# Evidence of Isomerization of 5-Methylenebicyclo[2.2.1] hept-2-ene Cation by $^{13}$C NMR Spectroscopy

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SUMMARY

Cations obtained by reaction of various protonic acids with 5-Methylenebicyclo[2.2.1]hept-2-ene (5-methylene-2-norbornene) have been studied by $^{13}$C NMR spectroscopy. The isomerization of initial carbocation has been pointed out. A correlation of these results with the structure of the corresponding polymers has been established

The cationic polymerization of 5-Methylenebicyclo[2.2.1]hept-2-ene (5-methylene-2-norbornene) has been investigated several times and KENNEDY (1974) published a review on this topic. A structure of the polymer obtained by classical cationic initiation has been suggested; this results from infrared and X.R. diffraction studies.

In a recent work IVIN et al. (1980) reported the $^{13}$C NMR spectrum of a poly[5-methylenebicyclo[2.2.1]hept-2-ene] resulting from a Ziegler-Natta initiation. We obtained the same $^{13}$C NMR spectrum as IVIN et al. when the initiator were $TiCl_4$, $CF_3COOH$, $CCl_3COOH$ and concentrated $H_2SO_4$ (see fig.1). Chemical shifts and coupling constants $J_{^{13}C-H}$ fit with the generally accepted structure of the polymers:
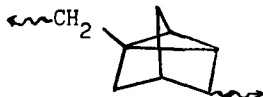


KENNEDY and MAKOWSKY (1967) suggested an isomerization of the active species :
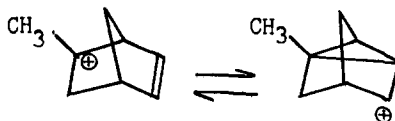
In order to confirm this hypothesis we used $^{13}$C NMR spectroscopy to study the protonation of 5-Methylenebicyclo[2.2.1] hept-2-ene by several acids: $CX_3COOH$ (X=F,Cl,H) and conc. $H_2SO_4$. The results are reported in this article.

EXPERIMENTAL

     Monomer (Aldrich) and acids (Prolabo Rectapur) were used without further purification. The acids were added to the monomer solution ($CDCl_3$, [M]= 3mole.l$^{-1}$) in NMR sample at room temperature.

     $^{13}$C NMR spectra were recorded at 25,15 MHz. Chemical shifts were determined by using the solvent as reference and converted to $Me_4Si$ with $\delta_{CDCl_3}$ = 76.9 ppm. Assigments were obtained by comparison with non decoupled spectra; coupling constants $J_{^{13}C-H}$ were determined by gated decoupling method.

     Respective contributions of M, I and II to the reaction mixture were obtained by comparison of the areas of the peaks. This quantitative determination has been carried out on solutions added with $Cr(Acac)_3$ and with a pulse delay of 7 sec. Under these conditions the relative error is about 10%.

     Polymerizations were carried out either at -70°C or at room temperature in $CH_2Cl_2$ or in $CHCl_3$ under nitrogen.

RESULTS AND DISCUSSION

     When 5-Methylenebicyclo[2.2.1] hept-2-ene (M) is protonated very little polymer is produced (<1%) and the reaction medium consists of a mixture of M and adducts I and II :
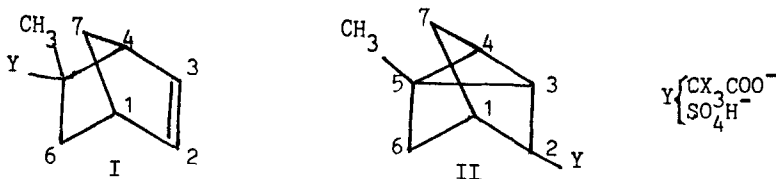


In the case where trifluoroacetic acid is the protonating agent it is very easy to observe the consecutive reactions reported below, by increasing the acid concentration :

$$A + M \longrightarrow I \longrightarrow II \qquad \text{A is the acid}$$
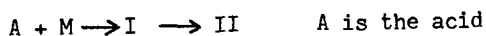
This allows an identification of the peaks which are relative to I and II; their chemical shifts are reported in table 1, see also fig. 2.

