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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The $BF_3 \cdot N_2O_4$ Complex as a Nitrating Agent[1]

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The stable, solid complex $BF_3 \cdot N_2O_4$ is an excellent nitrating agent for aromatic compounds and is somewhat more powerful than concentrated nitric acid (70%). In comparison with the latter it gives a different distribution of isomers and nitrates satisfactorily some substances which behave anomalously with nitric acid. Aliphatic compounds with a few exceptions are oxidized by the complex.

Dinitrogen tetroxide appears to be unique among simple molecules in the ease with which it can be dissociated homolytically or heterolytically in several ways. The equilibria shown here illustrate

$$\begin{tikzcd}
O_2N^- + NO_2^+ \arrow[r, shift left, "A"] & O_2N{:}NO_2 \arrow[l, shift left] \arrow[r, shift left, "B"] \arrow[d, shift right, "\text{heat}"'] & O_3N^- + NO^+ \arrow[l, shift left] \\
 & O_2N\cdot + \cdot NO_2 \arrow[u, shift right] &
\end{tikzcd}$$

A = generalized acids B = generalized bases

these dissociations and indicate the reagents and conditions favoring each of them. The homolytic dissociation into $\cdot NO_2$ radicals is too well known to require extensive comment. It has been studied quantitatively by Verhoek and Daniels[2] among others, and proceeds to the extent of 20% at 27° and atmospheric pressure.

The base-promoted dissociation occurs quite readily with even very weak bases such as amines, nitriles, ethers, ketones, carboxylic acids and their anhydrides and esters.[3] This type of dissociation has been so strongly emphasized that some authors consider it to be the only type of heterolytic dissociation which N_2O_4 can undergo.[4] Actually liquid N_2O_4 itself is very weakly ionized and is a poor conductor of electricity. However, tetramethylammonium nitrate containing N^{15} in the nitrate ion equilibrates completely with ordinary liquid N_2O_4 in 36 hours, suggesting the presence of some NO_3^- in the liquid.[5] Bases increase the extent of this dissociation, and complexes of the types $N_2O_4 \cdot B$ and $N_2O_4 \cdot 2B$ are known in considerable variety. Presumably their structures are[6]

$$(B \rightarrow NO)^+ (NO_3^-) \text{ and } B \rightarrow \underset{\overset{\uparrow}{B}}{NO^+}(NO_3)^-$$

although Sisler finds no spectral evidence for ions in complexes with weak bases such as ethers. In any event the polarizing action of the base would be expected to promote the formation of the most acidic ion from N_2O_4, and on this basis NO^+ may be taken as more acidic than NO_2^+, the other possible acidic ion from N_2O_4.

The acid-promoted dissociation of N_2O_4 would be expected to proceed in such a way that the most basic ion would be produced. Of the two possibilities, NO_2^- and NO_3^-, the former is the more basic as evidenced by the fact that HNO_2 is more weakly ionized than HNO_3. However, since NO_2^- is still not very basic this dissociation would only be caused by relatively strong acids. Weak acids might form complexes with N_2O_4 which are undissociated molecules. However BF_3 is one of the strongest acids known and as such should cleave N_2O_4 heterolytically into NO_2^- and NO_2^+ and then combine with the NO_2^- ion.

The above reasoning has led us to formulate the $BF_3 \cdot N_2O_4$ complex as $(F_3B \leftarrow NO_2)^-(NO_2)^+$, a structure which is also in accord with its physical and chemical properties. Unfortunately the substance does not lend itself readily to spectral measurements since it is non-crystalline, is insoluble in all inert solvents, is very reactive, is readily dissociated at elevated temperatures, and cannot be melted under pressure below 300°. Chemically it is a powerful nitrating agent, especially for aromatic compounds and this is perhaps the best evidence for the presence in it of an NO_2^+ ion.

In addition to the theoretically interesting consideration of its structure there is also the practically interesting consideration of the use of $BF_3 \cdot N_2O_4$ as a nitrating agent. Results obtained in a series of reactions are summarized in Table I.

