rect, but heat capacities are not available in the literature. However, we think that such a correction would not substantially modify our values of excess entropy. This view is supported by comparison with the Ga-Bi system *(9)* which is analogous to the Ga-Pb system in many aspects. In fact, excess entropies are positive in bismuth-rich alloys ($\sim$0.07 e.u. at 90 at. % Bi) and negative at intermediate compositions ($-$0.2 e.u. at 30 at. % Bi). This is not surprising, because lead and bismuth are neighbors in the sixth period of the Periodic Table and have similar properties as shown in Table III. As one can see, the difference in electronegativity for Ga-Bi alloys is greater than or at least equal to that for Ga-Pb alloys. Taking into account the errors which affect the electronegativity values, one could attribute the differences of excess entropies between Ga-Bi and Ga-Pb alloys to electronic peculiarities. This seems supported by the maximum mixing enthalpy of Ga-Pb alloys which is larger than that of Ga-Bi alloys (920 and 504 cal/g-atom, respectively).

At present, we cannot regard the excess entropies of Ga-Pb alloys as more reliable than those of Predel and Stein for our assumption on Newman-Kopp law validity. Further calorimetric measurements of mixing enthalpies at 1143K should be carried out to get entropy values from direct experimental data.

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ORGANIC SECTION

Survey of Alkanone Reactivity Based on Time Required for 50% Oximation

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The 50% oximation times for 238 alkanones have been determined. Several empirical rules have been derived for estimating the 50% oximation times of many other alkanones.

The oximation studies previously reported (5) have been extended to alkanones of other structural types. For the purpose of this investigation the alkanones were divided into 25 classes (A_1–A_{12}, B_1–B_5, C_1–C_5, D, E, and F) as shown in Table I.

Results and Discussion

The 50% oximation times for 238 alkanones are listed in Table I. At least one member of each class was prepared and tested. The following empirical rules were derived from the results.

The first rule is based on the following considerations: All of the alkanones may be formally derived from 2-propanone by the successive introduction of methyl groups as illustrated in Figure 1. Although there is a well-defined exception (see Rule I), the oximation rates decrease with increasing carbon content as the arrows are followed from left to right. Conversely, the rates increase with decreasing carbon content as the arrows are followed from right to left. It must be emphasized that any number of similar diagrams may be made starting with any alkanone, thus deriving sequences with increasing or decreasing carbon content having correspondingly lower or higher oximation rates. The first rule was therefore formulated as follows:

Rule I. The successive introduction of methyl groups into an alkanone always decreases the oximation rate while the successive removal of methyl groups always increases the oximation rate. However, the successive introduction or removal of methyl groups in the R of $RCH_2CH_2COR_{prim,\ sec,\ tert}$ or $(RCH_2CH_2)_2CO$ has little or no effect on the oximation rate.

Several exceptions were found to the above rule. For example, ketone numbers $C_{3\text{-}4}$ and $C_{3\text{-}5}$ were markedly more reactive than the corresponding straight chain compounds, while an impure sample of the highly branched ketone $C_{3\text{-}6}$ was less reactive. Further work is required to determine the extent of these exceptions.

Rule II. Alkanones of the type RR′CHCOR″ have a lower oximation rate than the corresponding alkanone RR′CO, when R″ is any alkyl group except methyl.

The following ratios are constant enough to have predictive value, particularly ratios A and B:

Rule III.

