

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLA.]

The Decarboxylation of β -Ketoacids: A Study of the Decarboxylation of 1-Carboxy-bicyclo[3,3,1]nonane Derivatives¹

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The synthesis of compounds V and VI is described. Compound V decarboxylates at 245°, while VI requires only 145°. This difference in reactivity has been explained by the difference in the degree of stabilization of the carbonium formed by the loss of carbon dioxide. The facile decarboxylation of lycotonamic acid (I) and the inert nature of the carboxyl group in III and its derivatives can be explained in the same manner.

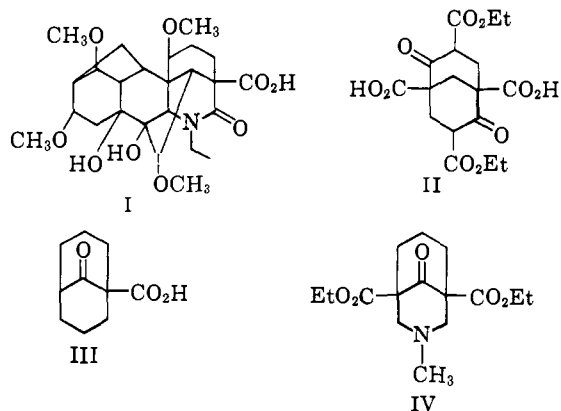
In 1902, Bredt² first began studies which led to his formulation of a rule stating that it is impossible for a double bond to exist at the bridgehead carbon atom of a bicyclic ring system. Since that time numerous investigations have resulted in the extension of the Bredt rule to reaction intermediates in the smaller bicyclic ring systems.² The basis for this empirical rule is the conflicting steric requirements of the planar double bond and the rigid bicyclic ring system.³

The reported facile decarboxylation of lycotonamic acid (I)³ prompted this investigation, as such bridgehead β -ketoacids usually do not decarboxylate or else do so with extreme difficulty. The commonly accepted mechanism⁴ for decarboxylation of β -ketoacids involves an enol intermediate which would place the double bond at the bridgehead carbon atom, thus a violation of the Bredt rule. Lycotonamic acid was reported to decarboxylate in three minutes at 205° and the closely related derivative, anhydrolycotonamic acid, decarboxylates in five minutes at 185°.³ These reactions take place at very low temperatures when compared with the results reported for other bicyclo[3,3,1]nonane systems. For example, a temperature of 246° was required to decarboxylate compound II⁵ while compound III and its derivatives do not decarboxylate at all when heated to 250°.⁶ It has been suggested^{7,8}

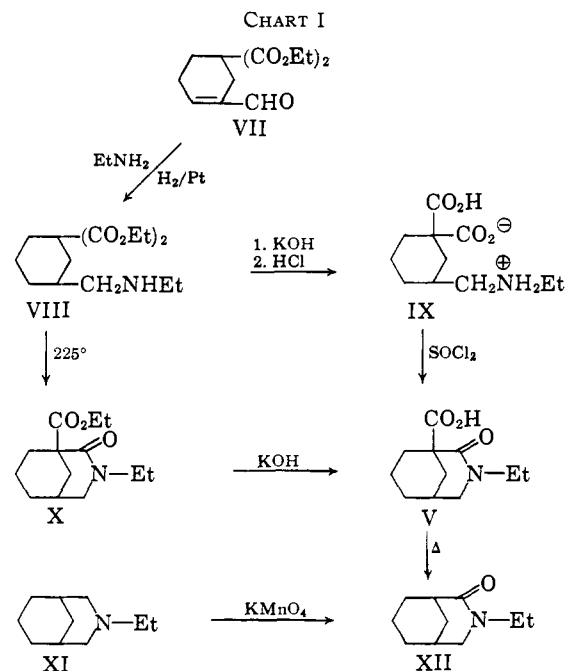
the enol in III would have to be in the one-carbon bridge of the bicyclononane system and therefore would be more difficult to form than in compounds of type III where the double bond of the enol would be in the three-carbon bridge. The hydrolysis and decarboxylation of compound IV to 9-oxo-3-methylazabicyclo[3,3,1]nonane appeared to be the first example of the decarboxylation of a compound of type III.⁹ However, recent work⁷ has shown that the initial step in the decarboxylation is ring-opening *via* a retrograde Mannich reaction to yield a monocyclic intermediate which decarboxylates and this then recycles to the bicyclic ring system.