Discussion of Results

Relative rate studies in which benzene reacted with $BF_3 \cdot N_2O_4$ and nitric acid of various concentrations are summarized in Table II. They show that the complex nitrates benzene under comparable conditions somewhat more slowly than does concentrated nitric acid (70%, d. 1.42) but produces considerable amounts of *m*-dinitrobenzene while the nitric acid produces none. This probably means that the complex nitrates nitrobenzene much more rapidly than concentrated nitric acid. These apparently anomalous results may be explained by assuming that the nitration rates with the complex are influenced by the physical state of the complex which is an insoluble solid. As such it introduces into the rate equations certain diffusion factors common to heterogeneous reactions between solids and liquids. These factors would be expected to disguise the power of the complex as a nitrating agent making it appear less reactive on the basis of over-all rate and more reactive on the basis of types of molecules attacked. On this assumption the complex is probably a considerably

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[1] From the Ph.D. thesis of Clifford M. Vogt, January, 1957.

[2] F. Verhoek and F. Daniels, THIS JOURNAL, **53**, 1250 (1931).

[3] H. H. Sisler, *et al.*, *ibid.*, **74**, 877 (1952); **75**, 5158, 5191 (1953); **76**, 4668 (1954).

[4] P. Gray and A. D. Yoffe, *Chem. Revs.*, **55**, 1092 (1955).

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[6] C. C. Addison, *et al.*, *J. Chem. Soc.*, 1390 (1952); *Chemistry & Industry*, 1338 (1953); *Quart. Revs.* (*London*), **9**, 115 (1955).

TABLE I

NITRATION PRODUCTS WITH $BF_3 \cdot N_2O_4$

Compound nitrated	Reactant ratio[a]	Solvent[b]	Time, hours	Temp.,[c] °C.	Products	M.p. or b.p. (mm.), °C.	Yield, %
Benzene	0.12	6	24		Nitrobenzene	120–125 (1–3)	36.6
					m-Dinitrobenzene	90	26.4
p-Cymene	1.70	2	36	0	2-Nitro-*p*-cymene	125 (1)	88.5
Naphthalene	2.14	4	48	27[d]	1-Nitronaphthalene[e]	58	91.0
			4	85[d]			
Naphthalene	2.14	4	48	27[d]	1,5-Dinitronaphthalene	216–217	43.9
			4	80[d]	1,8-Dinitronaphthalene	173	29.4
Chlorobenzene	1.12	4	132	27[d]	*p*-Nitrochlorobenzene	83–84	60.1
			6	80[d]	*o*-Nitrochlorobenzene	31–32	38.5
o-Nitrotoluene	1.12	4	72	50	2,4-Dinitrotoluene	70	60.5
					2,6-Dinitrotoluene	66	39.0
Phenol	1.00	4	12	0	*o*-Nitrophenol	45	4.6
Phenol	2.63	2	12	0	*o*-Nitrophenol	45	17.0
					p-Nitrophenol	114	Trace
					2,4-Dinitrophenol	114	14.2
2,6-Di-*t*-butylphenol	2.00	4	4	0	2,6-Di-*t*-butylquinone	67–68	28.3
					2,2′,6,6′-Tetra-*t*-butyl-4,4′-biphenylquinone	244	14.6
2,6-Di-*t*-butylphenol	3.16	1	8	0	2,6-Di-*t*-butylquinone	67–68	20.9
					2,2′,6,6′-Tetra-*t*-butyl-4,4′-biphenylquinone	244	27.8
					2,4-Dinitro-6-*t*-butylphenol	122–123	22.3
Thymol	2.75	2	1	0	4-Nitrosothymol	159–160	90.5
Thymyl methyl ether	2.60	2	16	0	4-Nitrothymyl methyl ether	125–127 (1)	76.5
Thymyl methyl ether	2.60	5	16	27	4-Nitrothymyl methyl ether	125–127 (1)	60.1
					Thymoquinone	45	21.2
Aniline	1.00	1	8	0	Diazonium salt	. . .	98.5
Benzophenone oxime	5.5	2	24	27	Benzophenone	48–49	98
Benzophenone oxime	5.5	4	193	27[d]	Benzophenone	48–49	44.3
			3	95[d]	2,3′-Dinitrobenzophenone	126	27.1
Ethylene	0.50	4	12	0	No prod. isolated, unstable	. . .	. .
Isobutane		7	6	130	Small amount of tar	. . .	. .
Vinyl chloride	0.50	1	6	0	1,1-Dichloro-2-nitroethane	41–42 (1–2)	13.9
2-Nitropropane	1.00	7	12	140	Recovered 2-nitropropane	. .	88
Sodium 2-propanenitronate	3.00	1	8	0[d]	2,2-Dinitropropane	54	19.8
			12	27[d]			
Dimethyl ether	1.0	2	6	0	No prod. isolated, oxidn.	. . .	. .
Dibutyl ether	1.00	4	24	0	Butyl butyrate	166–167 (760)	18.0
					Butyric acid	160–161 (760)	4.0
					1-Butanol	70–71[f]	3.5
					Butyraldehyde	122[g]	2.8
Dibutyl ether	3.00	2	24	0	Butyl butyrate	166–167 (760)	51.0[h]
Epichlorohydrin	1.12	2	48	27	Polymeric oil	>200 (2)	71
2-Chlorobutane	1.00	4	4	60[d]	Recovd. 2-chlorobutane	67–68 (760)	88.1
			48	27[d]			
1-Bromobutane	1.00	4	48	27	2-Bromobutane	91–92 (760)	11.8
1-Bromobutane	1.25	4	192	27	2,2-Dibromobutane	145–146 (760)	21.8
					sec-Butyl nitrate	51–52 (7)	17.4
					2-Butanol	99–100 (760)	7.3
					2-Bromobutane	91–92 (760)	5.4
2-Bromobutane	1.25	4	192	27	2,2-Dibromobutane	145–146 (760)	29.1
					sec-Butyl nitrate	51–52 (7)	22.0
					2-Butanol	99–100 (760)	11.0
t-Butyl chloride	1.00	3	2	0	Fume off	. . .	. .
t-Butyl bromide	1.00	3	6	0	Fume off	. . .	. .
1-Butanol	1.00	2	8	0[d]	*sec*-Butyl nitrate	123–124 (760)	17.1
			16	27[d]	Butyl butyrate	166–167 (760)	12.5
					Butyric acid	160–161 (760)	9.2
					Butyraldehyde	73–76 (760)	6.5
					2-Butanol	98–101 (760)	3.2
Dibutylamine	1.78	4	96	27	Addn. compd. $(C_4H_9)_2NH:BF_3$	258–260 dec.	98.0
N,N-Dibutylacetamide	1.09	4	192	27	Recovered amide	90–91 (1.0)	77.0

