denser over a period of one hour while the temperature was slowly brought to 100°.[7] The reaction mixture was held at this temperature for 5–6 hr. During the reduction of *o*-chloro-N-acetylarsanilic acid to *o*-chloroaniline purple fumes of iodine were observed. The reaction mixture became very dark, all starting material went into solution, and metallic arsenic appeared to be present. It was noted during base runs that if an excessive amount of hydriodic acid was available, an iodinated crystalline compound was formed. If, on the other hand, just the six molecular proportions theoretically needed to remove the arsonic group was added, reduction was incomplete. This is undoubtedly a stepwise reaction with an arseno compound, 2,2′-dichloro-N,N′-diacetyldiaminoarsenobenzene (II) being formed as intermediate, and the acetyl group being removed before removal of the arseno group. After complete reduction the reaction mixture was made alkaline with an excess of saturated sodium hydroxide and steam distilled. *o*-Chloroaniline-Cl^{36} came over as a slightly yellowish oil.

_o_-Chloroacetanilide-Cl^{36}.—The distillate containing *o*-chloroaniline-Cl^{36} was saturated with sodium chloride and twice extracted with benzene. The benzene solution was distilled off after acetylation of the compound with acetic anhydride. The product was recrystallized to radioactive purity[8] in 50% ethanol to a specific activity of 105,000 d./m./mg. Final yield of *o*-chloroacetanilide-Cl^{36} was 0.92 g., m.p. 88°.[9] The yield was 27% based on N-acetylarsanilic acid and 43.8 μc. or 21.9% of the original radioactivity was incorporated.

Preparation of _m_-Chloroacetanilide-Cl^{36}. _m_-Nitrobenzenemercuric Acetate (III).—*m*-Nitrobenzenemercuric acetate was prepared from the sodium salt of *m*-nitrosulfinic acid[10] in a modification of Kharasch and Chalkley's preparation of *m*-nitrobenzenemercuric chloride.[11]

_m_-Chloronitrobenzene-Cl^{36}.—Five and one-tenth grams (0.0135 mole) of *m*-nitrobenzenemercuric acetate, m.p. 173°, dissolved in 25 ml. of glacial acetic acid kept at 80–90° was gassed slowly with Cl_2^{36} (0.027 mole). Two hundred μc. of chlorine-36 was used in this preparation. The radioactive hydrochloric acid was oxidized to Cl_2^{36} in the first generator and swept out with inactive Cl_2 from the second generator as described for the preparation of *o*-chloroacetanilide. The reaction mixture was left to stand overnight, neutralized with sodium hydroxide and steam distilled. Crystalline *m*-chloronitrobenzene-Cl^{36}, m.p. 45°,[12] was collected.

_m_-Chloroaniline-Cl^{36}.—The *m*-chloronitrobenzene-Cl^{36} was reduced by refluxing 5 hr. with 40 ml. of 60% acetic acid and 2 g. of powdered iron. The mixture was made alkaline with saturated sodium hydroxide and steam distilled. *m*-Chloroaniline-Cl^{36} came over as a pale yellow oil.

_m_-Chloroacetanilide-Cl^{36}.—*m*-Chloroaniline-Cl^{36} was twice extracted with benzene and acetylated with acetic anhydride. Recrystallization to radioactive purity from 25% ethanol yielded 1.1 g. of *m*-chloroacetanilide-Cl^{36} m.p. 73°[9] (yield 48.5% based on *m*-nitrobenzenemercuric acetate). Specific activity of the purified compound was 77,000 d./m./mg.; 38μc., or 19% of the original activity, was utilized.

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[7] G. W. Raiziss and J. L. Gavron, "Organic Arsenical Compounds," Reinhold Publ. Corp. Inc., (Chemical Catalog Co.) New York, N. Y., 1923, p. 151.

[8] J. L. Wood and H. R. Gutmann, *J. Biol. Chem.*, **179**, 535 (1949).

[9] F. Beilstein and A. Kurbatow, *Ann. Chem.*, **182**, 94 (1876).

[10] H. Limpricht, *Ber.*, **25**, 75, 3477 (1892).

[11] M. S. Kharasch and L. Chalkley, THIS JOURNAL, **43**, 611 (1921).

[12] W. W. Hartman and M. R. Brethen, "Organic Syntheses," Coll. Vol. I, H. Gilman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 156.