No 1-carboxy-2-oxobicyclo[3,3,1]nonane derivatives have been prepared which would serve as appropriate models for the heterocyclic ring system of lycotonamic acid and anhydrolycotonamic acid. We wish to report the syntheses of V and VI and the results of our decarboxylation studies on these model compounds.

The starting material for the synthesis of model compound V (Chart I) was aldehyde VII.¹⁰ Reductive amination of VII with ethylamine yielded the amino diester VIII which was converted to the desired model compound *via* two routes. Saponification and subsequent acidification of the reaction mixture yielded a crude aminodiacid (IX). The crude acid was cyclized



that the difference in lability of the carboxyl group in compounds of type II and those of type III can be explained on the basis of the usual mechanism⁴ for the decarboxylation of β -ketoacids. The double bond of



in low yield to the desired lactam acid V with thionyl chloride. A better yield was obtained by heating VIII at 200–225° *in vacuo* to yield the lactam ester X, which had infrared bands at 1725 cm^{-1} (ester) and 1624 cm^{-1}

(1) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Presented at the 142nd National American Chemical Society Meeting, Atlantic City, N. J., p. 47Q of the abstracts.

(2) F. A. Fawcett, *Chem. Rev.*, **47**, 219 (1950).

(3) O. E. Edwards and L. Marion, *Can. J. Chem.*, **30**, 627 (1952); O. E. Edwards, L. Marion and D. K. R. Stewart, *ibid.*, **34**, 1315 (1956).

(4) F. H. Westheimer and W. A. Jones, *J. Am. Chem. Soc.*, **63**, 3283 (1941).

(5) V. Prelog and R. Seiwerth, *Ber.*, **74**, 1644 (1941).

(6) A. C. Cope and M. Synerholm, *J. Am. Chem. Soc.*, **72**, 5228 (1950); V. Prelog, P. Barman and M. Zimmerman, *Helv. Chim. Acta*, **32**, 1284 (1949).

(7) H. O. House and H. C. Müller, *J. Org. Chem.*, **27**, 4436 (1962).

(8) E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 302.

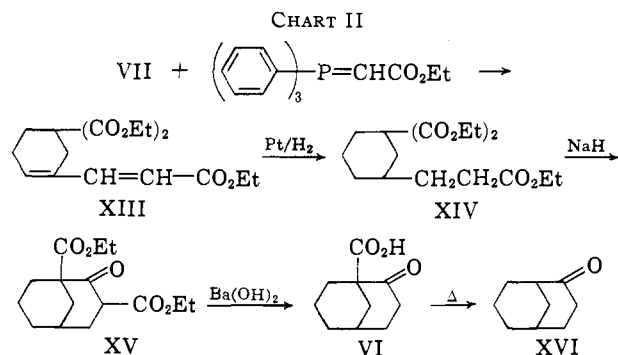
(9) W. Schneider and H. Götz, *Arch. Pharm.*, **294**, 506 (1961).

(10) D. T. Warner and O. A. Moe, *J. Am. Chem. Soc.*, **70**, 3470 (1948); O. A. Moe, D. T. Warner and M. I. Buckley, *ibid.*, **73**, 1062 (1951).

(lactam) of approximately equal intensity. Saponification of X gave a good yield of V which was identical in all respects with that prepared by the former synthetic route. The model compound V had strong maxima in the infrared at 1598 cm^{-1} (lactam) and 1736 cm^{-1} (acid). The C-methyl group was evidenced by a triplet in the n.m.r. spectrum at 8.78τ ($J 8.5\text{ c.p.s.}$).

The synthesis of model compound VI (Chart II) also utilized VII as starting material. The aldehyde group of VII was condensed with triphenylcarbethoxymethylenephosphorane¹¹ to yield the diene XIII which was hydrogenated to the completely saturated derivative XIV. Dieckmann cyclization of XIV yielded the enolic ketoester XV, which when hydrolyzed with barium hydroxide yielded the desired non-enolic ketoacid VI.