TABLE I (*Continued*)

Compound nitrated	Reactant ratio[a]	Solvent[b]	Time, hours	Temp.,[c] °C.	Products	M.p. or b.p. (mm.), °C.	Yield, %
Ethyl methylmalonate	1.03	2	72	27	Ethyl nitromethylmalonate	66–67 (0.5)	62.6
Ethylene 1,2-bis-(malonic ester)	1.12	2	72	27	Fume off		
	3.80	4	72	27	Fume off	. . .	. .
	2.00	7	72	27	Fume off		

[a] Mole ratio of complex to compound. [b] Solvents: 1 = chloroform, 2 = carbon tetrachloride, 3 = nitromethane, 4 = nitroethane, 5 = 2-nitropropane, 6 = benzene, 7 = no solvent. [c] All reactions started at 0°. [d] Times at two successive temperatures for a single reaction. [e] For this experiment benzene was refluxed in a Soxhlet extractor over the complex in an Alundum thimble. The temperature at the point of reaction probably averaged 35–45°. [f] M.p. of the α-naphthylurethan. [g] M.p. of the 2,4-dinitrophenylhydrazone. [h] Grams. [i] One mole equivalent of water was present in this run.

more powerful nitrating agent than 70% nitric acid.

TABLE II

RELATIVE NITRATION RATES FOR BENZENE[a]

Nitrating agent	Time, hours	Conversions, %	
		$C_6H_5NO_2$	m-$C_6H_4(NO_2)_2$
HNO_3, 16%	4.0	10.0	0
	6.0	15.6	0
HNO_3, 70%	1.0	61.2	0
	2.0	76.2	0
	3.0	84.0	0
	6.0	91.5	0
HNO_3, 90%	0.25	95.7	Trace
Complex	3.0	20.7	10.9
	6.0	35.1	23.8

[a] All experiments were run at 80° with a 1.5-mole ratio of nitrating agent/benzene.

