August, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (8), 2013—2016 (1977) 2013

Deoxygenation of Nitrobenzene by Tributylphosphine in the Presence of Alcohols. Synthesis of 2-Alkoxy-3*H*-azepines

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(Received January 5, 1977)

Deoxygenative reduction of nitrobenzene by tributylphosphine in the presence of primary or secondary alcohols gave 2-alkoxy-3*H*-azepines in good yields. The use of acidic hydroxylic compounds, such as phenol or acetylacetone, in place of the alcohols did not lead to ring enlargement. Triphenylphosphine could be used as a reducing agent, but the yields of the azepines were relatively low. 2-Alkoxy-3*H*-azepines were converted into 2-amino-3*H*-azepine in good yields by the reaction with ammonium carbonate. 2,3-Dihydro-1*H*-azepin-2-one was prepared by the hydrolysis of 2-butoxy-3*H*-azepine or 2-amino-3*H*-azepine.

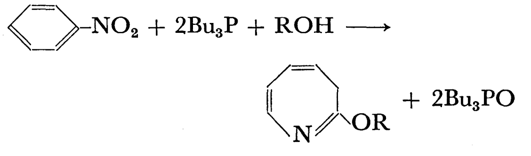
Deoxygenation of nitro- and nitrosobenzene by tervalent phosphorus reagents in the presence of primary or secondary alkylamines results in the ring enlargement giving 2-alkylamino-3*H*-azepines.[1)] Phenylnitrene is postulated as an intermediate for this reaction. It is accepted that nucleophilic attack of amines on 7-azabicyclo[4.1.0]heptatriene, assumed to be in equilibrium with phenylnitrene, leads to ring enlargement.[2)] Such a ring enlargement is also observed in the thermolysis[3)] or photolysis[4)] of phenyl azide and in the photolysis of oxaziridines[5)] or anthranils.[6)] Although the formation of 2-methoxy-3*H*-azepines by photolysis of phenyl azide[7,8)] or anthranils[6)] in methanol is known, no report has appeared on the ring enlargement of nitro- and nitrosobenzene in the presence of alcohols as the nucleophile. Sundberg and Smith, Jr. observed the formation of alkoxyanilines in the deoxygenation of nitrosobenzene by triethyl phosphite in the presence of alcohols.[7,9)]

This paper deals with the deoxygenation of nitrobenzene by tertiary phosphines in the presence of alcohols, providing a convenient method for the preparation of 2-alkoxy-3*H*-azepine, 2,3-dihydro-1*H*-azepin-2-one and several other azepine derivatives in good yields.

Results and Discussion

Tervalent phosphorus reagents for the deoxygenation of nitrobenzene include phosphorus triamide, trialkyl phosphite and phosphonite. Cadogan and Todd studied the order of reactivity of the reagents in the deoxygenation of 2-nitrobiaryl, and observed that tributyl- and triphenylphosphine are not reactive as phosphorus triamide or diethyl methylphosphonite,[1b)] while Odum and Brenner reported the deoxygenative ring enlargement of nitrosobenzene by means of triphenylphosphine in the presence of alkylamines.[1a)] We have confirmed that tributylphosphine and tripiperidinophosphine are most reactive for the deoxygenation of nitrobenzene in piperidine giving 2-piperidino-3*H*-azepine.

When nitrobenzene was treated with tributylphosphine in refluxing 1-butanol for 1 h, 2-butoxy-3*H*-azepine (**1d**) was formed in 89% yield. The structure of **1d** was determined by IR, NMR, and mass spectra as well as elemental analysis. The IR spectrum exhibited a strong intensity band at 1615 cm^{-1} and a medium band at 1515 cm^{-1}, both of which are due to C=C and C=N stretching vibration. The NMR spectrum shows peaks at τ 7.43 (d, 2H), 4.85 (q, 1H), 4.20 (m, 1H), 3.88 (m, 1H), and 3.21 (d, 1H) other than peaks due to protons of butyl group. The peak pattern indicates 3*H*-azepine skelton since it is very close to that reported for 2-diethylamino-3*H*-azepine.[4a)] The mass spectrum of **1d** shows the molecular ion (*m/e* 165) as the highest mass feature, which corresponds to the parent peak of the expected structure.