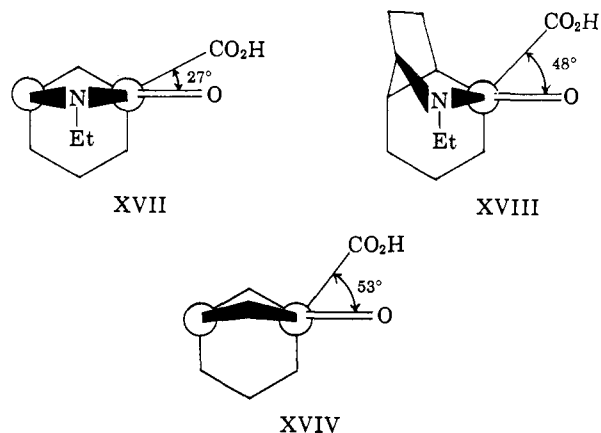
The decarboxylation of V and VI was studied by heating weighed portions of the compounds at various temperatures for half-hour periods. The amount of acid that was not decarboxylated was determined from the absolute intensity of the acid carbonyl band in the infrared. From these data it was possible to determine the temperature at which these acids would be completely decarboxylated in thirty minutes. We found that V would completely decarboxylate in thirty minutes at 245° while VI required only a temperature of 145° to decarboxylate completely in the same period of time.



Proof that no unforeseen rearrangements took place during these decarboxylations or in the preceding synthetic steps was obtained by comparison of the compounds produced by decarboxylation with those of authentic samples prepared by other routes. The product from the decarboxylation of V was synthesized from XI in a remarkably specific amine oxidation.¹² The product of the decarboxylation of VI had been synthesized previously, m.p. 135° (lit.¹³ m.p. 150°); semicarbazone m.p. $179\text{--}181^\circ$ (lit.¹³ m.p. $180\text{--}181^\circ$).

Our results indicate a one hundred degree difference in the temperatures at which V and VI decarboxylate. Lycoctonamic acid and anhydrolycoctonamic acid appear to lose carbon dioxide in five minutes or less at temperatures intermediate to V and VI. The explanation of this wide range of temperatures does not seem to be based on the difference in steric strain in the enol intermediate in the decarboxylation^{7,8} because molecular models indicate that the enol intermediate in the lycoctonine derivatives is the most highly strained due to the additional five-membered ring bridged across the bicyclononane ring system. However, one consequence of the bridged five-membered ring in the lycoctonine series is the distortion of the bicyclic ring system (see XVIII) making the

dihedral angle (measured from Dreiding models) between the carbonyl group and the carboxyl group 48° . The corresponding angle in model compound V (see XVII) is only 27° , while in VI (see XIV) this angle is 53° .¹⁴ The differences in rate of decarboxylation can be



explained if one makes the reasonable assumption that, due to the rigid structure of the bicyclic systems, the geometry of the ground state of these molecules closely resembles that of the transition state for the decarboxylation reaction. The carbanion formed by loss of carbon dioxide from these compounds would have practically the same dihedral angle with respect to the carbonyl group as did the carboxyl group that was originally in that position. The activation energy for the formation of this carbanion would depend on the degree to which the charge on the ion is dispersed in the transition state by overlap with the π -electrons of the adjacent carbonyl group. As the dihedral angle between the carbonyl group and the carbanion increases (up to the optimum angle of 90°), the greater will be the overlap and consequently the lower the activation energy for decarboxylation. Therefore, there should be a direct correlation between the rates of decarboxylation and the dihedral angle in the starting material; which is what we observed. The inert nature of the carboxyl group in the 9-oxo-bicyclo[3,3,1]nonanes^{7,8} (III) can also be explained on this basis. Here the dihedral angle between the carboxyl group and the carbonyl group is zero so that the carbanion formed by loss of carbon dioxide will not be stabilized by overlap with the π -electrons of the carbonyl.