The results with naphthalene also are pertinent to a consideration of relative rates of nitration. With fresh, completely anhydrous complex naphthalene yields no mononitronaphthalene but only a mixture of dinitronaphthalenes. If water is present, either through prolonged contact with undried air or through deliberate addition, the product contains mononitronaphthalene. With one mole of added water per mole of complex mononitronaphthalene is the sole product. The dinitronaphthalenes formed contain the 1,5- and 1,8-isomers in a ratio of about 1.5/1. This experiment has been repeated many times following the published criticism of Ward[7] and the isomers have been separated by several different procedures. In all cases the ratio of about 1.5/1 was found. This is nearly the reverse of the ratio (31/69) found for nitric acid nitrations by Ward and Hawkins.[8] In general, isomer ratios were determined as nearly as possible by the methods used by the authors quoted.

One advantage of the complex as a nitrating agent is its tendency to produce a different ratio of isomers from those obtained with nitric acid. *Ortho* substitution is favored relative to *para* substitution. In this respect the complex resembles acetyl nitrate and mixtures of acetic anhydride with nitric acid. The complex, however, is far safer to handle than acetyl nitrate and shows no explosive tendencies alone. Chlorobenzene reacts rapidly at room temperature with the complex to produce quantitative yields of a 40/60 mixture of *o*- and *p*-nitrochlorobenzenes. Bird and Ingold[9] give the ratio of these products as 31/69 using nitric acid at 35°. Similarly *o*-nitrotoluene formed 2,4- and 2,6-dinitrotoluenes with the complex in a 61/39 ratio as compared to a 68/32 ratio using nitric acid.

Another advantage of the complex is the ease with which it accomplishes certain nitrations which proceed anomalously with nitric acid. *p*-Cymene is reported to be converted by nitric acid to difficultly separable mixtures containing various oxidation products and considerable amounts of nitrotoluenes,[10–12] except under highly specialized conditions![13] On the other hand, the complex in carbon tetrachloride converts *p*-cymene to 2-nitro-*p*-cymene in 85–90% yields and the product offers no difficulties in purification. Similarly thymol and its ethers with nitric acid give primarily nitrocresols or nitrocresyl ethers.[14] The complex in carbon tetrachloride converts thymyl methyl ether to 2-nitrothymyl methyl ether in 75% yield.

Some of the results with the complex are apparently anomalous in that they lead to nitrosation rather than nitration. Thus aniline is diazotized by the complex and thymol is converted to 6-nitrosothymol (thymoquinone monoxime). It is our belief that such results depend in part on the basicity of these reactants which is great enough to remove BF_3 from the weakly basic N_2O_4 thus destroying the complex. The nitrosating action of N_2O_4 is well known and depends on the base-promoted ionization of N_2O_4 to NO_3^- and NO^+ the latter of which is the nitrosating ion. However this explanation does not suffice to account for all of the results with phenols as evidenced by the variety of products obtained with different phenols.

In the aliphatic series methylmalonic ester is nitrated satisfactorily in good yields, but ethers and alcohols are oxidized and give no nitro compounds. 2-Nitropropane is not nitrated by the complex at temperatures up to 140° and explodes at slightly above this temperature. On the other hand, sodium 2-propanenitronate yields 2,2-dinitropropane in low yields (20%) at room temperatures or below. Of special interest are the reactions of the 1- and 2-bromobutanes. These halides were selected as probably inert to the complex but to our surprise reacted vigorously at room temperature. The principal products from both halides were 2-butyl nitrate and 2,2-dibromobutane. No isomeric dibromobutanes were found. A reasonable mech-

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(12) A. Leeds, *ibid.*, **2**, 277 (1880); *Ber.*, **13**, 1993 (1880); **14**, 482, (1881).

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anism for this reaction leading to 2,2-dibromobutane has not occurred to us since, if the bromine is reacting as bromine atoms, it should attack 2-bromobutane at all positions rather than at just the 2-position, and if it is reacting as a bromonium ion and adding to an unsaturated hydrocarbon then the product should also have some other atom or group introduced on a position adjacent to the 2-position. If the reaction proceeds *via* the oxidation product 2-butanone, then some at present unknown mechanism for replacing an oxygen atom by two bromine atoms is operating. It is difficult to see how $C_2H_5CBr{=}CH_2$ or HBr could be present in the reaction mixture, although, if present, they probably would react to form 2,2-dibromobutane.

