TABLE III

SYMMETRICAL CARBONATES $ROCO_2R$

R	B.P.	M.P.	n_D^{25}	Analysis Calcd. C	Calcd. H	Found C	Found H
$C_6H_5OCH_2CH_2$—	180–183° (0.4 mm.)	92–93°		67.6	6.0	67.5	5.8
$C_6H_5(CH_2)_3$—	176° (0.4 mm.)		1.5318	76.5	7.4	76.9	6.9
$C_4H_7OCH_2$—[a]	114°		1.4658	55.5	7.5	55.9	7.7

[a] Tetrahydrofurfuryl.

and the mixture was washed successively with water, dilute hydrochloric acid, water, dilute sodium carbonate, and water. The organic material was dried over calcium chloride and distilled to give 658 g. (76.0% of theoretical) of ethyl tetrahydrofurfuryl carbonate. The physical properties are listed in Table II.

Table III summarizes the properties of new symmetrical carbonates isolated from the disproportionation reactions of the unsymmetrical carbonates.

Catalysts. The catalysts were prepared or purified in a nitrogen atmosphere under dry conditions.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, MCLAUGHLIN GORMLEY KING CO.]

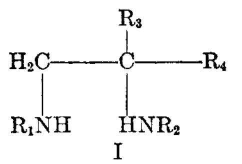
5-Membered Heterocyclic Compounds Derived from Piperonal. I. A Study of the Reactions between Piperonal and 1,2-Diamines

PETER F. EPSTEIN

Received August 19, 1958

A number of 1,2-diamines were allowed to react with piperonal. The nature of the products obtained varied with the type of amine used. When both the amine groups were primary, a di-Schiff's base was formed; with one primary and one secondary amine group the product was an imidazolidine; while in the case of a di-secondary amine there was either no reaction or an imidazolidine was formed, depending on the nature of the substituent groups.

Riebsomer[1] described the formation of some imidazolidines derived from benzaldehyde and furfural. Other workers[2–6] have reported similar results. It seemed to the author to be of interest to discover if the less reactive piperonal would behave in a similar manner, and accordingly attempts were made to condense piperonal with a number of 1,2-diamines of the general Formula I.



$$\begin{array}{ccc} & R_3 & \\ & | & \\ H_2C & —C— & R_4 \\ | & | & \\ R_1NH & HNR_2 & \end{array}$$

I

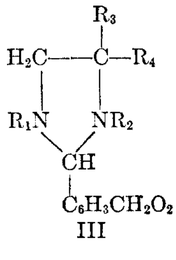
In the simplest case of all, using 1,2-diaminoethane (I; $R_1 = R_2 = R_3 = R_4 = H$) the only product which could be isolated was the di-Schiff's base *N,N'*-di(3,4-methylenedioxybenzal)-1,2-diaminoethane (II).

$CH_2O_2C_6H_3CH{=}NCH_2CH_2N{=}CHC_6H_3CH_2O_2$

II

This result was obtained regardless of the proportions of reagents used, and in no case could any of the imidazolidine be isolated. These findings agree with the work of van Alphen[5] regarding the corresponding benzaldehyde compounds.

In the case of diamines with one primary and one secondary group, of the type used by Riebsomer[1] the reaction proceeded smoothly to give imidazolidines. Thus, for example, N_1-phenyl-2-(3,4-methylenedioxyphenyl)-4,4-dimethylimidazolidine.



III

(II; R_1 = Ph, R_2 = H, $R_3 = R_4$ = Me) was prepared in 89% yield from piperonal and 1-phenyl-

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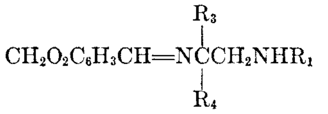
(1) J. L. Riebsomer, *J. Org. Chem.*, **15**, 237 (1950).
(2) F. Moos, *Ber.*, **20**, 732 (1887).
(3) C. A. Bischoff, *Ber.*, **31**, 3248 (1898).
(4) M. Scholtz and K. Jaross, *Ber.*, **34**, 1504 (1901).
(5) J. van Alphen, *Rec. Trav. Chim.*, **54**, 93 (1935).
(6) W. L. C. Veer, *Rec. Trav. Chim.*, **57**, 989 (1938).

amino-2,2-dimethyl-2-aminoethane (I; $R_1 = Ph$, $R_2 = H$, $R_3 = R_4 = Me$).