(1)

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	a	**b**	**c**	**d**	**e**	**f**
R:	Me	Et	*i*-Pr	*n*-Bu	*n*-C_6H_{13}	cyclo-C_6H_{11}

	g	**h**	**i**
R:	*n*-C_7H_{15}	$PhCH_2$	CF_3CH_2

The deoxygenative ring enlargement of nitrobenzene by tributylphosphine was then studied in the presence of various hydroxylic compounds. The results are summarized in Table 1.

Deoxygenation in the presence of primary or secondary alcohols led to ring enlargement to give the corresponding 2-alkoxy-3*H*-azepines (**1**) in moderate or good yields (Eq. 1). Attempted reactions in the presence of tertiary alcohols (2-methyl-2-propanol and 2-phenyl-2-propanol) failed to give the azepine, probably owing to the bulkiness of the nucleophiles. The use of 2,2,2-trifluoroethanol (pK_a 12.3) results in a formation of 2-(2,2,2-trifluoroethoxy)-3*H*-azepine (**1i**) but only in 19% yield.[9)] Phenol (pK_a 9.98) and acetylacetone (pK_a 8.24) were also examined as a nucleophile in the deoxygenation, but no ring enlargement product was obtained.

The results show that hydroxylic compounds whose pK_a value is greater than *ca.* 12 are available as the nucleophiles for the ring enlargement.[10)]

Solvent and temperature effects on the ring enlargement reaction were examined by means of deoxygenation in the presence of benzyl alcohol as a nucleophile. The solvent effect was hardly observed, since the reactions in dioxane, pyridine, 4-methyl-2-pentanone and toluene at the same temperature led to the formation of 2-benzyloxy-3*H*-azepine (**1h**) in nearly equal yields. On the other hand, temperature effect was remarkable. The results of the reactions in xylene at various tempera-

TABLE 1. DEOXYGENATION OF NITROBENZENE BY TRIBUTYLPHOSPHINE IN THE PRESENCE OF HYDROXYLIC COMPOUNDS (ROH)

	Reactants, mmol			Reaction conditions				3*H*-Azepine (Yield, %)	$PhNO_2$ recovered, %
	ROH	$PhNO_2$	Bu_3P	Solvent (ml)	Temp, °C	Time, h	Method[b]		
MeOH	624	75	172		110	25	A	**1a** (60)	0
EtOH	890	25	55		110	30	A	**1b** (71)	0
i-PrOH	400	50	125		120	25	A	**1c** (62)	0
n-BuOH	720	120	240		127—139	4	B	**1d** (89)	6
	150	25	50[a]		120	6.5	B	**1d** (22)	62
t-BuOH	318	50	125		120	25	A	(0)	0
n-$C_6H_{13}OH$	150	25	55	Pyridine (50)	124	10	C	**1e** (66)	—
cyclo-$C_6H_{11}OH$	950	50	105		165	6	B	**1f** (65)	4
n-$C_7H_{15}OH$	705	50	110		160	2	B	**1g** (69)	0
$PhCH_2OH$	600	100	250	Pyridine (200)	120	6	C	**1h** (84)	0
	485	25	62[a]		160	6	B	**1h** (28)	38
$PhC(Me)_2OH$	150	25	55	Xylene (50)	150	5	C	(0)	0
CF_3CH_2OH	150	25	55	Benzene (50)	110	24	A	**1i** (19)	0
PhOH	150	25	55	Pyridine (50)	125	7	C	(0)	0
Acetylacetone	487	25	63		110	7.5	B	(0)	0

a) Triphenylphosphine was used in place of tributylphosphine. b) See Experimental.

TABLE 2. TEMPERATURE EFFECT ON THE FORMATION OF 2-BENZYLOXY-3*H*-AZEPINE (**1h**) IN XYLENE

Reaction conditions		Yield of **1h**, %	$PhNO_2$ recovered, %
Temp, °C	Time, h		
80	20	51	33
100	20	70	16
120	7	76	12
150	3	93	4
180	1	94	5

tures are summarized in Table 2. **1h** was obtained in 99% yield based on nitrobenzene consumed at 180 °C, and in 76% yield at 80 °C. Lowering the reaction temperature decreases the yield of **1h** based on nitrobenzene consumed. This might be related to the fact that the deoxygenation of nitrosobenzene in the presence of methanol at 0 °C gives *o*- and *p*-anisidine.[7]

