

On the Beckmann Rearrangement, XIV. Distillation of the Sodium Salts of Oximes under Reduced Pressure.

By

Shigeru Komatsu and Teikichi Hiraidzumi.

(Received March 23, 1925)

Benzophenone oxime when heated alone above its melting point decomposes into benzophenone and diphenylmethane imine¹ while its hydrochloride and acetyl esters² which contain the acyloxyl radical derived from a strong acid, suffer by heat to rearrange into its isomeric benzanilide. According to Mignonac³, the oxime by reduction at ordinary temperature, in presence of reduced nickel, was converted into diphenyl methane imine. Recently, S. Yamaguchi⁴ in our laboratory observed that the same oxime, when it came into contact with reduced copper heated at 200° in an atmosphere of hydrogen, was converted into benzophenone, diphenyl methane imine, diphenyl methane and tetraphenyl ethane, and other ketone oximes such as the oxime of acetophenone, camphor and dibenzyl ketone by the same treatment as in the case of the benzophenone oxime, suffers to decompose into the corresponding acid amide, nitrile, carboxylic acid and ketone.

As a consequence of the observations by Hollemann, Lachman and Kuhara, it was expected that the ketoximes, when brought into contact

1 Hollemann: *Rec. trav. Chim.*, **13**, 429 (1894); A. Lachman: *J. Am. Chem. Soc.*, **46**, 1477 (1924).

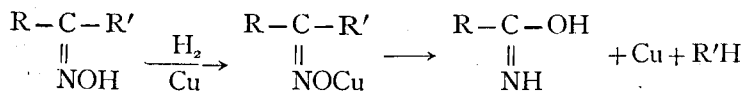
2 M. Kubara, N. Agatsuma and K. Araki: *These Memoirs*, **3**, 1 (1917).

3 *C. R.* **169**, 237 (1919).

4 *These Memoirs*: **7**, 281 (1924).

action with reduced copper in an atmosphere of hydrogen, would suffer either decomposition into the ketone and the ketimine, or rearrangement into its isomeric acid amide. The formation of these compounds indicated by Yamaguchi, being contrary to our expectation, would not be explained entirely by the analogy of the chemical behavior of reduced copper and reduced nickel and also by referring to the behavior of the oximes toward heat. With regard to the formation of acid amides and nitriles from oximes we have, however, no definite knowledge, though it might be explained in the following way, as one of the authors (S. K.) and M. Kurata have conjectured, that the nitriles resulted from the acid amides by the contact action of reduced copper, but the origin of the acid amide has remained still in obscurity. For obtaining more definite knowledge on the formation of the acid amide and the nitrile from the oxime, the authors have started the present experiment to ascertain whether the nitrile would be formed by the contact action of the metal on an acid amide which resulted from an oxime by virtue of the same catalyst or by other chemical reactions.

In the catalytic action of reduced copper, it was supposed by the authors that an oxime when passed in a vapor state over the finely divided metal, according to the recent view of contact action¹, would be condensed in a thin layer on the surface of the catalyst, and temporarily form a copper salt, though its combination was in a labile state, and the oxime regenerated from the compound by dissociation into its components was then evaporated on the metal, whereupon it suffers the chemical changes mentioned above, which will be illustrated in the following scheme :



For confirmation of the above idea, the authors have endeavoured to distil a sodium salt of the oximes (aldo and ketoximes) under reduced pressure with the expectation of obtaining reaction products similar to those obtained by the contact action of reduced copper, since metallic copper was sometimes regarded² to act like the monad sodium as these metals were arranged in the same column in the periodic system of the elements.

-
- 1 E. F. Armstrong and T. P. Hilditch: Fourth Report on Colloid Chemistry, 343 (1922);
W. C. Mc. Lewis: A. System of Physical Chemistry, I, 469 (1920).
2 Refer. H. Collins: Chem. News, **129**, 157 (1924) (S. K.).

The sodium salt of the benzophenone oxime prepared according to the method proposed by E. Spiegler¹, was suddenly heated to a high temperature in a flask connected by a delivery tube to two receivers arranged in series and cooled with ice-water, by dipping the flask in a nitre bath heated at 45°, the first receiver was an empty flask and the second one contained dilute hydrochloric acid to absorb the basic volatile substances generated by the reaction.

