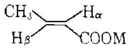
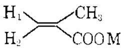
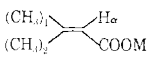
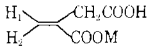
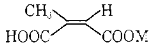
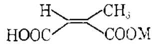
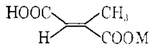
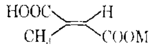
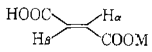
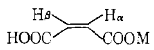
TABLE I

PROTON RESONANCE LINE POSITIONS FOR OLEFINIC CARBOXYLATO LIGANDS IN PENTAAMMINE COBALTIC COMPLEXES[a,b]

Complex	Structural formula[c]	Proton group	Line position, $\tau^{d,i}$ pH ≈1	Line position, $\tau^{d,i}$ pH ≈7[e,f]
trans-Crotonato		H_α	4.18	Same at both pH values
		H_β	3.30	
		CH_3	8.20	
Methacrylato[g]		H_1	4.57	
		H_2	4.17	
		CH_3	8.17	
β,β-Dimethyl-acrylato[g]		H_α	4.37	
		$(CH_3)_1$	8.17	
		$(CH_3)_2$	8.04	
Itaconato[g]		H_1	4.44	4.59
		H_2	3.94	4.08
		CH_2	6.66	6.87
Citraconato A		H	4.11	4.75
		CH_3	8.01	8.06
Citraconato B		H	4.28	4.09
		CH_3	8.01	8.17
Mesaconato C		H	3.49	3.34
		CH_3	7.90	8.14
Mesaconato D		H	3.26	3.74
		CH_3	8.01	8.00
Fumarato[h]		H_α	3.21	3.59
		H_β	3.45	3.40
Maleato[h]		H_α	3.56	4.39
		H_β	3.88	3.62

[a] The NH_3 protons give two broad lines, similar in appearance to those illustrated in ref 3, whose positions are approximately the same for each complex, with the *cis*-NH_3 at τ 6.0–6.1 and the *trans*-NH_3 at τ 7.0–7.1. These lines disappear at pH 7 as each NH_3 is converted to ND_3. [b] The solutions were 0.2–2 *M* in D_2O. [c] M = $Co^{III}(NH_3)_5$; hence, each formula shown represents a cation with an over-all charge of +2. At pH 7, the complexes from dibasic acids, having lost the carboxyl proton, have an over-all charge of +1. [d] Line positions were measured relative to the methyl line of the internal reference, *t*-butyl alcohol; this line was taken to have τ 8.75[i] in converting the measured positions to the τ scale. The errors in the quoted values are about ±0.015. [e] The line positions have reached constant values by pH 7; hence, the free carboxylate groups can be taken as being completely ionized. [f] To check for the absence of appreciable hydrolysis during the measurements at pH 7, the pH was afterward lowered to 1, when the lines were observed to go back to their previous positions; any lines from free acid would have had a different pH dependence. [g] The line assignments for groups 1 and 2 are assumed to be the same as for the free acids.[4] [h] Measurements at intermediate values of pH confirm that the two lines cross over and are coincident at one pH. [i] R. A. Y. Jones, A. R. Katritzky, J. N. Murrell, and N. Sheppard, *J. Chem. Soc.*, 2576 (1962); M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *ibid.*, 4854 (1961); R. J. Abraham and W. A. Thomas, *ibid.*, 3739 (1964).

The citraconate product gives two sets of lines which are attributed to the two isomeric complexes; they can be distinguished by the different intensities of lines in the two sets. One isomer (A) can be isolated by repeated recrystallization of the product from water; its spectrum at a given pH coincides with one of the sets of lines at the same pH. It was assigned the structure shown in the table since, on ionization, the =CH proton moves to a considerably higher τ value, suggesting that it is β to the free carboxyl, whereas the CH_3 proton line moves only slightly, suggesting that it is α to the free carboxyl. In contrast, ionization of isomer B makes the =CH line move (to a lesser extent) to lower τ while the τ of the CH_3 line increases by an amount typical of a β-methyl group in a monobasic olefinic acid.

