ՀԱՅԱՍՏԱՆԻ ՀԱՆՐԱՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ
ԱԶԳԱՅԻՆ ԱԿԱԴԵՄԻԱ
НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ
АРМЕНИЯ

Հայաստանի քիմիական հանդես 50, №3-4, 1997 Химический журнал Армении

ОРГАНИЧЕСКАЯ И ПОЛИМЕРНАЯ ХИМИЯ

HYDROBORATIONS: NEW METHOD FOR PREPARATION OF SUBSTITUTED 1- AND 2-NAPHTOLS

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ABSTRACT. The hydroboration followed by oxidation with chromic acid of 1- and 2-alkyl (or aryl)-3,4-dihydronaphthalenes and 2-alkyl (or aryl)-1,4-dihydronaphthalenes, leads to the corresponding substituted naphtols. The 1- and 3-substituted 2-naphtols are formed in better yields than the 2-substituted 1-naphtols.

INTRODUCTION

The derivatives of 1- and 2-naphtols are interesting compounds in medicinal chemistry due to their antiseptic and antifungic activities (1-4). Furthermore, naphtols are the starting intermediates for preparation of synthetic vitamins K (6-8) and natural substances corresponding to the type of Isoeleutherin (9).

Although there are many available routes for the preparation of phenolic compounds via the already known hydroxylation reactions of organic chemistry, a survey of the literature showed that the regioselective synthesis of naphtols remains still a tedious task which gave rise to the devepement of various procedures. These can be grouped in three categories: aromatization (10-17), C-alkylation (18-26) and total synthesis (27-33).

Examination of the described methods shows their lack in generality and often their low overall yields. In some cases, their application needs not easily available intermediates.

A general synthetic and regioselective method for the synthesis of subtituted naphtols was therefore interesting and led us to the systemetic investigation of the applicability of hydroboration followed by oxidation with chromic acid (34)

to the substituted derivatives of 3,4-dihydronaphthalene and 1,4-dihydronaphthalene.

It is noteworthly that this method was already developed for the preparation of aldehydes and ketones (35,36), chroman-4-ones (37-39), isoflavan-4-ones (40,41), homoisoflavanones (42), susbtituted indan-2-ones (43), chroman-3-ones (44) and 3,4-dihydronaphthalen-2(1H)-ones (45).

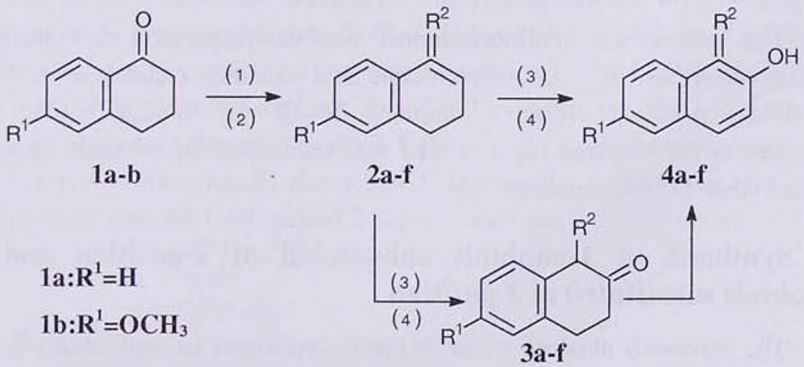
RESULTS

1. Synthesis of 1-alkyl(or aryl)2-naphthols

Previous work related to the preparation of benzo-[b]-cyclan-2-ones from benzo[b]-cyclenes via hydroboration followed by oxidation with chromic acid (44,45), showed that under identical experimental conditions, 1-alkyl(or aryl)3,4-dihydronaphthalene-2(1H)-ones are obtained in lower yields than 1-alkyl(or aryl)-indan-2-ones. Furthermore, thin layer chromatography of the reaction mixtures shows besides the expected ketones, the presence of more polar compounds. The examination of the experimental conditions of the hydroboration followed by chromic acid oxidation, indicates that an excess of the oxidizing reagent is used during the oxidation step of the intermediate organoborane (36). This observation led us to consider that hydroboration followed by chromic oxidation of 1-alkyl or 1-aryl-3,4-dihydronaphthalenes **2a-f**, could lead to more oxidized compounds corresponding to naphtols **4a-f**, instead of the expected 3,4-dihydronaphthalene-2(1H)-ones **3a-f**. We therefore applied this reaction to the known 3,4-dihydronaphthalenes **2a-f** using an excess of chromic acid and a longer oxidation step.

