Tetrahedron. Vol. 29, pp. 4205 to 4209. Pergamon Press 1973. Printed in Great Britain

STUDIES ON ORGANOPHOSPHORUS COMPOUNDS—III[a]

REACTION OF α-SUBSTITUTED SECONDARY CARBOXAMIDES WITH HMPA—AMIDINE AND/OR NITRILE SYNTHESES

E. B. PEDERSEN* and S.-O. LAWESSON
Department of Organic Chemistry, Chemical Institute, Aarhus University, DK-8000 Aarhus C, Denmark

(*Received in the UK 26 June 1973; Accepted for publication 16 August 1973*)

Abstract—Secondary carboxamides (R^1CONHR^2) undergo different reactions when heated in HMPA at about 220°. If R^1 or R^2 can form stable carbonium ions, fragmentation reactions are observed and the corresponding nitriles R^2CN or R^1CN, respectively, are formed. Also amidines are produced. N-benzyl-acetamide rearranges when heated in HMPA to give β-phenyl-propionitrile. It is suggested that in all the reactions investigated the first step is the formation of a phosphorodiamidate followed by formation of a nitrilium carbonium ion. The fragmentation reactions can be used as an alternative to the Sandmeyer reaction (nitrile synthesis).

INTRODUCTION

During the last ten years chemists have paid increasing attention to the effect of HMPA as a solvent[1,2] in chemical reactions. Until recently, only a few publications[3,4] dealt with possible reactions of HMPA as a reagent (especially when the reactions were run at elevated temperatures), but during the last few years an increasing number of papers[5-13] has appeared on this subject. It was thus found that gentle reflux of a series of secondary carboxamides in HMPA[11] produced N,N-dimethylamidines in fair yields (Eq 1).

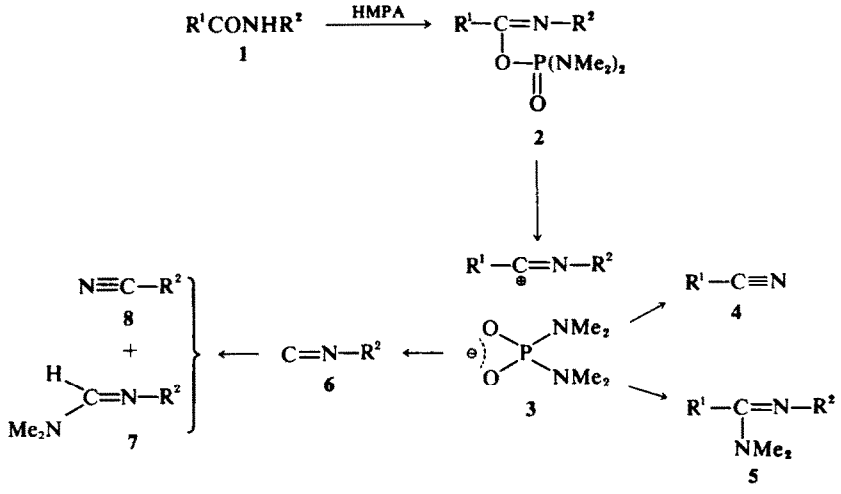
$$R^1CONHR^2 \xrightarrow{HMPA} R^1{-}C(=N{-}R^2){-}NMe_2 \qquad (1)$$

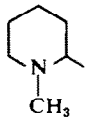
In light of the known propensity of HMPA[1,2] to exchange with hydroxylic compounds it is suggested that the initial step in the reaction of the amide **1** with HMPA forming the amidine **5** would be the formation of the phosphorodiamidate derivative **2**, which is supposed to give the ion pair **3**, the postulated intermediate in the Beckmann rearrangement.[14] Then on bond formation between one of the N atoms of the anion and the C atom of the nitrilium carbonium ion, followed by a fragmentation reaction, the amidine **5** is formed. Also it should be taken into account that **5** may be formed by the reaction of **3** with dimethyl amine present in the reaction mixture. Furthermore it is obvious that in these reactions there should be some similarities to the Beckmann rearrangements. In the Beckmann fragmentation reaction of α-trisubstituted oxime tosylates no correlation has been found between percentage of fragmentation and the rates of rearrangement. However, the stability of the cationic fragments correlates with the degree of fragmentation, indicating that fragmentation to nitriles occurs after the rate-determining migration step.[15] As the nitrilium carbonium ion is the common intermediate of rearrangement and fragmentation products in certain Beckmann reactions, it can easily be foreseen that in the amidine synthesis from **1** the intermediate nitrilium carbonium ion **3** should also undergo fragmentation reactions if the groups R^1 or R^2 can form stable carbonium ions.