Experimental¹⁵

1-Formal-5,5-dicarbethoxy-1-cyclohexene (VII).¹⁰— β,β -Dicarbethoxybutyraldehyde¹⁰ (216 g.), 500 ml. of benzene and 0.10 g. of sodium in 10 ml. of dry ethanol were combined and cooled to 0° . Acrolein (56 g.) was added dropwise with stirring over a period of 1 hour, then an additional 0.20 g. of sodium in 20 ml. of ethanol was added. Stirring was continued for 2 hours at 0° ; then the reaction mixture was acidified with acetic acid. After washing with water and drying with sodium sulfate, the solution was concentrated under reduced pressure and flash distilled at about 200° (2 mm.). Fractionation of the distillate yielded 68.9 g. (31.9%) of product; λ_{max} 227.5 $\text{m}\mu$ (ϵ 18,000), 307 $\text{m}\mu$ (ϵ 70); γ_{max} 2800, 2710, 1735, 1650 cm^{-1} (CCl_4 , Infracord). The 2,4-dinitrophenylhydrazine derivative after recrystallization from ethyl acetate melted at $161\text{--}163^\circ$ (lit.¹⁰ m.p. $162\text{--}163^\circ$).

(14) The chair-boat form of VI is favored; E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 296. If the cyclohexanone ring of VI is in the boat conformation there is only one unfavorable hydrogen-hydrogen interaction and this would be favored over a chair cyclohexanone ring with two such interactions.

(15) Infrared spectra were run on a Perkin-Elmer model 221 spectrophotometer in chloroform except when noted otherwise, and ultraviolet spectra were run on a Cary model 14 in 95% ethanol by Mrs. K. Osmond and Mrs. D. DeTar. N.m.r. spectra were run in CCl_4 or CDCl_3 on a Varian HR60 spectrometer. Melting points were determined in open capillaries and are uncorrected. Analyses were carried out by Messrs. Weiler and Strauss, Oxford, Eng.; Midwest Microlab, Indianapolis, Ind.; and F. Pascher, Bonn, West Germany.

(11) D. B. Denny and S. Ross, *J. Org. Chem.*, **27**, 998 (1962).

(12) Previous attempts to prepare this compound were unsuccessful; H. K. Hall, Jr., *J. Am. Chem. Soc.*, **80**, 6412 (1958).

(13) H. Meerwein, F. Kiel, G. Klosgen and E. Schoh, *J. prakt. Chem.*, [2] **104**, 161 (1922).

N-(3,3-Dicarbethoxycyclohexyl)-methyl-N-ethylamine (VIII).—A mixture of 14 g. of 33% aqueous ethylamine, 25 g. of 1-formyl-5,5-dicarbethoxy-1-cyclohexene (VII), 25 ml. of absolute ethanol and 100 mg. of PtO_2 was hydrogenated at 4 atmospheres for 24 hours, with absorption of 2 molar equivalents of hydrogen. The solvent was removed under reduced pressure and the product distilled at 105–108° (0.1 mm.) to yield 18.5 g. (66%); end absorption in ultraviolet, ϵ 900 at 220 μ , ν_{max} 1720 cm^{-1} (Infracord).

Anal. Calcd. for $\text{C}_{15}\text{H}_{25}\text{NO}_4$: C, 63.13; H, 9.54; N, 4.91. Found: C, 63.16; H, 9.19; N, 4.93.

1-Carbethoxy-2-oxo-3-ethylazabicyclo[3.3.1]nonane (X).—N-(3,3-Dicarbethoxycyclohexyl)-methyl-N-ethylamine (VIII), 35 g. was heated at 135–140° under vacuum (0.25–0.05 mm.) for 20 hours, then distilled. The low boiling portion was again heated for 2 hours at 200° (1 mm.), then added to the higher-boiling portion of the distillate. The distillate was dissolved in ether, washed with dilute hydrochloric acid, and the ether layer was dried, concentrated and distilled at 116–118° (0.1 mm.) to yield 7.42 g. (24%); ν_{max} 1624, 1725 cm^{-1} .

Anal. Calcd. for $\text{C}_{13}\text{H}_{21}\text{NO}_3$: C, 65.24; H, 8.85. Found: C, 65.12; H, 8.87.