The use of these experimental conditions resulted in the formation of the corresponding 1-alkyl(or aryl)-2-naphtols **4a-f** instead the 3,4-dihydronaphthalene-2(1H)-ones(45) (scheme 1).

Scheme 1



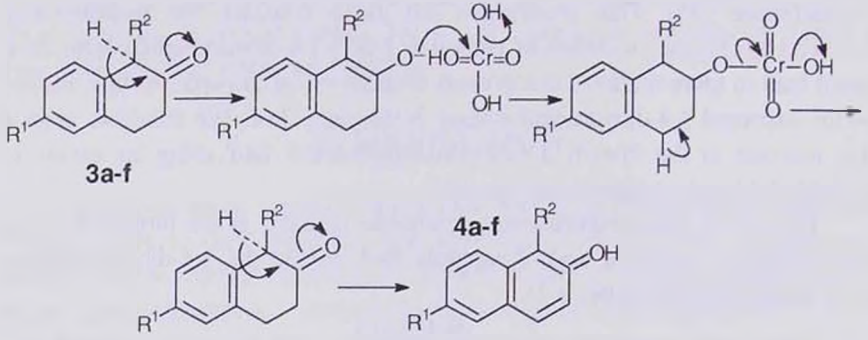
(1): R^2MgX, NH_4Cl-H_2O (3): 9-BBN-THF

(2): H_2SO_4-H_2O, T° (4): H_2CrO_4

Compounds 2, 3, 4	R^1	R^2	Naphtols (Yields %)
a	H	CH_3	**4a** : (63)
b	H	C_2H_5	**4b** : (67)
c	H	C_6H_5	**4c** : (67)
d	CH_3O	CH_3	**4d** : (61)
e	CH_3O	C_6H_5	**4e** : (61)
f	CH_3O	C_6H_4-OCH_3(P)	**4f** : (58)

The mechanism of this reaction can be interpreted according to scheme 2, leading to the initial formation of the 3,4-dihydronaphthalene-2(1H)-ones **3a-f**, followed by their oxidative aromatization to 2-naphtols **4a-f** involving possible enolization step (scheme 2).

Scheme 2



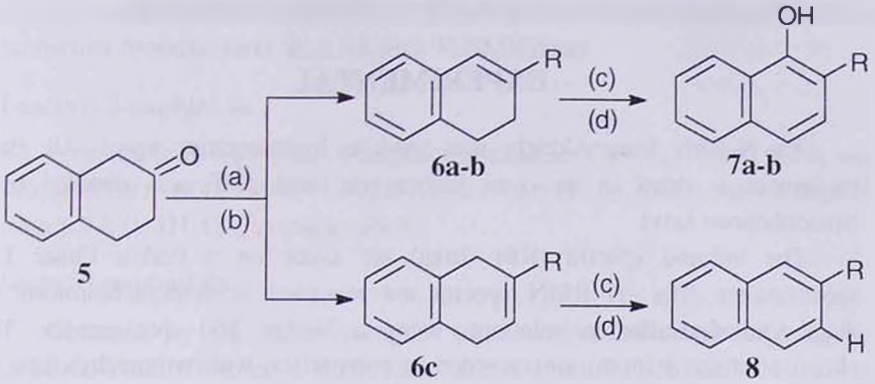
This scheme was confirmed further with the preparation of 1-phenyl-2-naphtol **4c** (R^1=H; R^2=C_6H_5) by chromic acid oxidation (scheme 1) from the previously prepared 1-phenyl-2-tetralone **3c** (R^1=H; R^2=C_6H_5) (45). The structure of the prepared naphtols **4a-f** was established by elemental analysis, infrared and ^1H NMR spectroscopy.

