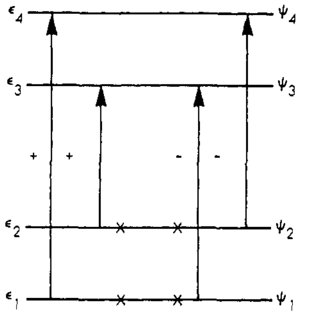

Figure 1. Molecular orbitals and excitations for the H–X–H system; sign of each contribution to contact term is given at the left of the corresponding excitation.

The most obvious features of the results in Table I is that J_{HPH} is negative for the tricoordinated phosphorus compounds and approximately zero or positive for the tetracoordinate species.[10] In the case of PH_3D^+, it was impossible to resolve the H–P–D coupling, and hence the value in Table I represents an upper limit for J_{HPD}. In the phosphorus-31 spectrum of a mixture of phosphonium and deuterated phosphonium cations all the species PH_4^+, PH_3D^+, $PH_2D_2^+$, PHD_3^+, and PD_4^+ give rise to their expected multiplets. Thus, we conclude that the unresolvable J_{HPD} is not the result of an exchange process.

Based on available structural data, it appears that opening out of the geminal H–P–H bond angle leads to an algebraic increase in the proton–proton coupling. In this sense J_{HPH} resembles J_{HCH} where increasing the H–C–H angle from tetrahedral to trigonal increases J_{HCH} from -12.5 to $+2.4$ Hz.[3] It is also apparent that the variation of the H–P–H angle is not the only significant factor because the anion O_2PHD^- has the largest J_{HPH}, yet the H–P–H angle is only about 92°.[11] At this point it is not clear whether the formal negative charge or the electronegative substituents contribute the most to increasing J_{HPH} in this anion. In the $-CH_2-$ fragment neighboring oxygen increases J_{HCH} algebraically by both inductive and lone-pair conjugative effects.[3,4]

Our results for this series of molecules may also be understood qualitatively in terms of the Pople and Bothner-By molecular orbital treatment of geminal H–X–H couplings.[4] In this model two bonding (ψ_1 and ψ_2) and two antibonding (ψ_3 and ψ_4) molecular orbitals are constructed from two H(1s) atomic orbitals and two sp hybrid orbitals centered on atom X. The excitations $\psi_1 \rightarrow \psi_4$ (see Figure 1) and $\psi_2 \rightarrow \psi_3$ lead to positive contributions to the contact term while the excitations $\psi_1 \rightarrow \psi_3$ and $\psi_2 \rightarrow \psi_4$ lead to negative contributions. The single most dominant term is $\psi_2 \rightarrow \psi_3$ because the excitation energies appear in the denominator of the contact coupling expression. As nitrogen is replaced by phosphorus in this treatment, it would be anticipated that the separation between the bonding and antibonding levels would decrease. Thus, the positive contribution from the $\psi_2 \rightarrow \psi_3$ excitation should become more important, making J_{HXH} more positive for phosphorus compounds than for nitrogen compounds.[12] This may explain why J_{HPH} is very small in the phosphonium cation [or slightly positive in $(CH_3)_2PH_2^+$] while J_{HNH} is negative in ammonium cation.[13] A similar variation in the energies of ψ_2 and ψ_3 may explain the sign inversion on changing the coordination number of phosphorus from three to four.

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(8) E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962).

(9) Performed with a modified HA-100 spectrometer whose 100- and 40.4-MHz frequencies were derived from the same source; details to be published.

(10) Our results are based on the assumption that J_{PH} and J_{PD} are always positive for both tri- and tetracoordinate phosphorus. This assumption has been discussed previously in detail [S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966)]; more recently it has been confirmed by double resonance studies on compounds with various coordination of phosphorus [W. McFarlane, *J. Chem. Soc., A*, 1148 (1967); S. L. Manatt, M. T. Bowers, and H. Goldwhite, unpublished work.

(11) In ammonium hypophosphite the H–P–H angle is 92°: W. H. Zachariasen and R. C. L. Mooney, *J. Chem. Phys.*, **2**, 34 (1934); M. L. Huggins, *Phys. Rev.*, **21**, 719 (1923).

(12) Similar arguments have been presented by H. Dreeschamp and C. Schumann, *Chem. Phys. Letters*, **1**, 555 (1968), to explain why the J_{HXH} couplings algebraically increase in the order X = Sn > Ge > Si > C.

(13) The sign of J_{HND} in deuterated ammonium ions has been determined to be opposite to the J_{ND} and J_{NH} couplings by W. McFarlane and R. R. Dean, *J. Chem. Soc., A*, 1535 (1968). There is good reason to believe that J_{ND} and J_{NH} are always positive; see J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(14) NRC Resident Research Associate, Jet Propulsion Laboratory, 1967–1968.