A. $t_{50\%}\ R_{prim,\ sec,\ tert}COC_3/t_{50\%}\ R_{prim,\ sec,\ tert}COC_2 = 1.35–1.62$ (1.54 av)

B. $t_{50\%}\ R_{prim,\ sec,\ tert}CH_2CH_2COC_2/t_{50\%},\ R_{prim,\ sec,\ tert}CH_2CH_2COC = 3.8$

C. $t_{50\%}\ R_{sec}CH_2COC_2/t_{50\%}\ R_{sec}CH_2COC = 6.69–8.15$ (7.6 av)

D. $t_{50\%}\ R_{sec}COC_2/t_{50\%}\ R_{sec}COC = 15.0–27.8$

Table I. Fifty Percent Oximation Times for Some Alkanones

	Preparation[a]		New compounds			
					CO	
Alkanone	Method	R of RMgX	$t_{50\%}$, min	Bp range (mm)	Calcd	Found
A R_pCOR_p[b]						
A_1 $R_{pst}CH_2CH_2COMe$						
1. 2-Pentanone			0.13			
2. 2-Decanone			0.13			
3. 5-Methyl-2-hexanone			0.13			
4- 5-Methyl-2-heptanone	B[c]	Me	0.12			
5. 5-Ethyl-2-heptanone	B[c]	Me	0.12			
6. 5,5-Dimethyl-2-hexanone	B[d,e]	Me	0.10			
A_2 $R_{pst}CH_2CH_2COEt$						
1. 3-Hexanone			0.45			
2. 3-Decanone			0.45			
3. 6-Methyl-3-heptanone			0.45			
4. 6-Methyl-3-dodecanone			0.47			
5. 6-Ethyl-3-octanone	B[c]	Et	0.45	90–92° (16)	17.92	17.2
6. 6-Ethyl-3-decanone	B[c]	Et	0.47	117–119° (14)	15.19	14.7
7. 6-Butyl-3-dodecanone	A	3-Butylnonyl	0.45	166–168° (16)	11.64	11.4
8. 6,6-Dimethyl-3-heptanone	B[d,e]	Et	0.38			
A_3 $R_{pst}CH_2CH_2COCH_2CH_2R_{pst}$						
1. 4-Heptanone			0.67			
2. 4-Nonanone			0.67			
3. 2-Methyl-5-dodecanone			0.62			
4. 7-Ethyl-4-nonanone	B[c]	Pr	0.62	109–111° (15)	16.44	16.0
5. 3-Ethyl-6-dodecanone	B[c]	Hexyl	0.62	144–146° (12)	13.18	12.6
6. 7-Ethyl-4-undecanone	B[c]	Pr	0.63	131–133° (15)	14.11	13.6
7. 8-Ethyl-5-dodecanone	B[c]	Butyl	0.62	146–148° (16)	13.18	12.6
8. 2,8-Dimethyl-5-nonanone	A[f]	Isopentyl	0.58			
9. 3,9-Diethyl-6-undecanone	[g]		0.57			
10. 2,2,8,8-Tetramethyl-5-nonanone	A[f]	3,3-Me_2butyl[e]	0.50			
A_4 R_sCH_2COMe						
1. 4-Methyl-2-pentanone			0.62			
2. 4-Methyl-2-hexanone			0.73			
3. 4-Methyl-2-heptanone	B[d]	Me	0.73			
4. 4,6-Dimethyl-2-heptanone	B[h]	Me	0.87			
5. 4,6,6-Trimethyl-2-heptanone	B[i]	Me	1.10			
6. 4,5-Dimethyl-2-hexanone	B[h]	Me	0.85			
7. 4-Ethyl-2-hexanone	B[d]	Me	1.00			
8. 4-Ethyl-2-octanone	B[d]	Me	1.12			
9. 4-Ethyl-5-methyl-2-hexanone	B[h]	Me	1.38	78–80° (12)	19.68	19.3
A_5 R_sCH_2COEt						
1. 5-Methyl-3-hexanone			4.2			
2. 5-Methyl-3-heptanone			5.3			
3. 5-Methyl-3-octanone	B[d]	Et	5.7			
4. 5-Methyl-3-undecanone	B[h]	Et	5.3			
5. 5,7-Dimethyl-3-octanone	B[h]	Et	6.3	83–85° (18)	17.92	17.7
6. 5,7,7-Trimethyl-3-octanone	B[i]	Et	8.7	90–92° (14)	16.44	16.0
7. 5,6-Dimethyl-3-heptanone	B[h]	Et	6.3			
8. 5-Ethyl-3-heptanone	B[d]	Et	7.7			
9. 5-Ethyl-3-octanone	B[h]	Et	8.5	90–92° (17)	17.92	17.2
10. 5-Ethyl-3-nonanone	B[d]	Et	8.3			
11. 5-Ethyl-3-undecanone	B[h]	Et	8.5	131–133° (17)	14.11	13.5
12. 5-Ethyl-6-methyl-3-heptanone	B[h]	Et	13.4	86–88° (14)	17.92	17.7
13. 5-Propyl-3-octanone	B[h]	Et	9.0			
14. 5-Butyl-3-nonanone	B[h]	Et	9.5	126–128° (16)	14.11	13.9
15. 5-Butyl-3-undecanone	B[h]	Et	9.0	157–159° (20)	12.36	12.1
A_6 $R_sCH_2COCH_2CH_2R_{pst}$						
1. 2-Methyl-4-heptanone			6.5			
2. 2-Methyl-4-undecanone			6.3			
3. 6-Methyl-4-octanone			8.5			
4. 3-Methyl-5-undecanone			8.5			
5. 6-Ethyl-4-octanone	B[d]	Pr	12.5			
6. 3-Ethyl-5-undecanone	B[d]	Hexyl	12.7	126–128° (12)	14.11	13.6
7. 6-Ethyl-4-decanone	B[d]	Pr	13.5	111–113° (13)	15.19	14.7
8. 5-Ethyl-7-tridecanone	B[d]	Hexyl	13.3			
9. 2,2-Dimethyl-7-ethyl-5-undecanone	B[d]	3,3-Me_2butyl	10.8	143–145° (10)	12.36	12.2
10. 4-Propyl-6-dodecanone	B[h]	Hexyl	13.8	156–158° (18)	12.36	11.9
11. 7-Butyl-5-undecanone	B[h]	Butyl	13.8	153–155° (16)	12.36	11.9

