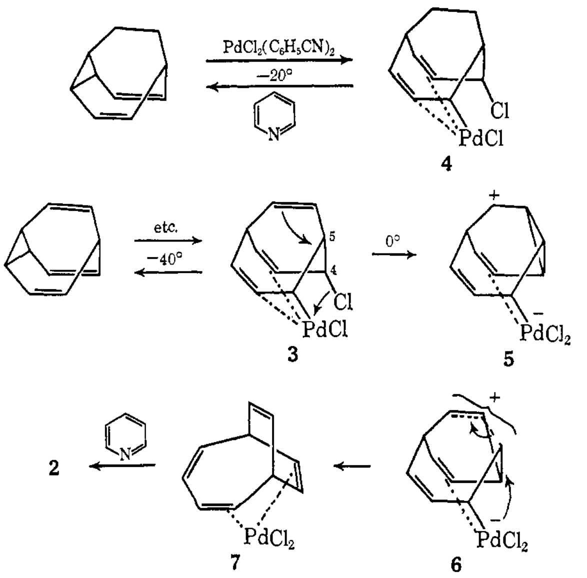
spin–spin coupling parameters. By analogy, the bullvalene complex **3** is tentatively assigned a similar allylpalladium structure.

Table I. Nmr Spectrum (100 Mc) of Dihydrobullvalene–Palladium Chloride Complex **4** at 10° in $CDCl_3$

Chemical shift, τ	Integral	Assignment	Coupling constants (by multiple spin decoupling)
4.0–4.4[a]	3	H_2, H_3, H_8	Complex multiplet
4.71	1	H_7	Triplet, $J_{6,7} = J_{7,8} = 8.0$ cps
4.82	1	H_4	Doublet of doublets, $J_{3,4} = 3.8$ cps, $J_{4,5} = 6.7$ cps
5.79	1	H_6	Doublet of doublets, $J_{6,7} = 8.0$ cps, $J_{5,6} = 8.9$ cps
6.84	1	H_1	Multiplet, $J_{1,2} = J_{1,8} = 8.0$ cps, $J_{1,9} = 3.0$ cps
7.6–8.6	5	H_5, H_9, H_{10}	Complex multiplet

[a] Olefinic hydrogens are slightly deshielded in π-olefin–palladium complexes when compared to the parent hydrocarbons: J. K. Stille and R. A. Morgan, *J. Am. Chem Soc.*, **88**, 5135 (1966); H. Takahashi and J. Tsuji, *ibid.*, **90**, 2387 (1968).

The rearrangement of bullvalene–palladium chloride complex **3** is a novel variant of the familiar homoallyl–cyclopropylcarbinyl interconversion. Ordinarily, it is expected that displacement of the C_4 chloride will be assisted by the bridging double bond to form a cyclopropylcarbinyl structure, **5**.[12] However, the remarkable ease of the rearrangement is best explained if vacant palladium coordination sites also assist the departure of the chloride ion, an effect which resembles silver ion induced polarization of carbon–halogen bonds.[16] The interaction[17] between palladium and the C_4 chloride is further apparent in the facile conversion of **3** and **4** to bullvalene and dihydrobullvalene,[9] respectively, upon treatment with coordinating solvents at −20°. Since **5** may equilibrate with its homoallyl isomer **6**, the occupied palladium d orbitals can now bond to the electron-deficient C_5, resulting in the formation of a π complex (**7**) of bicyclo[4.2.2.]deca-2,4,7,9-tetraene to complete the rearrangement.



The thermal behavior of other homotropilidene–palladium chloride complexes is under investigation and will be described in a future publication.

Acknowledgments. We are grateful to the Research Corporation for financial support and to Badische Anilin und Sodafabrik for a gift of cyclooctatetraene.

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[12] A substituted bicyclo[3.2.1]octadienyl bromide rearranges to its cyclopropylcarbinyl isomer at 80°;[13] a related chloride is stable up to 180°.[14] Bicyclo[3.2.2]nonatrienyl carbonium ion also affords cyclopropylcarbinyl products.[15] To our knowledge, no work has been done with bicyclo[3.3.2]decatrienyl derivatives which might be analogous to complex 3.

[13] W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

[14] D. C. F. Law and S. W. Tobey, *J. Am. Chem. Soc.*, **90**, 2376 (1968).

[15] M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967).

[16] N. Kornblum and D. E. Hardies, *ibid.*, **88**, 1707 (1966).

[17] Other examples of the palladium(II)-induced polarization of a carbon–chlorine bond include carbonylation[18] and alcoholysis[2a,19] of the butadiene–palladium chloride complex.

[18] J. Tsuji and S. Hosaka, *J. Am. Chem. Soc.*, **87**, 4075 (1965).

[19] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963).