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF ORGANIC DIVISION AND THE CHEMICAL RESEARCH DEPARTMENT, RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL COMPANY]

N-Substituted-amides[1]

BY ARTHUR H. SCHLESINGER AND ERHARD J. PRILL

RECEIVED MAY 7, 1956

The synthesis of various N-substituted-amides, R–$CONR_1R_2$ is described. The novel formation of 2,2′-oxybis-(phenyl-

$$\begin{array}{c} ArCHCONR_1R_2 \\ | \\ O \\ | \\ ArCHCONR_1R_2 \end{array}$$

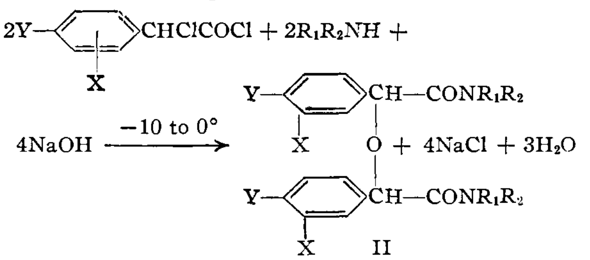
acetamides) from certain 2-chlorophenylacetyl chlorides under conditions normally expected to give 2-chlorophenylacetamides is discussed. The amides described failed to show appreciable phytotoxicity.

N-Substituted-2-chloroacetamides have shown high herbicidal activity.[2] As a continuation of the study of the relationship of structure to phytotoxicity, a large number of unreported chloroacyl amides have been synthesized.

The amides of Tables I–IV were prepared by the reaction of equivalent amounts of acid chlorides and amines in the presence of aqueous sodium hydroxide at −10 to 0°, usually in a solvent such as *sym*-tetrachloroethane or 1,2-dichloroethane. The low temperature was employed in order to reduce the possibility of hydrolysis of aliphatic chlorine atoms and/or elimination of HCl from many of the resultant chloro-N-substituted-amides.

$$R—COCl + R_1R_2NH + NaOH \longrightarrow R—CONR_1R_2 + NaCl + H_2O \qquad \text{I}$$

While attempting to prepare 2-chlorophenylacetamides of structure I (R = C_6H_5CHCl–), the previously unreported 2,2′-oxybis-(N-substituted-phenylacetamides) (II) listed in Table V were obtained as the sole products.



II

The transformation of a benzyl type chlorine atom in the α-position into a benzyl type ether is usually accomplished under more strenuous conditions

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[1] Presented before the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 16–21, 1956.

[2] P. C. Hamm and A. J. Speziale, Abstracts 127th National Meeting, American Chem. Soc., Cincinnati, O., March 30–April 2, 1955.

TABLE I

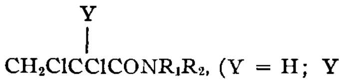
2- OR 3-CHLOROPROPIONAMIDES, $CH_3CHCl{-}CONR_1R_2$ AND $CH_2ClCH_2{-}CONR_1R_2$

