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Reaction of dialkyl acetylenedicarboxylates with ninhydrin in the presence of secondary amines: synthesis of alkyl 4-(benzyl(alkyl)amino)-1',3',5-trioxo-1',3'- dihydro-5*H*-spiro[furan-2,2'-indene]-3-carboxylate derivatives

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A three-component domino reaction approach between a secondary amine, dialkyl acetylenedicarboxylate and ninhydrin that affords novel alkyl 4-(benzyl(alkyl)amino)-1',3',5-trioxo-1',3'-dihydro-5*H*-spiro[furan-2,2'-indene]-3-carboxylate derivatives is reported. The reaction sequence consists of an initial Michael-addition of secondary amines to dialkyl acetylenedicarboxylates, followed by aldol-like reaction with ninhydrin, and then γ-lactonization to afford the products. This cascade reaction sequence represents a rapid and unprecedented route to the described biologically interesting molecules.

Key words: dialkyl acetylenedicarboxylates, ninhydrin, furan, Michael-addition, secondary amine

INTRODUCTION

Multicomponent reactions allow more than two simple and flexible building blocks to be combined in practical, timesaving one-pot operations. Due to their valued features such as atom economy, inherent simple experimental procedures and one-pot character, they are perfectly suited for automated synthesis [1]. Therefore, MCRs have attracted much attention because of their exceptional synthetic efficiency [2–5]. Since all the organic reagents employed are used and moved toward the target compound, purification of products resulting from MCRs is simple [6], [7]. Isocyanide based multicomponent reactions (abbreviated to IMCRs by Ugi and Dömling) have an advantageous position. The special features of IMCRs including unique synthetic potential, high atom economy, convergent nature, ease of implementation, and the generation of molecular diversity are considered as acceptable factors in the relative advantage of the reactions [6–14].

For years, acetylenic esters have attracted the attention of organic chemists, mostly as Michael acceptors [7, 15, 16]. In recent years, there has been an increasing interest in the

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applications of acetylenic esters in multicomponent syntheses [1, 7–9], specially for preparing stabilized phosphonium ylides [17–22]. Due to atom economy, convergent character and simplicity of one-pot procedures, multicomponent condensation reactions have great potentials in synthesis. The development of novel multicomponent condensation reactions is also receiving growing interest from industrial-chemistry research groups, and represents a challenge for organic chemists [1, 7].

Furans, benzofurans, and their reduced forms are important core structures in many biologically active natural products. Moreover, they are useful building blocks in the total synthesis of natural products and pharmaceuticals [23–26]. Many naturally occurring furans have exhibited considerable biological activities, such as antitumor and cytotoxic properties [27, 28], as well as antimicrobial [29, 30], antispasmodic [31], and several other potentially useful activities [32]. In addition, furans are also present in commercially important products, such as agrochemical bioregulators, essential oils, cosmetics, dyes, photosensitizers, flavoring and fragrance compounds [32–34]. As part of our ongoing program to develop efficient and robust methods for the preparation of heterocyclic compounds [35–47], we sought to develop a convenient preparation of alkyl 4-(benzyl(alkyl)amino)-1',3',5-trioxo-1',3'-dihydro-5*H*-spiro[furan-2,2'-indene]-3-carboxylate derivatives **4a–e**. Herein we report a hitherto unknown, one-pot three-component reaction, which, starting from readily available ninhydrin **3**, affords **4a–e** (Scheme 1).

RESULTS AND DISCUSSION

We examined the reaction of the secondary amines with dialkyl acetylenedicarboxylate in the presence of ninhydrin in dry CH_2Cl_2 at room temperature (25 °C) and obtained the corresponding alkyl 4-(benzyl(alkyl)amino)-1',3,5-trioxo-1-',3'-dihydro-5*H*-spiro[furan-2,2'-indene]-3-carboxylates **4** in 83–87% yields; the full results are summarized in Table. ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of alkyl 4-(benzyl(alkyl)amino)-1',3,5-trioxo-1',3'-dihydro-5*H*-spiro[furan-2,2'-indene]-3-carboxylates **4**. We also used secondary amines such as *N*-benzyl-*N*-(*tert*-butyl) amine and *N,N*-dibenzylamine in this reaction, but they have not participated in the reaction. The presence of fairly high steric intractions in the amines may be plausible factors in the reduction of their reactivity.