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On the Stereochemistry of Quaternization of Pseudotropine[1]

Sir:

More than 15 years ago, Fodor, Koczka, and Lestyán assigned structure III to the major quaternization product of pseudotropine (I) and ethyl iodoacetate and structure IV to the major product of N-ethoxycarbonylnorpseudotropine (II) and methyl iodide.[2] These assignments were based on the observations that the latter product, but not the former, could be converted in poor yield to a substance that had an elemental analysis and ir spectrum consistent with a lactone structure. If the structures are as proposed, then the major quaternization products are formed from the less stable amine conformers.[3,4] In contrast, recent studies[7,8b,9] indicate that, for most alkyl-substituted piperidines, the major quaternization products from reactions with alkyl iodides or sulfonates are formed from the more stable amine conformer. We describe here results that lead us to conclude that the actual structures of these quater-

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[1] Supported in part by Grant CA-05528 from the National Cancer Institute of the Public Health Service.

[2] G. Fodor, K. Koczka, and J. Lestyán, *Magy. Kem. Folyoir.*, **59**, 243 (1953); *J. Chem. Soc.*, 1411 (1956).

[3] (a) G. L. Closs, *J. Amer. Chem. Soc.*, **81**, 5456 (1959); and (b) G. Fodor, *Alkaloids*, **9**, 269 (1967).

[4] The results of an X-ray diffraction study of "N-ethylnortropine methobromide"[5,6] seem to indicate that the major quaternization product of tropine and ethyl iodide is formed from the less stable amine conformer. Also, very recently, Fodor, Medina, and Mandava,[6] on the basis of nmr data, have concluded that the major products of quaternizations of tropine and pseudotropine with deuteriomethyl iodide are formed from the *more* stable amine conformers, but that the major products with ethyl iodide are formed from the less stable amine conformers. Because of other work,[7-9] we find it difficult to accept this latter conclusion.

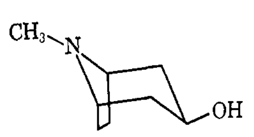
[5] C. H. McGillavry and G. Fodor, *J. Chem. Soc.*, 597 (1964).

[6] G. Fodor, J. D. Medina, and N. Mandava, *Chem. Commun.*, 581 (1968).

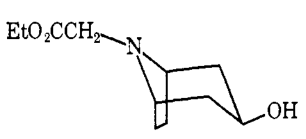
[7] H. O. House, B. A. Tefertiller, and C. G. Pitt, *J. Org. Chem.*, **31**, 1073 (1966).

[8] (a) A. T. Bottini, B. F. Dowden, and R. L. VanEtten, *J. Amer. Chem. Soc.*, **88**, 3250 (1965); (b) A. T. Bottini and M. K. O'Rell, *Tetrahedron Lett.*, 423 (1967).

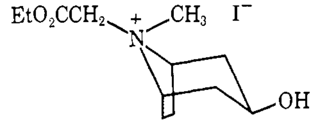
nization products of I and II are the reverse of those previously assigned.[9–11]



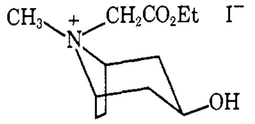
I



II



III



IV

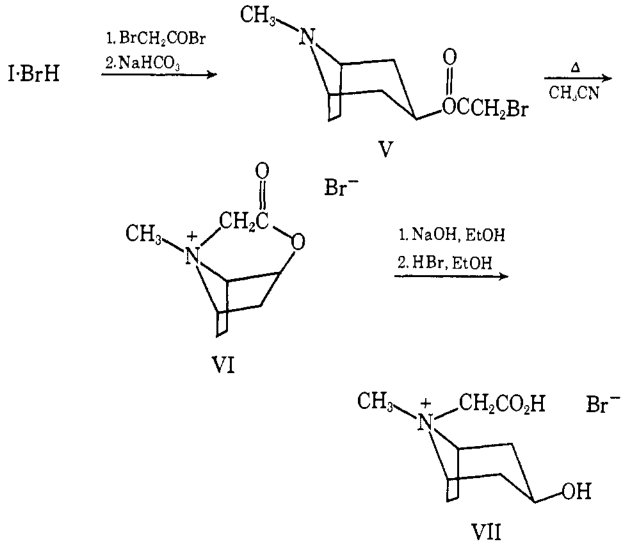
I and II with the appropriate iodides in ethanol–benzene or acetonitrile gave *ca.* 8:1 and 0.08:1 mixtures, respectively, of diastereomeric products as determined by the relative intensities of their N-methyl bands at δ 3.42 and 3.20.[12] The major products were purified by crystallization from ethanol,[13,14] and each was treated successively with ethanolic sodium hydroxide and ethanolic hydrogen bromide to convert it into the corresponding acid, isolated as the mixed bromide iodide. These salts, in turn, were converted[2] into betaines,[14,15a] by treatment with silver oxide, and picrates.[14,15b] The chemical shifts of the N-methylene and N-methyl bands of these derivatives are summarized in Table I.