Triphenylphosphine could also be used in place of tributylphosphine for the deoxygenation of nitrobenzene in the presence of 1-butanol or benzyl alcohol, but the

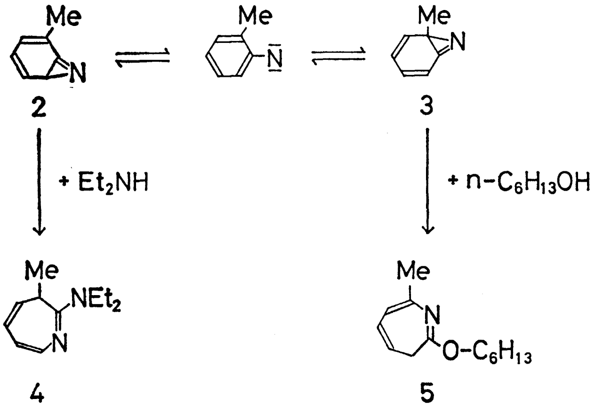
TABLE 3. ANALYTICAL AND SPECTRAL DATA OF 2-ALKOXY-3*H*-AZEPINE (**1**)

	Bp °C/Torr	Found %	Calcd %	IR cm^{-1}	NMR[a] τ	MS *m/e*
a	74—6/32	C, 68.00 H, 7.12 N, 11.40	68.27 7.37 11.37	1620, 1525, 1320, 1250, 1160	7.41(d, 2H), 4.81(q, 1H), 4.14(m, 1H), 3.85(m, 1H), 3.14(d, 1H)	123(M^+), 108(M−Me)
b	105/78	C, 69.98 H, 8.11 N, 10.10	70.04 8.08 10.21	1610, 1525, 1310, 1245, 1205, 1160	7.45(d, 2H), 4.86(q, 1H), 4.20(m, 1H), 3.90(m, 1H), 3.20(d, 1H)	137(M^+), 122(M−Me), 109($M-CH_2{=}CH_2$), 108(M−Et)
c	89/31	C, 71.64 H, 8.65 N, 9.56	71.49 8.67 9.26	1610, 1515, 1310, 1245, 1205, 1160	7.44(d, 2H), 4.81(m, 1H), 4.15(m, 1H), 3.83(m, 1H), 3.15(d, 1H)	151(M^+), 109($M-CH_3CH{=}CH_2$)
d	126/49	C, 72.69 H, 9.16 N, 8.62	72.69 9.15 8.48	1615, 1515, 1325, 1250, 1210, 1165	7.43(d, 2H), 4.85(q, 1H), 4.20(m, 1H), 3.88(m, 1H), 3.21(d, 1H)	165(M^+), 150(M−Me), 136(M−Et), 109($M-CH_2{=}CHEt$)
e	98/3.5	C, 74.56 H, 10.06 N, 7.21	74.57 9.91 7.25	1610, 1525, 1310, 1245, 1205, 1160	7.43(d, 2H), 4.85(m, 1H), 4.19(m, 1H), 3.89(m, 1H), 3.20(d, 1H)	193(M^+), 164(M−Et), 150(M−Pr), 109($M-CH_2{=}CHBu$)
f	104—6/5.5	C, 75.53 H, 10.40 N, 6.70	75.32 10.21 6.76	1610, 1525, 1320, 1245, 1205, 1160	7.42(d, 2H), 4.83(q, 1H), 4.19(m, 1H), 3.88(m, 1H), 3.19(d, 1H)	207(M^+), 109($M-CH_2{=}CHPe$)
g	86/1	C, 75.49 H, 9.18 N, 7.43	75.35 8.96 7.32	1605, 1525, 1325, 1245, 1205, 1160	7.47(d, 2H), 4.90(q, 1H), 4.21(m, 1H), 3.90(m, 1H), 3.21(d, 1H)	
h	173/27	C, 78.10 H, 6.86 N, 7.02	78.36 6.58 7.03	1610, 1525, 1315, 1245, 1205, 1160	7.38(d, 2H), 4.84(q, 1H), 4.16(m, 1H), 3.88(m, 1H), 3.15(d, 1H)	199(M^+), 108($M-PhCH_2$)
i	69/27	C, 50.57 H, 4.44 N, 7.48	50.27 4.22 7.33	1615, 1415, 1330, 1245, 1205, 1160,	7.34(d, 2H), 4.78(q, 1H), 4.08(m, 1H), 3.85(m, 1H), 3.18(d, 1H),	191(M^+), 172(M−F), 108($M-CF_3CH_2$)

a) The peaks due to alkoxy group in 2-position are omitted.

yield of the azepine (**1d** or **1h**) was relatively low.

