

*Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)*

PYRIDINES WITH LONG ALKYL SUBSTITUENTS AS LIGANDS IN OLIGOMERIZATION OF ISOPRENE**

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The oligomerization of isoprene in the presence of a catalyst system containing pyridines with long alkyl substituents is described. The synthetic route and compounds identification is presented.

These new ligands **2a-i** were prepared from direct conversion of corresponding pyrylium perchlorates **1a-i**.

All new compounds were characterized by ¹H-, ¹³C-NMR, IR, UV, GC/MS, ESR spectra and by elemental analysis.

INTRODUCTION

In a series of previous papers we have reported the synthesis of a series of pyridinium salts with long alkyl substituents in α or γ positions derived from the corresponding pyrylium salts.^{1,6,11-18}

The transition-metal catalysed oligomerization of isoprene by nitrogen or phosphorus derivatives as ligands is frequently used in organic synthesis.²

At the present time, there are over 30.000 naturally occurring isoprenoid compounds and 10 different ways for joining the five-carbon isoprene have been reported.³

The insertion of olefins into the transition – metal alkyl bond is the fundamental process in Ziegler – Natta polymerization. The problem in determining the mechanism arises from the fact that most Ziegler – Natta catalysts are heterogeneous.⁴

Indeed, very interesting chemistry has been developed following synthetic Ziegler – Natta catalyst applications pertinent to terpene or terpenoids synthesis. Many ligands and intermediates have been disclosed.⁵

Our first concern was to get a new class of ligands with long alkyl substituents which reacts and increase the homogeneity of Ziegler – Natta catalysts.^{6,18} On the other hand, pyridine can form both σ -donor and hexahapto π - complexes with molybdenum, chromium, nickel and other transition metals.⁷

This paper describes herein our results related to the oligomerization reaction of isoprene with pyridines with long alkyl substituents **2a-i** as ligands. Needless to say, the favorable stable and homogeneous catalysts which were obtained pertinent to added this new ligands to the general interest in the terpene or terpenoids synthesis.

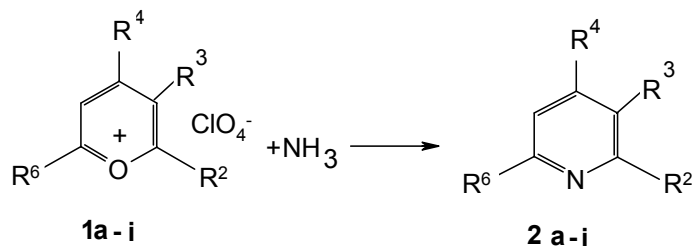
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** This is contribution no. 11 in the series “Pyrylium Salts with Long Alkyl Substituents”. For some previous papers in this series see ref. ^{1,6,11-18}

RESULTS AND DISCUSSION

Preparation and spectra of ligands

The synthesis of pyridines with long alkyl substituents derived from corresponding pyridinium salts has been described in detail elsewhere.^{1, 6, 8-18} By reaction between salts **1a-i** with aqueous ammonia, the **2a-i** compounds were obtained.



Scheme 1 – Pyridines synthesis.

Table 1 presents the various compounds used in this study.

Table 1

The synthesized pyridines with long alkyl substituents.

Cpd.	R ²	R ³	R ⁴	R ⁶
2a	C ₁₁ H ₂₃	H	CH ₃	CH ₃
2b	CH ₃	H		CH ₃
2c	C ₅ H ₁₁	H	CH ₃	C ₅ H ₁₁
2d	C ₁₁ H ₂₃	H	CH ₃	C ₁₁ H ₂₃
2e	C ₁₁ H ₂₃	CH ₃	CH ₃	C ₁₁ H ₂₃
2f	C ₁₅ H ₃₁	H	CH ₃	C ₁₅ H ₃₁
2g	C ₁₇ H ₃₅	H	CH ₃	C ₁₇ H ₃₅
2h	C ₁₁ H ₂₃	C ₆ H ₅	CH ₃	C ₁₁ H ₂₃
2i	C ₁₅ H ₃₁	C ₆ H ₅	CH ₃	C ₁₅ H ₃₁

NMR spectra

The ¹H and ¹³C-NMR chemical shifts of the pyridines **2a-i** were in agreement with previously reported data. The assignments in the one dimensional ¹H- and ¹³C-NMR spectra have been assisted with additional H-H COSY, H-C HMQC and H-C HMBC spectra. Practically all individual signals could be resolved in the ¹³C-NMR spectra, but as expected for such long chains some overlapping signals occur in the ¹H-NMR spectra (see Experimental Part).

