with the right half of model A) would have involved the further arranging of carbon atoms 8 and 9 and a hydrogen atom on the latter.

The evidence for this selectivity is threefold: (1) one symmetrical peak for the 2-hydroxycyclobutanone with vapor phase chromatography of each reaction mixture; (2) the absorption band at 1775 cm.$^{-1}$, and none at 1700–1720 cm.$^{-1}$, in the infrared spectra of these products; and (3) a single band observed with chromatography on silicic acid[14] of the *p*-nitrophenylhydrazones (prepared with excess reagent and long reaction times). Items 1 and 3 reveal a further specificity. Two asymmetric carbon atoms result from the formation of 2-hydroxy-3-methyl-2-propylcyclobutanone and 2-butyl-3-ethyl-2-hydroxycyclobutanone, but one of the two possible racemates predominates (probably the *trans*).

Preliminary experiments suggest that the excited state A is a triplet since oxygen, naphthalene and anthracene exert a quenching effect. Solutions of 2,7-dimethyl-4,5-octanedione (each 7 ml., 0.84 *M* in ethanol; in 40 ml. serum bottles, soft glass—1% transmittancy at 2900 Å. and 10% at 3000 Å.) with these additives (naphthalene, 0.002 *M*, absorbed ~2% of light from 2900 to 4700 Å.; oxygen, ~0.001 *M;* and anthracene, 0.0005 *M*, absorbed ~5% of this light; control and those containing aromatics swept with nitrogen) were irradiated simultaneously (G. E. Sunlamp, 275 w.; from 12 cm. distance). In all experiments, analyses each hour (F and M Model 500 Chromatograph, 61 cm. Silicone rubber column, 125°, helium flow 70 ml. per min.) showed that 3,3-dimethyl-2-hydroxy-2-(2-methylpropyl)-cyclobutanone was the only product (symmetrical peak, retention time 3.7 min., ultimate yield 95%). All plots of cyclobutanone formed *versus* time were linear through the origin (rates zero order in dione; dependent on constant light intensity completely absorbed). Rate ratios were: control, 1.0; with naphthalene, 0.88; oxygen, 0.62; and anthracene, 0.41 (duplicated to ±0.02 with interchange of vessels). These results imply paramagnetic quenching by oxygen and triplet–triplet conversion by the aromatics,[15,16] and are striking since such destruction of the diketone-derived triplet must compete with an intramolecular reaction.

Supporting evidence is: (1) 2,3-butanedione when irradiated in solution undergoes almost complete intersystem crossing to its phosphorescent triplet state,[17] and (2) a triplet intermediate is suggested since cyclobutane ring formation (B → C) is slow enough to permit domination by conformational factors.

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[14] B. E. Gordon, F. Wopat, Jr., H. D. Burnham and L. C. Jones, Jr., *Anal. Chem.*, **23**, 1754 (1951). *p*-Nitrophenylhydiazones were used since acidic 2,4-dinitrophenylhydrazine reagent gave partial dehydration to give some α,β-unsaturated hydrazones.

[15] W. G. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

[16] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958).

[17] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 53 (1960).

CARBONIUM ION SALTS. III. SPECTRA AND DECOMPOSITION OF TROPENIUM HALIDES IN METHYLENE CHLORIDE[1]

Sir:

The colors of solid tropenium halides (chloride white, bromide yellow, iodide red) have been attributed to charge-transfer.[2] Winstein[3] has demonstrated charge-transfer complexing between tropenium ion and aromatics, but only one brief report[4] has appeared concerning measurements of the visible solution spectra of the halides.

The ${}^1E_{3u}$ band[5] of tropenium ion in 96% sulfuric acid (λ_{min} 244 (420), λ_{max} 268 (sh), 273.5 (4350), 280 mμ),[6] water (λ_{max} 275 (4350), 280 mμ),[7] and acetonitrile (λ_{max} 275 (4200), 280 mμ)[2c] is not anion dependent, and at spectral concentrations (about 10^{-4} mole/l.) such solutions are colorless unless the anion is colored (as I_3^-, HgI_3^-, etc.). The spectrum of tropenium fluoroborate in dry methylene chloride (λ_{min} 253.5 (785), λ_{max} 271.5 (sh), 278 (4270), 283 mμ (sh)) is similar to that in sulfuric acid, and the solution is colorless. However, tropenium halides dissolve in methylene chloride to give colored solutions at spectral concentrations (chloride light yellow, bromide deep orange, iodide deep violet) with new absorption bands. The new chloride band (λ_{max} 298 mμ (1820)) lies under the tropenium ion band; its position and intensity are estimated by subtracting from the chloride spectrum the absorption of a solution of tropenium fluoroborate of equivalent concentration. The bands of the bromide (λ_{max} 402 mμ (1380)) and the iodide (λ_{max} 422 (1120), 575 mμ (1880))[8] represent discrete new maxima. In addition the tropenium ion ${}^1E_{3u}$ band loses its structure and shows a smooth peak with a higher minimum but almost unchanged maximum (chloride: λ_{min} 249 (2380), λ_{max} 276 mμ (4070); bromide: λ_{min} 253 (1480), λ_{max} 277 mμ (4270); iodide: λ_{min} 264 (3180), λ_{max} 278 mμ (4270)[8]).