Fragmentation of R^1

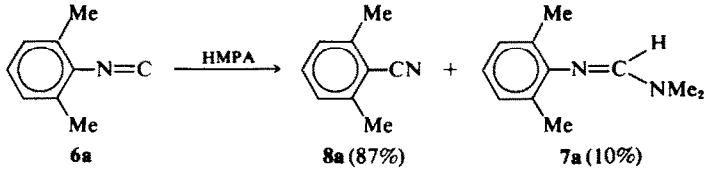
The amides **1a-i** were heated in HMPA at 215–230° and although the R^1 groups can form stable carbonium ions in all cases no fragmentation of the amides **1a-d** could be observed. In all four cases high yields of the corresponding amidines **5** were isolated. However, for the α-chloro-amides **1e** and **1f** low yields (~20%) were obtained of the corresponding fragmentation product **8**. The α-chloroamides were only heated for 2 h as prolonged heating at high temperature caused polymerization. The best yields for the fragmentation product **8** (40–67%) were obtained for the α-amino-amides **1g-i**. It should be noted that in all cases where fragmentation reactions were observed also the formamidine **7a** was obtained in small yields. The formamidine **7a** had identical properties with authentic sample prepared from 2',6'-formoxylidide. In fact, on refluxing the isonitrile **6a** in HMPA (Eq 2) the same nitrile and formamidine observed in the above fragmentation reactions could be isolated clearly indicating the intermediacy of the isonitrile in the fragmentation reactions. This again indicates that **3** is a common intermediate for the fragmentation reactions as well as for the amidine formation. It

*Part II. N. O. Vesterager, R. Dyrnesli, E. B. Pedersen and S.-O. Lawesson, *Synthesis* 548 (1972).



	R^1	R^2		R^1	R^2
a	t-Bu	2,6-xylyl	i	Et_2NCHCH_3	2,6-xylyl
b	$EtOCH_2$	2,6-xylyl	j	Et_2NCHCH_3	*m*-CH_3O—C_6H_4
c	$MeSCH_2$	2,6-xylyl	k	Et_2NCHCH_3	*p*-CH_3O—C_6H_4
d	$(C_6H_5)_2CH$	2,6-xylyl	l	Et_2NCHCH_3	*m*-CF_3—C_6H_4
e	$ClCH_2$	2,6-xylyl	m	Et_2NCHCH_3	2-diphenyl
f	CH_3CHCl	2,6-xylyl	n	Et_2NCHCH_3	2-naphtyl
g	Et_2NCH_2	2,6-xylyl	o	Et_2NCHCH_3	2-pyridyl
h*		2,6-xylyl			

SCHEME 1

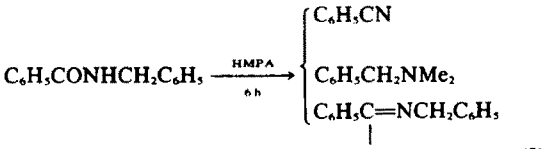


(2)

was confusing that **1a** did not undergo a fragmentation reaction as it is known that a t-Bu group easily splits off from the nitrilium carbonium ion in the Beckmann fragmentation reaction.[15] However, it should be noted that the reaction conditions, the counter ion and the R^2 group were different from those used in the Beckmann fragmentation reactions.

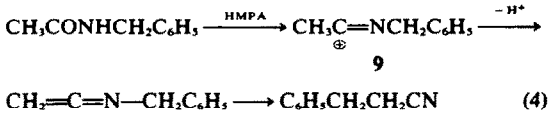
Fragmentation of R^2

In the reaction depicted in Eq 3 a fragmentation reaction is observed besides that the expected amidine is produced. Benzonitrile and benzyl dimethyl amine are isolated as a mixture and their mass spectra when separated by GLC connected to the mass spectrograph, were identical with those of authentic samples. The appearance of those products is probably best explained by the existence of the nitrilium carbonium ion **3**.