The pressure of the apparatus was kept at 12 mm. throughout the reaction by means of a pump. The oxime salt melted at 180°, and then a yellow tarry matter began to distil at about 220°, and the reaction was completed in a few minutes, leaving a coke-like substance in the distilling flask. On opening the apparatus the presence of ammonia in the reaction product was perceived by its odour. The reaction product was treated with ether to separate into an aqueous alkaline solution and the ether soluble substance. From the aqueous solution a phenolic compound, together with benzophenone oxime which escaped from the reaction, was isolated, and this showed a colour reaction with ferric chloride, similar to that of phenol. The tarry reaction product was obtained from the ethereal solution after evaporating off the solvent, which was subjected to fractional distillation.

The fraction B. p. 187-190°, forming the main part of the product, was confirmed to be composed of benzonitrile by analysis after it was purified: C=81.28; H=4.87; theory requires C=81.55 H=4.85. for C₆H₅CN. Some ammonium chloride was isolated from the second receiver and benzophenone oxime was also found in the residue in the flask and confirmed to be so by determination of its melting point, [140°]. No aniline or acid amide could be isolated from the reaction product.

Acetophenone oxime and camphor oxime were changed into their sodium salts; the former salt was prepared from the oxime and metallic sodium and was confirmed to have the composition (C₆H₅)(CH₃)NONa. H₂O by determination of the content of the sodium giving Na=12.85, theory requiring Na=13.14, and the latter salt was prepared from d-camphor oxime $[\alpha]_D^{25} = -40.66$ in an alcohol solution, following the direction by Nägeli².

Both salts were then subjected to distillation separately in a flask under 15 mm. pressure. Benzoic acid [M. p. 120-121°], acetophenone, acetophenone oxime, benzonitrile, ammonia, a nitrogenous compound [M.

1 Ber. D. Chem. Ges., 17, 810 (1884).

2 Ibid., 16, 298 (1883).

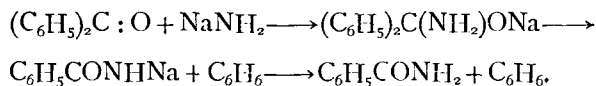
p. 186-196°] and a basic compound were isolated from the reaction product of the acetophenone oxime. The acid was identified by analysis; C=68.52; H=5.63; theory requiring C=68.85; H=4.92 for $C_7H_6O_2$, and the nitrile was confirmed by saponification into benzoic acid and ammonia, due to the difficulty of separating the compound in a pure state by fractional distillation from acetophenone, which formed simultaneously and accompanied the former. The endeavour to isolate the acid amides supposed to be formed by the Beckmann rearrangement of the oxime, was failure. We were unable to settle the constitution of the nitrogenous compound indicating a melting point of [186-190°]; and the basic substance which gave the hydrochloride, was analysed by conversion into the double salt of platinum; C=1.75; H=2.82; Pt=45.17.

The camphor oxime resulted analogously in yielding α -campholen nitrile of $d_4^{25}=0.9116$; $n_D^{25}=1.4613$; $[\alpha]_D^{25}=+25.45^\circ$, α -campholenic acid, and a small quantity of ammonia. The nitrile was confirmed by analysis: C=80.67; H=10.34, theory requiring C=80.47; H=10.13 for $C_{10}H_{15}N$.

The ketoximes when their sodium salts were subjected to distillation under reduced pressure, so far as we have studied, yield nitriles, ketones and ammonia, sometimes accompanied by some quantities of the acids corresponding to the nitriles, the results of which may be seen in the table.

When these facts are compared with the observation by Prof. Kuhara and his co-workers¹ on the rearrangement of chlorimido-diphenylketone by fusion with caustic potash, it seems very strange that the sodium salt of the ketoxime should suffer nitrile decomposition by heat as was noticed by Kötze and Wunsdorf² on the thermal decomposition of ketoximes, but not the Beckmann rearrangement.

Now, it is a well-known fact that sodium plays an important role in synthetic organic chemistry as in the Wurtz-Fittig reaction and in the soda-amide synthesis. Among these syntheses, we cite here the reaction between benzophenone and soda-amide, which was studied by Haller,³ and resulted in yielding benzamide and benzene as the final reaction products as may be seen in the following scheme;



¹ These Memoirs, **3**, 13 (1917).

² J. prak. Chem., **88**, 519 (1913).

³ Ann. d. Chim., **1**, 987 (1908); Lieb. Ann., **436**, 205 (1924).

