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A. G. GASANOV, E. G. MEMMEDBEYLI, I. G. AYYUBOV,
I. M. MEMMEDOVA, M. M. GURBANOVA, G. D. GASANOVA

Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan, Baku

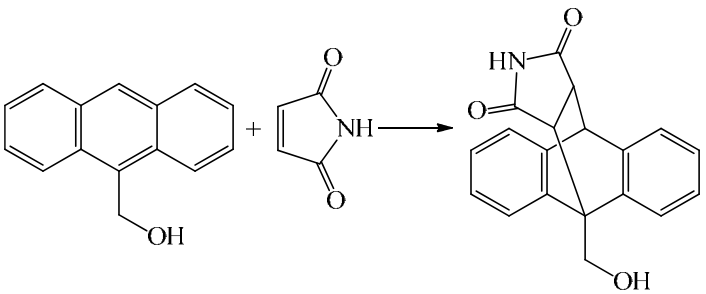
STUDY OF INFLUENCE THE TEMPERATURE ON THE REACTION OF DIENESYNTHESIS OF MONOESTERS OF NORBORNENDICARBONIC ACID ON THE TOTAL AND OPTICAL YIELD OF THE ADDUCT

Abstract. The influence of temperature of Diels-Alder reaction between cyclopentadiene and monoesters of maleic acid to the yield of obtained adducts has been studied. The optimum conditions of reaction have been founded. It is showed that at low temperatures the total yield of adduct has been decreased, but its optically yield increased. The increasing of temperature lead to increasing of total yield. But optically yield is decrase.

Key words: cyclopentadiene, diene synthesis, monoesters of maleic acid, norbornenedicarboxylic acid.

It is known that maleic derivatives are one of the classical dienophiles in the reaction of diene synthesis and a huge amount of work has been done in this direction. However, research in this field continues to develop intensively and the search for new applications of the adducts obtained remains relevant to this day. Thus, the kinetic regularities of a second-order reaction between cyclopentadiene and a series of dienophiles, including maleic anhydride and N-phenylmaleimide, were studied in [1]. It is shown that in the dioxane medium, the reaction rate constant for maleic anhydride is $1.22 \cdot 10^{-1}$ 1 / mole c, and for N-phenylmaleimide $1.22 \cdot 10^{-1}$ 1 / mole c, respectively, while the optimal rate for maleic anhydride is 2, $45 \cdot 10^{3}$ 1 / mole c, and for N-phenylmaleimide $2{,}30 \cdot 10^{3}$ 1 / mole s. The authors note that the yield of the adduct in the case of maleic anhydride is 99.5%, and for N-phenylmaleimide, respectively, exceeds 99.8%.

The reaction of anthracene-9-methanol and maleimide in an aqueous medium under the conditions of "green chemistry" was studied in [2]. It is shown that in this reaction water serves not only as a solvent but also as an active catalyst. The reaction proceeds according to the scheme:



The authors studied in detail the effect of solvents and the duration of the reaction on the yield of the adduct.

Solvent	Duration, h	Yield of adduct, %
Heptane	4	42
n-Propanediol	4	47
Dioxane	4	51
H_2O	1	78
H_2O / LiCl	0,5	87
H_2O /NaCl	1	76

In [3], the rate constants of the reaction of diene synthesis between cyclopentadiene (CPD) and various dienophiles, including those of maleic series, were calculated. The authors give the results of the studies in table 1.

Table 1 – The values of the rate constants of Diels-Alder reactions between cyclopentadiene and certain dienophiles

Diene	Dienophile	Configuration of adduct	Rate constant, 1/mol c
CPD	Maleic anhydride	endo	0,008
CPD	Maleic anhydride	exo	0,002
CPD	N-maleimide	endo	0,001
CPD	N-maleimide	exo	0,024
CPD	Di-n-propylmaleat	endo	0,005

Diene condensation of maleic anhydride with isoprene in various media (ethyl ether, butanol, isopropanol, diphenyl ether, dichloromethane, dioxane, ace-tone, benzene, nitrobenzene, nitromethane, chloroform, THF) has been studied [4].

