EXPERIMENTAL

Condensation with *p*-Nitrobenzaldehyde. A mixture of *p*-nitrobenzaldehyde (3.022 grams, 0.02 mole), methanol (25 ml.) and β-ethoxyethylamine (2.228 grams, 0.025 mole) was refluxed for 30 minutes and the resulting yellow solution cooled in the refrigerator for 1 hour. The precipitate was filtered and washed three times with 25-ml. portions of distilled water. The slightly cream-colored needles were air-dried, then dried over $CaCl_2$ for 24 hours in a desiccator. The yield was 4.1 grams (84.5%) (m.p. 55.0-55.5° C.). Recrystallization gave the same melting point.

Analysis. Calculated for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35; N, 12.60. Found: C, 59.27; H, 6.42; N, 12.52.

Condensation with *p*-Acetamidobenzaldehyde. A mixture of *p*-acetamidobenzaldehyde (3.259 grams, 0.02 mole), methanol (25 ml.), and β-ethoxyethylamine (1.780 grams, 0.02 mole) was refluxed 30 minutes and the methanol evaporated on the water bath. The resulting oily residue or yellow solid which formed on cooling was dissolved in 5 ml. of ethyl acetate with warming on the water bath and stirring to effect dissolution. Cyclohexane (50 ml.) was then added with stirring and the resulting precipitate was filtered and washed with 20 ml. of cyclohexane. The cream-colored, very fine needles were then air-dried. The yield was 3.2 grams (63.51%) (m.p. 93-94° C.). Repeated purification with cyclohexane gave the same melting point.

Analysis. Calculated for $C_{16}H_{21}N_3O_2$: C, 66.87; H, 7.37; N, 14.62. Found: C, 66.71; H, 7.40; N, 14.55.

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Synthesis and Thermal Decomposition of Tetrasubstituted Ureas

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A number of new tetraalkylureas, aryltrialkylureas, dialkyldiarylureas, alkyltriarylureas, and tetraarylureas were prepared and characterized. Several new acetamides, amines, and disubstituted carbamoyl chlorides were synthesized as intermediate compounds for the urea syntheses. A study of the thermal decompositiion of several tetraalkylureas indicated that the first step of degradation involves a β-elimination reaction.

A STUDY of the synthesis and thermal decomposition of a variety of tetrasubstituted ureas was conducted as part of a program dealing with the development of new synthetic lubricants.

EXPERIMENTAL

Synthetic Methods. TETRASUBSTITUTED UREAS (Table I). *Method A. Preparation of Tetra-n-decylurea* (Compound V, Table I). Di-*n*-decylamine (42.8 grams, 0.48 mole) and 500 ml. of toluene were placed in a 1-liter flask equipped with thermometer, stirrer, reflux condenser, and gas inlet tube. Phosgene (23.8 grams, 0.24 mole) was bubbled into the stirred reaction mixture while the temperature was held below 35° C. by applying external cooling. After the addition was complete, the reaction mixture was slowly heated to 110° C. and held there for 16 hours with stirring. The toluene was distilled off and the residue refluxed and stirred with 200 ml. of KOH solution for 1.5 hours. This reaction mixture was extracted with 300 ml. of ether. The ether layer was separated and dried over anhydrous Na_2SO_4, and the ether was stripped off, leaving a crude residual liquid. Purified product was obtained after two distillations. It was a yellow oil (b.p. 246–47° C./0.08 mm., volatilization temperature 428–35° C., n_D^{25} 1.4622, $d_4^{26.4}$ 0.8582, MR_D^{25} 199.00 observed; 194.33 calculated). On cooling, the product solidified to a pale yellow solid (m.p. 25.5–27.0° C.). The yield was 70.0 grams, equivalent to 47.0% of the theoretical.

