to be acetate derived,¹² and hispidin, isolated from *Polyporus hispidus*.¹³ Compound Ia could be isolated in small quantity (*ca.* 6 mg./l.) from 4-day cultures of *P. stipitatum*, whereas stipitatic acid could not be detected until the seventh day. The possible role of Ia in the biosynthesis of stipitatic acid is therefore under further investigation.

$$\begin{array}{c} OR\\ CH_3\\ C$$

Acknowledgment.—This work was supported by grants from the American Cancer Society and the U. S. Public Health Service.

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DEPARTMENT OF MICROBIOLOGY COLLEGE OF PHYSICIANS AND SURGEONS COLUMBIA UNIVERSITY New York 32, New York PAUL E. BRENNEISEN TERESE E. ACKER STUART W. TANENBAUM

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Stable Carbonium Ions. VII.¹ Nuclear Magnetic Resonance Investigation of the Triphenyl-C¹³carbonium Ion

Sir:

Recently we reported² on the nuclear magnetic resonance investigation of the trimethylcarbonium ion and were able to show that the C¹³ resonance of 2-C¹³-2-methyl-2-chloropropane (1-C¹³-t-butyl chloride) is shifted by 273 p.p.m. downfield in the trimethyl-C¹³-carbonium ion, $(CH_3)_3C^{13}$ +, formed via complexing the halide with antimony pentafluoride. We expressed our view that the observed substantial shift is due both to the change of hybridization of the involved carbon atom from sp³ to sp² and to the presence of positive charge on the carbon atom.

It was felt of interest to extend our investigations to the triphenyl-C¹³-carbonium ion, where charge delocalization through conjugative interaction with the three benzene rings was expected to decrease the C¹³ chemical shift of the carbonium ion, as compared with that of the trimethylcarbonium ion.

Labeling the aliphatic carbon atom with C^{13} (58%) allowed us to compare the nuclear magnetic C^{13} shifts of the covalent, sp³-hybridized triphenyl- C^{13} methanol (in tetrahydrofuran solution) with that of the labeled triphenylcarbonium ion, $(C_6H_5)_3C^{13+}$ - HSO_4^- (triphenyl- C^{13} -methanol in sulfuric acid solution). The data in Table I indicate a shift of 129.6 p.p.m. to less shielding in the triphenylcarbonium ion, as compared with the covalent triphenylmethanol.

In order to improve the signal-to-noise ratio the samples of enriched materials were put into 0.25-in. o.d. thin wall tubes and the spectra were recorded using the high resolution frequency-swept and proton stabilized n.m.r. spectrometer of Baker and Burd³ with the use of a frequency synthesizer. Using dispersion mode, rapid passage conditions spectra could also be obtained in standard size Varian sample tubes. Improved spectra were obtained using Overhauser enhancement by simultaneous H' irradiation.

TABLE I

$\begin{array}{rl} (C_6H_5)_3C^{13}OH\ (in\ THF)\ at\ 15.090646\ Mc.\\ (C_6H_5)_3C^{13}\mbox{+}HSO_4\mbox{-}\ (in\ H_2SO_4)\ at\ 15.092603\ Mc.\\ \delta_{C^{13}(C_6H_5)_3C^+}\ &-\ \delta_{(C_6H_5)_5COH}\ =\ 1957\ c.p.s.\ =\ -129.6\ p.p.m.\ (CS_2) \end{array}$

(reference) at 15.092330 Mc.)

The coupling with the ring protons is small which means that the spectra are concentrated essentially into a single line. There is however some coupling, about 5 c.p.s. to the ortho protons ($J_{\rm CCCH} = 5 \pm 0.2$ c.p.s.) and considerably less with the meta and para protons. The long range coupling with the ortho protons ($J_{\rm CCCH}$) is in accordance with similar observation of Frei and Bernstein⁴ in the case of C₆H₅-C¹³OC1.

To assess, at least qualitatively, how much of the observed shift in the triphenylcarbonium ion is due to the change of hybridization from sp³ to sp² and how much to the effect of the positive charge, a comparison of the chemical shifts of the triphenyl- C^{13} -carbonium and trimethyl- C^{13} -carbonium ions with their parent sp³ hybridized, covalent precessors and with some C^{13} compounds having sp²-hybridization is useful.

The C¹³ shift of an uncharged sp²-hybridized compound is found around +45 to +70 p.p.m. (from CS₂ as reference).^{5–7} The observed C¹³ shift at -18.1 p.p.m. in the triphenylcarbonium ion shows the additional deshielding effect (about 60–80 p.p.m.) of the positive charge. As the positive charge is much more delocalized in the triphenylcarbonium ion than it is in the trimethylcarbonium ion, the larger deshielding effect observed in the case of the latter (-146.9 p.p.m. from CS₂) is to be expected.