Table I. *Continued*

			New compounds			
	Preparation[a]				CO	
Alkanone	Method	R of RMgX	$t_{50\%}$, min	Bp range (mm)	Calcd	Found
A R_pCOR_p[b]						
A_7 $R_sCH_2COCH_2R_s$						
1. 2,6-Dimethyl-4-heptanone			78			
2. 2,6-Dimethyl-4-octanone	C[c]	Isobutyl	116			
3. 2,6-Dimethyl-4-nonanone	C[d]	Isobutyl	112			
4. 3,7-Dimethyl-5-nonanone	A[f]	2-Mebutyl	142			
5. 3,7-Dimethyl-5-decanone	C[d]	2-Mebutyl	165	111–113° (13)	15.19	14.8
6. 4,8-Dimethyl-6-undecanone	A[f]	2-Mepentyl	160	130–132° (20)	[j]	
7. 6-Ethyl-2-methyl-4-octanone	C[d]	Isobutyl	172	96–98° (13)	[j]	
8. 3-Ethyl-7-methyl-5-nonanone	C[d]	2-Mebutyl	240	110–112° (13)	[j]	
9. 3-Ethyl-7-methyl-5-decanone	C[d]	2-Mepentyl	259	125–127° (16)	14.11	13.7
10. 3,7-Diethyl-5-nonanone	A[f]	2-Etbutyl	380	122–124° (15)	14.11	13.6
11. 6-Ethyl-2-methyl-4-decanone	C[d]	Isobutyl	203	123–125° (16)	14.11	13.7
12. 7-Ethyl-3-methyl-5-undecanone	C[d]	2-Mebutyl	254	140–142° (17)	13.18	12.7
13. 8-Ethyl-4-methyl-6-dodecanone	C[d]	2-Mepentyl	280	157–159° (25)	12.36	11.9
14. 3,7-Diethyl-5-undecanone	C[d]	2-Etbutyl	400	158–160° (24)	12.36	11.9
15. 5,9-Diethyl-7-tridecanone	A[f]	2-Ethexyl	424	176–178° (20)	[j]	
A_8 R_tCH_2COMe						
1. 4,4-Dimethyl-2-pentanone	[k]		6.2			
2. 4,4-Dimethyl-2-hexanone	[l]	Me	9.8			
3. 4,4-Diethyl-2-hexanone	B[m]	Me	37	88–90° (15)	17.92	17.7
A_9 R_tCH_2COEt						
1. 5,5-Dimethyl-3-hexanone	B[n]	Et	99			
2. 5,5-Dimethyl-3-heptanone	[l]	Et	175	166–167° (745)	19.68	19.4
3. 5,5-Dimethyl-3-octanone	[l]	Et	186	182–183° (740)	17.92	17.7
4. 5,5-Dimethyl-3-decanone	[l]	Et	187	115–117° (21)	15.19	15.0
5. 5,5,7-Trimethyl-3-octanone	[l]	Et	205	88–90° (12)	16.44	16.2
6. 5,5,6-Trimethyl-3-heptanone	[l]	Et	214	85–87° (15)	17.92	17.8
7. 5,5-Diethyl-3-heptanone	[l]	Et	1312	108–110° (20)	16.44	15.9
A_{10} $R_tCH_2COCH_2CH_2R_{pst}$						
1. 2,2-Dimethyl-4-heptanone	B[n]	Pr	151			
2. 2,2-Dimethyl-4-dodecanone	B[n]	Octyl	152	142–144° (18)	13.18	12.7
3. 6,6-Dimethyl-4-octanone	B[m]	Pr	277	84–86° (20)	17.92	17.6
4. 3,3-Dimethyl-5-tridecanone	B[m]	Octyl	275	156–158° (18)	12.36	11.9
5. 6,6-Dimethyl-4-nonanone	B[m]	Pr	285	97–99° (17)	16.44	16.0
6. 7,7-Dimethyl-5-dodecanone	B[m]	Butyl	289	138–140° (18)	13.18	12.7
7. 3,3-Diethyl-5-undecanone	B[m]	Hexyl	2115	155–157° (16)	12.36	12.1
A_{11} $R_tCH_2COCH_2R_s$						
1. 2,2,6-Trimethyl-4-heptanone	C[n]	Isobutyl	3645			
A_{12} $R_tCH_2COCH_2R_t$						
1. 2,2,6,6-Tetramethyl-4-heptanone	C[n]	Neopentyl	[o]			
B R_sCOR_p						
B_1 R_sCOMe						
1. 3-Methyl-2-butanone			0.30			
2. 3-Methyl-2-pentanone			0.83			
3. 3-Methyl-2-hexanone			0.85			
4. 3-Methyl-2-heptanone	B[c]	Me	0.83			
5. 3-Methyl-2-nonanone	B[c]	Me	0.83			
6. 3,5-Dimethyl-2-hexanone	B[c]	Me	0.80			
7. 3,4-Dimethyl-2-pentanone	B[c]	Me	14.5			
8. 3,4-Dimethyl-2-hexanone	B[c]	Me	16.0			
9. 3-Ethyl-2-pentanone	A	Me	11.0			
10. 3-Ethyl-2-hexanone	B[c]	Me	11.3			
11. 3-Ethyl-2-heptanone	A	Me	11.3			
12. 3-Ethyl-5-methyl-2-hexanone	B[c]	Me	15.5	71–73° (16)	19.68	19.3
13. 3,5-Diethyl-2-heptanone	B[c]	Me	18.0	95–97° (12)	16.44	16.0
14. 3-Ethyl-4-methyl-2-pentanone	B[c]	Me	253			
15. 3-Ethyl-4-methyl-2-hexanone	B[c]	Me	335	78–80° (23)	19.68	19.3
16. 3-Propyl-2-hexanone	B[c]	Me	11.0			
17. 4-Methyl-3-propyl-2-pentanone	B[c]	Me	286			
18. 3-Isopropyl-2-nonanone	B[c]	Me	341	110–112° (13)	15.19	15.0
19. 4-Methyl-3-propyl-2-hexanone	B[c]	Me	338	93–95° (25)	17.92	17.6
20. 3-Butyl-2-heptanone	B[c]	Me	11.5			
21. 3-Isobutyl-5-methyl-2-hexanone	B[c]	Me	26.5			