GC-MS spectra

Based on assignments of the reported GC-MS¹⁸ for various pyridines with long alkyl substituents having either a short alkyl group or an isoprenoid alkyl C₁₁ in the γ-position (**2a**), the fragmentation pattern under electron impact of the new compounds follows similar trends. For example, for the pyridine **2f** which has a methyl group in the γ-position the parent peak in the EI mass spectrum appeared at m/z = 513. The base peak appeared in the EI mass spectrum at m/z = 317 and corresponds to the substituted benzylic type cation (C₂₂H₃₉N⁺) after a McLafferty fragmentation of the alkyl group and elimination of C₁₄H₂₈. The peak at m/z = 121 (abundance 33.30) corresponds to the substituted benzylic type cation (C₈H₁₁N⁺).

The oligomerization reaction

Two systems were used for oligomerization reaction of isoprene :

- a classical Ziegler – Natta catalyst;
- a catalyst which contains Ni(acetylacetonate)₂.

Table 2
Oligomerization of isoprene in the presence of pyridines with long alkyl substituents. Experimental results

Cpd.	Yield, %														
	2a			2b			2d			2f			2h		
	Ni:a 1:1.5	Ni:a 1:2.3	Ti:a ^a 1:2.3	Ni:b 1:1.5	Ni:b 1:2.3	Ti:b ^a 1:2.3	Ni:d 1:1.5	Ni:d 1:2.3	Ti:d ^b 1:2.3	Ni:f 1:1.5	Ni:f 1:2.3	Ti:f ^b 1:2.3	Ni:h 1:1.5	Ni:h 1:2.3	Ti:h ^b 1:2.3
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
Monoterpenes															
β-Myrcene	46.3	3.8	6.5	13.5	5.4	3.4	2.8	2.5	36.2	5.9	37.3	6.1	1.2	-	
β-Ocimene	10.8	2.9	1.9	2.4	7.8	1.8	2.5	1.9	8.9	1.8	6.9	3.2	-	-	
allo(neoallo)Cimene	8.2	1.7	-	-	3.9	1.9	-	-	7.6	1.7	9.1	2.1	3.0	-	
Limonene	14.3	7.8	17.8	7.7	18.2	38.3	8.9	3.9	18.9	29.1	20.4	28.1	-	-	
Dipentene	2.5	-	-	-	-	-	-	-	8.2	6.4	9.9	6.3	-	-	
α/β-Felandrene	5.3	7.3	-	-	-	-	-	-	2.1	4.5	1.8	3.9	-	-	
Terpinolene	2.4	-	-	-	-	-	-	-	2.3	4.8	-	2.9	-	-	
1,4 +2,8-Mentadiene	3.2	5.6	-	-	-	-	-	-	-	-	-	5.1	-	-	
α/β-Tuien		10.1	-	-	-	-	-	-	-	5.1	-	7.2	-	-	
α/β-Silvestrene		12.2	-	-	2.9	5.6	-	-	-	3.3	-	4.9	-	8.3	
Sabinene		6.7	-	-	-	6.5	-	-	-	4.4	-	2.9	2.1	2.4	
2+3-Carene		8.3	-	-	1.8	4.4	2.9	2.8	-	2.8	-	6.1	3.2	6.1	
α/β-Pinene		7.5	-	-	-	2.8	-	-	-	3.3	-	4.1	3.3	3.0	

Table 2 (continues)