R_1	R_2	–Chloro–	B.p. or m.p. °C.	Mm.	$n^{25}\text{D}$	Yield, %	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
C_5H_5O–[a]	H	2	118–120	3		93	$C_8H_{10}ClNO_2$	51.20	51.05	5.34	5.13	7.46	7.73
CH_3–	H	2	70–72	3	1.4670	55	C_4H_8ClNO	39.50	39.14	6.59	6.09	11.52	11.06
$CH_3(CH_2)_4$–	H	2	105–107	3	1.4600	88	$C_8H_{16}ClNO$	54.08	54.48	9.01	8.74	7.88	7.58
$(CH_3)_3C$–	H	2	M.p. 109–110[e]			63	$C_7H_{14}ClNO$	51.38	51.45	8.55	8.49	8.55	8.18
$CH_2{=}CHCH_2$–	H	2	83–85	3	1.4773	75	$C_6H_{10}ClNO$	48.81	49.05	6.77	6.52	9.49	9.00
$(CH_3)_2CH$–	H	2	M.p. 96–97[e]			42	$C_6H_{12}ClNO$	48.22	48.44	8.04	8.08		
$CH_3(CH_2)_5$–	H	2	87–93	1	1.4608	90	$C_9H_{18}ClNO$	56.39	56.78	9.40	9.67		
$CH_3(CH_2)_{15}$–	H	2	M.p. 62–63[f]			50	$C_{19}H_{38}ClNO$	68.77	69.94[g]	11.48	11.22		
$CH_3(CH_2)_3CH(C_2H_5)CH_2$–	H	2	115–119	3	1.4626	88	$C_{11}H_{22}ClNO$	60.14	60.46	10.03	10.25		
$(CH_2)_5CH$–	H	2	M.p. 107–108[e]			48	$C_9H_{16}ClNO$	57.00	56.91	8.45	9.53		
$C_6H_5CH(CH_3)$–	H	2	M.p. 101–102.5[e]			65	$C_{11}H_{14}ClNO$	62.41	62.90	6.63	6.74		
$C_6H_5CH_2CH_2$–	H	2	(M.p. 64–65) 150–152	3		83	$C_{11}H_{14}ClNO$	62.41	62.65	6.63	6.35	6.63	6.24
$(C_2H_5)_2N(CH_2)_3CH(CH_3)$–	H	2	124–128[h]	3	1.4680	77	$C_{12}H_{25}ClN_2O$	57.93	57.52	10.05	9.87		
$C_7H_{14}NO$–[b]	H	2	153–157[h]	3	1.4953	64	$C_{10}H_{19}ClN_2O_2$	51.17	50.93	8.10	7.94		
$(CH_3)_2CH$–	1-$C_{10}H_7$–[c]	2	79–88[i]	4	1.4548	24	$C_9H_{18}ClNO$	56.39[i]	57.37	9.40	9.72		
C_2H_5–	1-$C_{10}H_7$–[c]	2	157–167[i]	2	1.5910	72	$C_{15}H_{16}ClNO$	68.83[i]	70.46	6.08	6.36		
$CH_3(CH_2)_3CH(C_2H_5)CH_2$–	$CH_3(CH_2)_3CH(C_2H_5)CH_2$–	2	173–178	7	1.4649	91	$C_{19}H_{38}ClNO$	68.78	69.38	11.48	11.67		
$C_6H_5CH_2$–	$C_6H_5CH_2$–	2	183–189[i]	1		68	$C_{17}H_{18}ClNO$	70.96[i]	72.49	6.26	6.56		
$(CH_3)_2CH$–	H	3	M.p. 75–76[j]			35	$C_6H_{12}ClNO$	48.40	48.57	8.04	8.05		
$CH_3(CH_2)_4$–	H	3	109–116	1		75	$C_8H_{16}ClNO$	54.08	54.58	9.01	9.42		
$CH_3(CH_2)_5$–	H	3	(M.p. 45–47) 139–141	2		89	$C_9H_{18}ClNO$	56.39	56.91	9.40	9.56		
$CH_2{=}CH{-}CH_2$–	H	3	(M.p. 49–50)[e] 103–107	2		87	$C_6H_{10}ClNO$	48.81	49.73	6.78	7.39		
$(CH_3)_3C$–	H	3	M.p. 93–94[e]			81	$C_7H_{14}ClNO$	51.38	51.69	8.56	8.56		
C_5H_5O–[a]	H	3	M.p. 78–80			60	$C_8H_{10}ClNO_2$	51.20	51.08	5.34	5.27		
2-C_3H_2NS–[d]	H	3	M.p. 166–167[h]			88	$C_6H_7ClN_2OS$	37.79	38.22	3.68	3.94		
$CH_3CH_2CH_2$–	$CH_3CH_2CH_2$–	3	91–93	2	1.4649	82	$C_9H_{18}ClNO$	56.39	55.83	9.40	8.52		
$C_6H_5CH_2$–	$C_6H_5CH_2$–	3	M.p. 55.5–56.5			73	$C_{17}H_{18}ClNO$	70.96	72.00[g]	6.27	6.47		
$(CH_3)_2CHCH_2$–	$(CH_3)_2CHCH_2$–	3	105–108	3	1.4628	65	$C_{11}H_{22}ClNO$	60.14	60.76	10.02	10.51		

[a] Furfuryl-. [b] 3-(4-Morpholinyl)-propyl-. [c] 1-Naphthyl-. [d] 2-Thiazolyl-. [e] Recrystallized from 60–70% ethanol. [f] Recrystallized from acetone. [g] Difficult to purify by recrystallization. [h] Product was not washed but distilled directly. [i] Flash distilled to avoid decomposition, carbon analysis somewhat high. [j] Recrystallized from absolute ethanol. [k] Recrystallized with difficulty from 80% ethanol, therefore analysis poor.