(Continued on page 96)

Table I. *Continued*

			New compounds			
	Preparation[a]				CO	
Alkanone	Method	R of RMgX	$t_{50\%}$, min	Bp range (mm)	Calcd	Found
B R_sCOR_p						
B_1 R_sCOMe						
22. 3-Isobutyl-5-methyl-2-heptanone	B^c	Me	28.5	103–105° (13)	15.19	14.9
23. 3-Isobutyl-5-methyl-2-octanone	B^c	Me	29.0	113–115° (13)	14.11	13.6
24. 3-(2-Methylbutyl)-5-methyl-2-heptanone	B^c	Me	29.5	116–118° (14)	14.11	13.6
25. 3-(2-Methylbutyl)-5-methyl-2-octanone	B^c	Me	30.5	125–127° (12)	13.18	13.0
26. 3-(2-Methylpentyl)-5-methyl-2-octanone	B^c	Me	30.5	137–139° (14)	12.36	12.0
B_2 R_sCOEt						
1. 2-Methyl-3-pentanone			4.3			
2. 4-Methyl-3-hexanone			13.9			
3. 4-Methyl-3-heptanone			14.4			
4. 4-Methyl-3-octanone	B^c	Et	14.4			
5. 4-Methyl-3-decanone	B^c	Et	14.0			
6. 4,6-Dimethyl-3-heptanone	B^c	Et	15.5			
7. 4,5-Dimethyl-3-hexanone	B^c	Et	277			
8. 4,5-Dimethyl-3-heptanone	B^c	Et	304	88–90° (40)	19.68	19.3
9. 4-Ethyl-3-hexanone	A	Et	219			
10. 4-Ethyl-3-heptanone	B^c	Et	236			
11. 4-Ethyl-3-octanone	A	Et	239			
12. 4-Ethyl-3-decanone	B^c	Et	241	113–115° (14)	15.19	15.0
13. 4-Ethyl-3-dodecanone	B^c	Et	248	138–140° (11)	13.18	13.0
14. 7,7-Dimethyl-4-ethyl-3-octanone	B^c	Et	270	107–109° (21)	15.19	14.8
15. 4,7,7-Triethyl-3-nonanone	B^c	Et	321	138–140° (6)	12.36	12.0
16. 4-Ethyl-6-methyl-3-heptanone	B^c	Et	379	98–100° (40)	17.92	17.6
17. 4,6-Diethyl-3-octanone	B^c	Et	472	123–125° (38)	15.19	14.8
18. 4-Ethyl-5-methyl-3-hexanone	B^c	Et	5658	163–164° (743)	19.68	19.3
19. 4-Ethyl-5-methyl-3-heptanone	B^c	Et	8885	93–95° (30)	17.92	17.6
20. 4-Propyl-3-heptanone	B^c	Et	262			
21. 5-Methyl-4-propyl-3-hexanone	B^c	Et	7165	78–80° (12)	17.92	17.4
22. 4-Isopropyl-3-decanone	B^c	Et	8744	126–128° (17)	14.11	13.7
23. 5-Methyl-4-propyl-3-heptanone	B^c	Et	8851	106–108° (30)	16.44	16.1
24. 4-Propyl-3-decanone	B^c	Et	253	126–128° (12)	14.11	14.0
25. 4-Butyl-3-octanone	B^c	Et	272			
26. 4-Butyl-3-decanone	B^c	Et	262	146–148° (20)	13.18	13.0
27. 4-Hexyl-3-decanone	B^c	Et	290	157–159° (12)	11.64	11.3
28. 4-(3,3-Dimethylbutyl)-7,7-dimethyl-3-octanone	B^c	Et	312	145–147° (18)	11.64	11.3
29. 4-Isobutyl-6-methyl-3-heptanone	B^c	Et	704	110–112° (27)	15.19	14.6
30. 4-Isobutyl-6-methyl-3-octanone	B^c	Et	786	111–113° (13)	14.11	13.8
31. 4-Isobutyl-6-methyl-3-nonanone	B^c	Et	816	122–124° (12)	13.18	12.9
32. 4-(2-Methylbutyl)-6-methyl-3-octanone	B^c	Et	814	123–125° (12)	13.18	12.9
33. 4-(2-Methylbutyl)-6-methyl-3-nonanone	B^c	Et	845	133–135° (13)	12.36	12.2
34. 4-(2-Methylpentyl)-6-methyl-3-nonanone	B^c	Et	850	158–160° (23)	11.64	11.4
B_3 $R_sCOCH_2CH_2R_{pst}$						
1. 2-Methyl-3-hexanone			6.5			
2. 2-Methyl-3-tridecanone			6.5			
3. 2,6,6-Trimethyl-3-heptanone	A	3,3-Me_2butyl[e]	5.3	81–83° (18)	17.92	17.3
4. 3-Methyl-4-heptanone			21.9			
5. 3-Methyl-4-decanone			21.5			
6. 3,7,7-Trimethyl-4-octanone	A	3,3-Me_2butyl[e]	18.0	100–102° (25)	16.44	16.2
7. 5-Methyl-4-octanone			22.8			
8. 4-Methyl-5-undecanone			23.5			
9. 2,2,6-Trimethyl-5-nonanone	A	3,3-Me_2butyl[e]	18.8	106–108° (16)	15.19	14.9
10. 5,7-Dimethyl-4-octanone	B^c	Pr	24.0	83–85° (13)	17.92	17.7
11. 2,4-Dimethyl-5-undecanone	B^c	Hexyl	25.0	122–124° (13)	14.11	13.6
12. 2,3-Dimethyl-4-heptanone	B^c	Pr	430			
13. 2,3-Dimethyl-4-decanone	B^c	Hexyl	404	111–113° (11)	15.19	15.0
14. 3,4-Dimethyl-5-undecanone	B^c	Hexyl	449	125–127° (11)	14.11	13.5
15. 3-Ethyl-4-heptanone	A	Pr	329			
16. 3-Ethyl-4-octanone	A	Butyl	329			

