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SYNTHESES AND PROPERTIES OF (Z)-1-ARYL-2-TROPYLIOETHENE PERCHLORATES

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(Z)-1-Phenyl- and (Z)-1(1-naphthyl)-2-tropylioethene perchlorate are isolated and characterized. The ions readily isomerize to the E-isomers in acetonitrile at room temperature, but are remakably stable in trifluoroacetic acid to show a marked solvent effect. Light also induces the Z → E isomerization.

Thermal and photochemical Z,E isomerization of olefins have long been an interesting subject in organic and physical organic chemistry.[1,2] In this regard, stilbene and its derivatives are among the most extensively studied compounds. With respect to thermal isomerization of stilbenes, polarization effects by substituents play an important role on lowering the activation energy.[3]

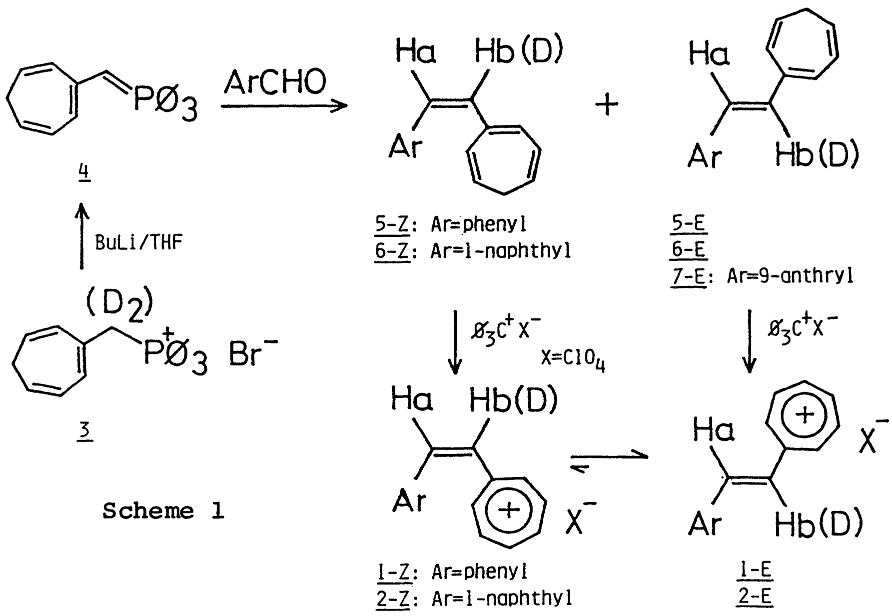
1-Phenyl-2-tropylioethene cation (1) is an analogue of stilbene having a tropylium ring in place of a phenyl ring, and might be expected to readily undergo thermal Z → E isomerization in view of its polar character and supposedly greater thermodynamic stability of the E-form over the Z-form.

In 1964, Jutz *et al.* reported the syntheses of 1 and its derivatives in two ways.[4] In these preparations, however, only the E-isomers were isolated in seemingly consonant with the above-mentioned expectation. Is it possible to isolate the Z-isomers ? If isolated, how different are the properties of the Z-isomers from those of the E-isomers, and how easy is the Z → E isomerization ? We here report the isolation and some properties of the perchlorate of 1-Z and (Z)-1(1-naphthyl)-2-tropylioethene cation (2-Z).

It was considered that the most promising way to the Z-cations should be abstraction of a hydride from the corresponding (Z)-1-aryl-2-cycloheptatrienylethenes at appropriate conditions. For the preparations of these precursors, we have used a Wittig reagent 4, (3-cycloheptatrienyl)methylenetriphenylphosphorane. Very recently, Ott and Rewicki have also employed 4 independently for their work on polymethines with heptafulvenyl terminal groups.[5]

Treatment of phosphonium bromide 3,[6] prepared from 3-bromomethylcycloheptatriene[7] and triphenylphosphine (88% yield), with n-BuLi (1 equiv) in THF followed by addition of benzaldehyde (1.1 equiv) at 20 °C gave 5-Z and 5-E[8] in 47 and 42% yield, respectively. 1-Naphthaldehyde also gave both 6-Z(43%) and 6-E(46%). However, 9-anthraldehyde produced only 7-E(82%).