We believe that these new colored bands in methylene chloride arise from charge-transfer from halide ion to tropenium ion in the ion pairs or aggregates which should exist[9] in this solvent of low dielectric constant[10] for the following reasons: (1)

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[1] Supported by the Petroleum Research Fund, the National Science Foundation, and Claremont University College.

[2] (a) E. M. Kosower and P. E. Klinedinst, Jr., *J. Am. Chem. Soc.*, **78**, 3493 (1956); (b) W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957); (c) K. M. Harmon, Ph.D. Thesis, U. of Washington, 1958, *Dissertation Abstr.*, **19**, 1563 (1959).

[3] M. Feldman and S. Winstein, *J. Am. Chem. Soc.*, **83**, 3338 (1961).

[4] K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961).

[5] J. N. Murrell and H. C. Longuet-Higgins, *J. Chem. Phys.*, **23**, 2345 (1955).

[6] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957); in this solvent the ${}^1E_{1u}$ band, at λ_{max} 217 mμ (41,000), may also be seen.

[7] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[8] The spectrum of tropenium iodide must be corrected for triiodide ion present from decomposition (see below). This is done by simultaneous solution at two wave lengths to find triiodide concentration, followed by subtraction of the indicated amount of absorption due to triiodide. The position and shape of the tropenium bands can be fixed, but the epsilon values must be compared to an arbitrary standard; values given are relative to 4270 for the 278 mμ absorption of tropenium ion.

[9] C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956), and references therein.

[10] Tropenium bromide shows an equivalent conductance at 1 × 10^{-4} moles/l. in methylene chloride of 21 mhos compared with the

these bands are most intense in fresh solutions; changes that occur in solution (see below) result in loss of these absorptions, (2) identical bands are produced when tropenium fluoroborate is treated with tetramethylammonium bromide or iodide in methylene chloride,[12] (3) a plot of ν in cm.$^{-1}$ against the ionization potential of the halide ions[15] gives a straight line, (4) the separation of the two bands of the tropenium iodide complex is in agreement with that expected[16] for the different electron affinities of the $P_{3/2}$ and $P_{1/2}$ states of iodine atom as observed in other[16,17] charge-transfer complexes of halide ion, (5) X-ray data[18] on solid tropenium iodide gives evidence for a weak charge-transfer bond between the iodide ion and the tropenium ion, which might be expected to persist in ion-pairs.

Solutions of the halides in methylene chloride are not stable unless rigorously protected from the atmosphere; decomposition begins with slight exposure. We find that this is due to preliminary hydrolysis of tropenium halide to tropenyl alcohol and hydrogen halide, followed by (1) hydride abstraction from tropenyl alcohol by tropenium to give cycloheptatriene and tropone (*i.e.*, hydroxytropenium),[19] and/or (2) oxidation of hydrogen halide to halogen[20] (as trihalide ion) followed by attack of halogen on tropenyl alcohol to cause an oxidative rearrangement to benzaldehyde.[21] Results of decomposition studies in dilute methylene chloride solution:[22] ((sample): (a) % recovered tropenium ion, (b) % tropone, (c) % cycloheptatriene, (d) % benzaldehyde, (e) % total recovered C_7 species, (f) % total recovered C_7 species if tropone assumed equal to cycloheptatriene) (tropenium chloride with one drop water): (a) 29.8, (b) 23.8, (c) 33.9, (d) 0, (e) 87.5, (f) 97.6; (tropenium bromide with one drop water): (a) 38.3, (b) 19.4, (c) 29.5, (d) 2.19, (e) 89.4, (f) 99.5; (tropenium bromide one week in glass stoppered flask): (a) 33.4, (b) 11.6, (c) 12.2, (d) 7.18, (e) 63.4, (f) 65.0; (tropenium iodide one week in glass stoppered flask: (a) 40.4, (b) 6.90, (c) not measured, (d) 33.9, (e) 81.4, (f) 88.2 (tropenium fluoroborate 48 hours with trace water): (a) 58, (b) 13, (c) 15, (d) 0, (e) 86, (f) 88. These results indicate that with the chloride and fluoroborate reaction (1) occurs, that reaction (2) predominates with the iodide, and that both are operative with the bromide.

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value of 150 mhos in acetonitrile at this concentration found by Dauben and Gadecki.[11]

[11] F. A. Gadecki, Ph. D. Thesis, University of Washington, 1957.

