4. E. A. Gruzinova, M. Yu. Svatikov, G. V. Kotrelev, and A. A. Zhdanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1145 (1987).

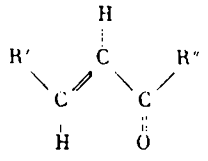
STEREOISOMERISM OF β-POLYFLUOROALKYL-α,β-ENONES

V. I. Filyakova, R. R. Latypov,
M. N. Rudaya, and K. I. Pashkevich

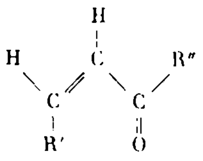
UDC 541.632:547.412.722+547.384

β-Polyfluoroalkyl-α,β-enones formed in the E,Z form are converted by the action of atmospheric oxygen into a 93:7 mixture of E,Z and Z,E isomers in the dark and 60:40 mixture of these isomers in the light. The Z isomer of 1-phenyl-4,4,4-trifluoro-2-buten-1-one was isolated preparatively for the first time and its E conformation relative to the C—C bond was established. The Z,E isomer spontaneously transforms into the indicated equilibrium mixtures.

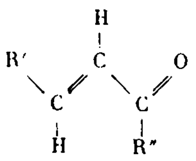
Theoretically, α,β-enones may exist as four spatial isomers:



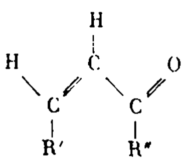
E, Z



Z, Z



E, E

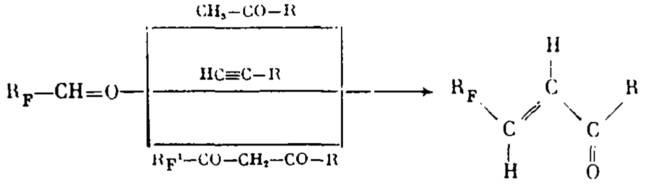


Z, E

Nonfluorinated α,β-enones are characterized by an equilibrium mixture of Z and E isomers with predominance of the E isomer [1]. The barrier to rotation about the double bond $\Delta G^{\neq} = 9$-19 kcal/mole [2]. The fraction of the Z isomer increases in the presence of acids [3] and upon the introduction of electron-withdrawing β-substituents [1].

Ogoshi et al. [4] reported the separation of 1,1,1-trifluoro-2-penten-4-one as a 95:5 equilibrium mixture of E and Z isomers relative to the double bond without considering s-Z,s-E isomerism.

In previous work [5-7], we used IR, Raman, and PMR spectroscopy to establish that β-polyfluoroalkyl-α,β-enones (Ia)-(If) are formed exclusively as the E,Z form independently of the method of preparation:



(Ia-e)

$R_F = CF_3$(a), C_4F_9 (b-d), C_6F_{13}(e,f); R = Me(b), t-Bu(c, f), Ph(a, d, e).

In the present work, we studied the isomerization of β-polyfluoroalkyl-α,β-enones (Ia)-(If) and established that the E,Z form does not undergo any change upon storage in the dark with access to air for one year as indicated by thin-layer chromatography and IR spectroscopy. On the other hand, in the light or upon storage in the dark with access to air, some of these β-polyfluoroalkyl-α,β-enones (Ia)-(If) form mixtures of E and Z isomers. The isomerization upon UV irradiation requires 24-48 h (s-E,s-Z isomerism is discussed below).

Division of Fine Organic Synthesis, Institute of Chemistry, Bashkir Science Center, Urals Branch, Academy of Sciences of the USSR, Sverdlovsk. Institute of Electrophysics, Urals Branch, Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1685-1689, July, 1991. Original article submitted November 13, 1990.

We developed a preparative synthesis for the Z isomer of 1-phenyl-4,4,4-trifluoro-2-buten-1-one (Ia). The IR spectrum of this compound lacks the band for the out-of-plane vibrations of the trans-HC= group at 985 cm^{-1} [8] but has a band at 680 cm^{-1} for the cis-HC= group [8]. The Raman band for the stretching vibrations of the asymmetrical C=C bond at 1640 cm^{-1} has reduced intensity in comparison with the E,Z isomer. The PMR signals of the olefinic protons of the Z isomer are doublets of quartets at 6.87 (H_α) and 6.10 ppm (H_β), J_{H-H} = 13 Hz. The PMR signals for the olefinic protons in E,Z isomer (Ia) are also doublets of quartets at 7.52 (H_α) and 6.83 ppm (H_β), J_{H-H} = 15 Hz.