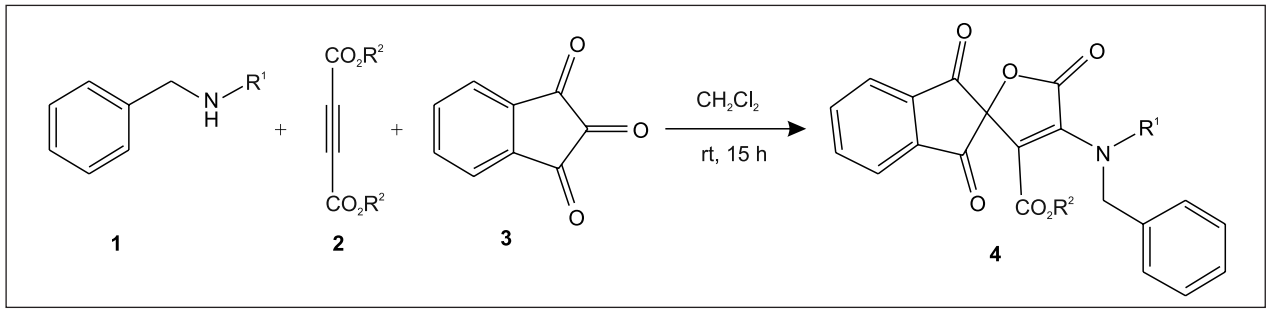
The structures of the products were deduced from their ^{1}H NMR, ^{13}C NMR, Mass and IR spectra. For example, the ^{1}H NMR spectrum of **4a** consisted of a doublet for 2 CH_3 (δ_H = 1.39 ppm), a singlet for OCH_3 (δ = 3.22 ppm), a singlet for CH_2 of the benzyl group at δ = 4.84 ppm, a multiplet for CH (δ = 4.89–4.97 ppm) and a multiplet at δ = 7.12–7.97 ppm for H-aromatic. The aryl groups exhibited characteristic signals in the aromatic region of the spectrum. The ^{1}H decoupled ^{13}C NMR spectrum of **4a** showed 17 distinct resonances, partial assignment of these resonances is given in the experimental section. The ^{1}H and ^{13}C NMR spectra of compounds **4b–e** were similar to those of **4a**, except for the aromatic and aliphatic moieties, which exhibited characteristic signals with appropriate chemical shifts. For the compounds **4b–c**, in the ^{1}H NMR spectra the signals corresponding to the methyl group of the CO_2Et moiety are unusually shifted upfield (δ: 0.46 (t, 3H, J = 7.0 Hz, CH_3 of OEt) and δ: 0.57 (t, 3H, J = 7.3 Hz, CH_3 of OEt) for **4b** and **4c**, respectively). It may be resulted from a strong shielding (probably due to spatial arrangement of CO_2Et moiety *vs* one of the benzene rings).

A possible mechanism for the present reaction is shown in Scheme 2, which envisages a tandem sequence. On the basis of the well established chemistry of trivalent nitrogen nucleophiles, the successful nucleophilic attack by amines on a carbon atom is facilitated when the latter is conjugated with a carbonyl group, or when it is a part of an unsaturated