Unsaturated compounds such as ethylene and propylene gave tarry mixtures which could not be worked up satisfactorily because of their great sensitivity to heat. However, vinyl chloride gave small yields (14%) of 1,1-dichloro-2-nitroethane,[15] a product which could arise only through oxidative degradation of part of the vinyl chloride.

Conclusions.—The $BF_3 \cdot N_2O_4$ complex is a useful new nitrating agent which is prepared readily as a stable white solid. In nitrations of aromatic compounds it differs from nitric acid in the relative rates of reaction, in the distribution of isomers produced, and in the ease with which it nitrates some substances which behave anomalously with nitric acid. With even weakly basic materials such as aniline and some phenols the complex may induce nitrosation rather than nitration. In the aliphatic series with few exceptions the complex acts as an oxidizing agent.

Experimental

Preparation of the Complex.—The previously described method of preparation was used.[16] We wish to correct a typographical error in the gravimetric data formerly published. By weight 136 g. rather than 100 g. of NO_2–N_2O_4 was found to combine with 99.5 g. of BF_3 on the average. The following experiments illustrate the techniques employed.

Reaction of the Complex with *p*-Cymene.—A slurry of 90 g. (0.560 mole) of the complex in 400 ml. of carbon tetrachloride was cooled to ice-bath temperature. *p*-Cymene (44.5 g., 0.332 mole) was added dropwise within two hours, and the reaction was stirred 36 hours at ice-bath temperature. The reaction was filtered, the organic layer washed several times with water, extracted with ether, dried and fractionally distilled. *p*-Cymene, 3.9 g., was recovered. The main product was 47.7 g. (88.5% yield) of 2-nitro-*p*-cymene,[17] b.p. 125° (1 mm.), $n^{20}D$ 1.5284.

Reaction of the Complex with Thymyl Methyl Ether.—A slurry of 69 g. (0.400 mole) of the complex in 250 g. of 2-nitropropane was cooled to ice-bath temperature. To this mixture 25 g. (0.152 mole) of thymyl methyl ether was added slowly. The reaction was stirred 8 hours at ice-bath temperature followed by 16 hours at room temperature. The reaction was filtered, washed several times with water, extracted with ether and dried. The excess solvents were distilled off and the remaining liquid fractionated under vacuum. The first fraction solidified upon cooling and was recrystallized from an ethanol–water (50–50) mixture to yield 5.3 g. (21.2%) of thymoquinone, m.p. 45°, mixture m.p. with an authentic sample, 45°. The other fraction contained 19.1 g. (60.1% theor.) of 4-nitrothymyl methyl ether, b.p. 125–127°.

Anal. Calcd. for $C_{11}H_{15}NO_3$: C, 63.11; H, 7.12; N, 6.70. Found: C, 63.22; H, 7.18; N, 6.81.

This new compound also was identified by reduction with tin and hydrochloric acid to the known 4-aminothymyl methyl ether hydrochloride,[18] m.p. 250°.

Reaction of the Complex with Aniline.—A slurry of 160 g. (1.00 mole) of the complex in 200 ml. of chloroform was cooled to 0° and 93.0 g. (1.00 mole) of aniline slowly was added. The reaction mixture turned black after most of the aniline had been added. It was held at 0° for 8 hours and then filtered. The solid obtained was washed several times with anhydrous ether and air-dried; yield 225.0 g. of a dark colored solid.

(a) **Thermal Decomposition of the Diazonium Salt.**—The above diazonium salt, 24.0 g., was decomposed by careful heating in a 500-cc. flask equipped for distillation. The product was washed with water, dried, and redistilled through a short column; yield 6.6 g. (65%) of fluorobenzene,[19] b.p. 84–85°, $n^{20}D$ 1.4653.

(b) **Coupling of the Diazonium Salt.**—The diazonium salt, 1.32 g., was dissolved in 10 ml. of 10% sodium hydroxide. To this was added a solution of 1.30 g. (0.009 mole) of β-naphthol in 15 ml. of 10% sodium hydroxide. An orange coupling product precipitated immediately, was filtered off, washed with 10% sodium hydroxide and water, and then dried. The solid was recrystallized from hot acetone to give the coupled product, 1-phenylazo-2-naphthol,[20] m.p. 134°, in quantitative yield.