Table I. *Continued*

			New compounds			
	Preparation[a]				CO	
Alkanone	Method	R of RMgX	$t_{50\%}$, min	Bp range (mm)	Calcd	Found
B R_sCOR_p						
B$_3$ $R_sCOCH_2CH_2R_{pst}$						
17. 3-Ethyl-4-nonanone	A	Pentyl	327	97–99° (12)	16.44	16.0
18. 3-Ethyl-4-decanone	A	Hexyl	327			
19. 3-Ethyl-4-undecanone	A	Heptyl	320	127–129° (12)	14.11	13.5
20. 3-Ethyl-4-dodecanone	A	Octyl	323	142–144° (13)	13.18	12.6
21. 3-Ethyl-4-tridecanone	A	Nonyl	324	152–154° (13)	12.36	11.9
22. 3-Ethyl-7-methyl-4-octanone	A	Isopentyl	315	100–102° (20)	16.44	16.2
23. 7,7-Dimethyl-3-ethyl-4-octanone	A	3,3-Me$_2$butyl[e]	291	105–107° (18)	15.19	14.9
24. 3,7,7-Triethyl-4-nonanone	A	3,3-Et$_2$pentyl[p]	300	158–160° (18)	[j]	
25. 5-Ethyl-4-octanone	B[c]	Pr	356	86–88° (18)	17.92	17.6
26. 4-Ethyl-5-undecanone	B[c]	Hexyl	352			
27. 5-Ethyl-4-nonanone	A	Pr	374			
28. 5-Ethyl-6-dodecanone	A	Hexyl	371	140–142° (18)	13.18	13.0
29. 2,2-Dimethyl-6-ethyl-5-decanone	A	3,3-Me$_2$butyl[e]	338	127–129° (13)	13.18	12.8
30. 5-Ethyl-4-undecanone	B[c]	Pr	384	131–133° (20)	14.11	13.9
31. 5-Ethyl-4-tridecanone	B[c]	Pr	386	156–158° (17)	12.36	12.2
32. 5-Propyl-4-octanone	B[c]	Pr	385			
33. 4-Propyl-5-undecanone	B[c]	Hexyl	389			
34. 6-Propyl-5-dodecanone	B[c]	Butyl	389	154–156° (20)	12.36	12.1
35. 5-Butyl-4-nonanone	B[c]	Pr	414	130–132° (22)	14.11	13.9
36. 6-Butyl-5-decanone	B[c]	Butyl	418			
37. 5-Butyl-4-undecanone	B[c]	Pr	414	157–159° (21)	12.36	12.1
B$_4$ $R_sCOCH_2R_s$						
1. 2,5-Dimethyl-3-hexanone	A	Isobutyl	79			
2. 2,5-Dimethyl-3-heptanone	A	2-Mebutyl	103	70–72° (16)	19.68	19.0
3. 2,5-Dimethyl-3-octanone	A	2-Mepentyl	115	88–90° (18)	17.92	17.4
4. 5-Ethyl-2-methyl-3-heptanone	A	2-Etbutyl	166	82–84° (16)	[j]	
5. 5-Ethyl-2-methyl-3-nonanone	A	2-Ethexyl	199	115–117° (20)	15.19	14.9
6. 2,5-Dimethyl-4-heptanone	A	Isobutyl	279			
7. 3,6-Dimethyl-4-octanone	A	2-Mebutyl	384			
8. 3,6-Dimethyl-4-nonanone	A	2-Mepentyl	391	101–103° (20)	16.44	15.8
9. 6-Ethyl-3-methyl-4-octanone	A	2-Etbutyl	528	97–99° (20)	[j]	
10. 6-Ethyl-3-methyl-4-decanone	A	2-Ethexyl	617	127–129° (20)	[j]	
11. 2,5-Dimethyl-4-octanone	A	Isobutyl	297	180–181° (752)	17.92	17.8
12. 3,6-Dimethyl-5-nonanone	A	2-Mebutyl	365	100–102° (16)	16.44	16.2
13. 4,7-Dimethyl-5-decanone	A	2-Mepentyl	394			