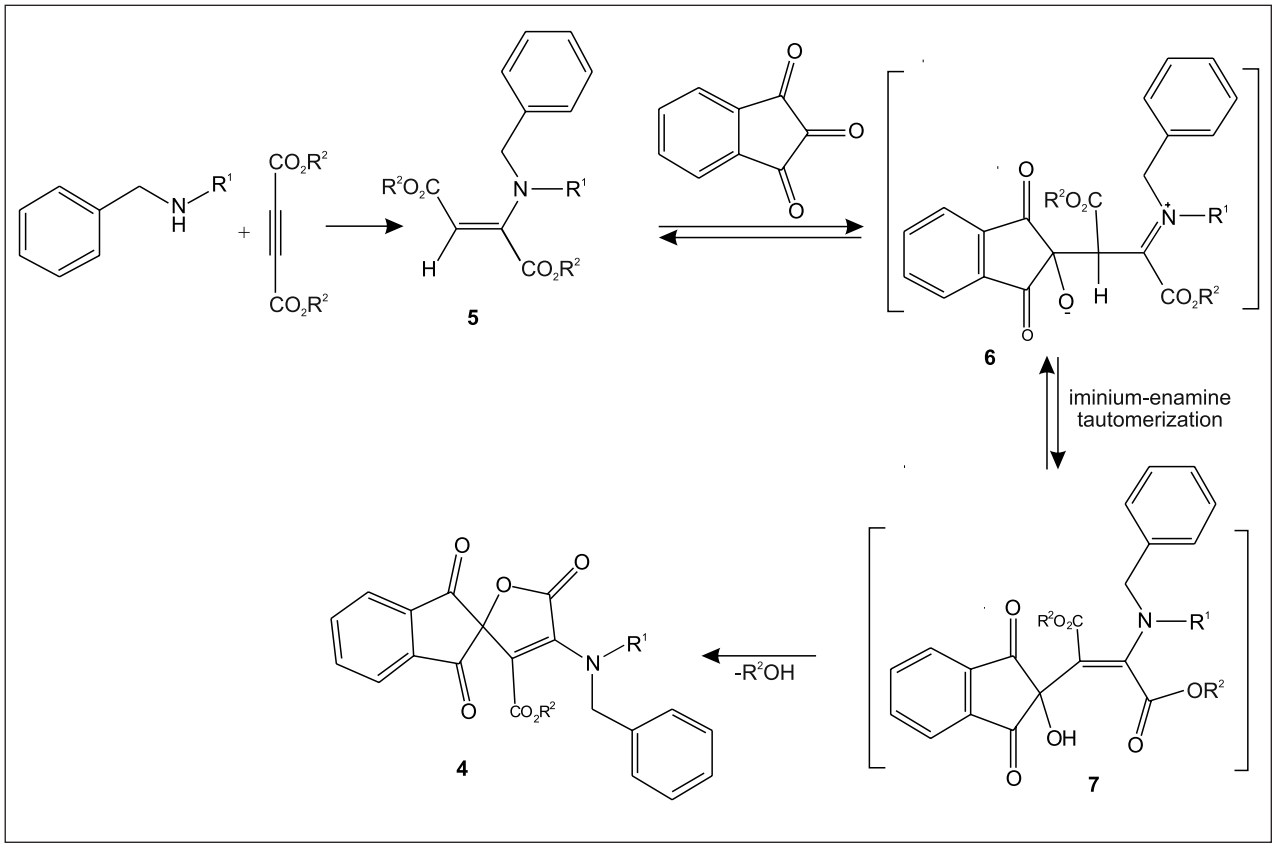
Table. **Preparation of alkyl 4-(benzyl(alkyl)amino)-1',3',5-trioxo-1',3'-dihydro-5*H*-spiro[furan-2,2-indene]-3-carboxylate derivatives 4 (See Scheme 1)**

Compounds	R^1	R^2	Yield[a] (%)
4a	Isopropyl	Methyl	86
4b	Isopropyl	Ethyl	84
4c	Methyl	Ethyl	87
4d	Ethyl	Methyl	85
4e	Methyl	Methyl	83

[a] Yield of isolated products



Scheme 1. Three-component synthesis of alkyl 4-(benzyl(alkyl)amino)-1',3',5-trioxo-1',3'-dihydro-5*H*-spiro[furan-2,2'-indene]-3-carboxylate derivatives **4a–e** (See Table 1 and Experimental)