Table 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Sesquiterpenes														
α -Farnesene	3.0	-	-	-	-	-	-	-	7.8	2.9	1.0	1.9	-	-
Nerolidol	2.0	-	-	-	-	-	-	-	2.9	1.9	6.0	2.1	-	-
Farnesol	1.0	-	-	-	-	-	-	-	-	1.3	2.0	2.0	3.0	5.2
Bisabolene	-	4.2	-	-	2.8	-	-	-	-	-	-	-	5.0	7.3
Zingiberene	-	2.8	-	-	2.7	-	-	-	-	-	-	-	7.1	8.6
TMDDDT ^c	-	4.9	-	-	3.9	5.6	-	-	-	4.5	-	1.7	6.1	7.5
α/β -Cadinene	-	3.5	-	-	-	4.5	-	-	-	-	-	-	9.3	10.7
Deriv. Azulene	-	3.5	-	-	-	4.1	-	-	-	-	-	-	7.1	4.9
α -Copaene	-	-	-	-	-	4.6	5.8	7.8	-	-	-	-	6.7	5.6
Selinene	-	-	-	-	-	3.8	6.7	6.9	-	-	-	-	9.3	5.8
Humulene	-	-	-	-	-	2.1	4.8	5.4	-	-	-	-	8.1	9.7
α/β -Cariofilene	-	-	3.9	5.9	-	3.1	-	-	-	-	-	-	10.2	8.0
Others C ₁₅	1.0	-	46.0	38.2	3.6	4.5	10.9	15.3	1.2	2.9	-	3.3	10.9	4.1
Di + Triterpen.														
Squalene	-	-	2.9	3.9	-	-	-	-	1.1	5.2	1.9	4.3	-	-
Others C ₂₀ + C ₃₀	-	4.0	21.0	28.2	-	3.0	54.7	53.5	2.8	2.3	1.8	1.8	4.4	2.8

^a TiCl₄; ^b TiI₂Cl₂; ^c Trimethyl-ciclododecatetraene.

Notable, for both systems and for all pyridines **2a-i**, stable and homogeneous catalysts were obtained.

Table 2 gives the yield values (%) of the most abundant components of the mixture reaction in various conditions. The yields (%) of compounds were calculated based on the weight of isoprene.

From the data reported, it is evident that the most significant differences in the composition of the mixture reaction are due to pyridine type and Ni:pyridine molar ratio.

For classical Ziegler – Natta catalysts (TiCl_4 or TiI_2Cl_2), some of monoterpenes like β -myrcene, β -ocimene, allocimene are present, but the major constituents of the mixture reaction are other isoprenoids or irregular isoprenoids.

The influence of ligand chemical structure on the composition resulted from the oligomerization reaction, is put in evidence by the differences between **2a** (having a linear α -undecyl side chain) and **2b** (having a isoprenoid γ -undecyl side chain). In the first case, at Ni:**2a** = 1:1.5 molar ratio, the reaction mixture is mostly composed (90 %) of acyclic monoterpenes (β -myrcene, β -ocimene, allocimene) and monocyclic monoterpenes, such as limonene, dipentene and acyclic sesquiterpenes (farnesene, nerolidol). Under identical conditions, for **2b**, the monoterpenes (acyclic, mono and bicyclic) are responsible for 85% of the total amount of the mixture reaction, but only monocyclic sesquiterpenes were obtain.

A second long chain (**2d** and **2f**) increases significantly the content in monocyclic monoterpenes and acyclic sesquiterpenes. At 1:1.5 Ni:ligand molar ratio, the results of GC-MS show the absence of cyclic sesquiterpenes.

The pyridine concentration has a pronounced effect on the composition of reaction mixture. The increase of the pyridine concentration (molar ratio at 1:2.3), for both ligands **2a** and **2b**, leads to increase of mono/bi/tricyclic components (25-35%). A similar, but smaller effect, (18-27 %), was observed for pyridines **2d** and **2f**.

As shown in **Table 2**, an opposite effect is present for **2h**. In this case, for both molar ratios, γ -phenyl group generated complex mixture reaction. Minor acyclic monoterpenes content and absence of acyclic sesquiterpenes were also obtain.

