as in the case of coumarin but λ_{max} is very much red-shifted suggesting that DMC-$BF_3 \cdot OEt_2$ complexation extends conjugation, probably resonance interaction between methoxy groups and BF_3 as shown in Fig. 4. The large contribution of resonance structure (II) may inhibit the photodimerization reaction because the 3,4-double bond character of DMC-$BF_3 \cdot OEt_2$ complex is greatly decreased by $BF_3 \cdot OEt_2$ complexation and photodimerization quantum yields decrease with increasing $BF_3 \cdot OEt_2$ concentration.

In conclusion, an increase or decrease of the photodimerization efficiency of coumarin and DMC on addition of $BF_3 \cdot OEt_2$ are not due to acceleration of the reaction rate of the excited states involved, but to complexation between the ground state of the compounds and $BF_3 \cdot OEt_2$ prior to excitation.

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Comparing the Stability of Geometrically rigid Tricyclopropyl Carbinyl Cations by ^{19}F NMR Spectroscopy

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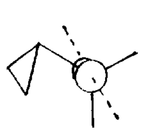
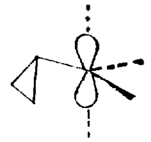
The relative stability as function of geometry in the rigid tricyclopropylcarbinyl cations with varied bond angle (α) between the plane of cyclopropane ring and the bond connecting cyclopropane ring to cationic carbon was examined by ^{19}F nmr spectroscopy. 7-p-Fluorophenyltricyclo[2.2.2.0^{2,6}]octan-7-yl(**4**) and 8-p-fluorophenyltricyclo[3.2.2.0^{2,7}]nonan-8-yl cation (**8**) were generated from corresponding tertiary alcohols under stable ion conditions, and their ^{19}F chemical shifts were compared with those of model compounds such as 7-nortricyclyl cation (**3**) and tricyclo[3.3.1.0^{2,7}]octan-8-yl cation (**7**). Consequently, it is concluded that the varied orientation of bond angle (α) within in the bisected conformation does not affect degree of the charge delocalization into cyclopropane ring.

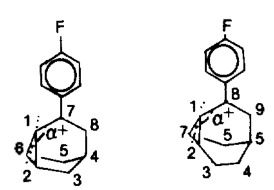
Among neighboring groups which provide stabilization to adjacent carbocationic center, the effectiveness of the cyclopropyl group is well documented.[1] The very large conjugative interaction between a strained cyclopropane bonds and adjacent empty or developing p orbital has been the object of continuing wide interest. The "bisected" conformation (**1**, $\theta = 0°$) of a cyclopropyl cation is energetically favored over the "perpendicular" one (**2**, $\theta = 90°$) by about



1



2



4 **8**

Figure 1

16 kcal/mol.[2] Recently, it has been demonstrated that a cyclopropylcarbinyl cation is also stabilized when the conformation of the system is locked by structural constraints at an intermediate position between bisected and perpendicular conformation.[3] Indeed, the change in energy of a cyclopropylcarbinyl cation upon rotation of the cation center

Conclusion

The studies of ^{19}F nmr on relative stability in closely related series of rigid tricyclopropylcarbinyl cations confirm that the bond angle (α) between the plane of cyclopropane ring and the bond connecting cyclopropane ring to the cationic carbon in the geometrically rigid tricyclopropylcarbinyl cations, appears to exert little influence on the degree of charge delocalization into cyclopropane ring. Futhermore, the bisected geometry may be the most favored for the interaction (σ-conjugation) between cyclopropane ring and the adjacent carbenium ion center.

Experimental Section

^1H nmr spectra were obtained in $CDCl_3$ at 100 MHz, using a Varian XL-100 instrument, and chemical shifts were referenced from interal TMS. Cationic solutions were made up to approximately 10% concentration by adding the corresponding carbinol in CD_2Cl_2 to a stirred FSO_3H-SO_2ClF solution at −120°C using a cation generation apparatus. The chemical shifts in ^{19}F nmr spectra were referenced from external $CFCl_3$.

Synthesis of ketones

Tricyclo[3.2.1.0^{2,7}]octa-3-one (A). The ketone was prepared according to the modified method of the procedure of W.R. Moore et al.[8]: 3,4-Dibromobicyclo[3.2.1.]octa-2,6-diene, prepared from the reaction of 31g (0.35 mole) of norbornadiene and 39g (0.25 mole) of bromoform in the presence of TEBAC in 50% KOH solution, was reduced with LAH to give 18g of 3-bromobicyclo[3.2.1]octa-2,6-diene (A-1). To the monobromodiene (A-1) was added 10ml of 90% sulfuric acid at once at 0°C. The mixture was stirred vigorously for 4 min and neutralized with Na_2CO_3. Column chromatography (Silica gel/n-hexane) gave 3.5g of yellow oil (A); ^1H nmr; 1.35-2.3 (m, 10H).

Tricyclo[3.2.2.0^{2,7}]nonan-3-one (B). The ketone was prepared according to modified method of W.v.E. Doering et al.[9]: Ethyl 3-cyclohexene-1-carboxylate was prepared from the Diels-Alder reaction of 10g (0.1 mole) of ethyl acrylate and 16.3 g (0.32 mole) of butadiene in the presence of $AlCl_3$, and was hydrolyzed and reacted with thionyl chloride to give 10g of 3-cyclohexene-1-carboxylic acid chloride (B-1). The diazoketone was prepared from 10g of the acid chloride (B-1) and diazomethane in ether, and rearranged to give 8g of 3-cyclohexene-1-yl acetic acid (B-2) in the presence of Ag_2O. And 8g of the acid (B-2) was chlorinated by thionyl chloride and reacted with diazomethane to give diazoketone, 6g of which was cyclized under the catalyst of Cu powder to give 1.5g of the ketone (B).

Synthesis of carbinols

The carbinols were prepared by the Grignard reaction of the corresponding ketone with p-fluorobromobenzene in dry ether.

7-p-Fluorophenyltricyclo[2.2.1.0^{2,6}]octan-7-ol; ^1H nmr; 1.0-2.5 (m, 11H) 7.0 (t, 2H) 7.5 (q, 2H), ^{19}F nmr = −116.4, mp = 59-62°C.

8-p-Fluorophenyltricyclo[3.2.2.0^{2,7}]nonan-8-ol; ^1H nmr; 0.9-2.5 (m, 10H) 2.8 (s, 1H) 6.9 (t, 2H) 7.3 (q, 2H) ^{19}F nmr = −115.6.

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