Scheme 2. Proposed mechanism for the formation of alkyl 4-(benzyl(alkyl)amino)-1′,3′,5-trioxo-1′,3′-dihydro-5*H*-spiro[furan-2,2′-indene]-3-carboxylate derivatives **4a–e**

bond otherwise activated [8, 9]. First, nucleophilic Michael-addition of the secondary amine **1** to the β-carbon of the electron-deficient alkyne **2** generates aminobutendioate **5** as an electron-rich enaminone [48]. The central carbonyl groups of the vicinal tri-carbonyl compounds such as ninhydrin possess outstanding electrophilic (electron-pair acceptor) properties [49]. The polar reactions with carbanion-like (electron rich) species such as enaminones give rise to nucleophilic addition reactions of carbonyl groups under exclusive C–C bond formation [50]. Subsequent nucleophilic aldol-like attack of aminobutendioate **5** to the central carbonyl group of ninhydrin **3** would yield iminium–oxoanion intermediate **6**, that can be tautomerized to dialkyl 2- (benzyl(alkyl)amino)-3-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)fumarate **7**. γ-Lactonization of **7** would produce the alkyl 4-(benzyl(alkyl)amino)-1′,3′,5-trioxo-1′,3′-dihydro-5*H*-spiro[furan-2,2′-indene]-3- carboxylate derivatives **4**.

EXPERIMENTAL

Starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. The methods used to follow the reactions are TLC and NMR, which indicated that there is no side product. IR spectra were measured on a Jasco 6300 FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were measured ($CDCl_3$) with a BRUKER DRX-250 AVANCE spectrometer at 250.0 and 62.5 MHz, respectively. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. Flash chromatography columns were prepared with Merck silica gel powder.

General procedure for the preparation of 4a–e

The solution of secondary amines **1** (1.0 mmol) and dialkyl acetylenedicarboxylate **2** (1.0 mmol) in CH_2Cl_2 (7 ml) was stirred for 1 h. Then ninhydrin **3** (1.0 mmol) was added, and the mixture was stirred for 15 h. The solvent was removed under reduced pressure and the viscous residue was purified by flash column chromatography (silica gel; petroleum ether–AcOEt (10 : 2)). The solvent was removed under reduced pressure and the products (**4a–e**) were obtained. The characterization data of the compounds are given below:

Methyl 4-(benzyl(isopropyl)amino)-1′,3′,5-trioxo-1′,3′-dihydro-5*H*-spiro[furan-2,2′-indene]-3-carboxylate 4a

Yellow oil, yield 360 mg (86%); R_f = 0.40 (petroleum ether – AcOEt (10 : 2)); IR: 2953, 1781, 1723, 1615, 1454, 1080, 736 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.39 (d, 6H, $2CH_3$, amine), 3.22 (s, 3H, OCH_3), 4.84 (s, 2H, CH_2 of benzyl group), 4.89–4.97 (m,

1H, CH of amine), 7.12–7.97 (m, 9H, H-Ar); ^{13}C NMR ($CDCl_3$) δ: 21.19, 47.58, 51.32, 52.95, 109.85, 124.09, 127.17, 127.26, 128.41, 128.64, 136.03, 136.50, 140.93, 141.05, 160.54, 167.59, 193.25. MS: m/e (%) 419 (M^+, 14), 376 (19), 316 (14), 248 (17), 198 (34), 163 (53), 149 (46), 134 (98), 121 (32), 104 (82), 91 (100), 76 (60), 65 (96), 43 (63). Anal. calcd. for $C_{24}H_{21}NO_6$ (419.43): C, 68.73; H, 5.05; N, 3.34. Found: C, 68.79; H, 5.01; N, 3.38.

Ethyl 4-(benzyl(isopropyl)amino)-1',3',5-trioxo-1',3'-dihydro-5*H*-spiro[furan-2,2'-indene]-3-carboxylate 4b

Yellow oil, yield 364 mg (84%); R_f = 0.45 (petroleum ether – AcOEt (10:2); IR: 2979, 1781, 1725, 1615, 1453, 1059, 761 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.46 (t, 3H, J = 7.0 Hz, CH_3 of OEt), 1.37 (d, 6H, J = 7.0 Hz, $2CH_3$, amine), 3.67 (q, 2H, J = 7.0 Hz, CH_2 of OEt), 4.84 (s, 2H, CH_2 of benzyl group), 4.89–4.97 (m, 1H, CH of amine), 7.11–7.97 (m, 9H, H-Ar); ^{13}C NMR ($CDCl_3$) δ: 12.80, 21.20, 47.51, 52.82, 60.50, 110.00, 124.05, 127.10, 127.30, 128.36 (CH and C), 136.18, 136.49, 141.11(CH and C), 159.83, 167.65, 193.34. Anal. calcd. for $C_{25}H_{23}NO_6$ (433.45): C, 69.27; H, 5.35; N, 3.23. Found: C, 69.23; H, 5.40; N, 3.20.