Similar behavior is found for the mesaconate product; again, one isomer (C) could be isolated. With itaconic acid, only one isomer could be detected. It is assigned the structure with the side chain carboxyl free, since on ionization the $=CH_2$ protons move only slightly, yet the τ of the CH_2 group increases by 0.21, about the same as is found for the α-CH_2 protons in simple aliphatic carboxylic acids. With the maleato and fumarato complexes, no isomers are possible, but the two =CH protons can be distinguished. The changes on ionization are similar for both complexes; one proton moves to lower τ and is assigned as the proton α to the free carboxyl, whereas the β proton moves to a greater extent in the opposite direction.

Presumably the isomeric monodentate complexes formed from other dibasic acids could be distinguished in a similar manner, once the pH dependence of the proton resonance lines of the appropriate simple acids was known.

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(Trimethylarsine)methylene

BY HUBERT SCHMIDBAUR AND WOLFGANG TRONICH

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In a recent communication[1] the preparation and properties of (trimethylphosphine)methylene, $(CH_3)_3PCH_2$, the basic member of the phosphorus ylid series have been described. Using a similar synthetic procedure, we were now able to isolate the corresponding arsenic analog, (trimethylarsine)methylene $(CH_3)_3AsCH_2$ (I). Though the existence of this compound, at least in solution and at low temperatures, seemed to be rather likely, no successful attempt of isolation has been documented.[2,3]

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(1) H. Schmidbaur and W. Tronich, *Angew. Chem.*, **79**, 412 (1967); *Angew. Chem. Intern. Ed. Engl.*, **5**, 448 (1967).

(2) A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966.

(3) S. O. Grim and D. Seyferth, *Chem. Ind.* (London), 849 (1959); M. C. Henry and G. Wittig, *J. Am. Chem. Soc.*, **82**, 563 (1960); D. Seyferth and H. M. Cohen, *J. Inorg. Nucl. Chem.*, **20**, 73 (1961).

The reaction of trimethylarsine–trimethylsilylmethylene[4] with trimethylsilanol leads to a desilylation of the ylid with formation of hexamethyldisiloxane

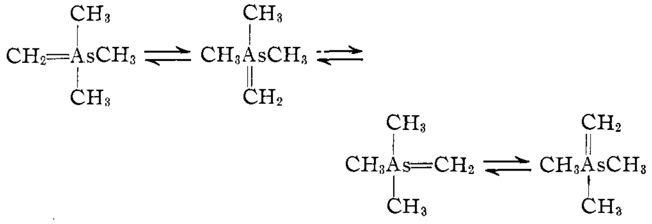
$$(CH_3)_3SiCH{=}As(CH_3)_3 + (CH_3)_3SiOH \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + \underset{\text{I}}{(CH_3)_3As{=}CH_2}$$

The high tendency of formation of the siloxane linkage promotes the reaction to proceed according to this equation. After evaporation of the siloxane under vacuum I is easily purified by sublimation at 30–35° under 0.1 mm of pressure. The compound forms beautiful colorless crystals, mp 33–35°, which are sensitive to air and moisture. On exposure to the atmosphere, a brown-violet color is developed almost instantaneously. Slow decomposition is also observed on heating above 38°. From cryoscopic molecular weight determinations I appeared to be monomeric in benzene solution.

As in the case of the phosphorus analog,[1] the proton nmr spectra of I merit special interest. The spectrum of a benzene solution at room temperature shows the expected two lines at $\delta_{CH_3} = -49$ and $\delta_{CH_2} = +11.5$ cps[5] with relative areas 9:2. The CH_2 resonance appears at very high field, thus indicating a preference of the ylid form (B) for the description of bonding according to the formulas

$$\underset{A}{(CH_3)_3As{=}CH_2} \longleftrightarrow \underset{B}{(CH_3)_3\overset{\oplus}{As}{-}\bar{C}H_2^{\ominus}}$$