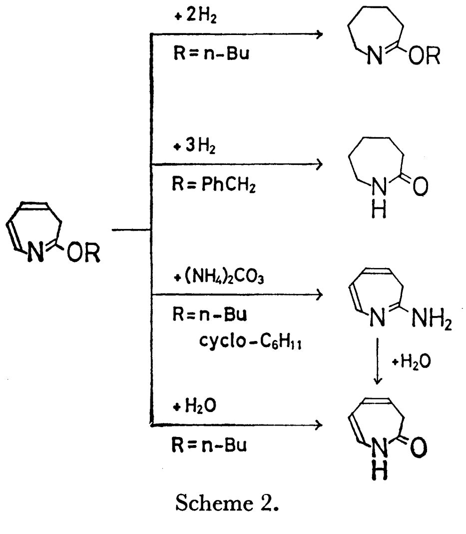
Deoxygenation of 4- and 2-nitrotoluene was also carried out in the presence of 1-hexanol, 5-methyl- (58%), and 7-methyl-2-hexyloxy-3*H*-azepine (**5**, 30%), respectively, being isolated. The position of the methyl group was determined by NMR spectroscopic examination. Although two isomeric products were possible in the deoxygenation of 2-nitrotoluene, no formation of 2-hexyloxy-3-methyl-3*H*-azepine took place. The deoxygenation of 2-nitrotoluene in the presence of diethylamine has been reported to give 2-diethylamino-3-methyl-3*H*-azepine (**4**, 36%) by de Boer *et al.*,[2] who explained the predominant formation of 3-methyl isomer by an attack of a relatively small nucleophile, diethylamine, on 5-methyl-7-azabicyclo[4.1.0]hepta-2,4,6-triene (**2**) which is expected to predominate in the equilibrium with 1-methyl isomer (**3**) of the azabicycle on steric grounds. The formation of **5** is due to the nucleophilic attack of 1-hexanol on the 1-methyl azabicyclic intermediate **3** (Scheme 1) as in the case where the nucleophile is triethyl phosphite.[11]



Scheme 1.

Transformation of 2-alkoxy-3*H*-azepines into some azepine derivatives was examined (Scheme 2).

Hydrogenation of 2-butoxy-3*H*-azepine (**1d**) on palladium-carbon gave 7-butoxy-3,4,5,6-tetrahydro-2*H*-azepine in 80% yield, and the hydrogenation of 2-benzyloxy-3*H*-azepine (**1h**) on the same catalyst gave hexahydro-2*H*-azepin-2-one in 77% yield. 2-Amino-3*H*-azepine was obtained in 90 and 75% yields by the reactions of 2-butoxy (**1d**) and 2-cyclohexyloxy-3*H*-azepine (**1f**), respectively, with ammonium carbonate in methanol, while the reactions of 2-cyclohexyloxy-3*H*-azepine (**1f**) with ammonium acetate and ammonium chloride[12] gave 2-amino-3*H*-azepine in 55 and 5% yields, respectively. Hydrolysis of 2-amino-3*H*-azepine afforded 2,3-dihydro-1*H*-azepin-2-one in 97% yield, which was alternatively obtained in 83% yield by the hydrolysis of 2-butoxy-3*H*-azepine (**1d**) under neutral conditions at 150 °C. The hydrolysis of 2-butoxy-3*H*-azepine hardly proceeds below 100 °C under neutral or alkaline conditions. Mineral acids promote the hydrolysis remarkably but subsequent hydrolysis of the product takes place. Paquette observed that 3,7-dimethyl- or 3,5,7-trimethyl-2,3-dihydro-1*H*-azepin-2-one is readily hydrolyzed under acidic conditions to give dihydro-2(3*H*)-furanones.[13]



Scheme 2.