14. 3-Ethyl-6-methyl-5-nonanone	A	2-Etbutyl	599	106–108° (17)	15.19	14.7
15. 7-Ethyl-4-methyl-5-undecanone	A	2-Ethexyl	675	138–140° (22)	[j]	
16. 5-Ethyl-2-methyl-4-heptanone	A	Isobutyl	4800			
17. 5-Ethyl-2-methyl-4-nonanone	A	Isobutyl	5340	108–110° (20)	15.19	14.7
18. 2,3,6-Trimethyl-4-heptanone	C[c]	Isobutyl	7920			
B$_5$ $R_sCOCH_2R_t$						
1. 2,5,5-Trimethyl-3-hexanone	C[n]	Isopropyl	4700			
C R_tCOR_p						
C$_1$ R_tCOMe						
1. 3,3-Dimethyl-2-butanone			6.5			
2. 3,3-Dimethyl-2-pentanone	B[d]	Me	55			
3. 3,3-Dimethyl-2-hexanone	B[i]	Me	67			
4. 3,3-Diethyl-2-pentanone	B[i]	Me	[q]			
C$_2$ R_tCOEt						
1. 2,2-Dimethyl-3-pentanone	B[d]	Et	613			
2. 4,4-Dimethyl-3-hexanone	B[d]	Et	6120			
3. 4,4-Diethyl-3-hexanone	B[i]	Et	[r]			
C$_3$ $R_tCOCH_2CH_2R_{pst}$						
1. 2,2-Dimethyl-3-hexanone	B[i]	Pr	970			
2. 2,2-Dimethyl-3-heptanone	B[i]	Butyl	952			
3. 2,2-Dimethyl-3-undecanone	B[i]	Octyl	958	125–127° (16)	14.11	13.5
4. 2,2,6-Trimethyl-3-heptanone	B[i]	Isopentyl	838			
5. 2,2,6,6-Tetramethyl-3-heptanone	B[i]	3,3-Me$_2$butyl	820			
6. 6,6-Diethyl-2,2-dimethyl-3-octanone	B[i]	3,3-Et$_2$pentyl	1065	138–140° (18)	[j]	
C$_4$ $R_tCOCH_2R_s$						
1. 2,2,5-Trimethyl-3-hexanone	C[i]	Isobutyl	[s]			
C$_5$ $R_tCOCH_2R_t$						
1. 2,2,5,5-Tetramethyl-3-hexanone	C[n]	*tert*-Butyl	[t]			

(Continued on page 98)

Table I. *Continued*

	Preparation[a]		New compounds			
					CO	
Alkanone	Method	R of RMgX	$t_{50\%}$, min	Bp range (mm)	Calcd	Found
D R_sCOR_s						
1. 2,4-Dimethyl-3-pentanone	A	Isopropyl	339			
2. 2,4-Dimethyl-3-hexanone	A	Isopropyl	1216			
3. 2,4-Dimethyl-3-heptanone	A	Isopropyl	1288			
4. 2,4-Dimethyl-3-decanone	C[c]	Isopropyl	1297	107–109° (12)	15.19	14.7
5. 3,5-Dimethyl-4-heptanone	A[f]	*sec*-Butyl	4372			
6. 2,4,6-Trimethyl-3-heptanone	C[c]	Isopropyl	1450			
7. 4-Ethyl-2-methyl-3-hexanone	A	Isopropyl	*u*			
8. 4-Ethyl-2-methyl-3-octanone	A	Isopropyl	*v*	95–97° (18)	16.44	16.0
9. 2,4,5-Trimethyl-3-hexanone	C[c]	Isopropyl	*w*			
E R_sCOR_t						
1. 2,2,4-Trimethyl-3-pentanone	A	*tert*-Butyl	*x*			
2. 2,2,4-Trimethyl-3-hexanone	A	*tert*-Butyl	*y*			
3. 2,2,4-Trimethyl-3-heptanone	A	*tert*-Butyl	*z*			
4. 2,2-Dimethyl-4-ethyl-3-hexanone	A	*tert*-Butyl	*aa*			
F R_tCOR_t						
1. 2,2,4,4-Tetramethyl-3-pentanone	*ab*		*ac*			