1-Carboxy-2-oxo-3-ethylazabicyclo[3.3.1]nonane (V). (a) From 1-Carbethoxy-2-oxo-3-ethylazabicyclo[3.3.1]nonane (X).—1-Carbethoxy-2-oxo-3-ethylazabicyclo[3.3.1]nonane (7.42 g.) in ethanol-water (10:35) was refluxed with 2 g. of KOH for 6 hours, then cooled and concentrated under reduced pressure. The residue was dissolved in water, acidified, and extracted with chloroform to yield 5.3 g. (81%) of crude product. Several crystallizations gave an analytical sample, m.p. 113.5–116°. A sample rapidly distilled at 225° and 0.05 mm. melted at 116–117° and had the same infrared spectrum as the recrystallized analytical sample material.

Anal. Calcd. for $\text{C}_{11}\text{H}_{17}\text{NO}_3$: C, 62.52; H, 8.11; N, 6.63. Found: C, 62.49; H, 8.13; N, 6.90.

(b) From N-(3,3-Dicarbethoxycyclohexyl)-methyl-N-ethylamine (VIII).—N-(3,3-Dicarbethoxycyclohexyl)-methyl-N-ethylamine (18.5 g.) was added to 8 g. of KOH in ethanol-water (4:1) and the mixture was refluxed on the steam-bath for 5 hours, then concentrated under reduced pressure to remove the alcohol. The aqueous solution was acidified with HCl to pH 3 and then lyophilized. The acid was extracted from the inorganic salts with methanol and the methanol was concentrated. The residue was dissolved in 23 ml. of thionyl chloride and refluxed for 2 hours and the thionyl chloride was removed under reduced pressure. The mixture was dissolved in cold dilute base and was washed with chloroform and the washings were discarded. The aqueous layer was acidified and extracted with chloroform to yield a small amount of material which on crystallization from ether gave 0.057 g. (0.41%), m.p. 106–108°. There was no depression in melting point when mixed with material obtained by route a, and the infrared spectra of the two samples were identical.

2-Oxo-3-ethylazabicyclo[3.3.1]nonane (XI). (a) From 1-Carboxy-2-oxo-3-ethylazabicyclo[3.3.1]nonane (V).—1-Carboxy-2-oxo-3-ethylazabicyclo[3.3.1]nonane (200 mg.) was heated for 1.5 hours at 225–230°, then distilled from the short-path apparatus, producing 97 mg. of 2-oxo-3-ethylazabicyclo[3.3.1]nonane.

(b) From 3-Ethylazabicyclo[3.3.1]nonane (XI).^{3,9}—3-Ethylazabicyclo-[3.3.1]nonane (7.77 g., 50.8 mmoles) was dissolved in 60 ml. of acetone (distilled from KMnO_4) and 3.8 ml. (67.72 mmoles) of acetic acid was added. The flask was cooled to 0°, and 14.6 g. (91.2 mmoles) of finely ground KMnO_4 was added in small portions over a period of 5 hours, with continued cooling. The MnO_2 was removed by centrifugation and the acetone was removed under reduced pressure. The residue was dissolved in chloroform and washed with three 150-ml. portions of water, dried, concentrated, and distilled at 71° (0.1 mm.). A vapor phase chromatogram (using a 2-foot 20% Craig polyester column) suggested the two isomers were present in a ratio of 19/1. A three-proton triplet at 8.93 τ (J 7 c.p.s.) proved that the desired isomer predominated. This material was redistilled and the fraction boiling at 62° (0.05 mm.) was taken; 3.0 g. (35.4%). The infrared spectrum of this material was identical in all respects with the material prepared by the former route; ν_{max} 1621 cm^{-1} .

Anal. Calcd. for $\text{C}_{10}\text{H}_{17}\text{NO}$: C, 71.83; H, 10.25; Found: C, 71.69; H, 10.03.