Table I. Chemical Shifts of N-Methyl and N-Methylene Bands of Derivatives of III, IV, and VI

	δ,[a] N–CH$_2$			δ,[a] N–CH$_3$		
Salt	I	II	VI	I	II	I·HBr
Br$^-$, I$^-$	4.00	4.32	3.90[b,c]	3.37	3.16	3.37[b,c]
Betaine	3.82	4.13	3.80	3.34	3.15	3.33
Picrate	4.10	4.38	4.11	3.40	3.18	3.40

[a] Parts per million. [b] Bromide. [c] The spectrum of a nearly equal mixture of this salt and the mixed halide salt derived from I had singlet N–CH$_2$ and N–CH$_3$ bands at δ 3.95 and 3.37.

Pseudotropinium bromide (I·HBr) was treated with a threefold excess of bromoacetyl bromide for 3 hr at 25°, the excess acid bromide was evaporated, and the residue was triturated with a dry acetone to give in 55% yield pseudotropinium bromide bromoacetate (V·HBr):[14] mp 180.8–183.0° (ethanol-benzene); ν 1735 cm^{-1} (C=O); δ 4.08 (s, 2 H, COCH$_2$Br), 2.82 (s, 3 H, NCH$_3$). V·HBr (2 g) was treated with saturated sodium bicarbonate solution (15 ml), and the mixture was extracted with ether (35 ml total). Most of the ether was removed from the turbid solution by distillation. Dry acetonitrile (30 ml) was added to the residue; the remaining ether was removed by distillation, and the acetonitrile mixture was heated at reflux for 24 hr.[16] Evaporation of the acetonitrile gave 0.53 g (35%) of hygroscopic lactone VI:[17] mp 224.8° (ethanol); ν 1740 cm^{-1} (C=O); δ 4.33 (s, 2 H, COCH$_2$N), 3.47 (s, 3 H, CH$_3$N). Successive treatment of VI with ethanolic sodium hydroxide and ethanolic hydrogen bromide gave the corresponding acid, VII, mp >300°;[18] VII was converted into the betaine[14,19] and picrate.[14,19] The chemical shifts of the N-methylene and N-methyl bands of these salts are given in Table I.



Comparison of the properties of the salts obtained from VI with those obtained from the diastereomeric quaternary iodides (Table I) show that the major quaternization product from II and methyl iodide must be III, and that IV is the major product from pseudotropine (I) and ethyl iodoacetate.

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(9) D. R. Brown, R. Lygo, J. McKenna, J. M. McKenna, and B. G. Hutley, *J. Chem. Soc., B*, 1184 (1967), have also had reason to question these structural assignments.

(10) Our efforts were motivated in part by a study of the effect of solvent on the stereoselectivity of quaternization reactions of pseudotropine with benzyl bromide and benzyl chloride, which indicated that the principal mode of quaternization in methanol, acetonitrile, and benzene was by axial attack (M. K. O'Rell, unpublished data). *Cf* ref 8.

(11) We have no reason to question other stereochemical assignments based on lactone formation made by Fodor[11a] and his coworkers to quaternization products of other tropane derivatives. See ref 3b.

(11a) NOTE ADDED IN PROOF. Professor Fodor has informed us that VI was prepared recently in his laboratory by treatment of pseudotropine with bromoacetyl bromide in the presence of butyllithium (reported at the 51st American Conference of the Chemical Institute of Canada, Vancouver, B. C., June, 1968; G. Fodor and N. Mandava, Abstracts, p 56), and that he is in complete agreement with our conclusions.

(12) Nmr spectra were determined for deuterium oxide solutions using a Varian Associates A-60A spectrometer. Chemical shifts were determined relative to sodium 3-trimethylsilylpropanesulfonate.

(13) Mp 206.5° dec (lit.[2] mp 204° dec) and 200° dec (lit.[2] mp 200, 209°), respectively.

(14) Satisfactory elemental analyses were obtained.

(15) (a) The betaines from the major quaternization products of I and II, after recrystallization from ethanol, began to decompose at 271 and 264°, respectively. On further heating (to >300 and 350°), they darkened gradually but did not give complete melts; lit.[2] mp 270° dec and >300°, respectively. (b) The corresponding picrates, after recrystallization from ethanol, had mp 170.8–171.5 and 165.5–166.5°; lit.[2] mp 188 and 168°, respectively. The former picrate, on remelting, had mp 177–182°.

(16) For description of similar preparations of seven-membered lactones, see ref 7.

(17) *Anal.* Calcd for $C_{10}H_{16}O_2NBr \cdot 1.4H_2O$: C, 41.8; H, 6.6; N, 4.9; Br, 27.8. Found: C, 42.1; H, 6.6; N, 4.8; Br, 27.5.

(18) VII was indistinguishable from the product obtained by similar treatment of the major quaternization product, mp 214.5° dec (lit.[2] mp 214°), of I and ethyl bromoacetate in acetonitrile.

(19) The betaine began to decompose at 273° but did not give a complete melt on further heating to >300°. The picrate had mp 170.8–171.8°. On remelting, it had mp 179–184°.