(15) Supported under Contract No. NAS 7-100 by the National Aeronautics and Space Administration.

(16) Supported by the Robert A. Welch Foundation and Jet Propulsion Laboratory Director's Discretionary Fund.

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Isolation of μ_4-Oxo-penta-μ-acetato-μ-trichloroacetato-tetraberyllium, $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$

Sir:

We have been unable to find an adequately documented report of the isolation of a pure metal mixed carboxylate. Perhaps this is because in many instances rapid ligand exchange would prevent the isolation of a compound containing a given mixed carboxylate ratio. In instances where ligand exchange would be slow, similar solubilities of compounds with varying ratios of different carboxylate groups would militate against the isolation of one member in a series. A number of attempts to prepare mixed basic beryllium carboxylates have been made. Tanatar and Kurowski[1] claimed to have prepared specific mixed carboxylates, *e.g.*, $Be_4O(CH_3CO_2)_3(C_2H_5CO_2)_3$. However, Marvel[2] and Hardt[3] have demonstrated that the "compounds" were actually mixtures of intramolecular mixed carboxylate compounds of the general formula $Be_4(RCO_2)_x(R^1CO_2)_{6-x}$ where $0 < x < 6$. A claim for the existence of acetate–monochloroacetate mixed carboxylates has been made by other workers[4] based on phase diagrams. For reasons presented below we do not believe pure compounds were present in the latter study.

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(1) S. Tanatar and E. Kurowski, *J. Russ. Phys.-Chem. Soc.*, **39**, 936 (1907); *Chem. Zentr.*, 791 (1908).

(2) C. S. Marvel and M. M. Martin, *J. Am. Chem. Soc.*, **80**, 619 (1958).

(3) H. Hardt, *Z. Anorg. Allgem. Chem.*, **314**, 210 (1962).

(4) A. V. Novoselenova and K. N. Semenenko, *Zh. Neorg. Khim.*, **1**, 2344 (1956).

Isolation of a pure mixed beryllium carboxylate seemed desirable for several reasons. We were interested in determining semiquantitatively the rate of carboxylate scrambling in a mixed derivative. The mechanism of the exchange reaction as well as the relative donor abilities of differing carboxylate ligands were also of interest. Therefore we sought to isolate a mixed compound in which the carboxylate groups would differ appreciably in base strength and in molecular weight. The trichloroacetate–acetate system fit these requirements nicely.

The usual precautions for working with beryllium compounds[5] were observed. μ_4-Oxo-hexa-μ-acetato-tetraberyllium was prepared by a standard method.[6] μ_4-Oxo-hexa-μ-trichloroacetato-tetraberyllium, a new compound, was prepared by thermal decomposition of ditrichloroacetatodiaquoberyllium(II). The details of this preparation will be reported separately.

Pure $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ was prepared in two ways. Amounts of materials involved in a typical run are given in parentheses. A 9:1 mole ratio of $Be_4O(CH_3CO_2)_6$ (6.57 g) to $Be_4O(CCl_3CO_2)_6$ (1.85 g) was allowed to equilibrate for 6 days in chloroform (50 ml). When no further change was observed in the proton nmr spectrum of the solution (Varian HA-100), petroleum ether (bp 60–110°) was added until a quantity of precipitate (*ca.* 0.9 g) appeared. This material was filtered, dissolved in chloroform, and reprecipitated with petroleum ether two times (final yield 0.4 g). No change in the nmr spectrum, melting point (217–18.5°), or ir spectrum was observed in going from the second to the third precipitation. $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ can be prepared by refluxing $Be_4O(CH_3CO_2)_6$ (30.0 g) with trichloroacetyl chloride (81.5 g) in benzene for 48 hr according to the reaction

$$Be_4O(CH_3CO_2)_6 + CCl_3COCl \longrightarrow Be_4O(CH_3CO_2)_5(CCl_3CO_2) + CH_3COCl$$

The yield after recrystallization from chloroform–petroleum ether was 9.8 g. We were surprised at this result as it had been our original intent to prepare $Be_4O(CCl_3CO_2)_6$ *via* this route. Evidently the above replacement reaction is sufficiently slow that it allows isolation of the monotrichloroacetate derivative even after 2 days of refluxing in benzene.