The compounds formed in this manner were colorless crystalline solids with well-defined melting points. Their identity as imidazolidines [rather than the corresponding mono Schiff's bases of (IV), having identical empirical formulas], was established partly by analogy with the results of Riebsomer[1] and partly by their stability to reduction with sodium and ethanol. Lob[7] showed that under these conditions Schiff's bases are reduced to secondary amines while imidazolidines are not affected. In the present investigation the presumed imidazolidines were recovered unchanged after treatment with sodium and ethanol, which is in accordance with the above findings.



$$CH_2O_2C_6H_3CH{=}N\overset{R_3}{\underset{R_4}{C}}CH_2NHR_1$$

IV

It was found impossible to prepare derivatives (*e.g.* benzoyl or acetyl) of these imidazolidines for further investigation. This also agrees with the experiences of Riebsomer.[1]

In the case of diamines with two secondary amine groups (I, $R_1 = R_2$ = alkyl, cycloalkyl, aryl or aralkyl, $R_3 = R_4 = H$) the results varied. When R_1 and R_2 are aryl, aralkyl, or cycloalkyl groups (*e.g.* phenyl, benzyl, 3,4-methylenedioxybenzyl, or cyclohexyl) the corresponding imidazolidines were formed as expected. (It is to be noted that in this case there is no possibility of Schiff's base formation.) When R_1 and R_2 were simple alkyl groups, however, no reaction occurred under the conditions used for this series of experiments. In these cases the starting materials were recovered unchanged in all experiments with the exception of one in which *N,N'*-di-*n*-butyl-1,2-diaminoethane (I, $R_1 = R_2 = n\text{-}Bu$; $R_3 = R_4 = H$) was used. This led to a compound whose melting point was much higher than expected for an imidazolidine; and which was shown by element analysis to be definitely not the desired compound. Its nature was not further investigated.

The di-secondary amines used in these experiments were prepared either by hydrogenation of the corresponding di-Schiff's base[7,8] (itself prepared by condensing the appropriate aldehyde with 1,2-diaminoethane) or by treating a suitable primary amine with 1,2-dichloroethane[9] or 1,2-dibromoethane.[10]

EXPERIMENTAL

All melting points are uncorrected. Microanalyses by Clark Microanalytical Laboratory, Urbana, Ill.

A. Amine with two primary amine groups.

N,N'-di(3,4-methylenedioxybenzal)1,2-diaminoethane. A solution of piperonal (30 g.) and 1,2-diaminoethane monohydrate (7.8 g.) in ethanol (50 ml.) was heated under reflux for 1 hr. On cooling, white crystals of the Schiff's base were formed, and were filtered off and dried. Yield 33.2 g. = 95%, m.p. 178–179° (from ethanol).

Anal. Calcd. for $C_{18}H_{16}N_2O_4$: C, 66.67; H, 4.94; N, 8.64. Found: C, 66.57; H, 4.96; N, 8.86.

In similar experiments performed as above but using twice and four times the above quantities of 1,2-diaminoethane monohydrate only the same compound was isolated, and in each case 95% of the piperonal used could be accounted for as the Schiff's base.

B. Amines with one primary and one secondary amine group. One example will suffice to illustrate the method of preparation of the imidazolidines listed in Table I.

N_1-isopropyl-2-(3,4-methylenedioxyphenyl)-4,4-dimethylimidazolidine (III, $R_1 = i\text{-}Pr$, $R_2 = H$, $R_3 = R_4 = Me$). A mixture of 1-isopropylamino-2,2-dimethyl-2-aminoethane (26 g.), piperonal (30 g.) and benzene (100 ml.) was heated together under reflux. The vapors were passed through a Dean-Stark water separator reflux head inserted between the reaction vessel and the condenser, thus enabling the water formed in the reaction to be collected and measured. The reaction was continued until the theoretical amount of water was evolved (2 hr.) The benzene was removed and the residue distilled, b.p. 157°/6 m.m. The distillate solidified to a waxy solid m.p. 37°–38°, soluble in all the usual organic solvents but insoluble in water. Yield 52.6 g. (quantitative).

Anal. Calcd. for $C_{15}H_{22}N_2O_2$: C, 68.67; H, 8.45; N, 10.68. Found: C, 68.65; H, 8.44; N, 10.51.

In the case of the other compounds listed in Table I, the products solidified as soon as the benzene was removed and distillation was not necessary. They were recrystallized from ethanol.

C. Amines with two secondary amine groups. Those imidazolidines listed in Table I which were prepared from disecondary amines were made as in the example quoted. In addition, the following di-secondary amines were treated with piperonal under the same conditions as above. In each case only the starting materials were recovered: *N,N'*-diethyl-1,2-diaminoethane, *N,N'*-di*iso*propyl-1,2-diaminoethane, *N,N'*-diallyl-1,2-diaminoethane, *N,N'*-di-*tert*-butyl-1,2-diaminoethane, *N,N'*-di(2-ethyl-butyl)-1,2-diaminoethane.