ESR spectra

The addition of different pyridines with long alkyl substituents (listed in **table 1**) to the catalytical systems influenced the composition / structure of the resulting complexes.

Addition of 2.3 equiv. of pyridine **2a** or **2b** to the Ni(acetylacetonate)₂ + 6 equiv. TIBA (triisobutylaluminum) systems aged for 8 h led to immediate conversion into corresponding complexes (orange for **2a** and cognac for **2b**). For ESR experiments each sample was analysed after concentration in vacuum and the electronic absorption spectra of the final reaction mixture were recorded. The ESR spectrum for complexes derived from pyridine **2a** and **2b** are presented in **fig. 1**.

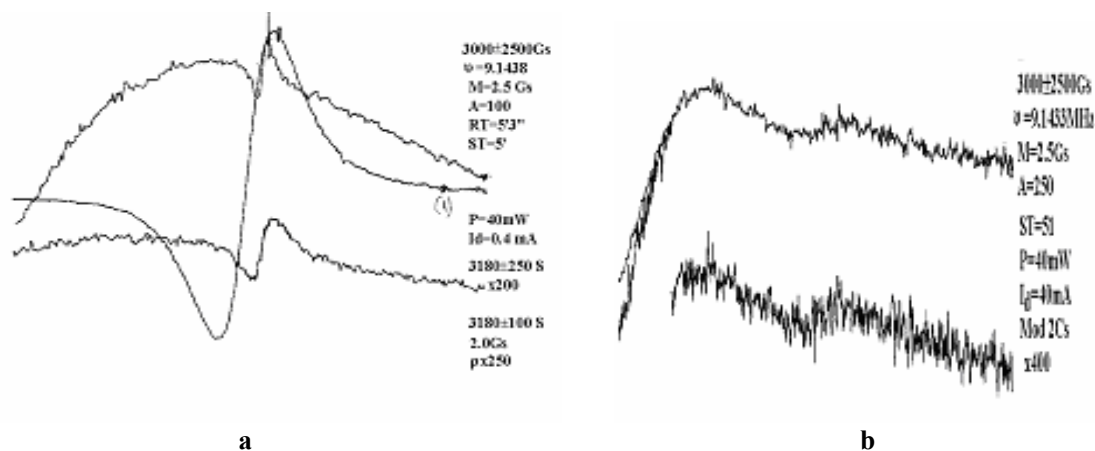


Fig. 1 – The ESR spectrum for complexes derived from pyridine 2a (a) and 2b (b).

The doublet observed in the ESR spectrum of the reaction mixture derived from pyridine **2b** (**fig. 1a**) having an isoprenoid side-chain in γ -position, indicated the presence of the $\text{R-CH}_2\cdot$ radical.

The opposite effect in the ESR spectrum (**fig. 1b**) was obtained for pyridine **2a** having a linear C₁₁ side chain in α -position, indicating the presence of a diamagnetic product. A similar result was observed earlier in the spectrum of complexes obtained from the reaction of Ni(acetylacetonate)₂ with pyridines. A notable feature of the ESR spectra can be explained by different Ni:pyridines complexes which are obtain.

EXPERIMENTAL

Materials and methods

Table 1 presents the various compounds used in this study. The synthesis of pyridines **2f** and **2g** has been described in detail. All oligomerization reactions were carried out under dry argon at constant flow put (10 l/min). For all syntheses dry solvents were used.

Procedures

Synthesis of 2,6-Dipalmitoyl 1-4-methylpyridine 2f and 2,6-distearoyl -4-methylpyridine 2g.

Pyrylium perchlorate **1f** (0.2 g, 0.32 mmoles) for **2f**, or **1g** (0.2 g, 0.30 mmole) for **2g** was treated with aqueous ammonia (20%). The pyridine **2f** or **2g** was extracted into diethyl ether, dried over potassium hydroxide pellets and concentrated in vacuum, yielding an yellow oil (0.11 g, 65.88%) for **2f** or (0.12 g, 70.69%) for **2g**.