The determination of the Z isomer of (Ia) permitted us to select between the s-Z and s-E forms. The experimental dipole moment (3.74 D) unequivocally excludes the formation of the Z,Z isomer. The theoretical dipole moments of the E,Z and Z,Z isomers are 3.73 and 6.54 D, respectively. The s-isomerism does not affect the dipole moment of the E isomer. The difference between the theoretical dipole moments of the E,Z and E,E isomers is 2.81 D.

Extension of the length of the alkyl substituents R_F and R in (I) hinders the isomerization. Thus, analytical samples of the E,Z isomers of (Ib) and (Id) are partially isomerized after storage in the light for one year. The Z,E isomers were detected using thin-layer chromatography and IR spectroscopy but the PMR spectrum of the mixtures displays only one set of signals, i.e., the content of the Z,E isomers in the mixtures is less than 5%. Enones (Ic), (Ie), and (If) do not isomerize under these conditions.

We studied the change in the composition of the isomer mixture in (Ia) by the action of light and atmospheric oxygen. The isomerization is indicated by thin-layer chromatography and IR and PMR spectroscopy. The E:Z ratio was determined using the integral intensities of the CF_3 group signals in the ^{19}F NMR spectra and the dipole moments.

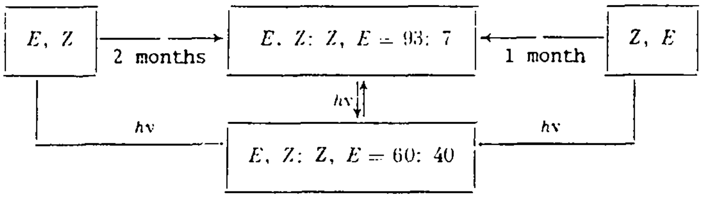
The significant difference in the theoretical dipole moments of the E,Z (or E,E) (2.81 D) and Z,E isomers (3.73 D) permitted us to monitor the composition of the mixture by measuring the experimental dipole moments.

The appearance of the Z,E isomer was indicated by thin-layer chromatography upon storage of a pure sample of the E,Z isomer of (Ia) over one month in the presence of air. The dipole moment of this mixture (2.98 D)[*] was invariant over the following two months.

The similarity of the experimental dipole moment of the E,Z isomer (2.97 D) and of the 93:7 mixture of E,Z and Z,E isomers leads to the circumstance that the difference between the calculated and experimental dipole moments is within the error in the calculations and experiments.

Irradiation of the sample by visible light over one month leads to a gradual increase in the dipole moment to 3.23 D.[†] The dipole moment of the mixture decreased after the cessation of irradiation for 30 days to 2.97 D[*] and then remains unchanged.

The dipole moment of a pure sample of the Z,E isomer of (Ia) decreases in the light over 30 days to 3.24 D[†] while this value decreases in the dark to 2.97 D.[*]



Thus, the same isomer mixtures (E,Z:Z,E = 60:40 in the light and E,Z:Z,E = 93:7 in the dark) obtained from pure samples of the E,Z and Z,E isomers with different dipole moments are probably equilibrium values.

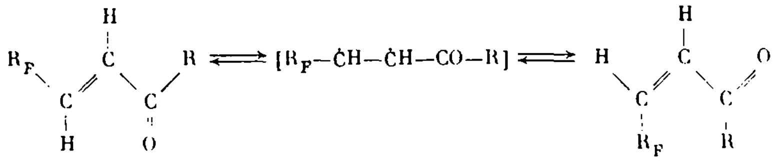
These results indicate greater thermodynamic stability of the E,Z isomers of β-polyfluoroalkyl-α,β-enones.

While such isomerization is possible for nonfluorinated α,β-enones with transfer of the γ-proton [9], this mechanism is impossible in the case of β-polyfluoroalkyl-α,β-enones and the process most likely proceeds with the formation of a diradical, which is readily generated in the light in the presence of atmospheric oxygen. This is also facilitated by the two electron-withdrawing substituents at the double bond:

---

[*] Corresponding to E,Z:Z,E ratio equal to 93:7.