Experimental

All the organic reagents and solvents were purified by distillation or recrystallization before use, while commercial inorganic materials were used without further purification. All the melting and boiling points were uncorrected. The GLPC analyses were carried out on a Shimadzu GC-4APT instrument with a thermal conductivity detector, using a 20% PEG 20 M on Celite 545 column (2 m; Temp: 180 °C; Carrier gas: He 30 ml/min; Internal standard: biphenyl). IR spectra were measured on a Hitachi G-2 instrument, NMR spectra on a JEOL C-60HL instrument in CCl_4 solution using TMS as an internal standard, and mass spectra on a Hitachi RMU-6E instrument.

Deoxygenation of Nitrobenzene by Tervalent Phosphorus Reagents in the Presence of Piperidine. A solution of nitrobenzene (3.08 g, 25 mmol) in piperidine (10 ml) was added drop by drop to a solution of tripiperidinophosphine[14] (bp 125 °C/0.5 Torr, 14.17 g, 50 mmol) and biphenyl (3.86 g, 25 mmol) in piperidine (40 ml) under reflux in nitrogen atmosphere. After being refluxed for 30 h, the mixture was analyzed by GLPC. 2-Piperidino-3*H*-azepine[1d] was formed in 88% yield.

When tributylphosphine (10.2 g, 50 mmol), triphenylphosphine (13.2 g, 50 mmol), and triethyl phosphite (8.35 g, 50 mmol) were used in place of tripiperidinophosphine, the yields of 2-piperidino-3*H*-azepine were 94, 16, and 24%, respectively.

Deoxygenation of Nitrobenzene by Tervalent Phosphorus Reagents in the Presence of Hydroxylic Compounds. The following three typical procedures are employed depending on the kind of hydroxylic compound or the reaction temperature. The results are summarized in Table 1, the analytical and spectral data of 2-alkoxy-3*H*-azepines (**1**) being given in Table 3.

Method A. A mixture of nitrobenzene (9.23 g. 75 mmol), tributylphosphine (34.89 g, 172 mmol), and methanol (20 g, 624 mmol) was heated in a sealed tube at 110 °C for 25 h and then evaporated by using a rotary evaporator under reduced pressure. Distillation of the residue afforded 2-methoxy-3*H*-azepine (**1a**, 5.5 g, 60%).

Method B. A mixture of nitrobenzene (14.77 g, 120 mmol), tributylphosphine (48.56 g, 240 mmol), and 1-butanol (57 g, 720 mmol) was heated under reflux (127—139 °C) for 4 h. The resulting mixture was stripped of 1-butanol and the product was distilled under reduced pressure. 2-Butoxy-3*H*-azepine (**1d**) was obtained 17.69 g (89%).

Method C. A solution of nitrobenzene (3.08 g, 25 mmol), tributylphosphine (11.13 g, 55 mmol), and 1-hexanol (15.33 g, 150 mmol) in pyridine (50 ml) was refluxed for 7 h. The mixture was fractionated under reduced pressure and the fraction (bp 65.5—146 °C/3.5 Torr, 7.32 g) was subjected to redistillation to yield 2-hexyloxy-3*H*-azepine (**1e**, 3.19 g, 66%).

*2-Hexyloxy-7-methyl-3*H*-azepine (5).* A mixture of 2-nitrotoluene (6.86 g, 50 mmol), tributylphosphine (22.26 g, 110 mmol) and 1-hexanol (100 ml) was heated under reflux for 3.5 h. The resulting mixture was fractionated under reduced pressure and the fraction (bp 53—141.5 °C/4.5 Torr, 21.4 g) was subjected to redistillation to give **5** (3.13 g, 30%): bp 81.5—82.5 °C/1.5 Torr; IR 1610, 1545, 1310, 1260, 1195, and 1150 cm^{-1}; NMR(16) $\tau=7.94$ (s, 3H), 7.45 (d, 2H), 4.95 (m, 1H), 4.31 (d, 1H), and 3.98 (q, 1H). Found: C, 74.71; H, 10.28; N, 6.97%. Calcd for $C_{13}H_{21}NO$: C, 75.36; H, 10.14; N, 6.76%.