The IR and UV-VIZ spectra for compound **2f** are:

IR (CCl₄), cm⁻¹: 1370 m, 1470 m, 1600 ms, 2855 vs and 2955 vs

UV (C₂H₅OH): λ_{\max} (nm): 217.8 and 265.0.

GC/MS (m/z, %):

513 (M⁺, 26.20), 498 (1.31), 484 (2.60), 470 (3.80), 456 (2.99), 414 (3.13), 386 (3.99), 373 (4.12), 344 (15.72), 330 (20.96), 317 (100), 274 (15.65), 246 (14.51), 190 (6.33), 134 (36.90), 121 (33.30), 57 (6.73), 43 (12.81), 28 (5.22) for **2f**.

569 (M⁺, 31.33), 554 (2.12), 540 (2.78), 5.12 (3.23), 442 (3.02), 429 (2.99), 400 (16.77), 386 (22.14), 373 (90.11), 330 (17.18), 302 (19.20), 246 (5.22), 194 (56.70), 177 (100), 113 (7.23), 99 (11.90), 84 (4.12), 43 (1.10) for **2g**.

¹H and ¹³C-NMR spectra, δ (ppm) in CDCl₃:

0.88 (t, 3H, J = 5.1 Hz, 16'-CH₃), 1.26 (m, 48H, 5'-15'-CH₂), 1.36 (m, 4H, 4'-CH₂), 1.68 (cv, 4H, 3'-CH₂), 2.36 (s, 3H, 4-CH₃), 2.77 (t, 4H, J = 7.60 Hz, 2'-CH₂), 6.83 (s, 2H, 3,5-H₂) for **2f**.

14.08 (16'-CH₃), 21.09 (4-CH₃), 22.68 (15'-CH₂), 30.25 (3'-CH₂), 31.85 (14'-CH₂), 37.27 (2'-CH₂), 121.36 (C-3), 148.56 (C-4), 160.78 (C-2) for **2f**.

0.88 (t, 3H, J = 5.4 Hz, 18'-CH₃), 1.26 (m, 52H, 5'-17'-CH₂), 1.36 (m, 4H, 4'-CH₂), 1.69 (cv, 4H, 3'-CH₂), 2.38 (s, 3H, 4-CH₃), 2.78 (t, 4H, J = 7.62 Hz, 2'-CH₂), 6.88 (s, 2H, 3,5-H₂) for **2g**.

14.10 (18'-CH₃), 21.10 (4-CH₃), 22.69 (17'-CH₂), 30.25 (3'-CH₂), 31.85 (16'-CH₂), 37.27 (2'-CH₂), 121.40 (C-3), 148.61 (C-4), 160.88 (C-2) for **2g**.

The IR and UV-VIZ spectra for pyridine **2g** are similar and in full agreement with the data presented for compound **2f**.

Elemental analyses:

C₃₆H₆₇N Calcd.: N 2.79%; found N 2.81% for **2f**.

C₄₀H₇₅N Calcd.: N 2.46%; found N 2.47% for **2g**.

The oligomerization reaction

In a typical experiment for the oligomerization reaction, in a glass autoclave a solution of 1 mmol Ni or Ti salts (10–20% in dry toluene), isoprene (10% of total amount) and 1.5–6 mmols pyridine **2** (70% solution in dry toluene) was stirred for one hour. To this homogeneous solution, after cooling to -10/-5 °C, 5.5–10 mmol TIBA (triisobutylaluminum) was added dropwise (30 min). The temperature was maintained at -10 °C and upon stirring for 30 minutes a yellow/cognac homogeneous solution was obtained.

To the first complex mixture, dry isoprene (300 mmol) was added dropwise. The temperature was maintained between -10 °C and 10 °C during 1 hour. After complete addition of isoprene, the mixture was heated at 36–42 °C and stirred for 8 hours.

The reaction mixture was cooled at 15–20 °C and 10 mL aqueous solution of HCl 6N were added dropwise. The aqueous layer (green, opalescent) was washed with diethyl ether (3×200 mL) and the combined extracts with organic layer were washed with saturated NaHCO₃ until pH=8 (2×200 mL) and with distilled water until pH= 6.5–7. The organic fraction was dried over MgSO₄ and, after filtration, afforded the crude mixture of the oligomerization reaction as a brown / orange oil which was maintained under refrigeration before analysis. The yields (%) were calculated based on the weight of the isoprene.