Reaction of the Complex with Sodium 2-Propanenitronate.—A slurry of 160 g. (1.00 mole) of the complex in 300 ml. of chloroform was cooled to 0° and 55 g. (0.495 mole) of sodium 2-propanenitronate was added. The reaction stood 72 hours at room temperature. The mixture was steam distilled, the distillate extracted with ether, dried and fractionated. 2,2-Dinitropropane,[21] 13.5 g. (20% yield), b.p. 48–50° (1–2 mm.), m.p. 53°, was isolated.

Reaction of the Complex with Dibutyl Ether.—A slurry of 160 g. (1.00 mole) of the complex in 200 ml. of nitroethane was cooled to 0° and 130 g. (1.00 mole) of dibutyl ether was added slowly enough to prevent the temperature from rising above 10°. All the complex disappeared during the ether addition. The reaction was held at 0° for 1 hour, washed with water, extracted with ether and dried. Fractional distillation yielded the products

	B.p., °C.	Yield g.	Yield %	$n^{20}D$
Butyraldehyde	74–76	2.0	2.8	....
1-Butanol	116–118	2.6	3.5	....
Butyric acid	160–161	3.5	4.0	1.3990
Butyl butyrate	166–167	24.9	18.0	1.4047

The butyraldehyde was identified as its 2,4-dinitrophenylhydrazone, m.p. 122°, the butanol as its α-naphthylurethan, m.p. 70–71°, and the remaining compounds by their physical constants.

Reaction of the Complex with 2-Bromobutane.—A slurry of 200 g. (1.25 moles) of the complex in 200 ml. of nitroethane was cooled to 0° and 137 g. (1.00 mole) of 2-bromobutane was added slowly. The reaction stood 8 days at room temperature. The mixture was filtered and the solid collected was added to water and extracted with ether. The two ether extracts were combined and dried. Fractional distillation yielded the products

	B.p., °C.	Yield g.	Yield %	$n^{20}D$	d^{20}_4
2-Bromobutane	91–92	19.4	14.2	1.4355	1.2585
2-Butanol	99–100	7.2	11.0	1.3970	0.8098
2-Butyl nitrate[a]	123–124	24.5	22.0	1.3711	1.0379
2,2-Dibromobutane[b]	145–146 51–52(7 mm.)	26.9	29.1	1.5053	1.7392

[a] *Anal.* Calcd. for $C_4H_9NO_3$: C, 40.33; H, 7.55; N, 11.75. Found: C, 40.56; H, 7.68; N, 11.61. [b] *Anal.* Calcd. for $C_4H_8Br_2$: C, 22.27; H, 3.70; Br, 74.03. Found: C, 22.50; H, 3.90; Br, 73.72.

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A small sample of the 2,2-dibromobutane was hydrolyzed in aqueous cuprous chloride to the corresponding ketone, 2-butanone, which was converted to its 2,4-dinitrophenylhydrazone, m.p. 117°.[22]

Reaction of the Complex with Dibutylamine.—A slurry of 160 g. (1.00 moles) of the complex in 200 ml. of nitroethane was cooled to 0° and 73.0 g. (0.565 mole) of dibutylamine was added slowly. The reaction stood 4 days at room temperature. The reaction was filtered and the organic liquid was washed with water, extracted with ether and the extract dried. The solvents were removed by vacuum distillation. The remaining solid was recrystallized from hot benzene, m.p. 258–260°. Mixture m.p. with a material prepared by bubbling gaseous boron trifluoride into dibutylamine in benzene, gave no depression. The total yield of the addition complex was 98%.

Reaction of the Complex with Ethyl Methylmalonate.—A slurry of 38 g. (0.238 mole) of the complex in 30 ml. of carbon tetrachloride was cooled to 0° and ethyl methylmalonate (40 g., 0.230 mole) was added dropwise within 2 hours. The reaction stood 3 days at room temperature and then was filtered, washed several times with water and dried. Fractionation yielded 10.1 g. of the starting ester and 23.6 g. (62.6%) of ethyl methylnitromalonate,[23] b.p. 66–67° (0.5 mm.), $n^{20}D$ 1.4361.