[a] Preparative details are not given for ketones previously described *(5)*. [b] Subscripts *p*, *s*, and *t* denote primary, secondary, and tertiary, respectively. [c] Acid was prepared by the malonic ester synthesis. [d] Acid was prepared by the carbonation of the corresponding Grignard reagent. [e] 3,3-Dimethylbutyl chloride was prepared from *tert*-butyl chloride and ethylene with an anhydrous aluminum chloride catalyst according to the procedure of Brandstrom *(1)*. [f] Carbinol was prepared by treating the Grignard reagent with ethyl formate. [g] Ketone was prepared by the laurone procedure of Sauer *(9)*. [h] Acid was prepared by the following reaction sequence: Reformatsky reaction → dehydration → catalytic hydrogenation → hydrolysis. [i] Acid was commercially available. [j] Analysis indicated an impure compound. However, the $t_{50\%}$ was always within the expected range except for ketone C_{3-6}. [k] Ketone was prepared by the oxidation of diisobutylene according to the procedure of Mosher and Cox *(6)*. Reaction time was reduced to less than one day by cooling the reaction flask in a bath of cold (15°) running water. [l] Ketone was prepared by treating a nitrile with a Grignard reagent. The nitrile was prepared by the 1,4 addition of a Grignard reagent (usually MeMgBr) to an ethyl alkylidenecyanoacetate followed by hydrolysis and decarboxylation according to the procedure of Prout *(7)*. [m] Acid was prepared by the hydrolysis of the corresponding nitrile according to the procedure of Prout *(7)*. [n] Acid was prepared by treating 4,4-dimethyl-2-pentanone with aqueous sodium hypobromite according to the procedure of Homeyer et al. *(4)*. [o] Analysis indicated 11.7% oximation after 15 days at room temperature, assuming 96% purity. [p] Acid prepared by the method of Prout *(7)* was reduced with lithium aluminum hydride and the resulting carbinol converted to the bromide by treating it with phosphorus tribromide. [q] Analysis indicated 58.5% oximation after 30 days at room temperature, assuming 96% purity. [r] Analysis indicated 2.1% oximation after 30 days at room temperature, assuming 96% purity. Another sample gave 4.1% oximation after 237 days at room temperature. [s] Analysis indicated 54.5% oximation after 30 days at room temperature, assuming 96% purity. [t] Analysis indicated 4.1% oximation after 30 days at room temperature, assuming 96% purity. [u] Analysis indicated 83% oximation after 30 days at room temperature, assuming 96% purity. [v] Analysis indicated 72% oximation after 30 days at room temperature, assuming 96% purity. Oximation was completed after 237 days at room temperature. [w] Analysis indicated 40% oximation after 15 days at room temperature, assuming 96% purity. [x] Analysis indicated 15.2% oximation after 30 days at room temperature, assuming 96% purity. [y] Analysis indicated 27% oximation after 313 days at room temperature, assuming 96% purity. [z] Analysis indicated 3.4% oximation after 30 days at room temperature, assuming 96% purity. [aa] Analysis indicated 5.5% oximation after 313 days at room temperature, assuming 96% purity. [ab] Ketone was prepared by the methyl iodide–sodium amide methylation of 2,2,4-trimethyl-3-pentanone. [ac] Analysis indicated 1.4% oximation after 30 days at room temperature, assuming 96% purity.

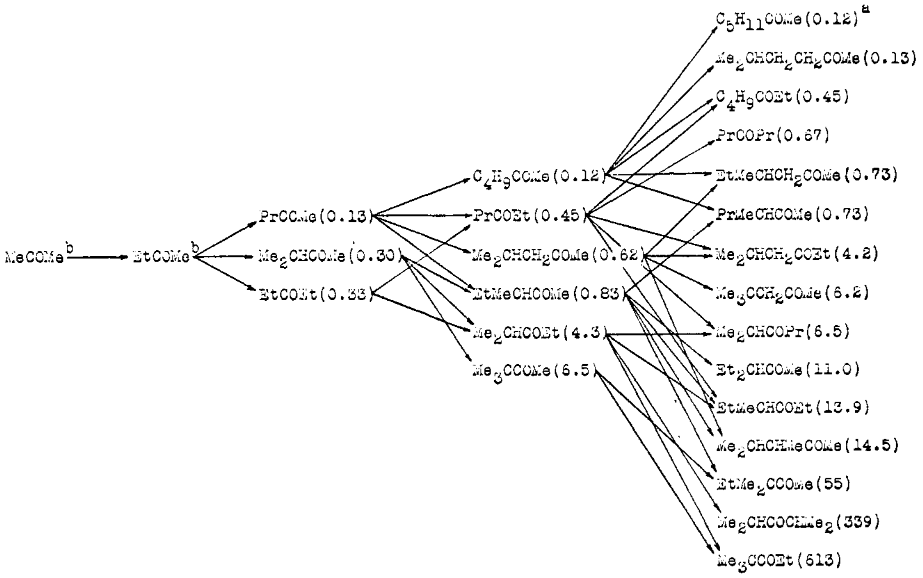

Figure 1. Formal derivation of alkanones from 2-propanone through the heptanones

[a] Time in minutes required for 50% oximation is given after the formulas
[b] $t_{50\%}$ was less than 0.083 min (5 sec)

As illustrated below, Rule I is useful for estimating the relative oximation rates of the various class members.