2. Synthesis of 1-naphtols substituted at 2-position and 2-naphtols substituted at 3-position

The previously obtained results led us to investigate its applicability for the preparation of other naphtols: 1-naphtols substituted at 1-position and 2-naphtols

substituted at 3-position. The application of hydroboration followed by oxidation with chromic acid was therefore applied to 2-substituted 3.4-dihydronaphthalenes **6a-b** and 2-phenyl-1.4-dihydronaphthalene **6c** and the expected naphtols **7a-b** and **8** were isolated according to scheme 3.

Scheme 3



(a): RMgX, NH_4Cl-H_2O; (b): H_2SO_4-H_2O; (c): 9-BBN-THF; (d): H_2CrO_4

Compounds	R	Naphtols (yields)
6a	CH_3	**7a** : (38%)
6b	C_6H_5	**7b** : (37%)
6c	C_6H_5	**8** : (70%)

It is noteworthy that the dehydration of the intermediate carbinol formed by the Grignard reaction of 2-tetralone **5** with phenylmagnesium bromide leads to a mixture of two compounds: 2-phenyl-3,4-dihydronaphthalene **6b** ($R=C_6H_5$) and 2-phenyl-1,4-dihydronaphthalene **6c** ($R=C_6H_5$), which were separated by column chromatography over silica gel and which are the starting intermediates used for the preparation of the two naphtols **7b** and **8**. The structure of these naphtols was also established by elemental analysis, infrared and ^1H NMR spectroscopy. The examination of these results shows that 2-substituted 1-naphtols are obtained in lower yields than the 1-substituted 2-naphtols **4a-f** and 3-phenyl-2-naphtol **8**.

CONCLUSION

This study shows that hydroboration followed by chromic acid oxidation constitutes a new general method for the preparation of 1- or 3-substituted 2-naphtols with good yields. In the case of 2-substituted 1-naphtols, although the yields are low, this method offers a new route for the preparation of 2-substituted 1-naphtols which are not easily available via the other known routes.

EXPERIMENTAL

The 9-BBN from Aldrich, was used as hydroborating agent. All glass equipment is dried in an oven before use, and THF was distilled over benzophenone ketyl.

The infrared spactra (KBr disks) are taken on a Perkin Elmer 117 spectrometer. The ^1H RMN spectra are recorded in deuterochloroform or deuterodimethylsulfoxide solutions, using a Varian T60 spectrometer. The chemical shifts ∂ (ppm) are recorded in comparison with tetramethylsilane as internal standard. Melting points are taken on an electrical bloc Maquenne and are not corrected. The elemental analysis data are in agreement with the molecular structures and are not indicated herein.

1-phenyl-2-naphtol 4c (Method A)

Typical procedure

To a nitrogen flushed round-bottom flask, fitted with a magnetic stirring bar and a reflux condenser, topped with a connecting tube leading to a mercury bubbler, a 0.5 molar 9-BBN solution in dry THF (10 *mmoles*, 20 *mL*) is added dropwise with a syringe via a septum inlet to a cooled solution (0-5°C) of 1-phenyl 3,4-dihydronaphthalene (1.6 *g*, 7.9 *mmoles*) dissolved in dry THF (50 mL, distilled from benzophenone ketyl). The reaction is left to come to r.t., while stirring is continued overnight. The next day the THF is evaporated and Et_2O (100 *mL*) added. The mixture is then oxidized. The chromic acid solution prepared from sodium dichromate dihydrate (1.2 *g*, 4 *mmoles*) and 96% sulfuric acid (1 *mL*, 1.835 *g*, 18.7 *mmoles*) diluted with water (6 *mL*), is added to the stirred etheral solution over a period of 15 minutes. After heating under reflux for 4 hours (reaction monitored by TLC), the ether layer is separated and the aqueous layer extracted with Et_2O (3×50 *mL*). The mixed organic extracts are then washed with sat. aq. NaCl to neutrality and dried (Na_2SO_4). After filtration, the solvent is removed and the residue is purified by column chromatography

over silica gel (solvent dichloromethane-ethanol 97-3). The fraction corresponding to the expected product is eveporated and the residue is recristallized from ethanol-water mixture. Isolated quanity: 1.15 *g* (67%). $C_{16}H_{12}O$, m.p.: 85, IR(KBr): 3500, 1600; ^1H NMR ($CDCl_3$/TMS): 7.2-7.8 (m, 11H, arom.), 8.3 (s, 1H, OH, exchangeable).