Method B. Preparation of 1-(2,4-Dimethylphenyl)-1-(4-phenoxyphenyl)-3-(1-naphthyl)-3-pheylurea (Compound XXXV in Table I). *N*-(1-Naphthyl)-*N*-phenylcarbamoyl chloride (44.0 grams, 0.156 mole) and *N*-(2-4-dimethylphenyl)-4-phenoxyaniline (45.3 grams, 0.156 mole) were heated in a 250-ml. flask for 2 hours at 200° to 210° C. One hour of this heating period was carried out in the presence of 0.5 gram of $AlCl_3$ catalyst. Upon cooling, 300 ml. of toluene were added and stirring and heating continued for 1 hour more. The reaction mixture was then poured into 500 ml. of water containing 1 mole of NaOH. The phases were separated, the organic layer was washed free of excess base, and the toluene was distilled off. The residues were vacuum-distilled through a Claisen head. A total of 51 grams of an amber glass (b.p. 305–14° C./0.55 mm.) was obtained. This material had an apparent melting point of 87–96° C. and volatilization temperature of 446–50° C. The glass when dissolved in toluene and shaken with concentrated HCl took on a deep-red coloration. The organic layer was separated, purged with N_2, and decolorized cold with Norit A. The resulting filtrate was stripped of solvent and flash-distilled. A center cut, when recrystallized from ethanol-water, yielded the product as a fine, snow-white crystalline material (m.p. 173–75° C., volatilization temperature, 460–70° C.). A total of 11 grams (13%) of pure material was obtained.

Method C. Preparation of 1,1,3,3-Tetrakis(4-biphenylyl)-urea (Compound XXXII in Table I). *N,N*-Bis(4-biphenylyl)carbamoyl chloride (335 grams, 0.875 mole) was dissolved in 1500 ml. of toluene in a 3-liter, 3-necked flask fitted with thermometer, stirrer, and reflux condenser. Metallic sodium (22.1 grams, 0.96 mole) was added piece by piece to the vigorously stirred, refluxing toluene solution over a 1½-hour period. Stirring and refluxing were continued for another 3 hours. The liquids were decanted from the cooled reaction mixture and the gelatinous semisolids filtered on a fritted glass funnel. The decantate was water-washed and separated. Filter cake solids were extracted with toluene-ethanol, then with water, and the organic phase was separated and combined with the decantate. Titration of the combined water washings indicated that 80% of the sodium had been consumed. The toluene liquors were reduced in volume and cooled in ice. Fractional crystallization of the concentrated extracts yielded 190 grams of crude urea. This product was recrystallized from acetone, yielding 107 grams of urea (m.p. 247–50° C.). Another 11 grams of pure material were obtained by decolorization and acid-wash purification of the mother liquors. Total yield was 118 grams (40%).

INTERMEDIATE COMPOUNDS (Table II). *Method A. Preparation of N-(4-Phenoxyphenyl)-3-phenoxyacetanilide* (Compound XXIV of Table II). 4-Phenoxyphenyl bromide (124.5 grams, 0.50 mole), 3-phenoxyacetanilide (113.7 grams, 0.50 mole), anhydrous potassium carbonate (76.0 grams, 0.55 mole), and 200 ml. of xylene were placed in a 1-liter flask equipped with stirrer, thermometer, reflux condenser, and Dean-Stark trap. In addition to the reactants, the copper catalyst was added in the following forms and amounts: copper foil (24 strips, 1.5 × 2.5 cm.), electrolytic copper dust (10 grams), and cuprous chloride (6 grams). The entire reaction mixture was refluxed for 18 hours and 3.7 ml. of water were collected (theory 4.5 ml.). The reaction mixture was filtered and the filter cake washed with hot toluene. The filtrate was decolorized with charcoal and the solvent distilled off. The residue was vacuum-distilled through a Claisen head. The product (90 grams, 45%) was a very viscous liquid (b.p. 233–37° C./0.05 mm., n_D^{30} 1.6217, d_4^{90} 1.2018, molar refraction calculated 116.30, found 115.52).