(3)

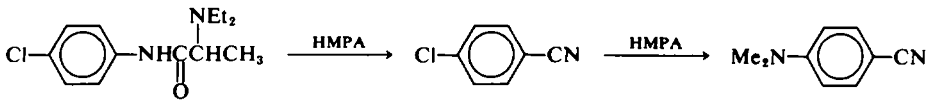
Rearrangement reaction



(4)

On treatment of N-benzylacetamide with HMPA at elevated temperature a low yield of β-phenylpropio-nitrile is obtained. The mechanism can best be explained by a deprotonation of the intermediate nitrilium carbonium ion **9** to give N-benzylketene-

*Kindly supported by dr. G. Claeson, Nobel-Pharma, Sweden.



12 13

imine **10**, which is then supposed to undergo a [1,3]-benzylmigration forming the nitrile, **11**. A precedent example[16,17] is known when tetramethylsuccinonitrile is formed by a [1,3]-migration reaction of dimethyl-N-(2′-cyano-2′-propyl)-keteneimmine.

The conversion of primary aromatic amines to nitriles

An aromatic amine reacts with ethylmagnesium bromide and the salt formed is then allowed to react with ethyl α-diethylamino-propionate to give the corresponding secondary carboxamide. Heating of the amide at 220° in HMPA gives the corresponding nitrile, **8**. This should therefore be one method of choice for conversion of an aromatic amine to the corresponding nitrile. As all steps are performed under basic conditions, this method should be suitable to acid-sensitive compounds. The first two steps are well known reactions, but also other routes are known for the formation of α-amino-carboxamides. Special attention was therefore given to the last step of conversion of the carboxamides to the nitriles (Table 1). An anomalous result was obtained on refluxing **12** in HMPA as the nitrile **13** was formed as the main product. This is best explained by the reaction sequence given in Eq 5 as it has been shown recently that chlorine in an aromatic ring activated by a cyano or a nitro group can be replaced by a dimethylamino group from HMPA at elevated temperature.[18]

EXPERIMENTAL

NMR spectra were recorded at 60 Mc/s on a Varian A-60 spectrometer. TMS was used as internal reference standard and the chemical shifts are expressed in δ-values (ppm), (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet). The IR spectra were recorded on a Beckmann 18 IR spectrometer. UV spectra were measured on a Perkin-Elmer 402. M.ps and b.ps are uncorrected. The microanalyses were performed by Løvens Kemiske Fabrik, Copenhagen. Commercial HMPA dried over molecular sieves (3A) was used in this investigation.

2-*Ethoxy*-2′,6′-*acetoxylidide* (**1b**). To ice-cooled and stirred EtMgBr (prepared from Mg (6 g) and EtBr (26 g) in 150 ml anhyd ether) were added dropwise 2,6-xylidine (23 g) in 100 ml anhyd ether. The mixture was then stirred for 1 h at room temp. Ethyl ethoxyacetate (24·8 g) in 50 ml anhyd ether were then added dropwise, with vigorous stirring and ice-cooling. The mixture was then refluxed for 3 h and 100 ml water were cautiously added. The ether-phase was decanted off. The water-phase and 200 ml ether were vigorously stirred and the ether-phase decanted off. This was repeated another 3 times. The ether-phases were washed with water and dried over $CaSO_4$. The ether was removed and recrystallization from light petroleum 60–80° gave 13·3 g (34%) of the title compound, m.p. 49°. (Found: C, 69·50; H, 8·27; N, 6·74. $C_{12}H_{17}NO_2$ requires: C, 69·54; H, 8·27; N, 6·76%).

2-*Methylthio*-2′,6′-*acetoxylidide* (**1c**). To 2,6-xylidine (19 g) and triethyl amine (20 g) in 250 ml benzene were added dropwise and with stirring methylthio-acetylchloride (19 g) and the mixture was refluxed for 2 h. The mixture was then filtered and the hot benzene soln was extracted twice with dil HCl. The benzene was stripped off and on recrystallization from EtOH and H_2O 14·5 g (45%) of **1c** were obtained, m.p. 116°. (Found: C, 62·97; H, 7·14; N, 6·62; S, 15·36. $C_{11}H_{15}NOS$ requires: C, 63·14; H, 7·23; N, 6·69; S, 15·29%).