The presence of bridging acetate and trichloroacetate groups in $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ was first qualitatively ascertained through an infrared spectrum of the compound. The analytical results were in excellent agreement with the proposed formulation. *Anal.* Calcd for $Be_4O_{13}C_{12}H_{15}Cl_3$: C, 28.28; H, 2.96; Cl, 20.87. Found: C, 28.77; H, 3.15; Cl, 20.38, 20.84. In addition, a molecular weight of 494 (calcd 509.7) was found cryoscopically in benzene. These results do not provide definitive evidence for a pure compound. It could be argued that we have isolated a mixture of materials which fortuitously gave the above results. Compelling evidence for the purity of $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ came from nmr and mass spectroscopic studies.

The mass spectra of a number of μ_4-oxo-hexa-μ-carboxylatotetraberyllium compounds have revealed very weak or nonexistent parent ion peaks. Instead the ion of highest mass (and also of high intensity) is $Be_4O(RCO_2)_5^+$.[7] Consistent with these observations, the highest mass peaks observed for $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ corresponded to the ions $Be_4O(CH_3CO_2)_4(CCl_3CO_2)^+$ and $Be_4O(CH_3CO_2)_5^+$ of 100 and 52% relative abundance, respectively. Peaks arising from $Be_4O(CH_3CO_2)_4(CCl_3CO_2)_2$ of less than 1% relative abundance were observed, indicating a negligible amount of contamination from this compound. Because the mixed carboxylate does not give rise to a parent ion, the presence of $Be_4O(CH_3CO_2)_6$ cannot be ruled out from a mass spectrometric study.

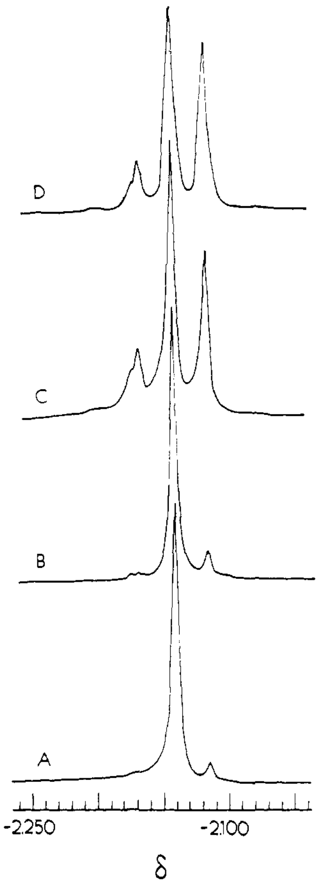

Figure 1. The proton nmr spectrum of $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ in chloroform *vs.* time (hr): A, 0.17; B, 3.33; C, 36.8; D, 109.

The proton nmr spectrum of the mixed derivative was of considerable aid in providing evidence for the existence of $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ as a pure mixed carboxylate. The proton nmr of this compound is shown in Figure 1, curve A. Despite the inequivalence of *trans* and *cis* acetate protons a single peak is observed for $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ at δ 2.140. The peak at δ 2.115 may be due to $Be_4O(CH_3CO_2)_6$ and was found to vary in relative intensity depending on the preparation. An average contamination of 4% of this compound was found. An alternative explanation of the nmr results is that the peak at δ 2.115 is due to *trans* protons while that at δ 2.140 is due to *cis* protons. The ratio of the peak heights is in poor agreement with this hypothesis, however.

The analytical, molecular weight, nmr, and mass spectrometric data strongly support the existence of

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[5] D. A. Everest, "The Chemistry of Beryllium," Elsevier Publishing Co., New York, N. Y., 1964.

[6] T. Moeller, *Inorg. Syn.*, 3, 9 (1950).

[7] J. G. Vogel and B. G. Hobrock, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

what we believe to be the first isolation of a well-characterized mixed carboxylate of a metal.

Solutions of $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ in chloroform are unstable. Scrambling of carboxylate groups occurs and may be followed conveniently by observing the nmr spectrum *vs.* time (Figure 1). New peaks arise at $\delta \sim 2.178$ and are tentatively assigned to $Be_4O(CH_3CO_2)_4(CCl_3CO_2)_2$. Interestingly, a 1:5 mole ratio mixture of $Be_4O(CCl_3CO_2)_6$ and $Be_4O(CH_3CO_2)_6$ in chloroform gave at equilibrium an nmr spectrum identical with curve D, Figure 1. In view of our observation of carboxylate scrambling, we believe that the claim of Novoselenova and Semenenko[4] for the preparation of pure acetate–monochloroacetate carboxylates simply by melting together an appropriate ratio of starting materials is untenable.

Current work is aimed at the isolation of other members in the series $Be_4O(CH_3CO_2)_x(CCl_3CO_2)_{x-6}$. By examining the rate of carboxylate scrambling for different members of the series we hope to postulate a reasonable mechanism for the scrambling reaction.