*2-Hexyloxy-5-methyl-3*H*-azepine.* A solution of 4-nitrotoluene (6.86 g, 50 mmol) and tributylphosphine (22.35 g. 60 mmol) in hexanol (100 ml) was heated under reflux for 6.5 h. The resulting mixture was distilled and the fraction (bp 117.5—148.5 °C/4.5 Torr, 7.92 g) was subjected to redistillation to give 2-hexyloxy-5-methyl-3*H*-azepine (6.05 g, 58%): bp 97—100 °C/3 Torr; IR 1610, 1535, 1325, 1250, 1195, and 1160 cm^{-1}; NMR(16) $\tau=8.13$ (s, 3H), 7.51 (d, 2H), 5.05 (q, 1H), 4.29 (d, 1H), and 3.28 (d, 1H). Found: C, 75.62; H, 10.40; N, 6.80%. Calcd for $C_{13}H_{21}NO$: C, 75.32; H, 10.41; N, 6.76%.

*Hydrogenation of 2-Butoxy-3*H*-azepine (**1d**).* 2-Butoxy-3*H*-azepine (**1d**, 6.73 g, 41 mmol) was hydrogenated at room temperature in 1-butanol (40 ml) with palladium catalyst (10% on carbon, 1.6 g) at an initial hydrogen pressure of 65 kg/cm^2. Hydrogenation was completed in 15 min. The catalyst and solvent were removed and the product was distilled to give 7-butoxy-3,4,5,6-tetrahydro-2*H*-azepine (3.8 g, 80%): bp 128—128.5 °C/48 Torr (lit, 214—216 °C;(15a) 80 °C/3.5 Torr,(15b) Found: C, 71.19; H, 11.25; N, 8.31%).

*Hydrogenation of 2-Benzyloxy-3*H*-azepine (**1h**).* Hydrogenation of **1 h** (4.96 g, 25 mmol) was performed in toluene (40 ml) with palladium catalyst (10% on carbon, 1.33 g) at 80 °C for 2.5 h, the initial hydrogen pressure being 70 kg/cm^2. Removal of the catalyst and solvent gave crude hexahydro-2*H*-azepin-2-one (2.61 g, 92%). The crude substance was dissolved in diisopropyl ether (60 ml) and extracted with water (50 ml × 10). The combined extracts were concentrated to *ca.* 45 ml and extracted with chloroform (40 ml × 7). The combined extracts were dried over anhydrous sodium sulfate and evaporated to give hexahydro-2*H*-azepin-2-one (mp 67—69.5 °C, 2.18 g, 77%), which was identified by comparing its retention time in GLPC and its IR spectrum with those of an authentic sample.

*6-Amino-3*H*-azepine.* A solution of 2-butoxy-3*H*-azepine (**1d**, 3.3 g, 20 mmol) and commercial ammonium carbonate (2.3 g) in methanol (50 ml) was kept at 40 °C for 3 days. The mixture was concentrated under reduced pressure and the residue was treated with benzene (100 ml) and the precipitate was removed by filtration. The filtrate was evaporated to give crude 2-amino-3*H*-azepine (1.94 g, 90%). Sublimation at 90 °C and 1 Torr yielded 1.74 g (81%) of 2-amino-3*H*-azepine: mp 90—91 °C (lit,(4a) 90—91 °C, Found: C, 66.40; H, 7.25; N, 25.69%).

2-Amino-3*H*-azepine was isolated by treatment of 2-cyclohexyloxy-3*H*-azepine (**1f**, 3.3 g, 17 mmol) with commercial ammonium carbonate (1.95 g) in methanol (50 ml) at room temperature for 4 days, treatment of **1f** (3.83 g, 20 mmol) with ammonium acetate (3.09 g, 40 mmol) in methanol (50 ml) at room temperature for 6 days, and treatment of **1f** (2.92 g, 15 mmol) with ammonium chloride (1.63 g, 30 mmol) in methanol (50 ml) at room temperature for 9 days in 75, 55, and 5% yields, respectively.

*2,3-Dihydro-1*H*-azepin-2-one.* *a) Hydrolysis of 2-Amino-3*H*-azepine*: A solution of 2-amino-3*H*-azepine (1.5 g, 14 mmol) in water (40 ml) was refluxed for 5 h, treated with aqueous hydrochloric acid (3 drops of a 3M solution), and extracted with chloroform (30 ml × 10). The combined extracts were concentrated to give 2,3-dihydro-1*H*-azepin-2-one (1.47 g, 97 %): mp 48—49 °C. Recrystallization from hexane afforded colorless crystals: mp 49—50 °C (lit, 48—50 °C;(17) 47.5—48.5 °C,(4a) Found: C, 66.06; H, 6.38; N, 12.91%).