Method F. Preparation of N-Methyl-N-(4-methylphenyl) carbamoyl chloride (Compound XXXI, Table II). Toluene (500 ml.) was placed in a 1-liter flask equipped with thermometer, stirrer, dry ice condenser, and gas inlet tube. The toluene was cooled to 15° C. and phosgene (248 grams, 2.5 moles) was dissolved in the solvent. *N*-Methyl-4-methylaniline (200 grams, 1.65 moles) was added dropwise to the phosgene solution while the temperature was maintained below 25° C. The dry ice condenser was replaced with a water condenser. The reaction mixture was slowly brought to reflux and held there for 3½ hours while a steady addition of phosgene was maintained. Finally, the reaction mixture was refluxed for 1½ hours to drive off excess phosgene. The mixture was concentrated to a 200-ml. volume, cooled, and filtered. The precipitated solids were recrystallized from Skellysolve B, washed with water, and recrystallized from toluene. The final product, a white crystalline powder (m.p. 75–77° C.,) was obtained after two recrystallizations from toluene. A yield of 225 grams (74%) was obtained.

Analytical Methods. Elemental analyses were performed by the Clark Microanalytical Laboratories, Urbana, Ill. The infrared spectra were obtained on all samples as liquids or melts using a Beckman Model IR-4 double-beam recording spectrophotometer equipped with a rock salt prism. The vapor phase chromatographic analysis of 1-octene and the volatile decomposition products of tetra-*n*-octylurea was performed on a Perkin-Elmer Model 154 recording Fractometer. A 2-meter column was packed with Perkin-Elmer column material A (dinonyl phthalate suspended on Celite). Helium was used as a carrier gas and a column temperature of 80° C. was employed. The thermal decomposition apparatus (*6*) consisted of a 20-ml. test cell equipped with an automatically controlled heater and a trap for volatiles. The test cell was operated under a stream of nitrogen at 365° C. for 1 to 10 hours, depending on the rate of decomposition.

DISCUSSION

Synthesis of Tetrasubstituted Ureas. All symmetrical tetrasubstituted ureas containing alkyl and alkaryl groups were prepared by the phosgenation of secondary amines.

$$COCl_2 + 2R_2NH \rightarrow R_2NCONR_2 + 2HCl$$

Inert solvents such as toluene (*15*) and xylene (*5*) have been used as reaction media, and aluminum chloride (*14*) has been employed as a catalyst. Basic materials, such as ZnO (*10*), MgO (*10*), pyridine (*15*), dimethylaniline (*5*), and aqueous alkali (*5*), have found use as acid acceptors. Toluene, in the presence of an excess of the secondary amine reactant, was preferred to the use of stoichiometric amounts of the secondary amine reactant, plus an acid acceptor.

Three symmetrical tetraaryl ureas of high molecular weight were obtained by the decarbonylative condensation of disubstituted carbamoyl chlorides using molten sodium dispersed in refluxing toluene.

$$2R_2NCOCl + 2Na \rightarrow R_2NCONR_2 + 2NaCl + CO$$

This type of reaction (*13*) proceeds exothermically at a fairly high rate and yields reaction products nearly free of contamination.

All new unsymmetrical tetrasubstituted ureas were synthesized by the reaction of disubstituted carbamoyl chlorides and secondary amines.

$$R_2NCOCl + R'_2NH \rightarrow R_2NCONR'_2 + HCl$$

Benzene (*15*), chloroform (*11*), ether (*1*), and pyridine (*4*) have been utilized as reaction solvents, and excess secondary as well as tertiary amines (*8*)are suitable as acid acceptors. Reactions with secondary amines which contained one or more alkyl substituents could be conducted without the aid of catalysts in the presence of toluene or pyridine, whereas