2,2-*Diphenyl*-2′,6′-*acetoxylidide* (**1d**). Diphenylacetic acid (50 g) and 22 ml $SOCl_2$ were heated for 1 h at 70–80°. Unreacted $SOCl_2$ was distilled off, and the diphenylacetylchloride formed was cautiously added to 2,6-xylidine (30 g) and triethylamine (35 g) in 500 ml benzene. After 1 h the amide and triethylammonium chloride was filtered off. The solid material was washed with 1 N H_2SO_4 and recrystallization from EtOH gave 63·9 g (86%) of **1d**, m.p.

Table 1. Nitrile syntheses

$$\underset{\displaystyle NEt_2}{CH_3\underset{|}{C}HCONHR^2} \xrightarrow{HMPA} R^2CN$$

Starting material	R^2	Reaction time (h)	Reaction temp (°C)	R^2CN (%)	R_f[a]	M.p. or n_D^{25}	Litt. m.p. or n_D
Ii	2,6-xylyl	5	220°	58	0·53	88–90°	89–91°[21]
Ij	m-CH_3O—C_6H_4	17	230°	9	0·37		
Ik	p-CH_3O—C_6H_4	24	215°	26	0·31	57–60°	60–61°[19]
Il	m-CF_3—C_6H_4	17	220°	23	0·47	1·4604	1·4616[20]
Im	2-diphenyl	17	225°	64	0·44	35–36°	37°[22]
In	2-naphtyl	18	230°	34	0·44	63–65°	65–66[23]
Io	3-pyridyl	16	230°	27	0·09	48–50°	49–50[19]

[a] Ether–light petroleum ether (3:7) on silica gel supporting material.

215°. (Found: C, 83·23; H, 6·77; N, 4·42. $C_{22}H_{21}NO$ requires: C, 83·77; H, 6·71; N, 4·44%).

2-*Diethylamino*-2',6'-*propionoxylidide* (**1l**) was prepared as **1b** from 2,6-xylidine (23 g) and ethyl 2-(diethylamino)-propionate (31 g) in 41% (18 g) yield, b.p. 149–151°/0·15 mm, m.p. 58° (from light petroleum b.p. 60–80°); lit.[25] m.p. 55°. (Found: C, 72·59; H, 9·73; N, 11·32. $C_{15}H_{24}N_2O$ requires: C, 72·54; H, 9·74; N, 11·28%).

2-*Diethylamino*-m-*propionanisidide* (**1j**) was prepared as **1b** from *m*-anisidine (24·6 g) and ethyl 2-(diethylamino)-propionate (31 g) in 49% (22·1 g) yield, b.p. 128–130°/0·06 mm, $n_D^{25} = 1·5301$. (Found: C, 67·14; H, 8·84; N, 11·06. $C_{14}H_{22}N_2O_2$ requires: C, 67·17; H, 8·86; N, 11·19%).

2-*Diethylamino*-p-*propionanisidide* (**1k**) was prepared as **1b** from *p*-anisidine (24·6 g) and ethyl 2-(diethylamino)-propionate (31 g) in 45% (20·1 g) yield, b.p. 168–170°/0·2 mm, $n_D^{25} = 1·5317$. (Found: C, 66·94; H, 8·78; N, 11·16. $C_{14}H_{22}N_2O_2$ requires: C, 67·17; H, 8·86; N, 11·19%).

2 - *Diethylamino* - α, α, α - *trifluoro* - m - *propionotoluidide* (**1l**) was prepared as **1b** from α, α, α - trifluoro - *m* - toluidine (32·2 g) and ethyl 2-(diethylamino)-propionate (31 g) in 54% (28 g) yield, b.p. 128–130°/0·2 mm, $n_D^{25} = 1·4832$; lit.[24] b.p. 159°/5 mm. (Found: C, 58·29; H, 6·61; N, 9·76. $C_{14}H_{19}F_3N_2O$ requires: C, 58·30; H, 6·64; N, 9·73%).