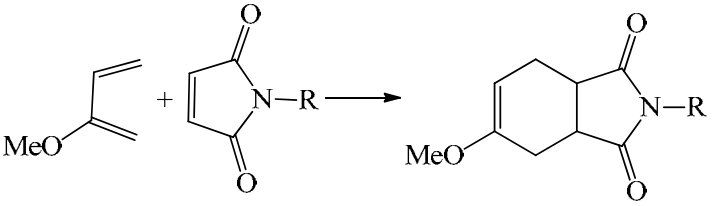
In continuation of these studies, diene condensation of CPD with various dienophiles of the maleic series has been studied [5]. The reaction was carried out at a temperature of 800°C. The authors give the results of the studies in table 2.

Table 2 – The yields of diene condensation adducts of the CPD with various maleic dienophiles

Diene	Dienophile	Yield of adduct, %
CPD	Maleic anhydride	67
CPD	Maleimide	70
CPD	N-phenylmaleimide	80
CPD	Diethylmaleat	43

In [6], the Diels-Alder reaction of CPD with maleic anhydride was studied at room temperature in the absence of a solvent with the formation of an endo-adduct in quantitative yield.

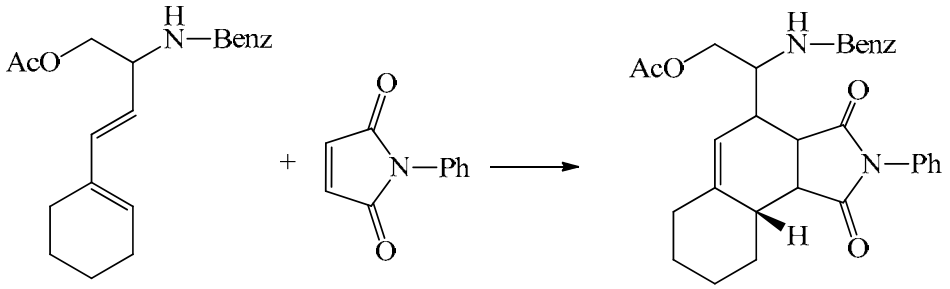
The Diels-Alder reaction of 2-methoxybutadiene with maleic anhydride in the presence of chiral Lewis acids (Al, B, Ti, Cu, La, Mg, etc. complexes), proceeding according to the scheme [7]:



The yield of the adduct was 98%, e.e. 93%.

In [8], diene condensation of 2,4-hexadiene-1-ol with maleic anhydride was studied. The structure of the obtained isomeric adducts was confirmed by IR and NMR spectroscopy.

The Diels-Alder reaction of a chiral cyclohexene derivative with N-phenylmaleimide was studied according to the scheme



The authors note [9] that the ratio of endo: exo isomers is 4.4: 1, and the yield of the adduct is 53%. The reaction was carried out in a 1M solution of $CDCl_3$ at a temperature of 250°C for 7 days.

The reaction of diene furo [3.4-b]-benzodioxin synthesis with various dienophiles, including maleic anhydride, is described in [10] and the formation of stable bis-adducts is shown.

Diene condensation of allocymene with maleic and citraconic anhydride has been studied, leading to the formation of preferentially endo-adducts [11]. As a result of these reactions, new synthetic sesquiterpenoids were synthesized. The structure of the adducts obtained is confirmed by X-ray spectroscopy.

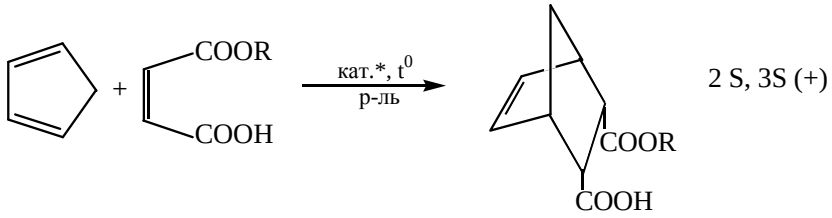
In [12], the [4+2]-cycloaddition of substituted Al- and Mg-cyclopenta-2,4-diones with dienophiles such as maleic anhydride, N-methylmaleimide and 1,4-benzoquinone was investigated.