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Contribution No. 115 Exploratory Research Laboratory Dow Chemical of Canada, Limited Sarnia, Ontario, Canada Physical Research Laboratory The Dow Chemical Company Midland, Michigan	George A. Olah Edward B. Baker Melvin B. Comisarow

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The Transition State in Methyl Radical Formation. The α -Deuterium Effect¹

Sir:

The magnitude of the α -deuterium isotope effect in many cases of "unimolecular" (*i.e.*, approaching limiting SN1) solvolyses is constant, about $k_{\rm H}/k_{\rm D} =$ 1.15 per deuterium atom, between ambient and 100° .²

⁽¹⁾ Part VI: G. A. Olah, J. Am. Chem. Soc., 86, 932 (1964).

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⁽¹⁾ Research performed under the auspices of the U. S. Atomic Energy Commission.

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It has been suggested that such effects are indicative of a rate controlling homolytic, or heterolytic, cleavage of the C-leaving group bond.3 Inverse effects of similar magnitude may be obtained when the reaction involves the reverse process: trigonal to tetrahedral carbon 4 These effects have served as a tool in ascertaining the one-step or two-step nature of decompositions of dialkyl azo compounds^{3,5} and a Diels-Alder adduct,6 and in the addition of diphenylketene to cyclohexene.7

These isotope effects have been described in terms of vibrational frequency changes from starting to transition state as the reacting carbon atom changes hybridization⁸

$$k_{\rm H}/k_{\rm D} = be^{0.171\Sigma(\nu_{\rm Hi} - \nu_{\rm Hi}*)/T}$$

where b is relatively constant over small temperature ranges, ν_{H_i} is the *i*th C–H fundamental vibrational frequency in the starting state, ν_{H_i*} the corresponding vibration in the transition state, and T is the absolute temperature. A net lowering of the sum of the frequencies results in $k_{\rm H}/k_{\rm D} > 1$.

A definite exception to the pattern of $k_{\rm H}/k_{\rm D}\cong 1.15$ for unimolecular homolytic or heterolytic bond cleavage is the small *inverse* effect observed in the formation of methyl radicals from gas phase pyrolysis of dimethylmercury; total $k_{\rm H}/k_{\rm D} = 0.92$ for the fully deuterated compound.⁹ This exception led to the suggestion that the secondary α -deuterium isotope effect may be an ambiguous criterion.¹⁰

We undertook the determination of the α -deuterium isotope effect in the formation of methyl radicals by carbon-carbon rather than carbon-mercury bond cleavage. The compound chosen was methyltrideuteriomethylphenylcarbinyl hypochlorite, whose de-composition has been studied.¹¹ It was prepared *via* the alcohol from acetophenone- d_3 and a twofold excess of methylmagnesium iodide. The possibility of deuterium exchange during acid hydrolysis of C₆H₅C- $(CH_3)(CD_3)OMgI$ was investigated by n.m.r. and none was found. Analysis of the alcohol for deuterium showed greater than 99% deuteration of one methyl The hypochlorite was obtained in high yield group. from the alcohol by treatment with a twofold excess of HOCl in the usual fashion.^{11b} Mass spectrometry indicated that 1.3% of the deuterated methyl group was $-CD_2H$ and all data were corrected for its presence.

The hypochlorite was irradiated by an incandescent lamp as a 0.5 M solution in carbon tetrachloride in the presence of cyclohexane (1.0 M); under these conditions the decomposition is a long chain reaction and complicating side reactions amount to less than 0.5%by gas-liquid chromatography (g.l.c.).

Path d leads to the formation of CH3' and CD3' in direct competition and $CH_3Cl/CD_3Cl = k_H/k_D$ for three deuterium atoms. The evolved mixture of

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methyl chlorides was purified by g.l.c. and analyzed by a Consolidated-Nier mass spectrometer used as a single collector. The spectrometer was calibrated for the relative sensitivity to the two compounds with standard mixtures of CH₃Cl and CD₃Cl. For equimolar mixtures the spectrometer ratio CH₃Cl/CD₃Cl was 1.01 ± 0.01 from the 52 and 55 peaks. A correction factor of 1.45 has been reported on the basis of the 50and 53 peaks.¹² We find 1.00 ± 0.04 in our mass

$$CH_{3} \qquad CH_{3} \qquad CH_{3}$$

$$C_{6}H_{5}-\dot{C}-O-Cl + R \cdot \longrightarrow C_{8}H_{5}-\dot{C}-O \cdot + RCl$$