The oligomerization proceeded smoothly until isoprene was completely consumed and it did not lead to high molecular weight polymer. Analysis by GC-MS of each compounds mixture revealed various content in acyclic / cyclic mono- and sesquiterpenes oligomers.

Analyses

The NMR spectra have been recorded on a BRUKER AVANCE DRX 400 instrument, equipped with a 5 mm inverse detection multinuclear probe head and field gradients on the z axis, operating at 400 MHz for ¹H and at 100 MHz for ¹³C nuclei. The COSY45, HMQC and HMBC spectra have been recorded with standard Bruker parameters in the versions employing pulsed field gradients. All spectra have been recorded in deuterated chloroform, and the chemical shifts have been reported as δ values referenced to TMS as internal standard. Infrared spectra were run on a Carl Zeiss UR 20 instrument.

GC/MS analyses

GC/MS analyses were performed on a Carlo – Erba -Fractovap gas Chromatograph equipped with a flame ionization detector 70-SE VG mass-selective detector.

The separations were performed using an SE-52 column (30 mx0.32 mm, 0.25 μm film thickness). The injector temperature and detector temperature was 275 $^{\circ}\text{C}$ and 250 $^{\circ}\text{C}$, respectively, with an oven temperature program of 60 $^{\circ}\text{C}$ (2 min), 4 $^{\circ}\text{C}/\text{min}$ to 250 $^{\circ}\text{C}$ (40 min). The carrier gas was hydrogen with a flow rate of 2 mL/min. The injection was made in the split mode (1:10 ratio). Quantitative data were based upon GC peak area measurements.

The volatile components were identified by comparison of their mass spectra with those in the Wiley library, our IDENT database, and with published data.¹⁹ The identifications were confirmed by comparison of the fragmentation pattern and their retention indices with those reported in the literature.²⁰

ESR spectra. Procedures

The ESR spectra were recorded on a JES-ME-3X (JEOL) spectrometer in X-band at room temperature. The g values were calibrated relative to the signal of a Ni^{+} standard at $g = 2.2490$ (950+/-20 Gs).

The solution of $\text{Ni}(\text{acetylacetonate})_2$ (1 mmol, 20 % in dry toluene) was mixed with solution of pyridine **2** (2.3 mmol, 20 % in dry toluene). After stirring for one hour the homogeneous solution was obtain. To this mixture, after cooling to -10/ -5 $^{\circ}\text{C}$, 6 mmol TIBA was added dropwise (30 min). The temperature was maintained at -10 $^{\circ}\text{C}$ and upon stirring for 30 minutes an orange (for **2a**) /cognac (for **2b**) solution was obtained. The reaction mixtures were usually stirred at room temperature for 8 h. For ESR experiments each samples was analysed after concentration in vacuum and the electronic absorbtion spectra of the final reaction mixture were recorded. Each spectrum was obtained as a sum of 10 scans recorded with an X-band JES-ME-3X (JEOL) apparatus at 9 GHz, at room temperature.