Table I. Tetrasubstituted Ureas

$R_1R_2NCONR_3R_4$

Compd. No.	R_1	R_2	R_3	R_4	Synthesis Method[a]	Yield,[b] %	M.P., ° C.	B.P., ° C./Mm.	N.B.P., ° C.[c]	UV Absorption in Ethanol		Recryst. Solvents[d]	Molecular Formula	Elemental Analysis			
										λ_{max}	ϵ				C	H	N
I	n-C_6H_{13}	n-C_6H_{13}	R_1	R_2	A	46	-20	156-58/0.03	380-85	...	...	...	$C_{25}H_{52}N_2O$	Calcd.	75.7	13.2	7.1
														Found	75.7	13.5	7.3
II	2-$C_2H_5C_6H_{12}$	2-$C_2H_5C_6H_{12}$	R_1	R_2	A	40	-40	176-78/0.03	400-05	...	...	...	$C_{33}H_{68}N_2O$	Calcd.	77.9	13.5	5.5
														Found	77.2	12.9	5.6
III	n-$C_{16}H_{33}$	CH_3	R_1	R_2	A	33	36-38	254-56/0.13	430-32	...	...	...	$C_{35}H_{72}N_2O$	Calcd.	78.3	13.5	5.2
														Found	78.2	13.2	5.3
IV	n-C_8H_{17}	n-C_8H_{17}	R_1	R_2	A	70	3.5-4.5	210-12/0.11	409-13	...	...	...	$C_{33}H_{68}N_2O$	Calcd.	77.9	13.5	5.5
														Found	77.4	12.9	5.7
V	n-$C_{10}H_{21}$	n-$C_{10}H_{21}$	R_1	R_2	A	47	25-27	246-47/0.08	428-35	...	...	...	$C_{41}H_{84}N_2O$	Calcd.	79.3	13.6	4.5
														Found	79.4	13.2	4.4
VI	4-n-$C_8H_{17}C_6H_4$	4-n-$C_8H_{17}C_6H_4$	R_1	R_2	A	60	152-55	...	436-44	275	43,075	1 + 2	$C_{57}H_{84}N_2O$	Calcd.	84.2	10.4	3.4
														Found	84.3	10.1	3.4
VII	n-$C_{18}H_{37}$	n-$C_{18}H_{37}$	R_1	R_2	A	22	67-70	...	444-50	...	...	2	$C_{73}H_{148}N_2O$	Calcd.	81.9	13.9	2.6
														Found	81.8	13.5	2.8
VIII	n-$C_{16}H_{33}$	CH_3	C_6H_5	C_6H_5	B	50	44-46	241-43/0.13	440-45	255	14,690	...	$C_{30}H_{46}N_2O$	Calcd.	80.0	10.3	6.2
														Found	79.9	10.1	6.7
IX	CH_3	C_6H_5	C_6H_5	C_6H_5	B	46	106-08	178-79/0.32	400-05	270	19,456	...	$C_{20}H_{18}N_2O$	Calcd.	79.4	6.0	9.3
														Found		(*4*)	
X	$C_6H_5CH_2$	C_6H_5	C_6H_5	C_6H_5	B	13	108-11	218-20/0.30	390-95	260	14,192	...	$C_{26}H_{22}N_2O$	Calcd.	82.5	5.9	7.4
														Found	82.1	5.6	7.6
XI	n-$C_{16}H_{33}$	2-Naphthyl	C_6H_5	C_6H_5	B	31	-15	285-90/0.30	410-18	...	...	...	$C_{39}H_{50}N_2O$	Calcd.	83.2	9.0	5.0
														Found	82.7	9.1	5.0
XII	n-C_4H_9	C_6H_5	C_6H_5	C_6H_5	B	64	15	191-96/0.06	406-15	264	14,560	...	$C_{22}H_{24}N_2O$	Calcd.	80.2	7.0	8.1
														Found	79.6	6.4	8.4
XIII	n-C_9H_{17}	C_6H_5	C_6H_5	C_6H_5	B	73	10	229-31/0.75	420-26	263	15,251	...	$C_{26}H_{33}N_2O$	Calcd.	81.0	8.1	7.0
														Found	80.8	7.6	6.9
XIV	n-$C_{16}H_{33}$	C_6H_5	C_6H_5	C_6H_5	B	66	44-47	267-68/0.40	444-50	263	15,481	...	$C_{34}H_{48}N_2O$	Calcd.	82.0	9.4	5.5
														Found	81.4	9.5	5.9
XV	2-Naphthyl	C_6H_5	C_6H_5	C_6H_5	B	31	130-32	281-83/0.70	476-79	250	33,560	1, 2	$C_{29}H_{22}N_2O$	Calcd.	84.0	5.4	6.8
														Found		(*12*)	