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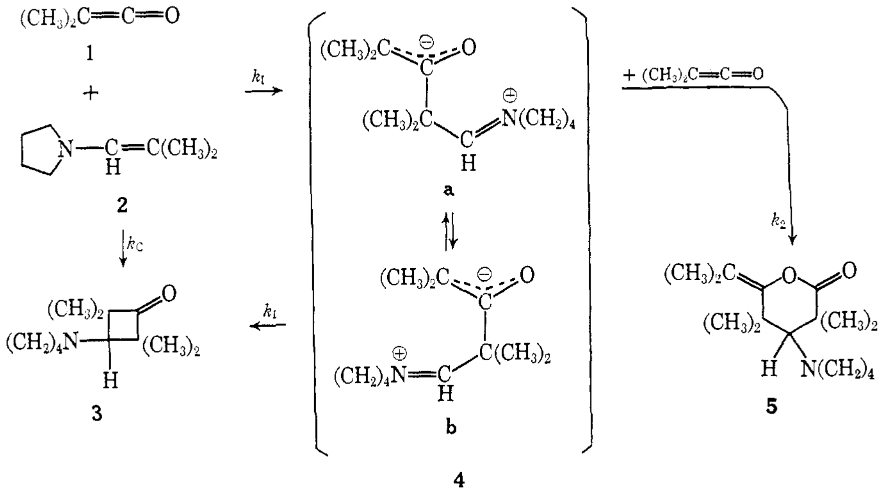
Demonstration of Two Mechanistic Pathways in the Reaction of Dimethylketene with N-Isobutenylpyrrolidine

Sir:

Kinetic[1] and stereochemical results[2-4] are consistent with a concerted mechanism for cyclobutanone formation from ketenes and olefins or vinyl ethers. Dimethylketene combines with isobutenyldialkylamines to give cyclobutanones and 2:1 adducts[5] which proved to be γ-methylene-δ-lactones like **5**.[6] We showed recently[7] that the ratio of the 2:1 adduct **5** and the 1:1 adduct **3** from N-isobutenylpyrrolidine (**2**) is strongly dependent on the concentration of dimethylketene (**1**). The formation of **5** is best interpreted as a 1,4-dipolar cycloaddition[8,9] of the zwitterionic intermediate **4** to the carbon–carbon double bond of **1**, especially since **3** is not converted to **5** by an excess of **1**. New kinetic and competition experiments now establish that two mechanisms participate in the formation of the cyclobutanone **3**.

Table I. Reactions of Dimethylketene (**1**) with N-Isobutenylpyrrolidine to give **3** and **5**

[**1**], *m*	**3**, mmoles	**5**, mmoles	**3** + **5**, %	mmoles of **3** × [**1**]/ mmoles of **5**	k_1/k_2
(1) 3.594 mmoles of **2** + 20.80 mmoles of **1** in benzene; 2.85 mmoles of **3** deducted for the evaluation of k_1/k_2					
1.962	2.87	0.722	100.0	7.8	0.056
0.473	2.93	0.665	100.1	2.1	0.057
0.269	2.98	0.627	100.2	1.3	0.053
0.145	3.06	0.539	100.0	0.8	0.055
(2) 3.594 mmoles of **2** + 25.23 mmoles of **1** in acetone; 1.91 mmoles of **3** deducted for the evaluation of k_1/k_2					
2.659	2.01	1.62	101.1	3.29	0.164
0.796	2.21	1.44	101.6	1.22	0.166
0.469	2.36	1.32	102.4	0.84	0.166
0.259	2.56	1.02	99.7	0.65	0.161
(3) 3.514 mmoles of **2** + 22.37 mmoles of **1** in acetonitrile; 1.51 mmoles of **3** deducted for the evaluation of k_1/k_2					
2.033	1.81	1.70	100.0	2.14	0.36
0.432	2.43	1.15	102.2	0.91	0.36
0.268	2.66	0.83	99.8	0.85	0.37
0.144	2.95	0.57	100.3	0.74	0.36



We treated **2** with an excess of **1** in several anhydrous solvents at room temperature under nitrogen. The effect of dilution was studied by carrying out four experiments in each solvent. The ratio **2**:**1** was kept constant, but the molar concentrations differed by more than one order of magnitude. After 5 days the solvent was removed and a weighed amount of tetrachloroethane as nmr standard was added. Nmr analysis of the mixture of **3**, **5**, and tetramethylcyclobutanedione established that virtually quantitative yields of **3** + **5**

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[1] R. Huisgen, L. A. Feiler, and P. Otto, *Tetrahedron Letters*, 4485 (1968); *Chem. Ber.*, **102**, in press.

[2] R. Huisgen, L. A. Feiler, and G. Binsch, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964).

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