TABLE II

2,3-DICHLOROPROPIONAMIDES AND 2,3-DICHLORO-2-METHYLPROPIONAMIDES,



$CH_2Cl\overset{\overset{\displaystyle Y}{|}}{C}ClCONR_1R_2$, $(Y = H;\ Y = CH_3)$

Y	R_1	R_2	B.p. or m.p. °C.	Mm.	$n^{25}\text{D}$	Yield, %	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
H	C_5H_5O–[a]	H	130–134 (M.p. 69–70)	2		90	$C_8H_9Cl_2NO_2$	43.24	43.43	4.05	4.16
H	$(CH_2)_5CH$–	H	M.p. 126–127			67	$C_9H_{15}Cl_2NO$	48.21	47.88	6.70	6.58
H	o-C_6H_4–C_6H_5	H	M.p. 109–110[c]			65	$C_{15}H_{13}Cl_2NO$	61.23	61.71	4.42	4.65
H	$CH_3CH_2CH_2$–	$CH_3CH_2CH_2$–	93–96	2		86	$C_9H_{17}Cl_2NO$	47.79	48.58	7.54	7.85
H	$CH_2{=}CHCH_2$–	$CH_2{=}CHCH_2$–	125–130[d]	4		95	$C_9H_{13}Cl_2NO$	48.65	47.66[d]	5.87	5.77

H	$-CH_2CH_2-O-CH_2CH_2-$[b]		116–118	1		73	$C_7H_{11}Cl_2NO_2$	39.62	39.41	5.20	5.45
CH_3	C_5H_5O-[a]	H	121–125	1.5	1.5185	71	$C_9H_{11}Cl_2NO_2$	45.76	46.11	4.66	4.39
CH_3	$(CH_2)_5CH-$	H	125–127 (M.p. 49.5–50.5)	1		69	$C_{10}H_{17}Cl_2NO$	50.42	50.91	7.15	7.28
CH_3	$CH_3O(CH_2)_3-$	H	122–124	1	1.4778	62	$C_8H_{15}Cl_2NO_2$	42.11	41.96	6.58	6.58
CH_3	$C_6H_5CH_2CH_2-$	H	141–143[d]	2		59	$C_{12}H_{15}Cl_2NO$	55.38	56.71[d]	5.78	5.93
CH_3	$-CH_2CH_2-O-CH_2CH_2-$[b]		123–126	1.5		66	$C_8H_{13}Cl_2NO_2$	42.48	42.76	5.75	5.73

[a] Furfuryl. [b] Radical derived from morpholine. [c] Recrystallized from absolute ethanol. [d] Tends to decompose upon distillation, hence poor analysis.

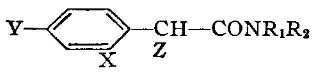
TABLE III

4-CHLOROBUTYRAMIDES, $Cl(CH_2)_3CONR_1R_2$

R₁	R₂	B.p. °C.	Mm.	$n^{25}D$	Yield, %	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
C_2H_5-	H	102–122	3		14[c]	$C_6H_{12}ClNO$	48.16	47.44	8.02	7.39		
$CH_3(CH_2)_4-$	H	139–146	3	1.4701	76	$C_9H_{18}ClNO$	56.39	55.83	9.41	9.58	7.30	6.96
C_5H_5O-[a]	H	158–165	3	1.5137	57	$C_9H_{12}ClNO_2$	53.58	53.55	5.96	6.21		
$-CH_2CH_2-O-CH_2CH_2-$[b]		140–143	3	1.5001	85	$C_8H_{14}ClNO_2$	50.13	49.65	7.31	7.56	7.31	7.65
CH_3-	CH_3-	90–95	3.5		21[c]	$C_6H_{12}ClNO$	48.16	49.18	8.03	7.56		
C_2H_5-	C_2H_5-	101–103	3	1.4662	81	$C_8H_{16}ClNO$	53.53	53.05	9.01	9.06		

[a] Furfuryl. [b] Radical derived from morpholine. [c] Low yield due to water solubility of product.