The other naphtols **4a, 4b, 4d, 4e, 4f, 7a, 7b** and **8** are prepared according to this same procedure (method A), from the corresponding dihydronaphthalenes (molecular formula, yield, m.p., IR and ^1H NMR data).

1-methyl-2-naphtol 4a

Prepared from 1-methyl 3,4-dihydronaphthalene. $C_{11}H_{10}O$, Yield: 63%, mp: 110; IR (KBr): 3400, 2900, ^1H NMR ($CDCl_3$): 2.6 (s, 3H, CH_3), 7.0-7.5 (m, 6H, arom.), 7.8 (s, 1H, OH, exchangeable).

1-ethyl-2-naphtol 4b

Obtained by the same reaction with 1-ethyl 3,4-dihydronaphthalene. $C_{12}H_{12}O$, Yield: 67%; mp: 105, IR (KBr): 3500, 1600, ^1H NMR ($CDCl_3$): 1.1 (t, 3H, CH_2-CH_3), 3.0 (q, 2H, CH_2-CH_3), 7.0-7.8 (m, 8H, arom.); 8.0 (s, 1H, OH, exchangeable).

1-methyl-6-methoxy-2-naphtol 4d

Prepared from 1-methyl 6-methoxy 3,4-dihydronaphthalene. Yield: 61%; mp: 154, $C_{12}H_{12}O_2$, IR (KBr): 3400, 2950; ^1H NMR ($DMSOD_6$): 2.75 (s, 3H, CH_3); 7.0-7.8 (m, 5H, arom.); 8.1 (s, 1H, OH, echangeable).

1-phenyl-6-methoxy-2-naphtol 4e

Prepared from 1-phenyl 6-methoxy 3,4-dihydronaphthalene. Yield: 61%, mp: 162; $C_{12}H_{12}O_2$, IR (KBr): 3400, 1600, ^1H NMR ($DMSOd_6$): 3.8 (s, 3H, OCH_3), 6.8-8.0: (m, 10H, arom.), 8.2 (s, 1H, OH, exchangeable).

1-(4-methoxyphenyl)-6-methoxy-2-naphtol 4f

This compound is prepared from 1-(4-methoxyphenyl) 6-methoxy 3,4-dihydronaphthalene. $C_{18}H_{16}O_3$, Yield: 58%, mp: 223, IR (KBr): 3400, 1600; ^1H NMR ($DMSOd_6$): 3.8 (s, 6H ($OCH_3)_2$); 6.8-8.0: (m, 9H, arom.); 8.1 (s, 1H, OH, exhangeable).

1-phenyl-2-naphtol 4 c (Method B)

To a 100 *mL* round-bottom flask, fitted with a magnetic stirring bar and a reflux condenser, 1-phenyl-3,4-dihydronaphthalene-2-one (670 *mg*, 3.3 *mmoles*) is dissolved in Et_2O (40 *mL*). The solution is then oxidized with a chromic acid

solution prepared from sodium dichromate dihydrate (894 *mg*, 2.98 *mmol*) and 96% sulfuric acid (0.7 *mL*, 1.28 *g*, 13 *mmoles*) diluted with water (4 *mL*). The mixture is heated under reflux during 4 hours. After cooling, water (20 *mL*) is added and the two phases are separated. The aqueous phase was extracted with Et_2O (3×30 *mL*). The mixed organic extracts are then washed with sat. aq. NaCl to neutrality and dried (Na_2SO_4). After filtration, the solvent is removed and the residue is purified by column chromatography over silica gel (solvent dichloromethane-ethanol 97-3). The fraction corresponding to the expected product **4c** is eveporated and the residue is recristallized from ethanol-water mixture. Isolated quantity 404 *mg* (61%) mp: 84. The mixed mp with the derivative **4c** prepared by method A is 84. The IR and ^1H NMR spectra of the two compounds are identical and superimposable.