Thus, a review of these reports shows that studies in the field of studying diene condensation based on maleic dienophiles continue to develop intensively and are of great scientific and practical interest. In connection with this, our studies have synthesized monoesters of norbornenedicarboxylic acid by the reaction of diene synthesis of cyclopentadiene and maleic acid monoesters, and optimization of this process has been carried out.

Results and discussions

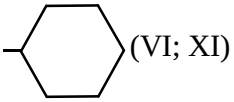
The aim of this work is to develop a regression mathematical model with the subsequent solution of the optimization problem, as well as to study the process of obtaining racemic and optically active forms of mono-esters of norbornene dicarboxylic acid on this model.

The synthesis of the optically active forms of the corresponding compounds was carried out in the presence of a catalyst, a chiral menthol complex with aluminum chloride in a benzene solvent medium according to:



I II - VI VII - XI

R = н - C_3H_7 (II; VII); i - C_3H_7 (III, VIII); н - C_4H_9 (IV; IX); i - C_4H_9 (V; X);



cat.* – $AlCl_2OMent$
temperature – -40 : $+20^0C$
solvent – C_6H_6;

Physic-chemical parameters and yields of synthesized adducts are presented in table 3 [14].

Table 3 – Physico-chemical parameters of synthesized monoesters of norbornene dicarboxylic acid

Compound	Configuration	Brutto-formule	T, ^0C		d_4^{20}, g/ml	n_D^{20}
			melt.	boil. (mm.Hg)		
VII	2S, 3S (+)	$C_{12}H_{16}O_4$	140-142	–	–	–
VIII	"–"	$C_{12}H_{16}O_4$	138-139	–	–	–
IX	"–"	$C_{13}H_{18}O_4$	135-137	–	–	–
X	"–"	$C_{13}H_{18}O_4$	138-139	–	–	–
XI	"–"	$C_{15}H_{20}O_4$	115	–	–	–

To find the optimal conditions that ensure the maximum total and optical yields of the compounds was obtained, the influence of temperature and the ratio of the catalyst: dienophile was studied. The molar ratio of the catalyst: dienophile was varied from 0.25: 1 to 0.5: 1, the reaction temperature was changed in the range (-) 50: (+) 40^0C.

The results of studies using isopropyl monoester of norbornenedicarboxylic acid (III) are presented in table 2, 3.

Table 2 – Effect of temperature on the total yield of the isopropyl monoester of norbornenedicarboxylic acid

Temperature, ^{0}C	Molar ratio catalyst : dienophile	Total yield of adduct, %
-50	0.5 : 1	77
-40	0.5 : 1	79,8
-30	0.5 : 1	82
-20	0.5 : 1	84,5
-10	0.5 : 1	87
0	0.5 : 1	89
10	0.5 : 1	93
20	0.5 : 1	96
30	0.5 : 1	99
40	0.5 : 1	99
-50	0.3 : 1	79
-40	0.3 : 1	81
-30	0.3 : 1	83
-20	0.3 : 1	85
-10	0.3 : 1	87
0	0.3 : 1	89
10	0.3 : 1	91
20	0.3 : 1	92,5
30	0.3 : 1	94
40	0.3 : 1	99
-50	0.25 : 1	78,5
-40	0.25 : 1	80
-30	0.25 : 1	82
-20	0.25 : 1	84,2
-10	0.25 : 1	86
0	0.25 : 1	88,6
10	0.25 : 1	91
20	0.25 : 1	93,5
30	0.25 : 1	96,5
40	0.25 : 1	99
-50	0.2 : 1	77,5
-40	0.2 : 1	79
-30	0.2 : 1	81
-20	0.2 : 1	83
-10	0.2 : 1	85
0	0.2 : 1	87
10	0.2 : 1	89
20	0.2 : 1	92
30	0.2 : 1	94,5
40	0.2 : 1	97,4

As can be seen from table 2, the greatest yield of the adduct is observed in the region of positive temperatures o f 30-40 C, whereas at low temperatures the total yield of the adduct decreases.