TABLE IV

2-PHENYLACETAMIDES, 

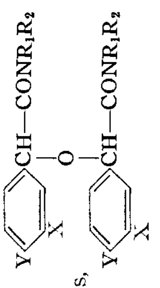
$Y-C_6H_3(X)-\underset{Z}{CH}-CONR_1R_2$

Z	Y	X	R₁	R₂	B.p. or m.p. °C.	Mm.	$n^{25}D$	Yield, %	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
H	H	H	H	C_5H_5O-[a]	M.p. 101–102			74	$C_{12}H_{13}NO_2$	72.56	72.51	6.05	6.24
H	H	H	H	$(CH_2)_5CH-$	M.p. 137–139			83	$C_{14}H_{19}NO$	77.42	77.76	8.78	8.76
H	H	H	H	$(C_2H_5)_2N(CH_2)_3-$	193–197	2	1.5150	70	$C_{15}H_{24}N_2O$	72.50	72.01	9.69	9.38
H	H	H	$-CH_2CH_2-O-CH_2CH_2-$[b]		M.p. 71–72			69	$C_{12}H_{15}NO_2$	70.24	70.20	7.32	6.55
H	H	H	$(CH_3)_2CHCH_2-$	$(CH_3)_2CHCH_2-$	152–155	3	1.5024	81	$C_{16}H_{25}NO$	77.74	77.73	10.20	10.37
H	H	H	$CH_2=CHCH_2-$	$CH_2=CHCH_2-$	221–225	3	1.5316	70	$C_{14}H_{17}NO$	78.14	78.18	7.91	7.54
H	Cl	H	H	C_5H_5O-[a]	M.p. 143–145			80	$C_{13}H_{12}ClNO_2$	62.52	61.89	4.82	4.86
H	Cl	H	H	$CH_3O(CH_2)_3-$	M.p. 58.5–61.0			72	$C_{12}H_{16}ClNO_2$	59.63	59.10	6.64	6.40
H	Cl	H	$-CH_2CH_2-O-CH_2CH_2$[b]		M.p. 107.5–109			71	$C_{12}H_{14}ClNO_2$	60.13	59.77	5.85	6.02
H	Cl	H	$CH_2=CHCH_2-$	$CH_2=CHCH_2-$	170–172	3	1.5450	93	$C_{14}H_{16}ClNO$	67.33	66.88	6.42	6.81
Cl	H	Cl	H	$CH_2=CHCH_2-$	162–167 (M.p. 44–46)	2		78	$C_{11}H_{11}Cl_2NO$	54.09	54.85	4.50	4.79
Cl	H	Cl	$CH_2=CHCH_2-$	$CH_2=CHCH_2-$	158–164	2	1.5500	74	$C_{14}H_{15}Cl_2NO$[c]	59.16	57.72[d]	4.94	5.53

[a] Furfuryl. [b] Radical derived from morpholine. [c] Calcd.: N, 4.94. Found: N, 5.09. [d] Carbon analysis poor due to tendency of product to decompose upon distillation.