2-methyl-1-naphtol 7a (Method A)

To 650 *mg* (4.5 *mmol*) of 2-methyl-3,4-dihydronaphthalene dissolved in anhydrous NHF (10 *mL*), a solution of 0.5 molar 9-BBN (5 *mmoles*) in THF (10 *mL*) is added and the reaction performed according to method A. The solution is then oxidized with a chromic acid solution prepared from sodium dichromate dihydtrate (4 *g*, 13.5 *mmoles*) and 96% sulfuric acid (3 *mL*, 5.5 *g*, 54 *mmoles*) diluted with water (17 *ml*). The product is isolated by column chromatography over silica gel (solvent dichloromethane-ethanol 97-3). The fraction corresponding to the expected product **4c** is eveporated and the residue is recristallized from petroleum ether. $C_{11}H_{10}O$, yield: 275 *mg* (38%), m.p.: 64, IR (KBr): 3400, 1600; ^1H NMR ($CDCl_3$/TMS): 2.65 (s, 3H, CH_3); 7.0-7.6 (m, 6H, arom.); 8.1 (s, 1H, OH, exchangeable).

2-phenyl-1-naphtol 7b et 3-phenyl-2-naphtol 8

These derivatives are prepared from from 2-phenyl 3,4-dihydronaphthalene **(6b)** and 2-phenyl 3,4-dihydronaphthalene **(6c).** In a three-necked round-bottom blask provided by a $CaCl_2$ drying tibe, a reflux condenser and N_2 bubbler, are introduced magnisium turnings (500 *mg*, 21 *mmol*), anhydrous THF (20 *mL*), and a iodine crystal. The reaction mixture is refluxed under N_2 (1 *hour*). After cooling, 2-tetralone (1.46 *g*, 10 *mmol*) dissolved in dry THF (30 *mL*) is added dropwise and the mixture refluxed (4 *hours*). After cooling hydrolysis is performed with a saturated ammonium chloride solution. The two phases are separated and the aqueous phase is extracted with Et_2O (3×50 *mL*). The mixed organic phase is washed with a saturated sodium chloride solution, dryed over anhydrous sodium sulfate. After filtration, the solvent is evaporated and to the residue a solution of 20% H_2SO_4 v/v (50 *mL*) is added and refluxed (1 *hour*). After cooling, Et_2O

(50 *mL*) is added and the two phases are separated. The aqueous phase is extracted with Et_2O (3×50 *mL*). The mixed organic phase is washed with a saturated sodium chloride solution, dried over anhydrous sodium sulfate, filtred and evaporated on a rotating eveporator. The residue is separated on column chromatography over silica gel (solvent dichloromethane). The fraction corresponding to the same product are mixed, concentrated and the residue is recristallized from methanol. Two compounds are separated:

2-phenyl 3,4-dihydronaphthalene **(6b):** yield 800 *mg* (38%), mp: 64 ^1H RMN: 2.9 (m, 4H, 3,4-CH_2CH_2, 6.9 (s, 1H, CH), 7.2-7.8 (9H, arom.);

2-pnenyl 1,4-dihydronaphthalene **(6c):** yield 360 *mg* (17%), mp 76, ^1H RMN: 3.2 (s, 4-CH_2), 3.6 (s, 2H, CH_2 benzylic, 7.0-7.5, (10H, arom. and benzylic).

2-phenyl-1-naphtol 7b (Method A)

This reaction is performed using 2-phenyl-3,4-dihydronaphthalene (200 *mg*, 1.0 *mmol*), dissolved in anhydrous THF (10 *mL*) and a 0.5 molar 9-BBN solution in THF (2.2 *mL*, 1.1 *mmol*)

The organoborane is oxidized with a chromic acid solution prepared from sodium dichromate dihydrate (1.2 *g*, 4 *mmol*) and a 96% m/v sulfuric acid (0.9 *mL*, 1.585 *g*, 16.2 *mmol*) and water (5.0 *mL*). The reaction mixture is worked up acording to method A. The isolated product is purified by column chromarography over silica gel (solvent: dichloromethane-ethanol 98/2). The product is recristallized from petroleum ether. $C_{16}H_{12}O$, Yield: 275 *mg* (37%), mp: 69; IR (KBr): 3500, 1600; 1H NMR ($CDCl_3$): 7.0-7.4 (m, 11H, arom.); 8.0 (s, 1H, OH, exchangeable).

