	0.13

^a The experimental uncertainties in *A* and *B* = *C* are ± 6 and ± 0.05 Mc./sec., respectively; conversion factor, 5.05531×10^8 a.m.u. \AA^2 Mc./sec.

Quadrupole splitting due to the ^{14}N nucleus was not resolved. The moments of inertia are listed in Table II.

The observed value of $\Delta = I_c - I_b - I_a$ (inertial defect) is typical of planar molecules. Any appreciable deviation from planarity should give a negative value easily detectable owing to the large masses of the atoms. However, slight deviations from planarity cannot be eliminated on this basis alone. It is reasonable to conclude, therefore, that the moments of inertia support a planar or very nearly planar species.

The N–N bond length can be determined from the moments of inertia of three isotopic species.⁶ Using the sets $O^{14}N^{14}NO_2$, $O^{14}N^{15}NO_2$, $O^{15}N^{14}NO_2$, and $O^{15}N^{15}NO_2$, $O^{15}N^{14}NO_2$, $O^{14}N^{15}NO_2$, almost identical values of 1.850 and 1.853 \AA . were obtained. Therefore, the N–N bond length is evaluated at $1.85 \pm 0.03 \text{ \AA}$. The large uncertainty is considered sufficient to include errors introduced because the “nitro” nitrogen lies close to the “a” axis and because $I_c - I_b$ was substituted for the more uncertain I_a in Kraitchman’s equations.⁷ For comparison, the N–N bond in N_2H_4

(6) J. Kraitchman, *Am. J. Phys.*, 21, 17 (1953).

(7) V. W. Laurie, D. T. Pence, and R. H. Jackson, *J. Chem. Phys.*, 37, 2995 (1962).