2-*Diethylamino*-2'-*phenyl*-*propionanilide* (**1m**) was prepared as **1b** from 2-amino-biphenyl (32 g) and ethyl 2-(diethylamino)-propionate (31 g) in 22% (11·5 g) yield, b.p. 185–187°/0·25 mm, m.p. 63° (from light petroleum b.p. 60–80°). (Found: C, 76·92; H, 8·13; N, 9·52. $C_{19}H_{24}N_2O$ requires; C, 76·99; H, 8·16; N, 9·45%).

2-*Diethylamino*-N-(2'-*naphtyl*)-*propionamide* (**1n**) was prepared as **1b** from β-naphtylamine (27 g) and ethyl 2-(diethylamino)-propionate (31 g) in 31% (15·2 g) yield, b.p. 191–193°/0·15 mm, $n_D^{25} = 1·5899$. (Found: C, 75·82; H, 8·21; N, 10·39. $C_{17}H_{22}N_2O$ requires: C, 75·52; H, 8·20; N, 10·36%).

2-*Diethylamino*-N-(3'-*pyridyl*)-*propionamide* (**1o**) was prepared as **1b** from 3-amino-pyridine (18·8 g) and ethyl 2-(diethylamino)-propionate (31 g) in 13% (5·0 g) yield, b.p. 141°/0·13 mm, $n_D^{25} = 1·5304$. (Found: C, 65·14; H, 8·62; N, 18·93. $C_{12}H_{19}N_3O$ requires: C, 65·12; H, 8·65; N, 18·99%).

2-*Diethylamino*-4'-*chloro*-*propionanilide* (**12**) was prepared as **1b** from *p*-chloro-aniline (24 g) and ethyl 2-(diethylamino)-propionate (31 g) in 51% (23 g) yield, b.p. 159–161°/0·2 mm, m.p. 70° (from light petroleum, b.p. 60–80°). (Found: C, 61·29; H, 7·51; N, 10·90; Cl, 13·98. $C_{13}H_{19}ClN_2O$ requires: C, 61·28; H, 7·52; N, 11·01; Cl, 13·92%).

N,N-*Dimethyl*-N-(2',6'-*xylyl*)-*formamidine* (**7a**) 2',6'-formoxylidide (10 g) in HMPA (50 ml) was heated at 215–220° for 5 h. The mixture was sllowed to cool to room temp and was then poured into water (400 ml) and extracted 4 times with ether. The combined ether phases were washed with water, dried with $CaSO_4$, the ether was stripped off and the amidine distilled to yield 10·4 g (89%), b.p. 63–65°/0·03 mm, $n_D^{25} = 1·5505$. (Found: C, 74·89; H, 9·17; N, 15·89. $C_{11}H_{16}N_2$ requires: C, 74·95; H, 9·15; N, 15·90%), NMR δ ($CDCl_3$): 2·13 (s, 6H), 2·95 (s, 6H), and 6·6–7·3 (m, 4H); IR^{film} shows strong C=N stretchings at 1650 cm^{-1}; UV (C_6H_{12}): $\lambda_{max} = 241$ nm (log $\epsilon = 4·06$).

2 - *Ethoxy* - N, N - *dimethyl* - N - (2', 6' - *xylyl*) - *acetamidine* (**5b**) was prepared as **7a** from 2-ethoxy-2',6'-acetoxylidide (10 g) in 73% (8·2 g) yield, b.p. 88–90°/0·07 mm, $n_D^{25} = 1·5303$. (Found: C, 72·02; H, 9·43; N, 12·06. $C_{14}H_{22}N_2O$ requires: C, 71·75; H, 9·46; N, 11·96%), NMR δ ($CDCl_3$): 1·08 (t, J = 7 C/S, 3H), 2·03 (s, 6H), 3·10 (s, 6H), 3·30 (q, J = 7 c/s, 2H), 3·79 (s, 2H), 6·6–7·1 (m, 3H); IR^{film} shows strong C=N stretchings at 1630 cm^{-1}; UV (C_6H_{12}): $\lambda_{max} = 245$ nm (log $\epsilon = 4·19$).