Ethyl 4-(benzyl(methyl)amino)-1',3',5-trioxo-1',3'-dihydro-5*H*-spiro[furan-2,2'-indene]-3-carboxylate 4c

Yellow oil, yield 352 mg (87%); R_f = 0.43 (petroleum ether – AcOEt (10:2); IR: 2982, 1781, 1725, 1623, 1454, 1088, 706 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.57 (t, 3H, J = 7.3 Hz, CH_3 of OEt), 3.14 (s, 3H, CH_3), 3.80 (q, 2H, J = 7.3 Hz, CH_2 of OEt), 4.99 (s, 2H, CH_2 of benzyl group), 7.29–8.09 (m, 9H, H-Ar); ^{13}C NMR ($CDCl_3$) δ: 12.88, 41.33, 56.68, 60.75, 106.71, 124.21, 127.75 (CH and C), 128.74 (CH and C), 136.50, 136.72, 141.21, 142.56, 160.43, 167.02, 193.98. Anal. calcd. for $C_{23}H_{19}NO_6$ (405.40): C, 68.14; H, 4.72; N, 3.46. Found: C, 68.11; H, 4.68; N, 3.51.

Methyl 4-(benzyl(ethyl)amino)-1',3',5-trioxo-1',3'-dihydro-5*H*-spiro[furan-2,2'-indene]-3-carboxylate 4d

Yellow oil, yield 344 mg (85%); R_f = 0.47 (petroleum ether – AcOEt (10:2); IR: 2963, 1781, 1723, 1625, 1454, 1079, 774 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.22 (t, 3H, J = 7.0 Hz, CH_3 of Et), 3.25 (s, 3H, OCH_3), 3.76 (q, 2H, J = 7.0 Hz, CH_2 of Et), 4.98 (s, 2H, CH_2 of benzyl group), 7.29–8.08 (m, 9H, H–Ar); ^{13}C NMR ($CDCl_3$) δ: 13.15, 46.37, 51.40, 54.70, 106.81, 124.19, 127.60 (CH and C), 128.64 (CH and C), 136.49, 136.63, 140.98, 141.54, 161.04, 167.04, 193.87. Anal. calcd. for $C_{23}H_{19}NO_6$ (405.40): C, 68.14; H, 4.72; N, 3.46. Found: C, 68.19; H, 4.75; N, 3.44.

Methyl 4-(benzyl(methyl)amino)-1,3,5-trioxo-1,3-dihydro-5*H*-spiro[furan-2,2-indene]-3-carboxylate 4e

Yellow oil, yield 324 mg (83%); R_f = 0.38 (petroleum ether – AcOEt (10 : 2); IR: 2989, 1781, 1725, 1623, 1453, 1088, 751 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 3.15 (s, 3H, CH_3), 3.31 (s, 3H, OCH_3), 4.99 (s, 2H, CH_2 of benzyl group), 7.29–8.10 (m, 9H, H-Ar); ^{13}C NMR ($CDCl_3$) δ: 41.31, 51.41, 56.78, 106.62, 124.23, 127.74 (CH and C), 128.76 (CH and C), 136.42, 136.72, 141.05, 142.53, 161.10, 166.98, 193.87. Anal. calcd. for $C_{22}H_{17}NO_6$ (391.40): C, 67.51; H, 4.38; N, 3.58. Found: C, 67.49; H, 4.42; N, 3.61.

CONCLUSIONS

The reported method offers a mild, simple and efficient route for the preparation of alkyl 4-(benzyl(alkyl)amino)-1',3',5-trioxo-1',3'-dihydro-5*H*-spiro[furan-2,2'-indene]-3-carboxylate derivatives **4**. Its ease of work-up, high yields, and fairly mild reaction conditions make it a useful addition to modern synthetic methodologies. Other aspects of this process are under investigation.