XVI	1-Naphthyl	C_6H_5	C_6H_5	C_6H_5	B	17	168-70	251-65/0.42	475-81	260(s)	16,346	2	$C_{29}H_{22}N_2O$	Calcd.	84.0	5.4	6.8
														Found	83.8	5.1	6.7
XVII	(*o*,*o*′-Diphenylene)		C_6H_5	C_6H_5	B	7	180-83	213-20/0.20	448-52	265	19,730	1	$C_{25}H_{18}N_2O$	Calcd.	82.9	5.0	7.7
														Found	82.5	5.5	8.2
XVIII	n-$C_{18}H_{37}$	C_6H_5	C_6H_5	C_6H_5	B	76	57-60	251-58/0.60	450-52	...	...	...	$C_{37}H_{52}N_2O$	Calcd.	82.2	9.7	5.2
														Found	82.0	9.8	5.0
XIX	2-Pyridyl	2-Pyridyl	C_6H_5	C_6H_5	B	46	214-17	...	344-58	255	19,170	1, 3	$C_{23}H_{18}N_4O$	Calcd.	75.4	5.0	15.3
														Found	75.5	5.3	15.1
XX	4-n-$C_8H_{17}C_6H_4$	4-n-$C_8H_{17}C_6H_4$	C_6H_5	C_6H_5	B	24	119-20	270-85/0.70	460-65	270	22,678	1	$C_{41}H_{52}N_2O$	Calcd.	83.6	8.9	4.8
														Found	83.9	9.2	5.0
XXI	4-$CH_3C_6H_4$	C_6H_5	C_6H_5	C_6H_5	B	30	108-10	240-60/0.15	470-78	265	20,872	2	$C_{26}H_{22}N_2O$	Calcd.	82.5	5.9	7.4
														Found	82.2	5.6	7.6
XXII	2,4-$(CH_3)_2C_6H_3$	C_6H_5	C_6H_5	C_6H_5	B	15	92-94	230-50/0.20	454-60	262	19,506	2	$C_{27}H_{24}N_2O$	Calcd.	82.6	6.2	7.2
														Found	82.1	6.0	7.3
XXIII	4-C_6H_5-C_6H_4	C_6H_5	C_6H_5	C_6H_5	B	20	160-62	260-300/0.15	481-89	280	28,950	4	$C_{31}H_{24}N_2O$	Calcd.	84.5	5.5	6.4
														Found	84.5	5.5	6.5
XXIV	n-$C_{18}H_{37}$	n-$C_{18}H_{37}$	C_6H_5	C_6H_5	B	31	28	317-20/0.15	451-62	267	37,898	...	$C_{49}H_{84}N_2O$	Calcd.	82.1	11.8	3.9
														Found	...	...	...
XXV	4-C_6H_5O-C_6H_4	C_6H_5	C_6H_5	C_6H_5	B	33	79-82	281-85/0.08	485-95	265	25,092	...	$C_{31}H_{24}N_2O$	Calcd.	81.6	5.3	6.1
														Found	81.3	4.9	6.3
XXVI	4-CH_3O-C_6H_4	C_6H_5	C_6H_5	C_6H_5	B	18	70-73	228-32/0.07	455-60	265	20,510	...	$C_{26}H_{22}N_2O_2$	Calcd.	79.2	5.6	7.1
														Found	78.7	5.2	7.6
XXVII	2-Naphthyl	n-$C_{16}H_{33}$	2-Naphthyl	n-$C_{16}H_{33}$	A	27	33-37	350-52/0.30	440-48	250(s)	22,990	...	$C_{53}H_{80}N_2O$	Calcd.	83.6	10.6	3.7
														Found	83.6	10.3	4.0
XXVIII	4-$(CH_3)_3Si$-C_6H_4	C_6H_5	C_6H_5	C_6H_5	B	16	82-85	224-29/0.09	450-60	270	22,455	...	$C_{28}H_{28}N_2OSi$	Calcd.	77.0	6.5	6.4
														Found	78.0	6.5	7.0
XXIX	3-F_3C-C_6H_4	C_6H_5	C_6H_5	C_6H_5	B	25	104-06	215-20/0.15	436-44	265	19,440	2, 5	$C_{26}H_{19}F_3N_2O$	Calcd.	72.2	4.4	6.5
														Found	72.8	4.6	6.5
XXX	4-FC_6H_4	C_6H_5	C_6H_5	C_6H_5	B	54	142-44	221-24/0.15	448-58	260	19,300	1	$C_{25}H_{19}FN_2O$	Calcd.	79.2	4.9	7.1
														Found	79.1	5.0	7.4
XXXI	R_3	R_4	C_6H_5	C_6H_5	C	75	183-85	212-34/0.20	458-62	267	19,983	6	$C_{25}H_{20}N_2O$	Calcd.	82.4	5.5	7.7
														Found		(*11*)	