$$CD_{3} \qquad \dot{C}D_{3}$$

$$C_{6}H_{5}-C-O \cdot \qquad k_{3}$$

$$C_{6}H_{5}-C-O \cdot \qquad k_{3} \qquad CH_{3}$$

$$C_{6}H_{5}-C-OH + C_{6}H_{11} \cdot \qquad \dot{C}D_{3}$$

spectrometer for this ratio. The isotope effect was determined at temperatures between -9° and 75° and the results are shown in Table I. A plot of log $(k_{\rm H}/k_{\rm D})$ vs. 1/T gave a good straight line relationship indicating a fairly constant pre-exponential term; $b = 0.93 \pm 0.02$ for three deuterium atoms. From the slope a net decrease of 270 ± 5 cm.⁻¹ is obtained for the frequency changes from starting to transition state. A net decrease of about 400 cm.⁻¹ can be calculated for the formation of a fully formed methyl radical with a tricoordinated sp² carbon atom.¹³ The experi-mentally determined change indicates that well over half of the vibrational changes accompanying the formation of the methyl radical have occurred in the transition state. The conclusion that the transition state is more akin to products than to reactants in this reaction, involving carbon-carbon bond cleavage and the formation of a methyl radical and a double bond, is consistent with the findings of Szwarc and co-workers^{4c}; they have concluded that the transition state for methyl radical addition to olefins is closer to the configuration of the reactants than to that of the products.

TABLE I

 α -Deuterium Isotope Effect in Methyl Radical Formation

Temp., °C.	CH_3Cl/CD_8Cl^a	$k_{\rm H}/k_{\rm D}^{b}$
9	1.588 ± 0.005	1.17 ± 0.01
20	1.486 ± 0.03	1.14 ± 0.01
50	1.429 ± 0.01	1.13 ± 0.01
75	1.401 ± 0.005	1.12 ± 0.01

^a Uncorrected for relative sensitivity. ^b Corrected values per deuterium.

The determination of the isotope effect in the pyrolysis of dimethylmercury9 was carried out in the gas phase at a pressure corresponding to 0.95 of the rate at the high pressure limit. Subsequent to this work, strong inverse secondary effects have been observed in the isomerization of CD3NC at low pressures in non-

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⁽¹²⁾ G. Ghiltz, et al., J. Chem. Phys., 38, 1053 (1963)

⁽¹³⁾ The C-H bond length in methyl radical is 0.013 Å. shorter than that in methane and about equal to that of ethylene [G. Herzberg, Proc. Roy. Soc. (London), A262, 291 (1961)]; ethylene was taken as a model for the vibrational frequencies of the methyl radical.

equilibrium thermal systems.¹⁴ These effects are strongly pressure dependent and become normal near the high pressure limit. This might contribute to the observed inverse effect of dimethylmercury. Effects of this type are known not to occur in solution.

The explanation for anomalous α -effects in the cleavage of the carbon-mercury bond¹⁵ is not obvious at present.

The demonstrated normal behavior of the methyl radical strengthens the usefulness and unambiguity of the secondary α -deuterium effect as a criterion for "unimolecular" cleavage.

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Received December 27, 1963

New Types of Organosulfur Derivatives of Metal Carbonyls¹

Sir:

Numerous unusual organosulfur transition metal compounds have been obtained by reactions of various metal carbonyls and cyclopentadienylmetal carbonyls with certain mercaptans, sulfides, disulfides, and dithietenes.^{2,3} Other types of organosulfur transition metal compounds have been obtained from metal sulfides and certain acetylene derivatives.⁴ This communication describes a new and entirely different synthesis of new types of organosulfur derivatives of metal carbonyls with metal-sulfur bonds. These new compounds have been obtained by thermal or photochemical decarbonylation of compounds of general formula $CH_3S(CH_2)_nM(CO)_x(C_5H_5)_y$ (n = 1, 2,or 3; M = Fe [x = 2, y = 1], Mo [x = 3, y = 1], or Mn [x = 5, y = 0]) without metal-sulfur bonds. These sulfur-containing transition metal alkyl derivatives, none of which has been previously reported, may in turn be obtained from metal carbonyl anions and the chloroalkyl methyl sulfides CH₃S(CH₂)_nCl.

Thus, the sodium salt NaMo(CO)₃C₆H₅⁵ reacts with chloromethyl methyl sulfide in tetrahydrofuran solution at 25° to give the yellow crystalline alkyl tricarbonyl derivative CH₃SCH₂Mo(CO)₃C₆H₅ (I), m.p. 66–67°.⁶ On heating to \sim 70° or ultraviolet irradiation this tricarbonyl derivative forms the likewise yellow crystalline *dicarbonyl* derivative CH₃SCH₂Mo(CO)₂-C₆H₅ in up to 60% yield, m.p. 66–67°.^{6,7} The infrared⁸ and proton n.m.r. spectra⁸ and close

The infrared⁸ and proton n.m.r. spectra⁸ and close analogies in stoichiometry, physical properties, and general method of preparation to π -cyclopentadienyl- π -allylmolybdenum dicarbonyl (II)⁹ lead us to propose structure III for the dicarbonyl derivative CH₃SCH₂-

(1) This work was supported in part by Grant AF-AFOSR-580-64 from the Air Force Office of Scientific Research.