TABLE V

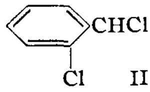
2,2'-OXYBISPHENYLACETAMIDES,



Y	X	R_1	R_2	B.p. or M.p. °C.	Mm.	$n^{25}D$	Yield, %	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
H	H	C_5H_5O–[a]	H	M.p. 99–100			79	$C_{26}H_{24}N_2O_5$	67.39	68.08	7.48	7.74	6.55	6.47
H	H	$(CH_3)_3C$–	H	M.p. 116–117			67	$C_{24}H_{32}N_2O_3$					7.06	7.14
H	H	$(CH_2)_5CH$–	H	M.p. 139–140			87	$C_{28}H_{36}N_2O_3$	75.00	75.62	8.03	8.17	6.25	6.16
H	H	$CH_3O(CH_2)_3$–	H	165–175	3	1.5257	79	$C_{24}H_{32}N_2O_5$	67.29	68.08	7.48	7.74	6.55	6.47
H	H	$(C_2H_5)_2N(CH_2)_3$–	H	185–192	3	1.5182	57	$C_{30}H_{46}N_4O_3$	70.59	70.79	9.01	9.51	11.00	10.70
H	H	–CH_2CH_2–O–CH_2CH_2–[b]		M.p. 70–71[c]			67	$C_{24}H_{28}N_2O_5$					6.62	6.59
H	H	$CH_2{=}CHCH_2$–	$CH_2{=}CHCH_2$	192–198	28	1.5350	100	$C_{28}H_{32}N_2O_3$	75.67	75.35	7.22	7.68		
H	H	$(CH_3)_2CHCH_2$–	$(CH_3)_2CHCH_2$–	152–157	3	1.5042	79	$C_{32}H_{48}N_2O_3$	75.60	76.85	9.46	9.69		
Cl	H	C_6H_5–	H	M.p. 141–143			40[d]	$C_{28}H_{22}Cl_2N_2O_3$	66.53	65.84	4.36	4.74		
Cl	H	CH_3–	C_6H_5–	205–210	4		68[d]	$C_{30}H_{26}Cl_2N_2O_3$					5.25	5.31
Cl	H	$CH_3O(CH_2)_3$–	H	205–210	2.5		77[d]	$C_{24}H_{30}Cl_2N_2O_5$					5.64	4.93
Cl	Cl	$CH_3O(CH_2)_3$–	H	207–211	3		83[d]	$C_{24}H_{28}Cl_4N_2O_5$					4.94	4.47

[a] Furfuryl. [b] Radical derived from morpholine. [c] Obtained by filtering reaction medium directly. [d] In these cases the procedure involved use of 2 moles alkali to 1 of amine (instead of 1:1) and reaction at reflux.

than employed here. The facile reaction at −10° appears unique in this respect. The steric inhibition of this reaction by an *ortho* chlorine atom in the phenyl ring is demonstrated by the fact that 2-chloro-2-(2-chlorophenyl)-acetyl chloride failed to give structure II even when refluxed with amine and excess aqueous sodium hydroxide. N-Substituted-2-chloro-2-(2-chlorophenyl)-acetamides (III) ar produced exclusively.

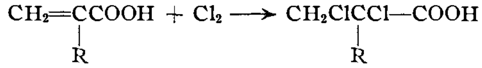


III

In contrast to this effect of the *o*-chlorine atom which must be steric rather than electronic is the facile formation of II when 2-chloro-2-(4-chlorophenyl)-acetyl chloride is employed under similar conditions.

While the amides described in the Experimental Section of this paper failed to exhibit herbicidal properties (indicating that the 2-chloroacetamide moiety is necessary for phytotoxic activity) several of the 2,2'-oxybis-amides showed interesting fungicidal properties.[3]

Several chlorinated acids were required for the preparation of the above amides. The previously unreported addition of chlorine to acrylic and methacrylic acids was successfully employed for the synthesis of the corresponding 2,3-dichloropropionic acids (IV). However, the acids IV were quite sensitive to elimination of HCl and had to be processed quickly.



$$\underset{\displaystyle R}{CH_2{=}\overset{}{C}}COOH + Cl_2 \longrightarrow CH_2Cl\underset{\displaystyle R}{C}Cl{-}COOH$$

IV, R = H
R = CH_3

Experimental[4]

Amides I.—The preparation of N,N-diethyl-4-chlorobutyramide is typical of the preparation of the amides of Tables I–IV, the appropriate acid chloride and amine being employed.

A stirred solution of 19 g. (0.26 mole) of diethylamine in 150 ml. of ethylene dichloride was maintained at −10° or less by means of an alcohol–Dry Ice bath while 44.3 g. (0.31 mole) of 4-chlorobutyryl chloride[5] and 63.0 ml. of 20% aqueous sodium hydroxide (0.31 mole) were added separately and simultaneously from separatory funnels over a one-hour period. After the mixture had warmed to room temperature, the organic layer was washed successively with 5% hydrochloric acid, 5% sodium bicarbonate and water. The solvent was removed *in vacuo* and distillation gave a small forerun, b.p. 70–90° at 3 mm. and 37 g. (81%) of N,N-diethyl-4-chlorobutyramide, b.p. 101–103° at 3 mm., $n^{25}D$ 1.4662.

Anal. Calcd. for $C_8H_{16}ClNO$: C, 53.53; H, 9.01. Found: C, 53.05; H, 9.06.

2,2'-Oxybis-amides II.—The preparation of 2,2'-oxybis-(N-cyclohexyl-2-phenylacetamide) is illustrative of the preparation of the amides II of Table V.