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LAFAYETTE, INDIANA

[CONTRIBUTION NO. 2273 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

On Some Cleavage Products of the Boron Trifluoride Complexes of α-Carotene, Lycopene and γ-Carotene

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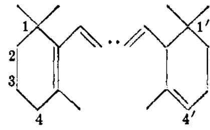
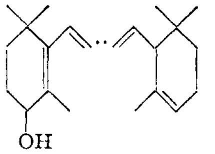
Hydrolysis of the deeply colored α-carotene–BF_3 complex yields mainly 4-hydroxy-α-carotene while the α-ionone end of the molecule remains unaltered. By dehydrogenation of the hydroxy compound 4-keto-α-carotene is obtained. Ethanolysis of the complex mentioned results in the formation of 4-ethoxy-α-carotene. Lycopene and γ-carotene were studied along similar lines. Upon cleavage of the complex, lycopene yielded 5,6-dihydroxy-5,6-dihydrolycopene, characterized by some conversions (Chart 2), while γ-carotene gave the 4-hydroxy compound. The cyclic terminal group of the γ-carotene complex appears to be more reactive than its acyclic end. Reaction mechanisms for the conversions mentioned are proposed (Charts 1, 3).

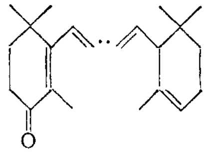
Although the formation of some deeply colored, rather sensitive carotenoid–boron halogenide complexes had been observed 18 years ago,[1] the cleavage products of such complexes were studied only recently, in our laboratory,[2–4] especially those obtained from the bicyclic, symmetrical β-carotene, $C_{40}H_{56}$, and some of its dehydrogenation products. We now have extended these experiments[5] to three structural isomers of β-carotene, *viz.*, the unsymmetrical, bicyclic α-carotene (I), the symmetrical, acyclic lycopene (XII) and the unsymmetrical, monocyclic γ-carotene (XXII).



I, α-carotene[6]



II, 4-hydroxy-α-carotene



III, 4-keto-α-carotene

α-Carotene.—When the dark blue complex of this polyene was treated with water, the original orange color of the carotene solution reappeared, and subsequent chromatographic analysis showed that about a third of the starting material had been converted into 4-hydroxy-α-carotene, $C_{40}H_{55}OH$ (II). This compound, although mentioned briefly before,[4] has been structurally clarified only in the present study. It is crystalline and forms crystalline alkyl ethers and an acetate. It shows the α-carotene spectrum (Fig. 1). The allylic position of the OH– group was indicated by the positive reaction with a dilute, anhydrous HCl solution in chloroform,[7] in that a considerable deepening of the color was observed almost immediately and, upon chromatographing, 3,4-dehydro-α-carotene[3] (IV) was shown to be present. The same com-

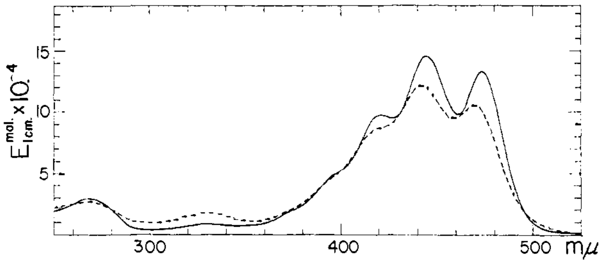


Fig. 1.—Molecular extinction curves (in hexane) of 4-hydroxy-α-carotene: ———, fresh solution of the all-*trans* compound; – – – –, mixture of *cis-trans* isomers after iodine catalysis.

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[1] G. N. Lewis and G. T. Seaborg, THIS JOURNAL, **61**, 1886 (1939); H. H. Strain, *ibid.*, **63**, 3448 (1941).

[2] L. Wallcave, J. Leemann and L. Zechmeister, *Proc. Nat. Acad. Sci. U.S.*, **39**, 604 (1941).

[3] G. Karmakar and L. Zechmeister, THIS JOURNAL, **77**, 55 (1955).

[4] F. J. Petracek and L. Zechmeister, *ibid.*, **78**, 3188 (1956).

[5] *Cf.* W. V. Bush, Thesis, California Institute of Technology, 1958.

[6] The two dots in the abbreviated formulas designate uninterrupted conjugation in an isoprenic structure.

[7] P. Karrer, *Helv. Chim. Acta*, **34**, 2160 (1951).