Ethyl 3-(3,3-Dicarbethoxy-6-cyclohexenyl)-2-propenoate (XIII).—A solution of 25.5 g. (0.1 mole) of 1-formyl-5,5-dicarbethoxy-1-cyclohexene (VII) in 200 ml. of benzene was added to a solution of 34.8 g. (0.1 mole) of triphenylcarbethoxymethylene-phosphorane¹¹ in 200 ml. of benzene. The system was flushed with nitrogen and allowed to stand at room temperature for 4 days. The clear, slightly yellow solution was concentrated under

reduced pressure, dissolved in benzene, and placed on a column of 500 g. of neutral alumina. The product (28.1 g.) was eluted with 500 ml. of benzene and was used directly in the next step. A sample was distilled for analysis at 120° (0.02 mm.); λ_{max} 263 μ (ϵ 18,910)¹⁶; ν_{max} 1730, 1635, 1625 cm^{-1} (Infracord).

Anal. Calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_6$: C, 62.94; H, 7.45. Found: C, 61.98, 63.71; H, 7.19, 7.50.

Ethyl-3-(3,3-Dicarbethoxycyclohexyl)propanoate (XIV).—A mixture of 28.1 g. of ethyl 3-(3,3-dicarbethoxy-6-cyclohexenyl)-2-propanoate and 100 mg. of platinum dioxide in 50 ml. of absolute ethanol was hydrogenated at 70 lb. pressure with absorption of two equivalents hydrogen. Distillation at 139–140° (0.1 mm.) afforded 23.4 g. of product, ν_{max} 1735 cm^{-1} (Infracord, CCl_4).

Anal. Calcd. for $\text{C}_{17}\text{H}_{28}\text{O}_6$: C, 62.17; H, 8.59. Found: C, 62.35; H, 8.24.

1,3-Dicarbethoxy-2-oxo-bicyclo[3.3.1]nonane (XV).—To 11.6 g. of sodium hydride (53% dispersion in mineral oil) in 75 ml. of dry toluene at 70° was added 42.8 g. of ethyl 3-(3,3-dicarbethoxycyclohexyl)-propanoate in 200 ml. of toluene over a 2-hour period. The mixture was stirred in a nitrogen atmosphere and heating was continued until no more hydrogen was evolved (7 hours). After the mixture was cooled, water was added, and finally 10% acetic acid. The toluene layer was separated and washed with 7% sodium carbonate and concentrated under reduced pressure. The residue was dissolved in methanol and washed with hexane to remove the mineral oil. The methanol portion was concentrated and the residue dissolved in ether and dried over sodium sulfate. The product distilled at 140° (0.5 mm.) yielding 7.77 g.; ν_{max} 1755, 1670, 1630 cm^{-1} (Infracord, CCl_4).

1-Carboxy-2-oxo-bicyclo[3.3.1]nonane (VI).—To 2.5 g. of 1,3-dicarbethoxy-2-oxo-bicyclo[3.3.1]nonane in 35 ml. of methanol, 10 g. of barium hydroxide was added and the mixture was heated at reflux for 20 hours. After concentration, the residue was taken up in water, acidified (10% HCl), and extracted with chloroform. The chloroform solution was dried over sodium sulfate, then concentrated to dryness and crystallized from ether-petroleum ether to give 0.65 g. of product, m.p. 102–104°. Further purification was achieved by sublimation at 90° (0.02 mm.), m.p. 104–106°; ν_{max} 1756 (shoulder), 1718 cm^{-1} .

Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}_3$: C, 65.92; H, 7.74. Found: C, 65.98; H, 7.49.

2-Oxo-bicyclo[3.3.1]nonane (XVI).—1-Carboxy-2-oxo-bicyclo[3.3.1]nonane (123 mg.) was heated at 150° for 0.5 hour, then dissolved in ether and washed with a saturated solution of sodium bicarbonate. The ether layer was dried over sodium sulfate, concentrated under reduced pressure, and sublimed at 40° (0.02 mm), m.p. 124–129°. Three additional sublimations raised the melting point to 135–137° (lit.¹³ m.p. 150°) and further sublimation did not result in any appreciable change in the melting point; ν_{max} 1720 cm^{-1} (Infracord, CCl_4).

Anal. Calcd. for $\text{C}_9\text{H}_{14}\text{O}$: C, 77.65; H, 10.14. Found: C, 77.80; H, 10.35.