3-phenyl-2-naphtol 8 (Method A)

This reaction is performed, using 2-phenyl-1,4-dihydronaphthalene (300 *mg*, 1.5 *mmol*), dissolved in anhydrous THF (10 *mL*) and a 0.5 molaire 9-BBN solution in anhydrous THF (3.3 *mL*, 1.65 *mmoles*). The organoborane is oxidized with a chromic acid solution oreoared from sodium dichromate dihydrate (1.9 *g*, 6.4 *mmol*) and a 96% m/v sulfuric acid (1.5 *mL* 2.64 *g*, 27 mmol) completed to 8.0 *mL* with water. The reaction mixture is worked up in the usual manner. The isolated product is purified by column chromatography over silica gel (solvent: dichloromethane-ethanol 98/2). The product is recristallized from methanol-water mixture. $C_{16}H_{12}O$, Yield: 230 *mg* (70%), mp: 117, IR (KBr): 3420, 1600; ^1H NMR ($CDCl_3$): 7.0-8.1 (m, 11H, arom.); 8.4 (s, 1H, OH, echangeable).

ՀԻԴՐՈԲՈՐԱՑՈՒՄ. ՏԵՂԱԿԱԼՎԱԾ 1- ԵՎ 2-ՆԱՖԹՈԼՆԵՐԻ ՍՏԱՑՄԱՆ ՆՈՐ ԵՂԱՆԱԿ

Ս. ԿԻՐԿԱՇԱՐՅԱՆ և Պ. ԿՈՒՐՏՍՈՒՐԱԿԻՍ

1- և 2-Ալկիլ(կամ արիլ)-1,4-դիհիդրոնաֆթալիններիի հիդրոբորացումը և քրոմական թթվով դրան հաջորդող օքսիդացումը բերում է համապատասխան նաֆթոլներին: 1- և 3-տեղակալված նաֆթոլները առաջանում են ավելի մեծ ելքերով, քան 2-տեղակալված 1-նաֆթոլները:

ГИДРОБОРИРОВАНИЕ: НОВЫЙ МЕТОД ПОЛУЧЕНИЯ ЗАМЕЩЕННЫХ 1- И 2-НАФТОЛОВ

С. КИРКИАШАРЯН и П. КУРТСУРАКИС

Гидроборирование с последующим окислением хромовой кислотой 1- и 2-алкил(или арил)-3,4-дигидронафталинов и 2-алкил(или арил)-1,4-дигидронафталинов приводит к соответствующим нафтолам. 1- и 3-замещенные 2-нафтолы образуются с более высоким выходом, чем 2-замещенные 1-нафтолы.

REFERENCES

1. *Lien E., Hansch C., Anderson S.J.* – J. Med. Chem., 1968, 11, 43.
2. *Duperray B., Chastrette M., Cohen M.M., Pacheco H.* – Eur. J. Med. Chem., 1976, 11, 433.
3. *Boyd J.C., Millership J.C., Woolfson A.D.* – J. Pharm. Pharmacol., 1982, 34, 158.
4. *Koster H., Scholtens E., Mulder G.* – J. Med. Biol., 179, 57, 340.
5. *Huisgen R., Feller L., Otto P.* – Chem. Ber., 1969, 102, 3405.
6. *Horitz Z.* – Japan Kokkai (1960), 4322. Chem. Abstr., 1960, 54, 6671h.
7. *Rama Rao A.V., Deshpande V.H., Ravishandran K.* – Ind. J. Chem., 1985, 24B, 233.
8. *Katsuri T.S., Slvarawakrisnan S.* – Proc. Ind. Acad. Sci. Sect A., 1977, 86A, 309.
9. *Li T., Ellison R.H.* – J. Am. Chem. Soc., 1978, 100, 6263.
10. *Nowicki A.W., Turner A.* – Chem. & Ind., 1981, p.501.
11. *Reetz M., Stephan W.* – Liebigs Ann. Chem., 1980, p.533.
12. *Przhiyalalyovskaya N.M., Shuez V.F., Belov N.* – Zhur. Obschchei Khim., 1961, 31, 1678.
13. *Fuson R.C., Armstrong M.D., Speck S.B.* – J. Org. Chem., 1945, 7, 297.
14. *Kost A.N., Terenin V.L., Yudin L.G., Sagituklin R.S.* – Khim. Geterotsikl. Soedin, 1980, p.1972.
15. *Minami K., Kijima S.* – Chem. Pharm. Bull. Japan, 1979, 27, 816.
16. *Bacchiocchi E., Rol C., Sebastiani G.V.* – J. Chem. Res. Synops, 1983, p.232.
17. *Newman M.S., Bye T.S.* – J. Am. Chem. Soc., 1952, 74, 905.
18. *Wenkert E., Youssefyeh R., Lewis R.G.* – J. Am. Chem. Soc., 1960, 82, 4675.
19. *Bram G., Geraghty N., Nec G., Seyden-Penne J.* – J. Chem. Soc. Chem. Commun., 1980, p.325.
20. *Leach B., Stacks C.* – Swiss Patent, 1978, 598, 170, Chem. Abstr., 1978, 89, 4291v.