The geometrical assignments of these compounds chiefly rest on the vicinal coupling constants (J_{ab}) between the ethene protons; for example, while J_{ab} of 5-Z is 12.0 Hz, that of 5-E 16.0 Hz.



Scheme 1

Hydride abstraction of 5-E with triphenylmethyl perchlorate in acetonitrile quantitatively yielded 1-E (orange solid) of which melting point and electronic absorption spectrum (ES) in acetonitrile are identical with those reported.[4] In this solvent, 5-Z also yielded only 1-E at 0°C to room temperature. However, desired 1-Z (yellow orange solid[9]) could be obtained in high yield when the hydride abstraction of 5-Z was performed briefly (5-10 min) in dichloromethane at 0°C followed by addition of ether or hexane to precipitate the salt. The precipitation after 1 h gave a mixture of 1-Z and 1-E, though the former was still predominant. Similarly, naphthyl compounds, 2-Z[4] and 2-E[9], were obtained from 6-Z and 6-E, respectively.

As already suggested above, the Z-isomers readily isomerize to the E-isomers on dissolution in acetonitrile at room temperature. However, it turned out that the Z-isomers are remarkably stable in trifluoroacetic acid (TFA): 1-Z isomerizes to 1-E slowly even at 100°C ($t_{1/2} \approx 8$ h by ^{1}H-NMR spectroscopy).

Light also causes the Z→E isomerization. Irradiation of a TFA solution of 1-Z in a NMR tube through a Pyrex filter at room temperature for 30 min gave rise to almost the same ^{1}H-NMR spectrum as 1-E,[10] which indicates that the photochemical equilibrium lies far (>95%) to the side of the E-form at the condition.

Figure 1 and Table 1 show the ^{1}H- and ^{13}C-NMR spectra and/or data of the cations. The averaged ^{13}C chemical shift of the tropylium ring of 1-Z is 2.3 ppm lower than that of 1-E, whereas the averaged one of the phenyl ring of the former is 0.9 ppm higher than that of the latter. The C-a of 1-Z is at 3.6 ppm higher field than of 1-E. These differences, though not very significant, indicate that the positive charge in 1-Z is less delocalized all over the molecule than in 1-E probably due to poorer coplanarity of the former as the case in Z-stilbenes. Naphthyl compounds, 2-Z and 2-E, show a similar tendency. The ethene protons (Ha and Hb) of 1-Z and 1-E are assigned unequivocally as indicated in Figure 1 by the comparison with the spectra of the monodeuterated cations prepared similarly starting from 3-bromodideuteriomethylcycloheptatriene[7] (Scheme 1).