The semicarbazone was prepared by dissolving 123 mg. of the ketone in 8 ml. of ethanol and adding a solution of 142.5 mg. of semicarbazide hydrochloride, 149.2 mg. of sodium acetate and 1 ml. of water in 10 ml. of ethanol, then refluxing the mixture for 1 hour. The product crystallized when the reaction mixture was cooled and diluted with water. One recrystallization from ethanol gave a product melting at 179–180° (lit.¹³ m.p. 180–181°).

TABLE I

A. DECARBOXYLATION OF V		B. DECARBOXYLATION OF VI	
Temp., °C.	Recovd. acid, %	Temp., °C.	Recovd. acid, %
200	78.5	120	37
210	57.5	130	23
220	43.5	140	10
230	27.5		

Rate Studies on the Decarboxylation of 1-Carboxy-2-oxo-3-ethylazabicyclo[3.3.1]nonane (V) and 1-Carboxy-2-oxo-bicyclo[3.3.1]nonane (VI).—Compounds V and VI were heated at the

(16) This is comparable with other compounds which have the same chromophore; A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

temperatures ($\pm 0.5^\circ$) indicated in Table I for 0.5-hour periods. After cooling, a known volume of chloroform was added and the intensity of the carbonyl carbonyl peak (1736 cm.^{-1} in V and 1750 cm.^{-1} in VI) in the infrared was measured. The amount of unreacted starting material was determined using a calibration curve prepared from known concentrations of V and VI.

Acknowledgment.—We wish to thank Professor H. W. Walborsky and Professor H. O. House for helpful discussions and Professor House for informing us of his results prior to publication. We also thank Mr. Gerald Caple for determining the n.m.r. spectra.

[CONTRIBUTION No. 87, EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LTD., SARNIA, ONTARIO, CAN.]

Stable Carbonium Ions. IV.^{1a} Secondary and Tertiary Alkyl and Aralkyl Oxocarbenium Hexafluoroantimonates. Formation and Identification of the Trimethylcarbonium Ion by Decarbonylation of the *tert*-Butyl Oxocarbenium Ion

BY GEORGE A. OLAH, WILLIAM S. TOLGYESI, STEPHEN J. KUHN, MARYANNE E. MOFFATT, IVAN J. BASTIEN AND EDWARD B. BAKER^{1b}

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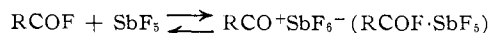
1:1-Addition compounds of di- and trialkyl(aryl)-acetyl fluorides with antimony pentafluoride were prepared and investigated. On the basis of infrared spectra it was found that in the crystalline state the ionic oxocarbenium structure ($\text{RCO}^+\text{SbF}_6^-$) prevails, with minor amounts of donor:acceptor complexes also present. Diphenylacetyl fluoride:antimony pentafluoride is practically exclusively the oxygen coordinated coordination complex. Triphenylacetyl fluoride gives only a very unstable coordination complex decarbonylating to the stable, ionic triphenylcarbonium salt. In solution there is evidence for an increased amount of coordination complex being present in addition to the ionic oxocarbenium salts, according to high resolution nuclear magnetic proton and fluorine resonance spectra. Decarbonylation of *tert*-butyl oxocarbenium hexafluoroantimonate could be followed spectroscopically and the trimethylcarbonium ion was identified. The isolated oxocarbenium salts are reactive acylating agents. Alkylation takes place as well in the case of tertiary and to some degree in secondary alkyl oxocarbenium salts due to prior decarbonylation.

Introduction

As a continuation of previous work^{1a,2} on *n*-alkyl and aryl oxocarbenium salts it was considered that it would be of interest to extend these investigations to secondary and tertiary alkyl (aralkyl) oxocarbenium systems. No previous data were available on any of these ions as stable entities.

Results and Discussion

Preparation of the new oxocarbenium complexes was achieved according to the previously reported "fluoride method."²



Some of the required acyl fluorides were available from previous work^{3,4} and the preparation of others will be reported in a future publication.⁵

The crystalline complexes were found by analytical data to be 1:1 addition compounds of high purity (see Experimental part). Their melting points (in sealed capillary tubes) are listed in Table I and are compared with those of the corresponding primary alkyl (aryl)-acetyl fluoride:antimony pentafluoride complexes.