(2) R. B. King, J. Am. Chem. Soc., 85, 1587 (1963), and references to previous work from various research groups cited therein.

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(4) G. N. Schrauzer and V. Mayweg, J. Am. Chem. Soc., 84, 3221 (1962).

(5) T. S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3, 104 (1955).

(6) These compounds gave satisfactory analyses for three to six elements. Detailed analytical data will be given in the full paper.

(7) A mixture of ${\sim}25\%$ CH_3SCH_2Mo(CO)_3C_8H_8 and ${\sim}75\%$ CH_8SCH_2-Mo(CO)_2C_8H_8 exhibited a melting point of 55-60° indicating the melting point depression to be small but detectable.

(8) Details of these spectra will be given in the full paper.

(9) M. Cousins and M. L. H. Green, J. Chem. Soc., 889 (1963).

 $Mo(CO)_2C_5H_5$. In structure III a carbon-sulfur double bond is π -bonded to the molybdenum atom and the neutral CH₃SCH₂ group donates three electrons¹⁰ to the molybdenum atom in a similar manner to the π -allyl ligand. The relationship between the metalligand bonding in CH₃SCH₂Mo(CO)₂C₅H₅ (III) and the π -allyl derivative (II) is very similar to the relationship between the metal-ligand bonding in benzene-chromium tricarbonyl and thiophene-chromium tricarbonyl¹¹ and is a further demonstration of the well-known

analogy between the groupings >C=C< and >S: A similar yellow liquid manganese derivative CH₃-SCH₂Mn(CO)₄ (IV) has been obtained from NaMn-(CO)₅ and chloromethyl methyl sulfide at $\sim 65^{\circ}.^{6}$



Analogous experiments with 2-chloroethyl methyl sulfide¹² and various metal carbonyl anions led to some surprising results. Thus, treatment of $NaMn(CO)_{b}$ with 2-chloroethyl methyl sulfide in boiling tetrahydro-furan gave a 26% yield of pale yellow diamagnetic¹³ crystalline volatile CH₃SCH₂CH₂Mn(CO)₅, m.p. 56.5-58.5°.⁶ The infrared spectrum of this new organo-manganese compound besides very strong bands at 2071, 1996, and 1972 cm.⁻¹ due to the terminal metal carbonyl groups exhibits a very strong band at 1622 cm.⁻¹, which may be assigned to an acyl carbonyl group suggesting structure VI rather than structure V.

Reaction between NaFe(CO)₂C₅H₅⁵ and 2-chloroethyl methyl sulfide in tetrahydrofuran solution at room temperature yields a rather unstable orange liquid indicated by analysis and other properties to be CH₃-SCH₂CH₂Fe(CO)₂C₅H₅ (VII). Ultraviolet irradiation of this material in benzene solution gives a complex mixture from which the following compounds can be isolated by chromatography on alumina in benzene solution followed by crystallization from pentane or ethanol of the fractions thus obtained: (1) unchanged CH₃SCH₂CH₂Fe(CO)₂C₅H₅; (2) brown crystalline [CH₃SFeCOC₅H₅]₂⁶ (VIII) identical with the compound of this composition previously isolated in low yield¹⁴ from the reaction between [C₅H₅Fe(CO)₂]₂

(10) Complexes III and 1V may possibly be regarded as derivatives of the unsaturated sulfonium ion $H_2C=S-CH_3$ where the carbon-sulfur double bond is π -bonded to the transition metal like a carbon-carbon double bond. (11) D. Discher and K. Gielle **Bar.** (24) 2005 (1058)

(11) E. O. Fischer and K. Öfele, Ber., 91, 2395 (1958).

(12) Although we have experienced no difficulties in handling 2-chloroethyl methyl sulfide apart from the usual obnoxious odor of divalent sulfur compounds, we advise caution in handling this compound due to its probable high toxicity based on its close chemical relationship to bis(2-chloroethyl) sulfide, highly toxic "mustard gas."

(13) From the proton n.m.r. spectrum.

(14) An improved preparation of $[CH_8SFeCOC_6H_6]_2$ from $[C_8H_8Fe(CO)_2]_2$ and dimethyl disulfide giving a 37% yield rather than a 9% yield has been developed and will be described in the full paper.