In the further case of *N,N'*-di-*n*-butyl-1,2-diaminoethane, also treated as in the example quoted, a solid of m. p. 179° (after purification) was formed.

Anal. Calcd. for $C_{18}H_{28}N_2O_2$: C, 71.02; H, 9.27; N, 9.20. Found: C, 66.72; H, 4.90; N, 8.59. This is obviously not the desired imidazolidine. The nature of this compound was not further investigated.

The di-secondary amines required were prepared either by the reduction of the corresponding Schiff's base[7,8] (Method 1) or by the action of the appropriate primary amine on an ethane-1,2-dichloride[9,10] (Method 2). They are listed in Table II.

One example will suffice to illustrate the method of preparation of these disecondary amines by Method 1. *N,N'-dibenzyl-1,2-diaminoethane*[7] (I, $R_1 = R_2 = —CH_2C_6H_5$; $R_3 = R_4 = H$). A solution of *N,N'*-dibenzal-1,2-diaminoethane[8] (19.3 g.) in methanol (50 ml.) was mixed with a catalyst consisting of a 10% suspension of palladium black on barium sulphate (5 g.) and hydrogenated with shaking at room temperature and an initial hydrogen pressure of 40 p.s.i.. When the reduction was complete (3 hr.) the catalyst was filtered off, the methanol removed, and the residue distilled, b. p. 203°C./2 m.m. Yield 17.1 g. = 87.1%.

Attempted benzoylation of an imidazolidine. N_1-isopropyl-2-(3,4-methylenedioxyphenyl)-4,4,-dimethyl-imidazolidine (III, $R_1 = i\text{-}Pr$, $R_2 = H$, $R_3 = R_4 = Me$) was treated with benzoyl chloride under the normal conditions of the Schotten-Baumann reaction. The only product formed was the

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(7) G. Lob, *Rec. Trav. Chim.*, **55**, 859 (1936).

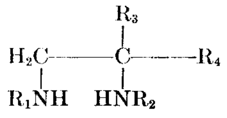
(8) A. Mason, *Ber.*, **20**, 270 (1887).

(9) G. H. Bennett, *J. Chem. Soc.*, **576** (1919).

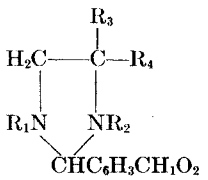
(10) W. R. Boon, *J. Chem. Soc.*, 307 (1947).

TABLE I

IMIDAZOLIDINES



I

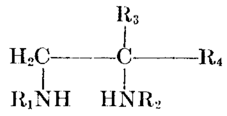


III

A. Amine Used	Radicals in I & III above				Formula of Product	M.P. °C.	Yield, %	Analysis					
								C		H		N	
	R_1	R_2	R_3	R_4				Calcd.	Found	Calcd.	Found	Calcd.	Found
a. Primary-secondary amines													
1-Isopropylamino-2,2-dimethyl-2-aminoethane	Isopropyl	H	Me	Me	$C_{15}H_{22}N_2O_2$	37–38	Quant.	68.67	68.65	8.45	8.44	10.68	10.5
1-Phenylamino-2,2-dimethyl-2-aminoethane	Phenyl	H	Me	Me	$C_{18}H_{20}N_2O_2$	102	89.0	72.95	72.81	6.80	6.86	9.45	9.45
1-(2-Hydroxyethylamino)-2,2-dimethyl-2-aminoethane	$HOCH_2CH_2$	H	Me	Me	$C_{14}H_{20}N_2O_3$	81–82	91.6	63.62	63.36	7.63	7.56		
1-(2-Hydroxypropylamino)-2,2-dimethyl-2-aminoethane	$HOCH(CH_3)CH_2$—	H	Me	Me	$C_{15}H_{22}N_2O_3$	89–90	93.0	64.72	64.55	7.97	7.80	10.06	9.75
1-(1,1-Dimethyl-2-hydroxyethylamino)-2,2-dimethyl-2-aminoethane	$HOCH_2CMe_2$	H	Me	Me	$C_{16}H_{24}N_2O_3$	78	77.0	65.73	65.56	8.27	8.25	9.58	9.44
b. Di-secondary amines													
N,N'-diphenyl-1,2-diaminoethane	Phenyl	Ph	H	H	$C_{22}H_{20}N_2O_2$	155	Quant.	76.72	76.85	5.85	5.71	8.13	8.17
N,N'-dicyclohexyl-1,2-diaminoethane	Cyclohexyl	Cyclohexyl	H	H	$C_{22}H_{32}N_2O_2$	120	86.0	74.12	73.97	9.05	8.85	7.86	7.76
N,N'-dibenzyl-1,2-diaminoethane	Benzyl	Benzyl	H	H	$C_{24}H_{24}N_2O_2$	112	Quant.	77.39	77.59	6.49	6.27	7.52	7.32
N,N'-di(3,4-methylene dioxybenzy)-1,2-diaminoethane	3,4-Methylenedioxybenzyl	3,4-Methylenedioxybenzyl	H	H	$C_{26}H_{24}N_2O_6$	155–156	Quant.	67.82	67.91	5.25	5.04	6.08	6.28