2-*Methylthio*-N, N-*dimethyl*-N-(2', 6'-*xylyl*)-*acetamidine* (**5c**) was prepared as **7a** from 2-methylthio-2',6'-acetoxylidide (10 g) in 82% (9·3 g) yield, b.p. 108/0·07 mm, $n_D^{25} = 1·5724$. (Found: C, 66·03; H, 8·52; N, 11·74; S, 13·56. $C_{13}H_{20}N_2S$ requires: C, 66·07; H, 8·53; N, 11·86; S, 13·54%), NMR δ ($CDCl_3$): 1·87 (s, 3H), 2·07 (s, 6H), 3·02 (s, 2H), 3·08 (s, 6H), 6·6–7·1 (m, 3H); IR^{film} shows strong C=N stretchings at 1630 cm^{-1}; UV (C_6H_{12}): $\lambda_{max} = 246$ (log $\epsilon = 4·19$).

2, 2-*Diphenyl*-N, N-*dimethyl*-N-(2', 6'-*xylyl*)-*acetamidine* (**5d**) was prepared as **7a** from **1d** (10 g) by heating for 13 h in 92% (10·0 g) yield, b.p. 185–187°/0·2 mm, m.p. 78° (recrystallized from light petroleum, 60–80°). (Found: C, 82·92; H, 7·67; N, 8·25. $C_{24}H_{26}N_2$ requires: C, 84·17; H, 7·65; N, 8·18%), NMR δ ($CDCl_3$): 1·87 (s, 6H), 2·89 (s, 6H), 5·35 (s, 1H), 6·5–7·5 (m, 13H), IR^{CCl_4} shows strong C=N stretchings at 1615 cm^{-1}, UV (C_6H_{12}) $\lambda_{max} = 226$ (log $\epsilon = 4·25$) and 245 (log $\epsilon = 4·22$).

Treatment of the amides **1e–i** *with HMPA.* The carboxamide (10 g) was heated in 50 ml HMPA at 215–220° for 2–5 h. The mixture was allowed to cool to room temp and was then poured into water (400 ml) and extracted 3 times with 200 ml ether (if the water and ether phases did not separate, NaCl was added). The combined ether phases were washed two times with 100 ml water, dried with $CaSO_4$, and the ether was distilled. Separation of this mixture by preparative TLC using silica gel as the supporting material and elution with ether–light petroleum ether (3:7) gave **7** ($R_f = 0·10$) and **8** ($R_f = 0·53$). (Starting material, reaction time (hrs), % yield of **7a**, and % yield of **8a** given): **1e**, 2, 7, 17; **1f**, 2, < 2, 18; **1g**, 5, 11, 40; **1h** 5, 6, 67; **1i**, 5, 12, 58.

Treatment of 2,6-*xylylisocyanide* **6a** *with HMPA.* **6a** (10 g) were treated as the amides **1e–i** and after using the same working up procedure as for the amides 1·3 g (10%) of **7a** and 8·7 g (87%) of **8a** were obtained.

Treatment of the amides **1j–o** *with HMPA.* The amides (10 g) were heated in 50 ml HMPA at 215–230° for 5–24 h. Using the same working up procedure as above, the yields of the nitriles obtained by preparative TLC are given in Table 1.

Treatment of **12** *with HMPA.* **12** (8 g) was heated in 50 ml HMPA at 225° for 16 h and worked up as above. Preparative TLC [silica gel support and eluted with ether–light petroleum ether (3:7)] gave 2·8 g (61%) of *p*-dimethylamino-benzonitrile ($R_f = 0·24$), m.p. 72–73°; lit.[26] 76°.

Treatment of N-*benzyl*-*benzamide with HMPA.* 10 g of N-benzyl-benzamide (10 g) was heated in 50 ml of HMPA at 230° for 6 h. The mixture was poured into 400 ml water and extracted as above. On distillation a small amount of a low boiling fraction was first collected, which was a mixture of benzonitrile and N,N-dimethyl-benzylamine (determined by IR, NMR, GLC and GLC-MS). Further distillation gave 4·5 g (40%) of N-benzyl-N,N-dimethyl-benzamidine (Ref 11), b.p. 118°/0·05 mm.

Treatment of N-*benzyl*-*acetamide with HMPA.* The amide (10 g) was gently refluxed for 6 h in 50 ml HMPA. After pouring the mixture on 400 ml water and extraction as above distillation gave 3-phenyl-propionitrile (1·1 g), b.p. 62°/0·1 mm, $n_D^{20} = 1·5226$; lit.[27] $n_D^{20} = 1·5231$. (Found: C, 82·31; H, 7·23; N, 10·52. C_9H_9N requires: C, 82·40; H, 6·92; N, 10·68%).