XXXII	R_3	R_4	$4\text{-}C_6H_5C_6H_4$	$4\text{-}C_6H_5C_6H_4$	C	40	248–50	. . .	446–60	. . .	. . .	6, 7	$C_{49}H_{36}N_2O$	Calcd.	88.0	5.4	4.2
														Found	87.6	5.4	4.2
XXXIII	R_3	R_4	$3\text{-}C_6H_5OC_6H_4$	$4\text{-}C_6H_5OC_6H_4$	C	17	90–95	ca. 333/0.02	470–90	262	21,689	. . .	$C_{49}H_{36}N_2O_5$	Calcd.	80.3	5.0	3.8
														Found	80.2	4.6	3.9
XXXIV	$2,4\text{-}(CH_3)_2C_6H_3$	$4\text{-}C_6H_5OC_6H_4$	$4\text{-}FC_6H_5$	C_6H_5	B	9	170–73	275–83/0.20	472–84	260	25,585	2	$C_{33}H_{27}FN_2O_2$	Calcd.	78.9	5.4	5.2
														Found	78.7	5.2	5.5
XXXV	$2,4\text{-}(CH_3)_2C_6H_3$	$4\text{-}C_6H_5OC_6H_4$	1-Naphthyl	C_6H_5	B	13	173–75	305–14/0.15	460–70	245	30,152	5	$C_{37}H_{30}N_2O_2$	Calcd.	83.1	5.7	5.2
														Found	83.5	6.0	5.0
XXXVI	$4\text{-}CH_3C_6H_4$	2-Naphthyl	$2,4\text{-}(CH_3)_2C_6H_3$	$4\text{-}C_6H_5OC_6H_4$	B	14	118–21	315–30/0.02	440–50	255	38,554	2, 1 + 2	$C_{38}H_{32}N_2O_2$	Calcd.	83.2	5.9	5.1
														Found	82.9	5.9	5.0
XXXVII	$2,4\text{-}(CH_3)_2C_6H_3$	$4\text{-}C_6H_5OC_6H_4$	CH_3	$4\text{-}CH_3C_6H_4$	B	43	155–57	248–53/0.30	437–52	260	23,206	1	$C_{29}H_{28}N_2O_2$	Calcd.	79.8	6.5	6.4
														Found	79.4	5.7	6.2
XXXVIII	CH_3	$3\text{-}C_6H_5OC_6H_4$	$2,4\text{-}(CH_3)_2C_6H_3$	$4\text{-}C_6H_5OC_6H_4$	B	25	100–03	278–84/0.15	454–60	262	19,655	. . .	$C_{34}H_{30}N_2O_3$	Calcd.	79.4	5.9	5.4
														Found	79.6	5.5	5.5
XXXIX	$2,5\text{-}(CH_3)_2C_6H_3$	$3\text{-}C_6H_5OC_6H_4$	2-Naphthyl	$4\text{-}C_6H_5OC_6H_4$	B	30	105–10	. . .	487–93	255(s)	32,712	. . .	$C_{43}H_{34}N_2O_3$	Calcd.	82.4	5.5	4.5
														Found	81.9	5.2	4.7
XL	$3\text{-}C_6H_5O\text{-}3\text{-}C_6H_4O\text{-}C_6H_4$	$4\text{-}C_6H_5O\text{-}C_6H_4$	CH_3	CH_3	B	8	44–46	280–83/0.04	432–46	260	19,514	. . .	$C_{33}H_{28}N_2O_4$	Calcd.	76.7	5.5	5.4
														Found	77.2	5.4	5.0
XLI	$3\text{-}C_6H_5OC_6H_4$	CH_3	CH_3	CH_3	B	42		148–50/0.10	350–58	. . .	. . .	. . .	$C_{16}H_{18}N_2O_2$	Calcd.	71.1	6.7	10.4
														Found	70.4	7.1	10.2
XLII	CH_3	CH_3	$3\text{-}C_6H_5OC_6H_4$	$4\text{-}C_6H_5OC_6H_4$	B	40	76–79	ca. 244/0.05	448–54	259	19,295	1	$C_{27}H_{24}N_2O_3$	Calcd.	76.4	5.7	6.6
														Found	76.1	5.8	6.5