## TABLE 1

Chemical shifts of peaks relative to M, I and II and to polymer P

| Assig | M $\delta$ ppm | M $J_{13C-H}$(Hz) | I $\delta$ ppm | I $J_{13C-H}$(Hz) | II $\delta$ppm | II $J_{13C-H}$(Hz) | P $\delta$ ppm | P $J_{13C-H}$(Hz) |
|---|---|---|---|---|---|---|---|---|
| 1 | 42.3(d) | 146.5 | 51.7(d) | 165 | 35.8(d) | 148 | 36.9(d) | 148 |
| 2 | 134.4(d) | 171 | 132.2(d) | 172 | 85.4(d) | 162 | 43.3(d) | 132 |
|  |  |  |  |  | 87(d) |  |  |  |
| 3 | 136.4(d) | 172 | 140.4(d) | 167 | 18.9(d) | 178 | 23.3(d) | 169 |
|  |  |  |  |  |  |  | 23.5(d) | " |
| 4 | 51.2(d) | 145.5 | 41.9(d) | 157.5 | 20.1(d) | 178 | 17.5(d) | 169 |
|  |  |  |  |  | 20.5(d) | " | 17.8(d) | " |
| 5 | 150.7(s) |  | 94.5(s) |  | 21(s) |  | 24.9(s) |  |
| 6 | 33.7(t) | 129.5 | 41.3(t) | 134 | 31.2(t) | 134 | 31.2(t) | 131 |
| 7 | 50.2(t) | 135.5 | 48.1(t) | 137 | 35.8(t) | 134 | 39.3(t) | 129 |
| $CH_2=$ | 103.4(t) | 156 |  |  |  |  |  |  |
| $CH_3$ |  |  | 22.2(q) | 127 | 14.1(q) | 126 |  |  |
|  |  |  |  |  | 14.8(q) |  |  |  |
| $-CH_2-$ |  |  |  |  |  |  | 31.8(t) | 123 |

The chemical shifts of I fits with the proposed structure. Two olefinic carbon sheildings, similar to those which were reported by STOTHERS (1972) in the case of methylnorbornene, can be observed. A quaternary carbon peaks at 94.5 ppm can be assigned to the carbon $C_5$ in $\alpha$ of the ester group.

The spectra of II and of the polymer can be compared. In both cases the shieldings of the unit tricyclo[3.3.1.0] can be identified by comparison with the work of LIPPMAA et al. (1973). The high coupling constants (169-178 Hz) can be attributed to the cyclopropane unit, and a peak corresponding to a tertiary carbon substituted by a polar group is observed at 85.4 ppm.

The splitting of several carbon resonances can be observed on the spectra of II and of the polymer. Both components have an
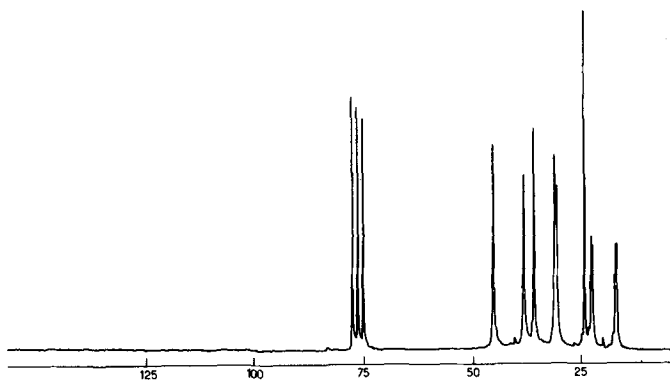
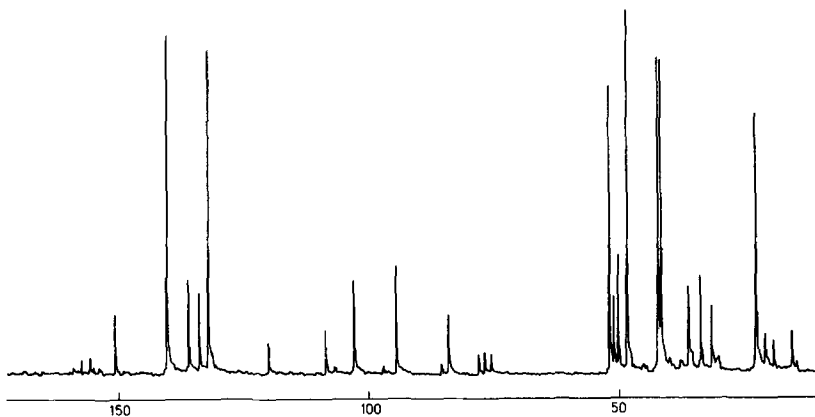Fig. 1. Spectrum of the polymer initiated by CF$_3$COOH.



Fig. 2. Spectrum of the mixture of M, I and II obtained by reaction of CF$_3$COOH with M in CDCl$_3$ solution.
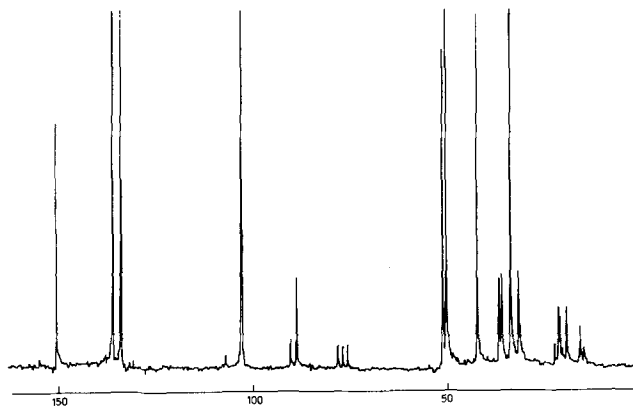


Fig. 3. Spectrum of the mixture of M and II obtained by reaction of conc. D$_2$SO$_4$ with M in CDCl$_3$ solution.

equal intensity in the case of polymer, and are unequal in the case
of II. The extent of the splitting depends on the nature of the acid
and is particularly important in the case of $H_2SO_4$. This fits with
the presence of two conformers corresponding to A or B position of
the substituant:
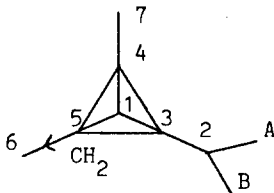
When the monomer is deuterated by conc. $D_2SO_4$ an increase of the
multiplicity of the peak relative to the methyl group is observed.
This confirms the formation of a $CH_2D$ group ($\delta$ =14.8ppm, $J_{13_{C-D}}$ = 19Hz)

The relative concentration of M,I and II depend on the nature of
the acid (see Table 2).