REFERENCES

[1]H. Normant, *Bull. Soc. Chim. Fr*, 791 (1968)
[2]N. Normant, *Russ. Chem. Rev.* **39**, 457 (1970)
[3]R. L. Heider, US P. 2 603 660; *Chem. Abstr.* **47**, 4900 (1953)
[4]J. Kopecky and J. Smejkal, *Chem. & Ind.* No. 36, 1529 (1966)
[5]E. A. Arutyunyan, V. I. Gunar, E. P. Gracheva and S. I. Zav'yalov, *Izv. Akad. Nauk SSSR, Ser. Khim.* (2) 445 (1968); *Chem. Abstr.* **69**, 8694u (1968)
[6]E. A. Arutyunyan, V. I. Gunar, E. P. Gracheva and S. I. Zav'yalov, *Ibid.* (3), 655 (1969); *Chem. Abstr.* **71**, 30453h (1969)
[7]E. Z. Arutyunyan, V. I. Gunar and S. I. Zav'yalov, *Ibid.* (12), 2857 (1969); *Chem. Abs.* **72**, 78979g (1970)
[8]E. A. Arutyunyan, V. I. Gunar, E. P. Gracheva, Z. S. Volkova and S. I. Zav'yalov, *Ibid.* (12), 2821 (1969); *Chem. Abstr.* **72**, 78986g (1970)
[9]E. A. Arutyunyan, V. I. Gunar and S. I. Zav'yalov, *Ibid.* (4), 904 (1970); *Chem. Abstr.* **73**, 35322r (1970)
[10]R. S. Monson, D. N. Priest and J. C. Ullrey, *Tetrahedron Letters* 929 (1972) and refes cited
[11]E. B. Pedersen, N. O. Vesterager and S.-O. Lawesson, *Synthesis* 547 (1972)
[12]N. O. Vesterager, R. Dyrnesli, E. B. Pedersen and S.-O. Lawesson, *Ibid.* 548 (1972)
[13]N. O. Vesterager, E. B. Pedersen and S.-O. Lawesson, *Tetrahedron* **29**, 321 (1973)
[14]R. T. Conley and S. Ghosh, *Mechanisms Molecular Migrations* (Edited by B. S. Thyagarajan) Part 4, 197. Wiley-Intersciences (1971)
[15]C. A. Grob, H. P. Fischer, W. Randenbush, and J. Zergenyi, *Helv. Chem. Acta* **47**, 1003 (1964)
[16]G. S. Hammond, O. D. Trapp, R. T. Keys and S. L. Neff, *J. Am. Chem. Soc.* **81**, 4878 (1959)
[17]G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin and R. T. Keys, *Ibid.* **82**, 5394 (1960)
[18]E. B. Pedersen, J. Perregård and S.-O. Lawesson, *Tetrahedron*, **29**, 4211 (1973)
[19]P. Oxley, M. W. Partridge, T. D. Robson and W. F. Short, *J. Chem. Soc.* 763 (1946)
[20]K. Inukai and Y. Maki, *Kogyo Kagaku Zasshi* **67**, 807 (1964); *Chem. Abstr.* **61**, 9418f (1964)
[21]R. R. Heer, T. Enkoji and J. P. Dailey, *J. Am. Chem. Soc.* **79**, 4229 (1957)
[22]S. H. Zaheer and S. A. Faseeh, *J. Indian. Chem. Soc.* **21**, 27 (1944)
[23]J. F. Norris and A. J. Klemka, *J. Am. Chem. Soc.* **62**, 1432 (1940)
[24]P. Malatesta, G. Migliaccio and U. Aliberti, *Farmaco Pavia, Ed. Sci.* **17**, 601 (1962); *Chem. Abstr.* **58**, 1377h (1963)
[25]N. Löfgren and B. Lundqvist, *Svensk Kem. Tid.* **57**, 206 (1946); *Chem. Abstr.* **43**, 1022h (1949)
[26]F. Sachs and P. Steinert, *Ber. Dtsch Chem. Ges.* **37**, 1733 (1904)
[27]G. van Brée, *Bull. Soc. Cheim. Belges* **57**, 71 (1948)