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REFERENCES

1. M. Bogățian, D. Simion (Nută), A. C. Corbu, C. Deleanu, F. Chiraleu, M. Maganu and G. Bogățian, *Rev. Roum. Chim.*, 51, in press.
2. S. L. Parisel, N. D. Moorcroft, A. Jutand, D. J. Aldous, K. K. Hii, *Org. Biomol. Chem.*, 2004, 2, 301; N. Burford, P. Losier, A. D. Philips, P. J. Ragona and T. S. Cameron, *Inorg. Chem.*, 2003, 42, 1087.
3. C. D. Paulter, *Acc. Chem. Res.*, 1993, 23, 70; D. Zang and C. D. Paulter, *J. Amer. Chem. Soc.*, 1996, 117, 1641.
4. R. J. McKinney, *J. Chem. Soc. Commun.*, 1980, 461; P. J. Cassel, *J. Catal.*, 1964, 3, 80; M. Brookhart and M. L. J. Green, *J. Organomet. Chem.*, 1983, 250, 396.
5. P. J. Steel and G. B. Caygill, *J. Organomet. Chem.*, 1990, 395, 359; G. Mignan, F. Girass, M. Aufrand and D. Morell, *Tetrahedron Lett.*, 1989, 30, 2383.
6. M. Bogățian, *Ph. D. Thesis*, Roumanian Academy, “Costin D. Nenitescu” Institute of Organic Chemistry, 1998.
7. I. Haiduc and J. Zuckermann, “Basic Organometallic Chemistry”, Eds. W. De Gruyer, Berlin, 1985, p. 342.
8. A. T. Balaban and C. D. Nenitescu, *Justus Liebigs Ann. Chem.*, 1959, 625, 66; A. T. Balaban and C. D. Nenitescu, *Justus Liebigs Ann. Chem.*, 1959, 625, 74; P. F. G. Prail and A. L. Whitear, *Proc. Chem. Soc.*, 1959, 312.
9. A. T. Balaban, A. Dinculescu, G. N. Dorofeenko, G. W. Fischer, A. V. Koblik, V. V. Mezheritskii and W. Schroth, “Pyrylium Salts. Syntheses, Reactions and Physical Properties”, Katritzky, A. R., Ed. Academic Press., New-York, Adv. Heterocyclic Chem., Suppl. vol. 2, 1984.
10. T. S. Balaban and A. T. Balaban “Pyrylium Salts” in Science of Synthesis - Houben-Weyl, Methods of Molecular Transformations, Volume 14, E. J. Thomas, Ed., Thieme: Stuttgart, 2003, Chapter 14.1, pp 11-200.
11. M. Bogățian, V. Cimpanu, C. Deleanu, A. C. Corbu, G. Bogățian and T. S. Balaban, *ARKIVOC*, 2005, (x), 272-284 (http://www.arkatusa.org/ark/journal/2005/110_Balaban/1275/AB-1275B.pdf).
12. M. Bogățian, M. Vanatoru, G. Bogățian, G. Mihai and T. S. Balaban, *Rev. Roum. Chim.*, 2004, 49, 819.
13. M. Bogățian, C. Deleanu, S. Udrea, F. Chiraleu, M. Plăveti, M. G. Daniilă, G. Bogățian and T. S. Balaban, *Rev. Roum. Chim.*, 2003, 48, 717.
14. M. Bogățian, V. Campeanu, S. Serban, G. Mihai and T. S. Balaban, *Rev. Roum. Chim.*, 2001, 46, 115.
15. M. Bogățian, G. Mihai, M. Plăveti, F. Chiraleu, M. Maganu, V. Bădescu and T. S. Balaban, *Rev. Roum. Chim.*, 1998, 43, 315.
16. M. Bogățian, G. Mihai, M. Plăveti, F. Chiraleu, C. Deleanu, V. Bădescu and T. S. Balaban, *Rev. Roum. Chim.*, 1996, 41, 979.
17. M. Bogățian, C. Deleanu, G. Mihai and T. S. Balaban, *Z. Naturforsch.*, 1992, 47b, 1011.
18. T. S. Balaban, M. Bogățian, M. Plăveti, V. Bădescu and G. Mihai, *Rev. Roum. Chim.*, 1991, 36, 229.
19. F.W. MacLafferty and D.B. Stauffer, “The Wiley/NBS Registry of Mass Spectral Data”, John Wiley & Sons, New York, 1989; R.P. Adams, “Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy”, Allured Publishing Corp., Carol Stream, IL., 1995.
20. E. Stehagen, S. Abrahamson, F. W. McLafferty, “Registry of Mass Spectral Data Base, Government Printing Office”, Washington DC, 1974; R. P. Adams, “Identification of Essential Oil Components by Gas Chromatography / Quadrupole Mass Spectroscopy”, Allured Publishing Corporation: Carol Stream, Illinois, USA, 2001.