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References

1. J. Zhu, H. Bienaymé (eds.), *Multicomponent Reactions*, Wiley-VCH, Weinheim (2005).
2. M. Bayat, H. Imanieh, N. Zabarjad Shiraz, M. Shah Qavidel, *Monatsh. Chem*., **141**, 333 (2010).
3. I. Yavari, A. Mirzaei, Z. Hossaini, S. Souri, *Mol Divers*., **14**, 343 (2010).
4. A. Ramazani, N. Shajari, A. Mahyari, Y. Ahmadi, *Mol Divers.*, **14**, 521 (2010).
5. F. Z. Nasrabadi, A. Ramazani, Y. Ahmadi, *Mol Divers*., **15**, 791 (2011).
6. I. Yavari, M. Sabbaghan, Z. Hossaini, *Mol Divers*., **11**, 1 (2007).
7. A. Domling, *Chem Rev*., **106**, 17 (2006).
8. I. Yavari, S. Seyfi, M. Nematpour, Z. Hossaini, *Helvetica Chimica Acta*, **93**, 1413 (2010).
9. I. Yavari, Z. Hossaini, M. Sabbaghan, M. Ghazanfarpour-Darjani, *Monatshefte fur Chemie*, **138**, 677 (2007).
10. I. Ugi, B. Werner, A. Dömling, *Molecule*s, **8**, 53 (2003).
11. R. W. Waller, L. J. Diorazio, B. A. Taylor, W. B. Motherwell, T. D. Sheppard, *Tetrahedron*, **66**, 6496 (2010).
12. A. Ramazani, Y. Ahmadi, M. Rouhani, N. Shajari, A. Souldozi, *Heteroatom. Chem*., **21**, 368 (2010).
13. A. Ramazani, Y. Ahmadi, R. Tarasi, *Heteroatom. Chem*., **22**, 79 (2011).
14. G. K. Nagaraja, G. K. Prakash, M. N. Kumaraswamy, V. P. Vaidya, K. M. Mahadevan, *Arkivoc*, **xv**, 160 (2006).
15. I. Yavari, M. Adib, M. H. Sayahi, *Tetrahedron Lett*., **43**, 2927 (2002).
16. S.-W. Zhang, T. Sugioka, S. Takahashi, *J. Mol. Catal. A: Chem*., **143**, 211 (1999).
17. J. Azizian, A. R. Karimi, H. Arefrad, A. A. Mohammadi, M. R. Mohammadizadeh, *Mol. Diversity*, **6**, 223 (2003).
18. P. J. Murphy, J. Brennan, *Chem. Soc. Rev*., **17**, 1 (1988).
19. H. Ahankar, A. Ramazani, I. Amini, Y. Ahmadi, A. Souldozi, *Heteroatom. Chem*., **22** (2011).
20. A. Ramazani, A. Azizian, M. Bandpey, N. Noshiranzadeh, *Phosphorus, Sulfur, and Silicon*, **181**, 2731 (2006).