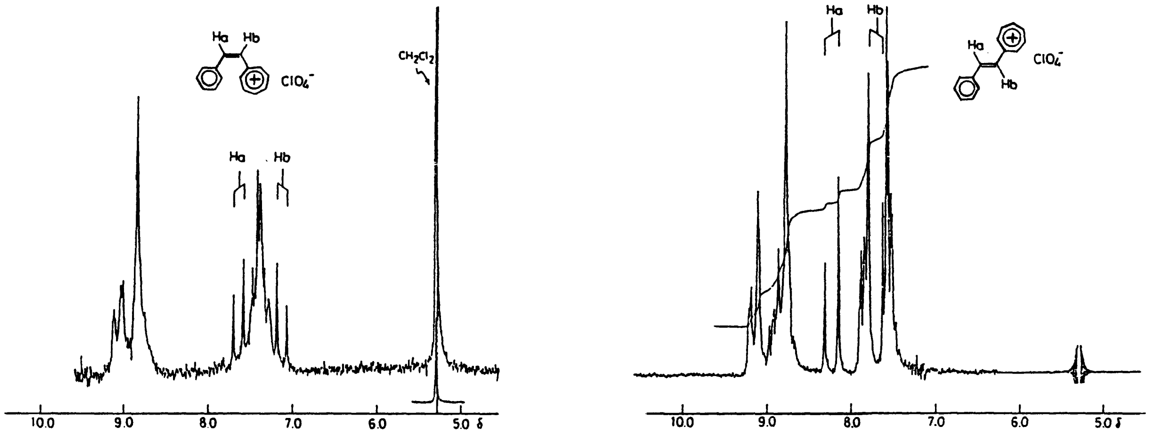


Fig. 1 ^{1}H-NMR spectra (100 MHz) of 1-Z (left) and 1-E (right) in CF_3COOD

Table 1 Spectral data of 1-Z, 1-E, 2-Z, and 2-E[a]

Compd.	^{1}H-NMR (δ ppm)[b]		(J Hz)	^{13}C-NMR (δ ppm)[c]	ES λ nm (ε)
1-Z	7.11	1H d	(11.4)	tropylium:153.9, 154.4, 156.0	278 (10000)
	7.2-7.6	5H m		171.4	463 (23400)
	7.62	1H d	(11.4)	phenyl:131.1, 131.8, 133.1, 135.3	
	8.6-8.9	4H m		ethene:130.9(C-b), 148.8(C-a)[d]	
	8.95-9.15	2H m			
1-E	7.5-7.7 7.7-7.9	6H m		tropylium:151.4, 152.8, 153.6	279 (13600)
				169.2	465 (39000)
	8.24	1H d	(15.8)	phenyl:131.7, 131.9, 135.5, 136.8	
	8.6-9.0	4H m		ethene:129.6(C-b), 152.4(C-a)[d]	
	9.0-9.2	2H m			
2-Z	7.2-7.5	3H m		tropylium:153.6, 154.2, 155.5	272 (13300)
	7.5-7.8	2H m		170.8	354 (8800)
	7.9-8.2	4H m		naphthyl & C-b:125.6-136.6	539 (10100)
	8.5-9.0	6H m		ethene:147.7(C-a)	
	AB q at 7.44 & 8.10		(12)		
2-E	7.5-8.4	8H m		tropylium:151.0, 152.2, 152.9	275 (15200)
	8.5-8.8	4H m		168.3	360 (9100)
	8.9-9.2	3H m		naphthyl & C-b:124.7-144.6	543 (27500)
	AB q at 7.74 & 9.04		(16)	ethene:147.8(C-a)	

[a] All the spectra were taken in CF_3COOH or CF_3COOD. [b] CH_2Cl_2 (δ 5.30) was used as an internal standard. [c] The solvent signals at δ 116.6 (q) were used as internal standards. [d] The assignments were deduced based on the proton off-resonance and selective decoupling.

The much weaker electronic absorption intensity of the Z-isomers than the E-isomers at the longest wavelength absorptions (Table 1) coincides with the poorer coplanarity of the Z-isomers. However, the differences in the absorption wavelengths are rather small as compared with those of Z- and E-stilbene. It has been observed a considerably large solvent effect on the absorption wavelengths of the E-isomers (e.g. for 1-E, 440 nm in CH_3CN and 466 nm in CH_2Cl_2),[4] and the data here obtained in TFA are close to those in dichloromethane.

How comes it that easiness of the Z→E isomerization of 1-Z and 2-Z is strongly solvent dependent ? Such a large solvent effect has been also observed on the Z→E isomerization of a quarternary stilbazolium salt, in which a correlation between the rate of the isomerization and Kosower's Z-value[12] was observed.[11] Although further study is needed for a conclusion, we at present think that tightness of the ion pairs between the cations and the counter anion in solutions should be largely responsible for the solvent dependence; for the polarization effect would work better in a loose ion pair than in a tight ion pair. Since trifluoroacetate ion can serve as a good counter anion, a tropylium salt in TFA may behave as a contact ion pair, whereas in acetonitrile it may exist as a free solvated ion or a solvent-separated ion pair due to the unshared electrons on the nitrogen and the large dielectric constant.

References

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and E. L. Eliel, Eds., Wiley-Interscience, New York, 1973, vol. 7, p. 295.