[†] Corresponding to E,Z:Z,E ratio equal to 60:40.



Evidence for this mechanism is found in the formation of the s-E isomer, which is facilitated upon cleavage of the double bond and destruction of the diene system.

EXPERIMENTAL

The IR spectra of 1-phenyl-4,4,4-trifluoro-2-buten-1-one (Ia) were taken neat on a Specord-75 IR spectrophotometer. The pathlength was 20 μm. The Raman spectrum of the Z,E isomer was taken on a DFS-24 spectrometer using an LG-38 excitation source ($\lambda = 623.8$ nm). The PMR spectra were taken on a Tesla BS-567A spectrometer at 100 MHz with TMS as the internal standard. The ^{19}F NMR spectra were taken on a Tesla BS-567A spectrometer at 94 MHz with C_6F_6 as the internal standard. The thin-layer chromatography was carried out on Silufol UV-254 plates using chloroform as the eluent. The spots were revealed using a KF-4M lamp and aqueous potassium permanganate.

The E,Z isomers of β-polyfluoroalkyl-α,β-enones (Ia)-(Id) were obtained according to our previous procedure [5]. The spectral indices were given in our previous work [5].

The experimental dipole moments were calculated using the Guggenheim–Smith formula [10,11] from the dielectric constant and refraction indices determined for solutions in CCl_4 in the concentration range from 0.01 to 0.1 mole/liter at 25°C. The dielectric constant of the solutions was determined using a Tangens-2M permittivity meter at 1 MHz. The refraction indices were determined on an IRF-454B refractometer. The theoretical dipole moments for the four conformers of the α,β-enones were calculated using an additive vector scheme from group dipole moments: $\vec{\mu}_{COPh} = 3.02$ D (direction of the vector along the C=O bond), $\vec{\mu}_{C-H} = 0.64$, $\vec{\mu}_{CF_3} = 2.54$ D.

Isomerization of 1-Phenyl-4,4,4-trifluoro-2-buten-1-one (Ia). a. A sample of 1 g (5 mmoles) E isomer of (Ia) was irradiated with a PRK ultraviolet lamp for 10 h. Thin-layer chromatography of the reaction mixture indicated two unsaturated compounds: $R_f(E) = 0.69$, $R_f(Z) = 0.52$. The elemental analysis data corresponded to (Ia). IR spectrum of the mixture (ν, cm^{-1}): 1685 (C=O), 1640 (C=C), 960 (trans-CH=), 680 (cis-CH=) [8]. ^{19}F NMR spectrum (δ, ppm, J, Hz): Z isomer: 101.38 d.d (CF_3, $J_{F-H_\beta} = 8.2$, $J_{F-H_\alpha} = 0.6$); E isomer: 97.02 d.d (CF_3, $J_{F-H_\beta} = 6.68$, $J_{F-H_\alpha} = 2$).

The E and Z isomers of (Ia) were separated by preparative thin-layer chromatography on glass plates coated with LS 5/40 silica gel with a luminescent indicator. The coating thickness was 1 mm. Chloroform served as the eluent. The Z isomer was first isolated in pure form. IR spectrum (ν, cm^{-1}): 1685 (C=O), 1640 (C=C), 680 (cis-CH=); the band at 960 cm^{-1} (trans-CH=) [8] is lacking. PMR spectrum (δ, ppm, J, Hz): 6.87 d.q (1H, H_α, $J_{H-F} = 0.6$), 6.10 d.q (1H, H_β, $J_{H-F} = 8.2$, $J_{H-H} = 13$), 7.0-8.0 m (5H, Ph).

b. A sample of 25 ml 0.01 mole/liter E isomer of (Ia) in CCl_4 was stored for two months in the dark with access to air. Monitoring by thin-layer chromatography showed two unsaturated compounds: $R_f(E) = 0.69$ and $R_f(Z) = 0.52$; the experimental dipole moment was 2.98 D. Upon storage of this solution for 30 days in daylight, the dipole moment of the mixture increased to 3.73 D. The dipole moment did not change upon storage for an additional two months (E:Z = 60:40).

c. A sample of 1.5 g (7.5 mmoles) Z isomer with experimental dipole moment 3.74 D was stored in the dark for 30 days. Thin-layer chromatography showed a mixture of the Z and E isomers of (Ia): $R_f(Z) = 0.52$, $R_f(E) = 0.69$. The IR spectrum of the mixture showed a band at 960 cm^{-1} (trans-CH=) [8]. The experimental dipole moment decreased to 2.97 D, which corresponds to an E:Z ratio equal to 93:7.