TABLE II

DI-SECONDARY AMINES



$$H_2C\text{—}C(R_3)(NHR_2)\text{—}R_4 \quad (R_1NH \text{ on } H_2C)$$

I

Amine	Method of Preparation	Schiff's Base M.P., ° C.	Dihalide Used	Over-all Yield, %	B. P., ° C.	R in I: R₁	R₂	R₃	R₄
N,N'-dibenzyl-1,2-diaminoethane	1	57–58	. . .	87.1	203/2 m.m.	—CH$_2$Ph	—CH$_2$Ph	H	
N,N'-di-(3,4-methylenedioxybenzyl)-1,2-diaminoethane	1	178–179	. . .	76.3	45[a]	—CH$_2$C$_6$H$_3$CH$_2$O$_2$	—CH$_2$C$_6$H$_3$CH$_2$O$_2$	H	
N,N'-di-*n*-butyl-1,2-diaminoethane	1[b]	184/18 m.m.[c]	. . .	86.5	265/760 m.m. 167/40 m.m.	*n*-Bu	*n*-Bu	H	H
N,N'-di-ethyl-1,2-diaminoethane	1[d]	Not isolated	. . .	40.3	60/8 m.m.	Et	Et	H	H
N,N'-di-cycohexyl-1,2-diaminoethane	2	. . .	1-2-Dibromo-ethane	59.3	89[a]	Cyclohexyl	Cyclohexyl	H	H
N,N'-diphenyl-1,2-diaminoethane	2	. . .	1-2-Dichloro-ethane	89.9	64–64.5	Ph	Ph	H	
N,N'-di-*iso*propyl-1,2-diaminoethane	2	. . .	1-2-Dibromo-ethane	62.0	169–173/750 m.m.	*i*-Pr	*i*-Pr	H	H
N,N'-diallyl-1,2-diaminoethane	2	. . .	1-2-Dibromo-ethane	64.2	198–201/760 m.m.	Allyl	Allyl	H	H
N,N'-di-(2-ethyl-butyl)-1,2-diaminoethane	2	. . .	1-2-Dibromo-ethane	38.0	116/5 m.m.	—CH(Et)C$_3$H$_7$	—CH(Et)C$_3$H$_7$	H	H
N,N'-di-*tert*-butyl-1,2-diaminoethane	2	. . .	1-2-Dibromo-ethane	61.0	193/760 m.m.	*tert* Bu	*tert* Bu	H	H

[a] M. p. [b] Using butyraldehyde. [c] B. p. [d] Using acetaldehyde.

dibenzoyl derivative of 1-isopropylamino-2,2-dimethyl-2-aminoethane with m.p. 146°. It gave a mixed m.p. 146° with an authentic sample. (Riebsomer[1] gives m.p. 146°–147°.)

Attempted acetylation of an imidazolidine. N_1-isopropyl-2-(3,4-methylenedioxyphenyl)-4,4-dimethyl-imidazolidine (III, R_1 = *i*-Pr, R_2 = H, R_3 = R_4 = Me) was treated with acetyl chloride under the usual conditions for acetylating an amine. No solid product could be isolated. The mixture, even −10°, formed a sticky tar which decomposed on attempted distillation.

Attempted hydrogenation of an imidazolidine using sodium and ethanol. To a solution of N_1-phenyl-2-(3,4-methylenedioxyphenyl)-4,4-dimethyl-imidazolidine (III, R_1 = Ph, R_2 = H, R_3 = R_4 = Me) (29.6 g.) in very dry ethanol[11] (250 ml.) was added sodium (9.2 g.) in large pieces at such a rate that a vigorous reflux was maintained. When all the sodium had been added and the reaction began to subside, the mixture was heated under gentle reflux till the last traces of sodium dissolved (30 min.). The mixture was cooled and poured on to ice (250 g.) and the alcohol removed under reduced pressure at 40°. On cooling white crystals (27.3 g.) were formed, which after purification melted at 102°. Mixed m.p. with starting material 102°; showing that only the unchanged starting material could be recovered.