21. *Saldi M., Dankwart J.W., Snieckus V.J.* – J. Org. Chem., 1986, 51, 271.
22. *Greenland H., Pickey J., Sternhell S.* – J. Chem. Soc. Perkin Trans 1, 1986, p.1789.
23. *Gates M., Webb W.G.* – J. Am. Chem. Soc., 1958, 80, 1186.
24. *Barton D.H.R., Chapriot B., Dehm H.T., Motherwell W.B., Pascard C., Pichon C.* – Helv. Chim. Acta 1984, 67, 586.
25. *Barton D.H.R., Bhatnagar N.Y., Finet S.P., Motherwell W., Barros Papoula M.T., Stanforth S.P.* – J. Chem. Soc. Chem. Comm. Perkin Trans 1, 1985, p.2657.
26. *Barton D.H.R., Bhatnagar N.Y., Finet S.P., Motherwell W.B.* – Tetrahrdron, 1986, 42, 3111.
27. *Hopf H., Thalmann P.* – Chimia, 1959, 13, 101.
28. *Saito N., Tanaka C., Okubo M.* – J. Pharm. Soc. Japan, 1956, 76, 359.
29. *Russel A., Lockhart L.* – Org. Synth. Coll. Vol. VI, 1955, 3, 463.
30. *Miller L.E., Hanneman W.W., St John W.L., Sweby R.R.* – J. Am. Chem. Soc., 1954, 76, 296.
31. *Khorana M.L., Pandit S.Y.* – Ind. J. Chem., 1963, 1, 489.
32. *Fields D.* – J. Org. Chem., 1971, 36, 3002.
33. *Giles R.G.F., Green I.R., York S.C.* – J. Chem. Soc. Perkin Trans. 1, 1984, p.2383.
34. *Brown H.C., Garg C.P.* – J. Am. Chem. Soc., 1961, 83, 2951.
35. *Brown H.C., Kulkarni S.U., Gundu Rao C.* – Synthesis 1979, p.702.
36. *Brown H.C., Kulkarni S.U., Gundu Rao C.* – Synthesis 1980, p.85.
37. *Kirkiacharian B.S., Elia G.H., Mahuzier G.* – C. R. Acad. Sci. (Ser C), 1974, 279, 151.
38. *Kirkiacharian B.S.* – C. R. Acad. Sci. (Ser C), 1980, 291, 73.
39. *Kirkiacharian B.S.* – J. Chem. Soc. Chem. Commun., 1975, p.162.
40. *Kirkiacharian B.S., Chidiack H.* – C. R. Acad. Sci. (Ser C), 1975, 280, 775.
41. *Kirkiacharian B.S., Brion J.D., Gomis M., Reynaud P.* – Heterocycles, 1980, 14, 1929.
42. *Kirkiacharian B.S., Gomis M.* – C. R. Acad. Sci. (Ser C), 1982, 295, 27.
43. *Kirkiacharian B.S., Koutsourakis P.G.* – Synthesis, 1990, p.815.
44. *Kirkiacharian B.S., Dahan A., Koutsourakis P.G.* – Synthesis, 1991, p.985.
45. *Kirkiacharian B.S., Koutsourakis P.G.* – Synth. Comm., 1993, 23, 737.
46. *Pappo R.* – J. Am. Chem. Soc., 1959, 81, 1010.