Isomerization of 1,1,1,2,2,3,3,4,4-Nonafluoro-5-octen-7-one (Ib). a. A sample of 1.5 g (5 mmoles) E isomer of (Ib) was stored in the light with access to air for two months. Thin-layer chromatography showed two unsaturated compounds: $R_f(E) = 0.61$, $R_f(Z) = 0.39$. The elemental analysis data corresponded to (Ib). The IR spectrum showed a band at

680 cm^{-1} (cis-CH=) [8]. The PMR spectrum in $CDCl_3$ had one set of signals corresponding to the E isomer [5].

b. A sample of 1.5 g (5 mmoles) E isomer of (Ib) was sealed in an ampul and stored in the dark for one year. Monitoring by thin-layer chromatography did not show any change in the system.

The formation of Z isomers was observed upon storing the E isomers of (Ia) and (Id) under analogous conditions in the light with access to air. The elemental analysis data corresponded to isomer mixtures of (Ia) and (Id).

The E isomers of (Ic), (Ie), and (If) did not undergo any change upon storage under these conditions for one year.

LITERATURE CITED

1. T. Vondrak and M. Prochazka, Coll. Czech. Chem. Commun., 48, No. 1, 82 (1983).
2. Y. Shuo and H. Shanan-Atidi, J. Am. Chem. Soc., 91, No. 24, 6683 (1969).
3. R. F. Childs, B. Diffev, and A. Miku-Gibala, J. Org. Chem., 49, No. 23, 4352 (1984).
4. H. Ogoshi, H. Mizushima, H. Toi, and Y. Aoyama, J. Org. Chem., 51, No. 12, 2366 (1986).
5. R. R. Latypov, V. D. Belogai, and K. I. Pashkevich, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 123 (1986).
6. K. I. Pashkevich, R. R. Latypov, and V. I. Filyakova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2576 (1986).
7. V. I. Filyakova, R. R. Latypov, A. L. Kotel'nikova, and K. I. Pashkevich, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 212 (1987).
8. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], Inostr. Lit., Moscow (1963).
9. D. Barton, W. D. Ollis, and J. F. Stoddart (eds.), Comprehensive Organic Chemistry [Russian translation], Vol. 2, Khimiya, Moscow (1982), p. 666.
10. E. A. Guggenheim, Trans. Faraday Soc., 45, 714 (1949).
11. I. W. Smith, Trans. Faraday Soc., 46, 394 (1950).

SYNTHESIS OF HYDROCARBONS FROM CO AND H_2 ON SUPPORTED NICKEL–PALLADIUM CATALYSTS

A. L. Lapidus, S. V. Yushin,
O. I. Mishchenko, A. A. Vedenyapin,
and L. T. Kondrat'ev

UDC 541.128.34:546.74+546.98+
546.623-31:542.91:547.21

The use of an Ni-Pd/Al_2O_3 catalyst in the synthesis of C_1–C_4 hydrocarbons from CO and H_2 permits us to increase the selectivity and total yield of these products by a factor of 1.5-2.0 relative to the corresponding nickel and palladium catalysts. The optimal temperatures and CO/H_2 ratios for obtaining hydrocarbons were determined. A structure was proposed for the active sites of the bimetallic catalyst.

Bimetallic Ni-Pd/Al_2O_3 catalysts differ markedly in their adsorption properties relative to H_2 and CO from Ni/Al_2O_3 and Pd/Al_2O_3 catalysts [1]. We studied such bimetallic catalysts in the synthesis of hydrocarbons from CO and H_2.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1689-1691, July, 1991. Original article submitted November 22, 1990.