Table 3 – Effect of temperature on the optical yield of the isopropyl mono ester of norbornenedicarboxylic acid

Temperature, ^{0}C	Molar ratio catalyst : dienophile	Optically l yield of adduct, %
-50	0.5 : 1	65
-40	0.5 : 1	60,5
-30	0.5 : 1	57
-20	0.5 : 1	55,1
-10	0.5 : 1	54,6
0	0.5 : 1	55,6
10	0.5 : 1	58
20	0.5 : 1	62
30	0.5 : 1	67
40	0.5 : 1	74
-50	0.3 : 1	95
-40	0.3 : 1	86
-30	0.3 : 1	78
-20	0.3 : 1	72
-10	0.3 : 1	68
0	0.3 : 1	63,5
10	0.3 : 1	61,5
20	0.3 : 1	61
30	0.3 : 1	62
40	0.3 : 1	64,5
-50	0.25 : 1	97,2
-40	0.25 : 1	87
-30	0.25 : 1	78
-20	0.25 : 1	70
-10	0.25 : 1	64,5
0	0.25 : 1	60
10	0.25 : 1	57
20	0.25 : 1	55
30	0.25 : 1	54,8
40	0.25 : 1	56
-50	0.2 : 1	97
-40	0.2 : 1	85,5
-30	0.2 : 1	75,4
-20	0.2 : 1	67
-10	0.2 : 1	60
0	0.2 : 1	54
10	0.2 : 1	50
20	0.2 : 1	47
30	0.2 : 1	45,8
40	0.2 : 1	45

From figure 2 it follows that the optimal optical yield of the adduct is observed in the region of negative temperatures (-) 50^0C at a molar ratio of 0.3: 1 to 0.2: 1. Under these conditions, the optical yield of the isopropyl monoester of norbornene dicarboxylic acid is 95-97%.

With the help of the developed mathematical model in the form of a regression polynomial adequately describing the experimental data, optimal values of the reaction input variables were found: catalyst: dienophile ratio equal to 0.3: 1, temperature equal to (+) 40^0C at which the maximum yield of the isopropyl monoester of norbornene dicarboxylic acid was 99 %. However, under these conditions, the optical yield of adduct was 64.3%. The maximum optical yield of adduct (97.2%) is observed at a temperature of (-) 50^0C and a catalyst: dienophile ratio of 0.25: 1, but the total yield of adduct is 78.5%.

REFERENCES

[1] Seguchi K., Sera R., Otsuki Y. An investigation of the endo product selectivity in the Diels-Alder reaction // Bulletin of the Chemical Society of Japan, 1975. Vol. 48, N 12. P. 3641-3644.

[2] Gbaguidi T., Kassehin U., Prevast J. Insight into the Diels-Alder reaction – a green chemistry revisitattion of the synthesis of a cantharidine-liketrypanocidal pilot-molecule // J. of Chemical and Pharnaceutical Reseach. 2015. Vol. 10. P. 172-174.

[3] Knall A-C., Hollauf M., Slugovc C. Kinetic studies of inverse electron demand Diels-Alder reactions of norbornenes and 5,6-di-pyridin-2-yl-1,2,4,5-tetrazine // Tetrahedron Letters. 2014. Vol. 55, N 34. P. 4763-4766.

[4] Silbert E. Solvent effects in the Diels-Alder reaction: Dissert. candidate work. USA, 2002. 124 p.

[5] Gieling R., Klunder A. Immobilized cyclopentadiene in the Diels-Alder/retro Diels-Alder concept // ARKIVOC. 2004. N 2. P. 91-108.

[6] Zhang Z., Oeng Z-W., Hao M. Mechanochemical Diels-Alder cycloaddition reactions for straight-forward synthesis of endo-norbornene derivatives. Synlett, 2010. Vol. 19. P. 2895-2898.

[7] Dias L. Chiral Lewis acid catalysts in Diels-Alder cycloadditions aspects and synthetic applications of recent systems // J. Braz. Chem. Soc. 1997. Vol. 8, N 4. P. 289-332.