TABLE 2

Dependence of the concentration (mole %) of M, I and II on the
nature of the acid A and on the ratio $[A]/[M]$. Solvent: $CDCl_3$;
temperature 25°C; $[M]$ =3 mole.$1^{-1}$.

| Acid | $\dfrac{[A]}{[M]}$ | M% | I% | II% |
|---|---|---|---|---|
| $CF_3COOH$ | 0.92 | 3 | 79 | 18 |
| $CCl_3COOH$ | 0.90 | 10 | 76 | 14 |
| $CH_3COOH$ | 1.35 | 100 | 0 | 0 |

Table 2 shows that even in presence of an excess of acetic acid
no adduct is formed and that the proportion of II increases with
increasing strength of acid. On the other hand no adduct I (fig.3)
is present when conc. sulfuric acid is used, and no other trans-
formation than M → II is observed.

The relative proportions of monomer and adducts depend also
on the amount of acid added to the monomer solution (see table 3).

The influence of temperature and of solvent polarity is too

## TABLE 3

Dependence of the relative proportion of M, I and II (mole %) on the amount of trifluoroacetic acid added to the solution. Solvent: $CDCl_3$; temperature: 25° C; $[M] = 3$ mole.$1^{-1}$.

| $\dfrac{[CF_3COOH]}{[M]}$ | M% | I% | II% |
|:---:|:---:|:---:|:---:|
| 0.35 | 68 | 28 | 4 |
| 0.52 | 50 | 43 | 7 |
| 0.92 | 3 | 79 | 18 |
| 1.26 | 0 | 46 | 54 |
| 1.73 | 0 | 0 | 100 |

## TABLE 4

Dependence of the polymerization yield on temperature, polarity of the solvent and the nature of the acid.

| A | T°C of polym. | solvent | [M] | $\dfrac{[A]}{[M]}$ | R% * |
|:---:|:---:|:---:|:---:|:---:|:---:|
| $CF_3COOH$ | -70 | $CH_2Cl_2$ | 0.6 | 0.054 | 1.6 |
| " | " | " | 0.6 | 0.3 | 23 |
| " | 25 | " | 2.5 | 0.95 | 3 |
| " | " | $CHCl_3$ | 3 | 0.95 | 0.5 |
| $CCl_3COOH$ | -70 | $CH_2Cl_2$ | 0.18 | 0.3 | 1.3 |
| " | 25 | $CHCl_3$ | 3 | 0.84 | 0 |
| $CH_3COOH$ | -70 | $CH_2Cl_2$ | 0.2 | 0.4 | 0 |

* R% is the yield of the polymer precipitated by pouring the polymerization solution in a large excess of methanol

low to observe any significant change by NMR study (see table 4).
It is therefore impossible to conclude that the isomerization of
the carbocation is an equilibrium.

On the contrary the yield of the polymerization depends on
the polarity of the solvent, temperature and the nature of acid.

If after elimination of polymer the residual solution is
dry-evaporated a mixture of adduct I and II is obtained whose
composition is close to those reported in table 3.

Infrared spectra of the polymers obtained by protonic
initiation exhibit an absorption between 1775 $cm^{-1}$ and 1754 $cm^{-1}$
assigned to $\vec{\nu}$ C=O vibration and NMR spectra show a weak peak at
84 ppm. These characteristics are not observed on spectra of polymer
initiated by $TiCl_4$. From these observations it can be concluded that
the end monomer unit of the polymers obtained by protonic initia-
tion has the structure of adduct II.


GENERAL CONCLUSION

The fact that the addition of the acid occurs on methylene
fits with BROWN and LIU (1975) results. They showed that the
addition in the bulk of trifluoroacetic acid to methylenenorbornane
is complete in approximately 15 sec. With norbornene, under the
same conditions, a time of 1 to 2 minutes is required.

The fact that no polymer is obtained when initiator is
$CH_3COOH$ is not surprising since the only monomer which could be
polymerized by this acid is N-vinylcarbazole (GANDINI and PIETRO
1977). No adduct is obtained due to the very weak extent of
dissociation of this acid.

The polymerization yield remains very low in the case of
trichloroacetic acid. However, adduct are formed. The very low
extent of the isomerization I→II fits with the high nucleophili-
city of the counter anion (BROWN and MATHIESON 1957).

Although weaker than most mineral acids, trifluoroacetic
polymerizes 2-methylenenorbornene. When the temperature of
polymerization increases the yield decreases, which is probably
due to transfer reaction.

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