Although the ketones occur actually in the reaction products from the sodium salt of the ketoximes and the formation of sodamide in the reaction system is highly probable, we hesitate to apply the above mechanism for the formation of the acid amide from the ketone oxime in our cases, since the reaction seems to take place instantly in the absence of water or hydrogen when the salt was heated, before it was decomposed into ketone and sodamide.

It is, however, evident that the molecular rearrangement of the ketoximes depends more or less upon the nature of the hydrocarbon radicals linked to the carbon atom of the diaryl or dialkyl methane nucleus of the molecule,¹ and that the mobility of the radicals from the carbon atom depending upon their electronic character, is in the order of methyl, benzyl and phenyl,² and moreover it was supposed that sodium played an important role in the disruption of the bonds between the carbon atoms as was noticed in the case of the decomposition of ethers³ by the aid of metallic sodium and in the sodamide synthesis.⁴

In the present case, the formation of nitrile from the sodium salt of ketoxime should be explained by assuming an intermediate formation of the acid amide resulting in two reactions—the molecular rearrangement of the oxime and the disruption of the bond between one of the hydrocarbon radicals and the carbon atom of dialkyl or diaryl methane, which take place simultaneously, and the acid amide, thus formed, by turne was converted into nitrile by the catalytic action of the sodium, and the cause of the reactions should be attributed to the special character of sodium as a donator of electrons⁵.

When we assume that the tendency of atomic groups to acquire an electron is in the order of $H > CH_3 > C_6H_5$, the formation of nitrile from various ketoximes as we noticed in the experiments, will be explained easily.

Consequently, it will be supposed that the conversion of an aldoxime into nitrile would take place with facility when compared with the ketoxime, owing to the mobility of the hydrogen atom combined with the carbon atom of the methane nucleus, and the above reactions would be modified in presence of hydrogen or water in the reaction system, so as

1 Kuhara & N. Agatsuma & K. Araki: These Memoirs, **3**, 8 (1919).

2 Meerwein: Lieb. Ann., **419**, 121 (1919); Ber. D. Chem. Ges., **55**, 636, 1080 (1922).

3 P. Schorigin: Ibid., **56**, 176 (1923). K. Ziegler & F. Thielmann: Ibid., **56**, 1740 (1923).

4 Loc. cit.

5 R. Robinson: Annual Reports of the Progress of Chemistry, **20**, 91 (1924).

to predominate in the yield of basic compounds and acid amide as we find in the case of the catalytic action of reduced copper on the oxime in the hydrogen atmosphere¹.

The sodium salt of α -benzaloxime was prepared according to the method proposed by Petraczek², which contained one molecule of the water of crystallization, it was then subjected to heating under 12-14 mm. pressure, and the reaction product was treated with ether. The alkaline solution was neutralized with dilute hydrochloric acid, whereas benzoic acid was separated from the solution, which was confirmed by the determination of the melting point [121°] and also by analysis; C = 68.66; H = 5.39; the theory requiring C = 68.85; H = 4.92 for $C_7H_6O_2$. Ammonium chloride was obtained from the mother liquor separated from the benzoic acid.

From the ether-extract, the oily residue was obtained after evaporating off the solvent, which was then subjected to fractional distillation:

	Fraction.	Yield.	Remark.
1	Below 120°	0.7 grm.	Colourless, containing nitrogen.
2	$120-188^\circ$	0.8 „	Colourless, containing nitrogen.
3	$189-190^\circ$	3.5 „	$d_4^{25}=1.0031$; $n_D^{26}=1.5230$
4	$190-200^\circ$	trace	Light yellow.
5	Residue,		

The third fraction was confirmed to be composed entirely of benzonitrile by analysis; C = 81.13; H = 5.37; N = 13.41, theory requiring C = 81.55; H = 4.85; N = 13.60 for C_6H_5CN .

The residue was treated with hot water, and on cooling the solution, crystals of benzamide [m. p. 127°] were separated which were analysed: C = 69.83; H = 5.77; N = 11.57, theory requiring C = 69.42; H = 5.80; N = 11.96 for $C_6H_5CONH_2$, and also other crystals with a melting point of [$78-80^\circ$] were isolated, which were assumed to be benzoyl amidine $C_6H_5C-NH_2$,
 $\backslash NH$

by keeping them in a bottle for a few months they were transformed into

¹ Refer. Yamaguchi's experiments.