In 150 ml. of carbon tetrachloride there was placed 10 g. (0.10 mole) of cyclohexylamine. This solution was held below −10° and 21.3 ml. of 20% aqueous sodium hydroxide (0.106 mole) and 20 g. (0.106 mole) of 2-chloro-2-phenylacetyl chloride were added separately and simultaneously during a 20-minute period with stirring. After the mixture had warmed to room temperature the solid was filtered off and the organic layer was separated. The latter yielded more solid upon solvent removal. The combined solid material

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(3) This will be described in a forthcoming publication by E. G. Jaworski, A. H. Schlesinger and E. J. Prill.

(4) All melting points listed are corrected.

(5) H. Kaltschnitt and A. Tartter, German Patent 804,567 (1951).

was boiled in ether, chilled and filtered to give 20 g. (87% based on amine) of 2,2′-oxybis-(N-cyclohexyl-2-phenylacetamide), m.p. 139–140°.

Anal. Calcd. for $C_{28}H_{36}N_2O_3$: C, 75.00; H, 8.03; N, 6.25. Found: C, 75.62; H, 8.17; N, 6.16.

N-(3-Chlorophenyl)-2-nitroacetamide.—This was prepared by a procedure of Boyd and Leshin[6] for similar compounds. A solution of 76.8 g. (0.5 mole) of 3-chlorophenyl isocyanate and 30.5 g. (0.5 mole) of nitromethane in 500 ml. of benzene was refluxed with 69 g. (0.5 mole) of potassium carbonate for 10 hr. After cooling and filtering, the solid was stirred in 2 liters of cold water and the filtrate from this was acidified to Congo Red paper with dilute hydrochloric acid. The precipitate was collected and crystallized from benzene to give 7 g. (7%) of yellow crystals, m.p. 119.5–120.5°.

Anal. Calcd. for $C_8H_7ClN_2O_3$: C, 44.76; H, 3.26. Found: C, 44.80; H, 3.45.

N-Furfurylacetamide.—A solution of 48.5 g. (0.5 mole) of furfurylamine in 100 ml. of benzene was added slowly to 91 g. (0.9 mole) of acetic anhydride over a 15-min. period. The benzene and excess anhydride were removed by distillation and there was obtained a 64-g. (92%) yield of N-furfurylacetamide, b.p. 114–116° at 3 mm. After standing two days the liquid set to a solid, m.p. 31–33°.

Anal. Calcd. for $C_7H_9NO_2$: C, 60.43; H, 6.47. Found: C, 59.97; H, 6.60.

N-Allyl-2-chlorobenzamide.—This was prepared by the reaction of 50 g. (0.29 mole) of 2-chlorobenzoyl chloride, 16.5 g. (0.29 mole) of allylamine, 150 ml. of benzene and 60 ml. of 20% sodium hydroxide (0.30 mole). After stirring for 30 minutes, the organic layer was separated, washed with dilute hydrochloric acid and distilled to give a 48 g. (86%) yield of yellow crystals, b.p. 145–150° at 2.0 mm., m.p. 67–68°.

Anal. Calcd. for $C_{10}H_{10}ClNO$: C, 61.38; H, 5.11. Found: C, 61.30; H, 5.06.

Acid Chlorides.—The following new chlorophenylacetyl chlorides were prepared from the appropriate phenylacetic acid by the method of Schwenk and Papa[7] utilizing thionyl chloride and sulfuryl chloride: 2-chloro-2-(2-chlorophenyl)-acetyl chloride, b.p. 146–149° at 35 mm.; 2-chloro-2-(2,4-dichlorophenyl)-acetyl chloride, b.p 158–161° at 22 mm.; 2-chloro-2-(3,4-dichlorophenyl)-acetyl chloride, b.p. 163–167° at 22 mm.

Other acid chlorides needed were prepared from the corresponding acids directly with thionyl chloride.

2,3-Dichloropropionic Acid.—This material has been previously described[8,9] and obtained by other routes. In our hands the following was a more convenient synthesis.