*b) Hydrolysis of 2-Butoxy-3*H*-azepine (**1d**)*: A mixture of **1d** (4.6 g, 28 mmol), ethanol (36 ml), and water (10 ml) was heated at 150 °C in a stainless steel autoclave for 3.5 h. The mixture was stripped of ethanol, water, and 1-butanol and the oily residue was dissolved in diethyl ether (50 ml). The solution was extracted with water (40 ml × 7) and the combined extracts were concentrated to give crude 2,3-dihydro-1*H*-azepin-2-one (2.52 g, 83%). Recrystallization from cyclohexane afforded colorless crystals of mp 48—50 °C, which showed no depression on admixture with the sample obtained above.

References

1) a) R. A. Odum and M. Brenner, *J. Am. Chem. Soc.*, **88**, 2074 (1966); b) J. I. G. Cadogan and M. J. Todd, *J. Chem. Soc., C*, **1969**, 2808; c) R. J. Sundberg, B. P. Das, and R. H. Smith, Jr., *J. Am. Chem. Soc.*, **91**, 658 (1969); d) F. R. Atherton and R. W. Lambert, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 1079.

2) T. de Boer, J. I. G. Cadogan, H. M. McWilliam, and A. G. Rowley, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 554.

3) a) R. Huisgen, D. Vossius, and M. Appl, *Chem. Ber.*, **91**, 1 (1958); b) M. Appl and R. Huisgen, *ibid.*, **92**, 2961 (1959).

4) a) W. von E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966); b) R. K. Smalley and H. Suschitzky, *J. Chem. Soc., Suppl.*, **1964**, 5922.

5) a) E. Mayer and G. W. Griffin, *Angew. Chem.*, **79**, 648 (1967); b) H. Shindo and B. Umezawa, *J. Pharm. Soc. Jpn.*, **1**, 492 (1962).

6) M. Ogata, H. Kano, and H. Matsumoto, *J. Chem. Soc., Chem. Commun.*, **1968**, 397; M. Ogata and H. Matsumoto, *Tetrahedron*, **25**, 5205 (1969).

7) R. J. Sundberg and R. H. Smith, Jr., *J. Org. Chem.*, **36**, 295 (1971).

8) A. C. Mair and M. F. G. Stevens, *J. Chem. Soc., C*, **1971**, 2317.

9) Deoxygenation of nitrosobenzene with triethylphosphite in the presence of trifluoroethanol gives 2′,2′,2′-trifluoro-*p*-phenethidine (21%) and 1-phenyl-1*H*-azepine (34%); R. J. Sundberg and R. H. Smith, Jr., *Tetrahedron Lett.*, **1971**, 267.

10) Deoxygenation of nitrobenzene with triphenylphosphine in hydrogen fluoride gives *p*-fluoroaniline; P. H. Scott, C. P. Smith, E. Kober, and J. W. Churchill, *Tetrahedron Lett.*, **1970**, 1153.

11) a) J. I. G. Cadogan, R. K. Mackie and M. J. Todd, *Chem. Commun.*, **1968**, 736; b) J. I. G. Cadogan, D. J. Sears, D. M. Smith, and M. J. Todd, *J. Chem. Soc., C*, **1969**, 2813.

12) Ammonium chloride is an effective reagent for the amination of 7-methoxy-3,4,5,6-tetrahydro-2*H*-azepine; R. E. Benson and T. L. Cairns, *J. Am. Chem. Soc.*, **70**, 2115 (1948).

13) L. A. Paquette, *J. Am. Chem. Soc.*, **85**, 3288 (1963).

14) M. Luyembourg, *Ber.*, **28**, 2207 (1895).

15) a) Ger. Patent 488447 (1926); *Chem. Abstr.*, **27**, 994^1 (1933); b) U. S. Patent 2516293 (1950); *Chem. Abstr.*, **45**, 640 g, (1951).

16) The peaks due to alkoxy group in 2-position are omitted.

17) E. Vogel and R. Erb, *Angew. Chem. Int. Ed. Engl.*, **1**, 53 (1962).