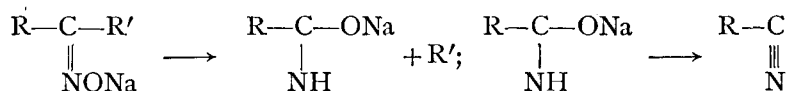
² Ber. D. Chem. Ges., **16**, 825 (1883).

a substance supposed to be benzoic acid from its melting point [105–107°], but further confirmation was lacking due to the small quantity of the substance. The second fraction was observed to contain a crystalline substance which melts at the same temperature as the melting-point of cyanphenine, and the formation of this compound was highly probable,¹ in the course of reaction, but confirmation was lacking owing to the small quantity of the sample.

Thus, the main reaction products from the sodium salt of the oxime by heat were observed to be the same as those obtained from the oxime by the contact action of reduced copper and with the fruitful yield of nitrile as we expected. When, however, the same reaction was applied on the sodium salt of isovaleraldoxime, valeronitrile and ammonia were the sole reaction product.

The difference between these aldoximes, in the reaction products, may be attributed to that of the chemical characters of the hydrocarbon radicals—aliphatic and aromatic—of the oximes, the same explanation was given to the different behavior noticed in the catalytic reduction of these oximes by means of colloidal palladium.²

Thus, the hypothesis we would put forward is, that, the sodium salt of oximes by the action of heat suffers the disruption of the linking between one of the hydrocarbon radicals or hydrogen atom and the carbon atom of the methane nucleus by the influence of the special character of sodium in the way of the molecular rearrangement which would take place simultaneously with the former, and consequently the detached radical or hydrogen atom was left in a free state without entering into combination with the nitrogen atom, resulting in the acid amide which was soon transformed partly into nitrile, as may be represented by the following scheme :



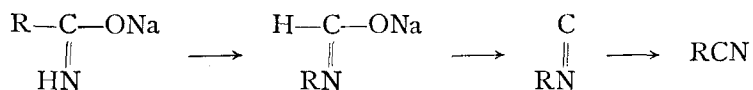
The latter phase of the reactions, the formation of nitrile from the acid amide, was also assumed to proceed in a similar way to the reaction between alkali and the halogen imino ethers in the formation of amines,³

¹ V. Meyer & P. Jacobson: *Lehrbuch d. Org. Chem.*, II, 1,552 (1921).

² Wl. Gulewitsch: *Ber. D. Chem. Ges.*, 57, 1645 (1924).

³ Kuhara and Matsui: *Mem. Coll. Sci. Engin., Kyoto*, 1, 187 (1902-1908); Hoogewerff and van Dorf: *Rec. trav. Chim.*, 6, 375 (1887); 8, 173 (1889); Jones: *Amer. Chem. J.*, 48, 25 (1912).

and also to the Hofmann reaction in the preparation of amines from acid amides,¹ as will be seen in the following scheme:



In the Beckmann rearrangement of an oxime, the hydrocarbon radicals as already noticed by Prof. Kuhara, seem to exert great influence for the exchange of the positions between the hydroxyl group and the hydrocarbon radical, and when one of the hydrocarbon radicals by some external or internal influence applied by heat or by the presence of a donator of electrons, was forced to detach very quickly from the methane carbon atom, the formation of the acid amide or nitrile will be resulted, and on the contrary the Beckmann rearrangement or the formation of an imine will occur when the dissociation of the combination between the hydroxyl group and the nitrogen atom takes place very easily.¹

When, however, both radicals—the hydrocarbon radical and the hydroxyl group, combine strongly, the hydrolysis of the oxime will take place yielding ketone or aldehyde and ammonia.

The conception respecting the conversion of acid amide into nitrile, being analogous to the rearrangement of the halogen imino esters by alkali² and also the Hofmann reaction for the formation of amines from acid amides,³ was confirmed experimentally with the sodium salt of benzamide; by heating the salt prepared by the method of Curtius³ under reduced pressure, it was converted into benzonitrile and ammonia, the former compound was confirmed by analysis: C=81.84; H=5.00; N=13.26; theory requiring C=81.55; H=4.85; N=13.60 for C₆H₅CN.

The results of the reaction products were shown in the table.

The several facts relating to the decomposition of the neutral potassium salt of dibenzohydroxamic acid into benzoic acid, carbon dioxide and diphenylurea,⁴ and the rearrangement of the potassium salt of the dihydroxamic acids into an isocyanate and a potassium salt of an acid⁵ may be regarded as giving strong support to the authors' view of the formation of nitrile:

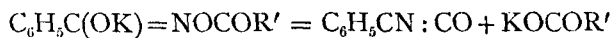
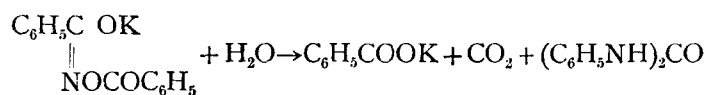
1 Loc. cit.