21. I. Yavari, A. Ramazani, *Phosphorus, Sulfur, and Silicon*, **130**, 73 (1997).
22. A. Ramazani, A. Bodaghi, *Tetrahedron Lett*., **41**, 567 (2000).
23. A. Padwa, M. Dimitroff, A. G. Waterson, T. J. Wu, *Org. Chem*., **62**, 4088 (1997).
24. O. C. Kappe, S. S. Murphree, A. Padwa, *Tetrahedron*, **53**, 14179 (1997).
25. D. S. Mortensen, A. L. Rodriguez, K. E. Carlson, J. Sun, B. S. Katzenellenbogen, J. A. J. Katzenellenbogen, *Med. Chem*., **44**, 3838 (2001).
26. H. Ding, Y. Zhang, M. Bian, W. Yao, C. J. Ma, *Org. Chem*., **73**, 578 (2008).
27. S. M. Kupchan, M. A. Eakin, A. M. J. Thomas, *Med. Chem*., **111**, 1147 (1971).
28. M. M. Bandurraga, W. Fenical, S. F. Donovan, J. J. Clardy, *Am. Chem. Soc*., **104**, 6463 (1982).
29. M. Hofnung, V. M. Quillardet, E. Touati, *Res. Microbiol*., **153**, 427 (2002).
30. M. W. Khan, M. J. Alam, M. A. Rashid, R. Chowdhury, *Bioorg. Med. Chem*., **13**, 4796 (2005).
31. J. Kobayashi, Y. Ohizumi, H. Nakamura, *Tetrahedron Lett*., **27**, 2113 (1986).
32. H. N. C. Wong, Y. Yang, *Tetrahedron*, **50**, 9583 (1994).
33. B. Gabriele, G. Salerno, E. J. Lauria, *Org. Chem*., **64**, 7687 (1999).
34. K. Koguro, T. Sugimura, A. Tai, *Tetrahedron Lett*., **34**, 509 (1993).
35. A. Souldozi, A. Ramazani, N. Bouslimani, R. Welter, *Tetrahedron Lett.*, **48**, 2617 (2007).
36. A. Souldozi, A. Ramazani, *Tetrahedron Lett*., **48**, 1549 (2007).
37. A. Ramazani, Y. Ahmadi, F. Z. Nasrabadi, *Z. Naturforsch.*, **66b**, 184 (2011).
38. A. Ramazani, A. Souldozi, *Phosphorus, Sulfur, Silicon Relat. Elem.,* **184**, 2350 (2009).
39. A. Ramazani, A. Souldozi, *Arkivoc*, **xvi**, 235 (2008).
40. A. Ramazani, Y. Ahmadi, A. Mahyari, *Synthetic Communications*, **41**, 2273 (2011).
41. A. Ramazani, A. Rezaei, *Org. Lett.*, **12**, 2852 (2010).
42. A. Souldozi, K. Ślepokura, T. Lis, A. Ramazani, *Z. Naturforsch*., **62b**, 835 (2007).
43. A. Ramazani, A. Morsali, B. Ganjeie, A. R. Kazemizadeh, E. Ahmadi, R. Kempe, I. Hertle, *Z. Naturforsch.*, **60b**, 569 (2005).
44. A. Ramazani, N. Noshiranzadeh, A. Ghamkhari, K. Slepokura, T. Lis, *Helv. Chim. Acta*, **91**, 2252 (2008).
45. A. Ramazani, A. Rezaei, A. T. Mahyari, M. Rouhani, M. Khoobi, *Helv. Chim. Acta*, **93**, 2033 (2010).
46. A. Ramazani, A. Mahyari, *Helv. Chim. Acta*, **93**, 2203 (2010).
47. A. Ramazani, F. Z. Nasrabadi, Y. Ahmadi, *Helv. Chim. Acta*, **94**, 1024 (2011).
48. F. Pohlki, S. Doye, *Chem. Soc. Rev.*, **32**, 104 (2003); B. Stanovnik, J. Svete, *Chem. Rev*., **104**, 2433 (2004); A. P. Brogan, T. J. Dickerson, K. D. Janda, *Angew. Chem*., **118**, 8278 (2006); J. Azizian, F. Hatamjafari, A. R. Karimi, M. Shaabanzadeh, *Synthesis*, 765 (2006).
49. M. B. Rubin, R. Gleiter, *Chem. Rev*., **100**, 1121 (2000).
50. K. Schank, R. Lieder, C. Lick, R. Glock, *Helv. Chim. Acta*, **87**, 869 (2004).

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DIALKILACETILENDIKARBOKSILATŲ REAKCIJA SU NINHIDRINU ESANT ANTRINIŲ AMINŲ: ALKIL-4-(BENZIL(ALKIL)AMINO)-1',3',5-TRIOKSO-1',3'-DIHIDRO-5*H*-SPIRO[FURAN-2,2'-INDEN]-3-KARBOKSILATO DARINIŲ SINTEZEI

S a n t r a u k a

Dėl reakcijos tarp antrinio amino, dialkilacetilendikarboksilato ir ninhidrino, gauti nauji alkil-4-(benzil(alkil)amino)-1',3',5-triokso-1',3'-dihidro-5*H*-spiro[furan-2,2'-inden]-3-karboksilato dariniai.