2) For reviews on photochemical Z,E isomerizations, see; (a) J. Saltiel et al., "Organic Photochemistry", O. L. Chapman Ed., Vol. 3, Dekker, New York, 1973, p. 1; (b) H. Meier, in "Photochemie I, Methoden der Organische Chemie", Gerog Thieme, Stuttgart, Band 4/5a, p. 189.

3) M. Calvin and H. W. Alter, J. Chem. Phys., 19, 768 (1951).

4) (a) C. Jutz and F. Voithenleitner, Chem. Ber., 97, 1337 (1964); (b) C. Jutz, ibid, 97, 1349 (1964).

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6) Mp 243-244°C (lit.^{5} 244-245°C): ^{1}H-NMR δ (CD_3CN) 2.02(2H,t,J=6.8 Hz), 4.60(2H, d,15.0), 4.9-5.5(2H,m), 5.86(1H,d,9.0), 6.07(1H,ddd,9.0,5.8,3.1), 6.53(1H,t, 5.8), 7.5-8.0(15H,m). This salt is usually contaminated with a varied amount of 1-cycloheptatrienyl isomer depending on the isomeric purity of the bromide.

7) S. Kuroda, M. Oda, and Y. Kitahara, Angew. Chem. Internat. Ed., 12, 76 (1973).

8) 5-Z: pale yellow oil; ^{1}H-NMR, δ ($CDCl_3$) 2.30(2H,t,J-6.9 Hz), 5.17(1H,dt,9.2, 6.9), 5.39(1H,dt,9.6,6.9), 5.97(1H,d,9.6), 6.15(1H,dd,9.2,6.0), 6.32(1H,d, 12.0), 6.47(1H,d,12.0), 6.59(1H,d,6.0). 7.1-7.4(5H,m); UV, λ (cyclohexane) 259(log ε 3.99), 306 nm(4.11); 5-E: pale yellow solid , mp 42-44°C; δ 2.34(2H, 4,6.9), 5.4-5.7(2H,m), 6.24(1H,dd,9.2,6.0), 6.46(1H,d,9.4), 6.62(1H,d,6.0), 6.68(1H,d,16.0), 6.92(1H,d,16.0), 7.1-7.5(5H,m); λ 263(4.06), 320 nm(4.48); 6-Z: pale yellow oil; δ 2.14(2H,t,6.9), 4.87(1H,dt,9.2,6.9), 5.35(1H,dt,9.2, 6.9), 5.69(1H,d,9.2), 6.10(1H,dd,9.2,6.0), 6.55(1H,d,6.0), 6.61(1H,d,12.0), 6.89(1H,d,12.0), 7.2-8.1(7H,m); λ 219(4.74), 288(4.08), 317 nm(4.12); 6-E: pale yellow oil; δ 2.40(2H,t,6.9), 5.4-5.7(2H,m), 6.27(1H,dd,9.2,6.0), 6.61(1H, d,9.2), 6.68(1H,d,6.0), 6.93(1H,d,16.0), 7.3-7.9(7H,m), 8.16(1H,m); λ 237(4.33), 289(sh 3.94), 336 nm(4.39); 7-E: yellow solid , mp 106-107°C; δ 2.44(2H,t,6.9), 5.4-5.8(2H,m), 6.27(1H,dd,9.2,6.0), 6.65(2H,m), 6.73(1H,d,16.0), 7.3-7.6(5H,m), 7.8-8.0(2H,m), 8.2-8.4(3H,m), λ 225.5(4.54), 230.5(4.54), 258(5.07), 306(4.05), 315(4.05), 350(sh 3.80), 368(sh 4.02), 388 nm(4.13).

9) Cation salts 1-Z and 2-Z do not show a distinct melting point probably because of Z → E isomerization during the measurements (1-Z: partially melting at ca 130°C and decomposing at ca 190°C; 2-Z (redish brown solids): somewhat darkening without melt above 150° and decomposing at ca 245°C).

10) Further irradiation caused appearance of new NMR signals, but the product(s) responsible for the signals has been yet unidentified.

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