TABLE I

MELTING POINTS OF SECONDARY AND TERTIARY ALKYL (ARYL)-ACETYL FLUORIDE:ANTIMONY PENTAFLUORIDE COMPLEXES

	M.p., °C.
$\text{CH}_3\text{CH}_2\text{COF} \cdot \text{SbF}_5$	110–112
$(\text{CH}_3)_2\text{CHCOF} \cdot \text{SbF}_5$	95
$(\text{CH}_3)_3\text{CCOF} \cdot \text{SbF}_5$	20 dec.
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COF} \cdot \text{SbF}_5$	58
$(\text{CH}_3\text{CH}_2)_2\text{CHCOF} \cdot \text{SbF}_5$	15 dec.
$(\text{CH}_3\text{CH}_2)_3\text{CCOF} \cdot \text{SbF}_5$	–5 to 0 dec.
$\text{C}_6\text{H}_5\text{CH}_2\text{COF} \cdot \text{SbF}_5$	132–135
$(\text{C}_6\text{H}_5)_2\text{CHCOF} \cdot \text{SbF}_5$	68–69
$(\text{C}_6\text{H}_5)_3\text{CCOF} \cdot \text{SbF}_5$	Dec. to $(\text{C}_6\text{H}_5)_3\text{C}^+\text{SbF}_6^-$, m.p. 211°

(1) (a) Part III, *Revue de Chimie*, C. D. Nenitzescu's 60th Birthday Issue, 1962. (b) Physical Research Laboratory, The Dow Chemical Co., Midland, Mich.

(2) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi and E. B. Baker, *J. Am. Chem. Soc.*, **84**, 2733 (1962).

(3) G. Olah, S. Kuhn and S. Beke, *Ber.*, **89**, 862 (1956).

(4) G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, **26**, 237 (1961).

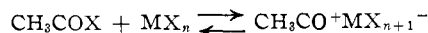
(5) G. A. Olah, S. J. Kuhn and W. S. Tolgyesi, unpublished results.

Spectroscopic Investigations. Infrared Investigations.

—A Perkin-Elmer model 421 grating spectrophotometer was used to record the spectra. Emulsions of the solids in mineral oil (Nujol) and a fluorinated hydrocarbon (Fluorolube, S30, Minnesota Mining and Manufacturing Co.) were pressed between silver chloride or Irtran plates, all operations being carried out in a drybox, as the compounds were extremely sensitive to moisture. No etching of these plates was observed, in marked contrast to the observation when sodium chloride plates were used. Even barium fluoride plates were slightly etched.

The main characteristic data obtained are summarized in Table II. As illustrative examples, the spectra of $(\text{CH}_3)_2\text{CHCO}^+\text{SbF}_6^-$ and $(\text{CH}_3)_3\text{CCO}^+\text{SbF}_6^-$ (as mixed mulls in Nujol-fluorolube) are shown in full in Fig. 1 and 2.

There has been general agreement^{6,7} that the spectra of acetyl halide:Lewis acid metal halide complexes contain a strong band at 2300 cm.^{-1} due to the methyl oxocarbenium ion (CH_3CO^+) formed in the process.



Similarly, aromatic acyl halide (benzoyl, etc.) complexes have given spectra containing a strong band at 2200 cm.^{-1} , indicating the presence of phenyl oxocarbenium ion.

The lower carbonyl frequency of the phenyl oxocarbenium ion than that of the methyl oxocarbenium ion was attributed to conjugation of the CO group with the ring (an effect often observed in infrared spectroscopy). Similarly, conjugation of the alkyl groups with the CO double bond caused a shift of the C=O stretching frequency to lower values in the secondary and tertiary alkyl substituted oxocarbenium ions.

In addition to the ionic oxocarbenium salts there are present also, but to a lesser extent, the polarized oxygen donor coordination compounds, as shown by the presence of the shifted C=O stretching frequencies. Table II shows the shift of the carbonyl stretching frequency of the donor-acceptor complexes and, as may be seen, the shift increases with the branching of the

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(7) D. Cook, *Can. J. Chem.*, **37**, 48 (1959).