[8] McDaniel K., Weekly M. The Diels-Alder reaction of 2,4-hexadiene-1-ol with maleic anhydride // J. of Chemical Education. 1997. Vol. 74, N 12. P. 1464-1467.

[9] Gebauer M. Synthesis and Diels-Alder reactions of chiral 1,3-dienes: Dissert. candidate work. University of Adelaide, Australia, 1996. 139 p.

[10] Bozzo C., Mur N., Constans P. Furo[3.4-b]benzodioxin cycloadditions – a one pot synthesis of functionalized bis-adducts // J. of Organic Chemistry. 2009. P. 2174-2178.

[11] Dzyurkevich M., Krivolapov D., Lodochnikova Q. Synthesis and molecular structure of alloocimene adducts with maleic and citraconic anhydrides // Russian Journal of General Chemistry. 2011. Vol. 81, N 6. P. 1181-1184.

[12] Khafizova L.O., Yakupova L.R., Tuktarova R.A. Diels-Alder reactions of alumina- and magnesacyclopentadienes // Russian Journal of General Chemistry. 2008. Vol. 44, N 9. P. 1314-1317.

[13] Mamedov Je.G., Gasanov A.G., Ajubov I.G., Alieva S.T., Gurbanova M.M. Stereo- i jenantioselektivnyj sintez monoalkilovyh jefirov norbornendikarbonovoj kisloty i izuchenie ih biologicheskoj aktivnosti // Azerb. Him. Zhurnal. 2005. N 1. P. 77-80.

[14] Gasanov A.G., Mamedbejli Je.G., Ajubov I.G., Gusejnov N.S. Dieny S5 frakcii piroliza v termicheskih i kataliticheskih reakcijah (4+2)-cikloprisoedinenija // Neftehimija. 2013. Vol. 53, N 1. P. 58-61.

Резюме

А. Г. Гасанов, Э. Г. Мамедбейли, И. Г. Аюбов, И. М. Мамедова, М. М. Гурбанова, А. М. Мамедова

НОРБОРНЕНДИКАРБОН ҚЫШҚЫЛЫНЫҢ МОНОЭФИРЛЕРІН ДИЕНДІ СИНТЕЗДЕУ РЕАКЦИЯСЫ ТЕМПЕРАТУРАСЫНЫҢ АДДУКТІҢ ЖАЛПЫ ЖӘНЕ ОПТИКАЛЫҚ ШЫҒЫМЫНА ӘСЕРІН ЗЕРТТЕУ

Циклопентадиен мен малеин қышқылының моноэфирлері арасындағы Дильса-Альдер реакциясы температурасының алынған аддуктердің шығымына әсері зерттелді. Реакция күйінің оңтайлы жағдайлары анықталды. төмен температураларда аддуктің жалпы шығымы азаятыны, ал оның оптикалық шығымы артатыны көрсетілді. Температура артқан сайын аддуктің жалпы шығымы артады, ал оптикалық шығымы төмендейді.

Түйін сөздер: циклопентадиен, диенді синтез, малеин қышқылының моноэфирлері, норборнендикарбон қышқылы.

Резюме

А. Г. Гасанов, Э. Г. Мамедбейли, И. Г. Аюбов, И. М. Мамедова, М. М. Гурбанова, А. М. Мамедова

ИЗУЧЕНИЕ ВЛИЯНИЯ ТЕМПЕРАТУРЫ РЕАКЦИИ ДИЕНОВОГО СИНТЕЗА МОНОЭФИРОВ НОРБОРНЕНДИКАРБОНОВОЙ КИСЛОТЫ НА ОБЩИЙ И ОПТИЧЕСКИЙ ВЫХОД АДДУКТА

Изучено влияние температуры реакции Дильса-Альдера между циклопентадиеном и моноэфирами малеиновой кислоты на выход полученных аддуктов. Определены оптимальные условия проведения реакции. Показано, что при низких температурах общий выход аддукта уменьшается, тогда как его оптический выход возрастает. С увеличением температуры общий выход аддукта закономерно возрастает, а оптический выход снижается.

Ключевые слова: циклопентадиен, диеновый синтез, моноэфиры малеиновой кислоты, норборнендикарбоновая кислота.