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CONCERNING THE STRUCTURE OF TRISHOMOCYCLOPROPENYL CATIONS

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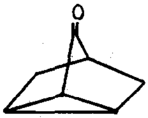
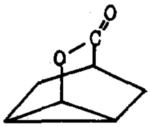
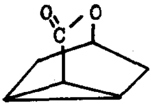
We wish to report some experiments which bear on the nature of trishomocyclopropenyl cations (I).[1] During the course of continuation of studies on the Baeyer-Villiger reaction,


I


II


III


IV

nortricyclanone (II) was oxidized with peracetic acid to give a high yield of a $C_7H_8O_2$ lactone. Evidence presented below establish structure IV, as opposed to III, for this compound. The n.m.r. spectrum of the lactone was not particularly revealing, showing a multiplet of area 1 at -273 cps. and a complex multiplet of area 7 at -113 cps.[2]

Since the lactone was found to be stable to concentrated sulfuric acid (80% recovery after 24 hrs.), the

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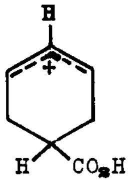
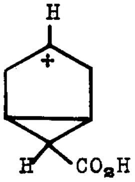
[1] S. Winstein and J. Sonnenberg, J. Amer. Chem. Soc. 83, 3244 (1961).

[2] The spectrum was determined on a Varian Model A-60 Spectrometer using TMS as internal standard.

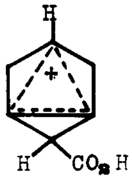
n.m.r. spectrum was determined in this medium with the hope of distinguishing between ions V and VI.[3] This



V



VI



VII

spectrum proved to be considerably more revealing, and is not consistent with ion V. In particular, no absorption due to alkenyl proton[3] was found at ca. 2 τ . The four methylene protons appeared as an $(AB)_2$ pattern at 6.91 and 7.10 τ (J = 15 cps.), in agreement with the assignments by Deno and co-workers for protons alpha to a positive charge. The three cyclopropyl protons form an A_2B system[4] (J = 7 cps) with ν_A at 6.13 τ and ν_B at 6.43 τ. The broad peak at 4.59 τ was assigned to the proton on the carbon bearing the positive charge.

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[3] Benzene capillary was used as external reference and τ values were calculated in the manner described by N. C. Deno, H. G. Richey, Jr., J. D. Hodge and M. J. Wisotsky, J. Amer. Chem. Soc. **84**, 1498 (1962).

[4] The line positions could be calculated to within 1 cps. assuming a value of 0.35 for the ratio of $J_{AB}/\nu_A - \nu_B$. The coupling constant for the cis cyclopropyl protons is in agreement with other values, cf. J.D. Graham and M. T. Rogers, J. Amer. Chem. Soc. **84**, 2249 (1962).

Of further interest is the fact that the spectrum does not change when determined in a mixture of D_2O and fuming sulfuric acid. This result is also inconsistent with ion V.[5] This evidence coupled with the fact that the cyclopropyl protons are deshielded more than the α-methylene protons leads to the conclusion that the species in sulfuric acid is best represented by formula VII in which the positive charge is partially delocalized. Presumably the ion is not completely symmetrical due to electron-withdrawing effect of the carboxyl group.

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[5] We are grateful to Prof. N. C. Deno for suggesting this experiment and for the information that α-protons of alkenyl cations exchange rapidly in sulfuric acid.