Acknowledgment. The author is pleased to express his appreciation to the Research Laboratory of Commercial Solvents Corporation for the generous gift of samples of some of the 1,2-diamines used in this investigation.

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(11) H. Lund and J. Bjerrum, *Ber.*, 64B, 210 (1931).

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF CHICAGO]

Metal Salt–Induced Homolytic Reactions. I. A New Method of Introducing Peroxy Groups into Organic Molecules[1,2]

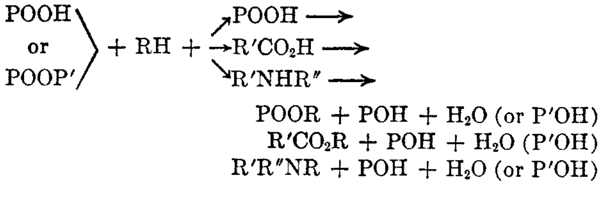
M. S. KHARASCH[3] AND ANDREW FONO[4]

Received July 30, 1958

A new and general method for the introduction of alkyl and aralkyl peroxy groups (ROO) into many types of organic molecules has been developed. This is accomplished by the use of a hydroperoxide and a copper, cobalt, or manganese salt catalyst. The versatility of this method is indicated by the fact that compounds of such diverse structure as cyclohexene, octene-1, cumene, α-methylcyclohexanone, cyclohexanone, dimethylaniline, xylene, and dioxane give good to excellent yields of the unsymmetrical peroxides.

Work done at this laboratory indicates that the metal-induced reaction of a hydroperoxide with organic compounds is as effective in introducing ROO groups as *N*-bromosuccinimide is in introducing bromine atoms into organic molecules. The two reactions are similar as both require an initiator and proceed by a free radical chain reaction. This similarity does not hold for the reactions in which the bromination by *N*-bromosuccinimide proceeds by an ionic mechanism, *e.g.*, the nuclear bromination of aromatic compounds.

Subsequent publications will extend this reaction to the introduction of acyloxy and imido groups:



$$\left.\begin{matrix}\text{POOH}\\ \text{or}\\ \text{POOP}'\end{matrix}\right\rangle + \text{RH} + \begin{matrix}\nearrow \text{POOH} \longrightarrow\\ \rightarrow \text{R}'\text{CO}_2\text{H} \longrightarrow\\ \searrow \text{R}'\text{NHR}'' \longrightarrow\end{matrix}$$

$$\begin{matrix}\text{POOR} + \text{POH} + \text{H}_2\text{O (or P}'\text{OH)}\\ \text{R}'\text{CO}_2\text{R} + \text{POH} + \text{H}_2\text{O (P}'\text{OH)}\\ \text{R}'\text{R}''\text{NR} + \text{POH} + \text{H}_2\text{O (or P}'\text{OH)}\end{matrix}$$

All of these reactions are promoted by copper salts, but most of them occur, to some extent, even in their absence. This study deals with reactions where the main function of the metal salts is only to initiate the decomposition of the hydroperoxides. Subsequent publications will discuss reactions where the metal salts also react with the free radicals initially formed, to alter the course of the reaction.

It has been previously shown that:

(*a*) If reactive free radicals are generated in a solution of *tert*-butyl hydroperoxide in cumene, *tert*-butyl-α-cumyl peroxide is formed. The free radicals were generated by the termal decomposition of acetylperoxide.[5a]

(*b*) Cobalt salts catalyze the decomposition of hydroperoxides, causing the formation of reactive free radicals.[5b]

(*c*) In the presence of a reactive substrate like cyclohexene[5c] or tetralin,[5d] cobalt salts catalyze the reaction of the hydroperoxides with the substrate to form peroxides.

The present work indicates that by careful choice of the catalyst and the reaction conditions, these reactions can be made very general and almost quantitative.

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(1) Previous communication, M. S. Kharasch and A. Fono, *J. Org. Chem.*, 23, 324 (1958).

(2) This work was made possible through the generous support of O. B. May, Inc. Newark, N. J.

(3) Deceased.

(4) Present address: Firestone Chemical and Physical Research Laboratories, Akron, Ohio.

(5) (a) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, 15, 753 (1950). (b) M. S. Kharasch, A. Fono, W. Nudenberg, and B. Bischof, *J. Org. Chem.*, 17, 207 (1952). (c) M. S. Kharasch, P. Pauson, and W. Nudenberg, *J. Org. Chem.*, 18, 322 (1953). (d) W. Treibs and G. Pellmann, *Ber.*, 87, 1201 (1954).