The CH_2 as well as the CH_3 signal clearly shows a line broadening at elevated temperatures, which is reversible on cooling. This phenomenon again[1] has to be interpreted by the assumption of a rapid proton exchange between both structural sites above room temperature



$$CH_2{=}\overset{CH_3}{\underset{CH_3}{As}}CH_3 \rightleftharpoons CH_3\overset{CH_3}{\underset{CH_2}{As}}CH_3 \rightleftharpoons CH_3\overset{CH_3}{\underset{CH_3}{As}}{=}CH_2 \rightleftharpoons CH_3\overset{CH_2}{\underset{CH_3}{As}}CH_3$$

The rapid decomposition of I above 60° prevents observation of the collapse and coalescence of both peaks, which formerly in $(CH_3)_3PCH_2$ has been observed without difficulties,[1] owing to the greater thermal stability of the latter. Merging of the resonances can be accomplished, however, already at room temperature on addition of traces of a protic species, *e.g.*, methanol. Obviously, proton catalysis favors rapid intermolecular proton exchange between the ylid molecules, for which now a single sharp line is observed. As expected, this resonance no longer shows $^1H-^{13}C$ satellites.

Chemically, I resembles its phosphorus analog.[1] It is alkylated by methyl iodide, almost quantitative yields of trimethylethylarsonium iodide being formed

$$(CH_3)_3As{=}CH_2 + CH_3I \longrightarrow [(CH_3)_3AsC_2H_5]^+I^-$$

The reaction with hydrogen halides converts I into tetramethylarsonium halides.

On prolonged standing at room temperature a 1:1 mixture of I and trimethylphosphine shows an interesting "transylidation" reaction, resulting in an equimolar mixture of trimethylarsine and (trimethylphosphine)-methylene

$$(CH_3)_3As{=}CH_2 + (CH_3)_3P \longrightarrow (CH_3)_3As + (CH_3)_3P{=}CH_2$$

This reaction is easily followed by nmr spectroscopy.

Among a number of products, which are formed under the thermal decomposition of I, trimethylarsine and ethylene have been detected by vapor phase chromatography to be the main components.

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(4) N. E. Miller, *Inorg. Chem.*, **4**, 1458 (1965).

(5) At 60 Mc, relative to TMS externally, positive sign for higher field.

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A Novel Synthesis of Bis(fluorocarbonyl) Peroxide[1]

BY RALPH CZEREPINSKI AND GEORGE H. CADY

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Bis(fluorocarbonyl) peroxide was first reported by Schumacher and co-workers.[2] Their elegant synthesis uniting fluorine, carbon monoxide, and oxygen at room temperature to give nearly quantitative yields of bis(fluorocarbonyl) peroxide has yet to be matched for convenience and simplicity. However, their preparation still requires handling elementary fluorine in the same system with carbon monoxide, introducing some potential hazard.

In the course of investigations of the chemistry of oxalyl fluoride, it was discovered that photolysis of oxalyl fluoride in the presence of oxygen led to the formation of bis(fluorocarbonyl) peroxide in yields approaching 50%. This discovery is consistent with Schumacher's proposed mechanism for the formation of the peroxide,[3] involving fluorocarbonyl groups which combine with oxygen.

Experimental Section

Oxalyl fluoride was prepared by treating oxalyl chloride with sodium fluoride in acetonitrile at reflux, essentially employing the method of Tullock and Coffman.[4] The crude product collected at −183° was found to be contaminated with carbonyl fluoride, carbon dioxide, and acetonitrile. The material was warmed to −78°, and materials volatile at that temperature were allowed to expand into a conventional vacuum system of 350-cc volume. The sample tube was closed and the volatiles pumped away. This procedure was repeated until the residual vapor pressure at −78° fell substantially below 1 mm. The sample was then

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(1) Presented, in part, at the Northwest Regional Meeting of the American Chemical Society, Richland, Wash., June 1967.

(2) A. Arvia, P. Aymonino, C. Waldow, and H. J. Schumacher, *Angew. Chem.*, **72**, 169 (1960).

(3) J. Heras, A. Arvia, P. Aymonino, and H. Schumacher, *Z. Physik. Chem.* (Frankfurt), **28**, 250 (1961).

(4) G. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).