A solution of 100 g. (1.39 moles) of acrylic acid (stabilized with methylene blue) in 400 ml. of carbon tetrachloride was stirred and treated with chlorine gas for 6 hr. The increase in weight was approximately 73 g. The solution was concentrated *in vacuo* and then distilled to give a 130-g. (66%) yield of 2,3-dichloropropionic acid, b.p. 83–86° at 3 mm., m.p. 57–58° (lit.[8,9] values, b.p. 83–86° at 2 mm.; m.p. 49°).

2,3-Dichloro-2-methylpropionic Acid.—In a manner similar to the preceding experiment, 86 g. (1.0 mole) of methacrylic acid in 500 ml. of carbon tetrachloride was treated with chlorine for 2 hr. Distillation, after solvent removal, gave 31 g. of methacrylic acid, b.p. 40–60° at 2 mm. followed by 2,3-dichloro-2-methylpropionic acid, yellow oil, b.p. 106–112° at 2 mm., $n^{25}D$ 1.4670. The yield was 47 g. (47%) and the conversion was 30%. The material is quite unstable, rapidly losing HCl.

Anal. Calcd. for $C_4H_6Cl_2O_2$: neut. equiv., 157. Found: neut. equiv., 151.

2,4-Dichlorophenylacetic Acid.—To a solution of 380 ml. of concd. sulfuric acid in 520 ml. of water there was added 500 g. (2.7 moles) of 2,4-dichlorophenylacetonitrile.[10] After heating to boiling and stirring for 3 hr. the mixture was filtered and the solid was crystallized from alcohol to give 104 g. (71.5%) of 2,4-dichlorophenylacetic acid, m.p. 52–53°.

Anal. Calcd. for $C_8H_6Cl_2O_2$: Cl, 34.63. Found: Cl, 33.85.

Herbicidal Assay.—The method employed has been described by Hamm and Speziale.[2] All of the amides described in this paper were shown to be relatively non-phytotoxic in pre-emergence tests.

Acknowledgment.—The authors wish to express their gratitude to Drs. P. C. Hamm and E. G. Jaworski for evaluation data and to Mrs. Winifred Harden, Mrs. Geneva Kratzer, Mr. Donald Stoltz and Mr. J. Danby for analytical data. Several helpful discussions with Dr. A. J. Speziale are gratefully acknowledged.

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[7] E. Schwenk and D. Papa, *ibid.*, **70**, 3626 (1948).

[8] G. S. Simpson, *ibid.*, **40**, 674 (1918).

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[10] E. A. Falco, S. DuBreuil and G. H. Hitchings, THIS JOURNAL, **73**, 3758 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

The Diazotization of 3,3-Dimethyl-1-butylamine-1-^{14}C

BY WILLIAM H. SAUNDERS, JR.

RECEIVED JULY 17, 1956

The reaction of 3,3-dimethyl-1-butylamine-1-^{14}C with nitrous acid yields an alcohol mixture which was shown to contain 57% 3,3-dimethyl-1-butanol and 43% 2,3-dimethyl-2-butanol. The former is produced with less than 1% isotope-position rearrangement. The significance of these results is discussed.

Isotopic tracer studies on the diazotization of amines of the type $RCH_2CH_2NH_2$ have revealed that the tendency of R to migrate follows the order $Ar > CH_3 > H > ArCH_2$.[1] Since very little is known about the migration aptitudes of branched alkyl groups, a study of the case where R = *t*-butyl was undertaken. This system is also of interest in that it bears structural resemblances to systems reported to undergo 1,3-shifts of methyl.[2]

The synthetic scheme employed is outlined in Fig. 1. Use of carbon-^{14}C dioxide in the first step led to the desired 3,3-dimethyl-1-butylamine-1-^{14}C

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[1] (a) A. W. Fort and J. D. Roberts, THIS JOURNAL, **78**, 584 (1956); (b) J. D. Roberts and M. Halmann, *ibid.*, **75**, 5759 (1953); (c) J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5493 (1952); (d) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953).

[2] (a) F. C. Whitmore, K. C. Laughlin, J. F. Matuszeski and J. D. Surmatis, *ibid.*, **63**, 756 (1941); (b) W. A. Mosher and J. C. Cox, *ibid.*, **72**, 3701 (1950); see, however, M. F. Ansell, M. A. Davis, J. W. Hancock and W. J. Hickinbottom, *Chemistry & Industry*, 1483 (1955), who cast doubt on the identity of the starting material used by Mosher and Cox.