2 V. Meyer & P. Jacobson: *Lehr. d. Org. Chem.*, I, 1,351 (1907).

3 *Ber. D. Chem. Ges.* **23**, 3038 (1890).

4 *Lieb. Ann.* **161**, 359 (1872); **175**, 257 (1875).

5 *Ibid.*, **309**, 189 (1899); **175**, 311, 312 (1875); *Ber. D. Chem. Ges.*, **27**, 1256 (1894); Meyer & Jacobson: *Lehrbuch d. Org. Chem.*, II, 1,560; *Amer. Chem. J.* **48**, 8 (1912); *These Memoirs*; **1**, 1 (1914-16).



When the results above mentioned are compared with those obtained by the contact action of reduced copper observed by Yamaguchi, the authors' interpretation of the chemical transformation of the oxime into acid amide or nitrile and the notion that sodium sometimes acts like copper will be admitted.

Sept, 1924, Laboratory of Organic- & Bio-Chemistry.

	Isovaleraldoxime	α -Benzaldoxime	Acetophenone oxime	Benzophenone oxime	Benzamide	α -Camphoroxime					
	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \cdot \text{CH}_2\text{CH} \\ \diagdown \\ \text{CH}_3 \end{array} \begin{array}{c} \text{CH} \cdot \text{CH}_2\text{CH} \\ \text{ } \\ \text{NONaH}_2\text{O} \end{array}$	$\begin{array}{c} \text{C}_6\text{H}_5\text{CH} \\ \text{ } \\ \text{NONa} \cdot \text{H}_2\text{O} \end{array}$	$\begin{array}{c} \text{C}_6\text{H}_5\text{C}-\text{CH}_3 \\ \text{ } \\ \text{NONa} \cdot \text{H}_2\text{O} \end{array}$	$\begin{array}{c} \text{C}_6\text{H}_5 \quad \text{CC}_6\text{H}_5 \\ \text{ } \\ \text{NONa} \end{array}$	$\begin{array}{c} \text{C}_6\text{H}_5\text{CO} \\ \text{ } \\ \text{NHNa} \end{array}$	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}-\text{CH}_2 \\ \quad \quad \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \quad \\ \text{H}_2\text{C}-\text{C}-\text{C} \\ \quad \quad \\ \text{CH}_3 \quad \text{NONa} \end{array}$					
Temperature of Nitre Bath.	400	350	435-440	450	440-450	440-450					
Pressure in Flask (m.m.)	20	12-14	14	12	18-20	15					
Reaction temperature	180-210	105	152	180-220	190-250	170					
Sample (gm)	16	21	12	20	15	14					
Reaction Products	$\left\{ \begin{array}{l} \text{Amide} \\ \text{Nitrile} \\ \text{Acid} \\ \text{NH}_3 \end{array} \right.$	yield (grm)		0.2		0.1		0.3		0.32	
		%		49.4		22.2		19.8		8.6	
		Mol %		31.5		16.6		12.6		39.3	
				3.3		60.0		4.2		32.54	
yield (grm)		3		0.9		0.8		0.1		0.35	
%		97		22.2		19.8		3.0		8.6	
Mol %		66.5		16.6		12.6		33.0		39.3	
yield (grm)		0.9		0.3		0.8		0.1		0.35	
%		81.0		7.0		19.8		3.0		8.6	
Mol %		60.0		4.2		12.6		33.0		39.3	
yield (grm)		0.3		0.25		0.3		0.1		0.35	
%		37.30		37.30		37.30		37.30		37.30	
Mol %		9.43		9.43		9.43		9.43		9.43	
yield (grm)		0.25		0.1		0.25		0.1		0.35	
%		14.9		14.9		14.9		14.9		14.9	
Mol %		4.44		4.44		4.44		4.44		4.44	
yield (grm)		0.1		0.1		0.1		0.1		0.1	
%		47.80		47.80		47.80		47.80		47.80	
Mol %		86.13		86.13		86.13		86.13		86.13	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)		0.32		0.32		0.32		0.32		0.32	
%		7.4		7.4		7.4		7.4		7.4	
Mol %		32.54		32.54		32.54		32.54		32.54	
yield (grm)											