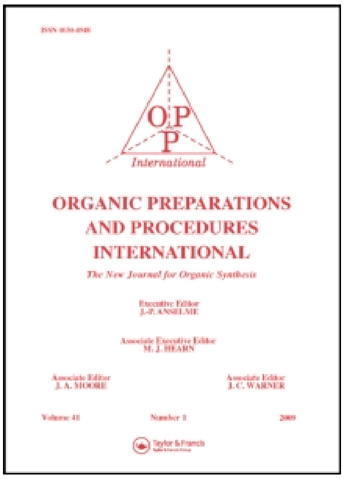

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FACILE OXIDATIVE CLEAVAGE OF CARBON-CARBON MULTIPLE BONDS WITH CHROMIUM(V) REAGENT [(BiPy)H_2CrOCl_5]

T. K. Chakraborty[a]; S. Chandrasekaran[a]
[a] Department of Chemistry, Indian Institute of Technology, Kanpur, INDIA

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10. Longer reaction times appear to be detrimental.

FACILE OXIDATIVE CLEAVAGE OF CARBON-CARBON MULTIPLE BONDS WITH CHROMIUM(V) REAGENT [(BiPy)H_2CrOCl_5]

Submitted (4/27/82)

by T. K. Chakraborty and S. Chandrasekaran*

Department of Chemistry
Indian Institute of Technology
Kanpur 208016, INDIA

Recently we reported[1] the use of chromium(V) reagents for the oxidation of alcohols to carbonyl compounds and of aldehydes to carboxylic acids. We now report a facile oxidative cleavage of carbon-carbon multiple bonds in the absence of readily oxidisable alcohol or aldehyde groups. The oxidation of carbon-carbon multiple bonds with different chromium(VI) reagents is often complicated by various side-reactions.[2] In general it has been observed that in a partially aqueous medium, chromic acid favors oxidative cleavage of carbon-carbon multiple bonds whereas anhydrous conditions favor either attack at allylic positions or partial oxidation of the double bond to form epoxides, diol derivatives or ketols; rearrangement of the intermediate oxidation products has also been observed.

We have now found that the chromium(V) complex [(BiPy)H_2-$CrOCl_5$][3] effects a fairly clean oxidative cleavage of carbon-

carbon multiple bonds under anhydrous conditions at room temperature, usually without any complicating side-reactions. In the case of compounds without alcohol or aldehyde functional groups, this oxidative cleavage reaction can serve as a useful and effective substitute for ozonolysis or osmium tetroxide-periodate cleavage process. However, attempted oxidative cleavage of simple alkyl substituted olefins in general lead to mixtures of products. It is also interesting to note that alcohols and aldehydes containing carbon-carbon multiple bonds gave only the corresponding carbonyl compounds and carboxylic acids, respectively, in good yields without any oxidative cleavage.[1]

EXPERIMENTAL

Preparation of (BiPy)H_2CrOCl_5.- Chromium trioxide (8 g, 0.08 mol) was added to distilled glacial acetic acid (300 ml) and the mixture was saturated with dry hydrogen chloride at room temperature, until all the chromium trioxide dissolved. A suspension of 2,2'-bipyridyl (10 g, 0.06 mol) in distilled glacial acetic acid (25 ml) (through which dry hydrogen chloride had been passed until precipitation of the amine hydrochloride was complete) was then added to the chromium trioxide solution and the mixture was resaturated with hydrogen chloride (0.5 hr). A dark brown precipitate started to appear at this stage. The mixture was vigorously stirred for 2 hrs (to ensure complete dissolution of the CrO_3) and allowed to stand overnight. The precipitate was collected and washed with about 250 ml of distilled glacial acetic acid and dried under vacuum to get dark brown free flowing powder (24 g, 92%) which was stored under vacuum.

TABLE. Oxidative Cleavage of C-C Multiple Bonds with $(BiPy)H_2CrOCl_5$[a]

Starting Material	Molar Ratio	Time (hr)	Product[b]	Yield[c] (%)
trans-Stilbene	1:4	4	Benzaldehyde	96
1,1-Diphenylethylene	1:4	4	Benzophenone	96
Diphenylacetylene	1:4	4.5	Benzaldehyde	96
Phenylacetylene	1:4	4.5	Benzaldehyde	92
1,1,4,4-Tetraphenyl-1,3-butadiene	1:8	6	Benzophenone	90
Camphene	1:2	0.5	Camphenilone	80
Ethylidene tetraphenyl fulvene	1:2	2	Tetracyclone	70[d]
9-Benzylidene fluorene	1:2	0.75	Fluorenone (+benzaldehyde)	90

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a) Oxidations were carried out at room temperature (28-30°) in CH_2Cl_2. b) Products were characterized by comparison with authentic samples (spectra, tlc, mp). c) All yields refer to isolated yields. d) Yield based on recovered starting material; acetaldehyde was not isolated and characterized.

Oxidative Cleavage of 1,1-Diphenylethylene. Typical Procedure.- To a magnetically stirred solution of 1,1-diphenylethylene (0.09 g, 0.5 mmol) at room temperature (30°) under nitrogen atmosphere was added $(BiPy)H_2CrOCl_5$ (0.8 g, 2 mmol). After 4 hrs, dry ether (15 ml) was added to the reaction mixture which was filtered through a pad of Celite and silica gel and washed with two or three 10 ml portions of dry ether. The combined organic filtrate was evaporated and benzophenone was obtained as a crystalline solid (0.087 g, 96%) mp. 48-49°;

its ir and nmr spectra were identical with those of authentic material.

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O-CYANOMETHYLOXIME OF NITROGLYOXYLONITRILE

Submitted by T. Perumal Pillai and Joseph H. Boyer*
(3/5/82)
Chemistry Department
Chicago Circle Campus
University of Illinois
Chicago, Illinois 60680

The formation of the O-cyanomethyl ether 3 (a nitrolate ester) of nitroglyoxylonitrile oxime from iodoacetonitrile and silver nitrite (Eq. 1) offers a new preparation of a nitrolate ester independent of an α-nitronitronate ester or anhydride.[1-3]