Every alkanone (except 2-propanone, 2-butanone, and 3-pentanone) may be assigned to one of the 25 classes listed in Table I. According to Rule I the oximation rate of a given alkanone would be the same or lower than the rate of the first member of the class to which it has been assigned. The reactivity of a given class would therefore be defined if class members of increasing branching were prepared and tested until an alkanone of low reactivity was found. This was easily and completely realized for classes A_{11}, A_{12}, B_5, C_4, C_5, E, and F and partially realized for classes A_9, A_{10}, B_2–B_4, C_1–C_3, and D. The alkanones nones in class B_1 roughly parallel the corresponding members of class B_2 (Rule III-D). The remaining classes A_1–A_8 are generally very reactive and therefore represent the greatest area of uncertainty.

Experimental

Unless otherwise indicated in Table I the ketones were prepared by the following methods.

Method A. A Grignard reagent was treated with an aldehyde and the resulting carbinol oxidized to the ketone according to the procedure of Sandborn (*8*).

Method B. A Grignard reagent was converted into the cadmium dialkyl and treated with an acid chloride according to the procedure of Cason and Prout (*3*).

Method C. An acid chloride was treated with a Grignard reagent and anhydrous ferric chloride catalyst according to the procedure of Cason and Kraus (*2*).

The intermediates were prepared by the methods indicated in the footnotes to Table I. The malonic ester syntheses and Reformatsky reaction sequences were performed according to the procedures previously described (*5*).

Analysis and rate determinations. The carbonyl percentages of new compounds and the 50% oximation times were determined by the methods previously described (*5*). An independent redetermination of the $t_{50\%}$ of 37 ketones gave an average precision of 3.1%.

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Preparation and Spectral Characterization of Substituted 2-Aminothiazoles

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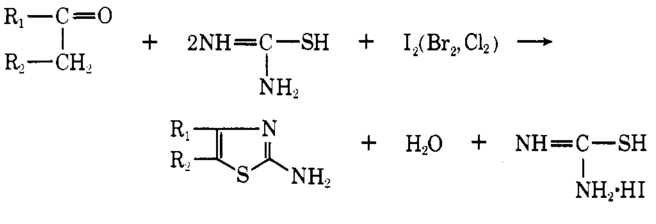
Ten 2-aminothiazole derivatives have been synthesized by the direct interaction of thiourea with a series of ketones in the presence of oxidizing agents (I_2, Br_2, Cl_2). α-Haloketones were also condensed with thiourea; the products were identical with those prepared by the direct method. The uv, ir, and nmr data for the synthesized 2-aminothiazoles are presented.

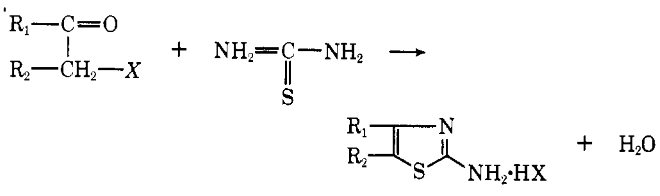
Ten 2-aminothiazoles were prepared by the method of Dodson et al. (*2–5*), by the interaction of 2 moles of thiourea and 1 mole of a ketone having a methyl or a methylene group adjacent to the carbonyl group in the presence of oxidizing agents (I_2, Br_2, Cl_2) (Method A). α-Haloketones (Table I) were also allowed to react with thiourea (*1, 6, 7*) (Method B); the products were identical with those prepared by the direct method. The structure and physical properties of the synthesized 2-aminothiazoles are given in Table II.

An examination of Table II reveals that Method A for the synthesis of 2-aminothiazoles gives excellent yield (60–90%), and can be carried out in a much shorter time than Method B. Furthermore, attempts to condense camphor with thiourea using bromine, iodine, or sulfuryl chloride as oxidizing agents, or to condense 3-bromocamphor with thiourea in alcoholic solutions were unsuccessful even on prolonged heating. This may be due to the great strain present in such bicyclic systems. It was also found during the present investigation that the condensation of cyclopentanone with thiourea, using different oxidizing agents and its corresponding α-bromoderivative with thiourea, could not be achieved. The condensation of some aliphatic ketones such as isobutyl methylketone, *n*-butyl methylketone, and mesityl oxide with thiourea using iodine or sulfuryl chloride were not successful. Sulfuryl chloride showed a violent reaction with the ketones used, and therefore it was added dropwise with cooling. Uv, ir, and nmr data for 2-aminothiazoles are given in Tables III and IV.

Method A



Method B



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