[12] Conversion in this process does not exceed 10%; if halide does replace fluoroborate in ion-pairs to any great extent the entity formed differs from that dissolved away from a halide crystal, perhaps by inclusion of solvent. Winstein[3] reports that addition of tetrabutylammonium bromide to tropenium fluoroborate in ethylene dichloride gives tribromide ion. We find that tetramethylammonium bromide alone in methylene chloride gives tribromide ion on standing; however, tribromide ion is not responsible for the 402 mμ band of tropenium bromide. Solutions of tropenium tribromide[13] in methylene chloride show no bands in the visible.

[13] M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2026 (1956), first reported the preparation of tropenium tribromide but did not recognize it as a tribromide salt. Its characterization is reported by Dauben and Harmon.[2c,14]

[14] H. J. Dauben, Jr., and K. M. Harmon, Abstracts, Pacific Southwest Regional Meeting of the American Chemical Society, Redlands, Calif., Oct. 25, 1958.

[15] L. Helmholz and J. E. Mayer, *J. Chem. Phys.*, **2**, 245 (1934).

[16] E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

[17] R. Platzmann and J. Franck, *Z. Physik*, **138**, 411 (1954).

[18] A. I. Kitaigorodskii, Yu. T. Struchkov, T. L. Khotsyanova, M. E. Vol'pin and D. N. Kursanov, *Izvest. Akad. Nauk, S. S. S. R., Otdel Khim. Nauk*, **1**, 32 (1960).

[19] Such hydride transfer has been reported by T. Ikemi, T. Nozoe and H. Sugiyama, *Chemistry and Industry*, 932 (1960).

[20] The production of halogen by homolysis of tropenium halide cannot be excluded, but seems unlikely in light of the stability of the halides in the absence of moisture.

[21] The rearrangement of tropenium derivatives to benzaldehyde by halogen was first reported by Dewar and Pettit[13] and has been investigated in detail by Dauben and Harmon.[2c,14]

[22] Decomposed solutions were analyzed by differential extraction followed by quantitative ultraviolet spectral analysis. Yields are based on the total original sample.

(22) (a) National Science Foundation Scholar, 1961; (b) National Science Foundation Scholar, 1960; (c) American Chemical Society—Petroleum Research Fund Scholar, 1961.

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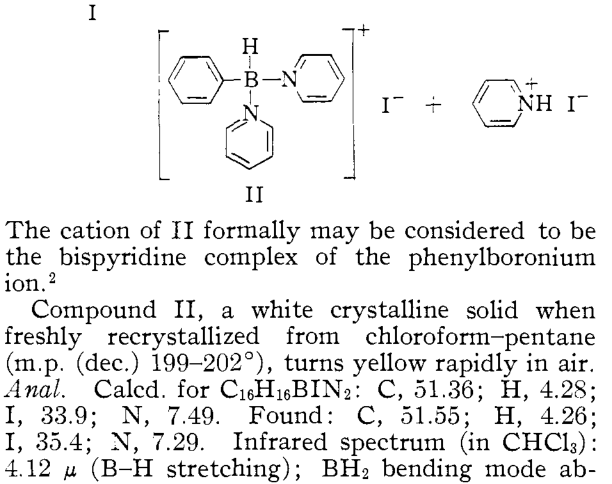
BISAMINE COMPLEXES OF BORONIUM IONS. THE REACTION OF IODINE WITH PYRIDINE PHENYLBORANE

Sir:

Hawthorne has reported that iodine reacts with pyridine phenylborane (I) in an aqueous medium to produce benzeneboronic acid.[1] We wish to report that in chloroform solution in the presence of excess pyridine I reacts with iodine to form, in addition to pyridinium iodide, a boron-containing iodide salt for which structure II is proposed.



I

II

The cation of II formally may be considered to be the bispyridine complex of the phenylboronium ion.[2]

Compound II, a white crystalline solid when freshly recrystallized from chloroform–pentane (m.p. (dec.) 199–202°), turns yellow rapidly in air. *Anal.* Calcd. for $C_{16}H_{16}BIN_2$: C, 51.36; H, 4.28; I, 33.9; N, 7.49. Found: C, 51.55; H, 4.26; I, 35.4; N, 7.29. Infrared spectrum (in $CHCl_3$): 4.12 μ (B–H stretching); BH_2 bending mode absorption found in I at 8.63 μ is absent in II.

Iodine fails to react with II (except for the formation of triiodide ion) indicating that the hydrogen bonded to boron is not hydridic.

In a chloroform slurry, II undergoes rapid metathesis with silver perchlorate to afford the corresponding perchlorate (III). The fine white needles (recrystallized from acetone–chloroform, m.p. (dec.) 182–184°) appear to be stable in air. *Anal.* Calcd. for $C_{16}H_{16}BClN_2O_4$: C, 55.45; H,

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[1] M. F. Hawthorne, *J. Am. Chem. Soc.*, **80**, 4291 (1958).

[2] The nomenclature of inorganic complex ions appears to offer the only unambiguous name for II, namely, phenylhydridobis(pyridine)boron(III) iodide.