[a] Synthesis methods used (see experimental for example of each method). A. $2\ R_1R_2NH + COCl_2 \rightarrow R_1R_2NCONR_1R_2 + 2\ HCl$. B. $R_1R_2NH + R_3R_4NCOCl \rightarrow R_1R_2NCONR_3R_4 + HCl$. C. $2\ R_3R_4NCOCl + 2\ Na \rightarrow R_3R_4NCONR_3R_4 + 2\ NaCl$.
[b] Value obtained by dividing number of moles of product by number of moles of limited reactant and multiplying the result by 100.
[c] Approximate normal boiling point (N.B.P.) given in terms of volatilization temperature as
[d] Recrystallization solvents: 1 = abs.

reactions between diaryl carbamoyl chlorides and weakly basic diarylamines required more vigorous reaction conditions. The latter reactions were conducted in the absence of solvent at about 200° C. using $AlCl_3$ and ZnO as a catalyst.

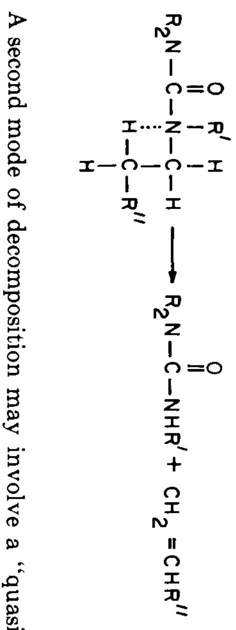
Preparation of Intermediate Compounds. A series of dialkyl and *N*-alkylarylamines was prepared by the direct alkylation of the corresponding primary amine (*9*). Preparation of diarylamines required a slightly more involved procedure. First, the primary amines were converted to the mono-*N*-arylacetamides and arylated by the Ullmann reaction (*19*) to obtain the *N,N*-diarylacetamides, which were subsequently hydrolyzed to the free diarylamines. Treatment of free secondary amines with an excess of phosgene afforded the required disubstituted carbamoyl chlorides (*15*).

Thermal Decomposition of Tetrasubstituted Ureas. Infrared spectral analysis was used to characterize and identify the volatile and nonvolatile products which were obtained by the partial thermal decomposition of several different tetrasubstituted ureas at 365° C. under a nitrogen atmosphere. The most characteristic and intense absorption band of tetrasubstituted ureas in the infrared region was the strong $C=O$ band (*2*), which usually appears at 1655 to 1680 cm.$^{-1}$ Most of the volatile decomposition products exhibited $CH_2=CH$- bands of moderate intensity in the 1645- to 1650-cm.$^{-1}$ region. In one case, benzyltriphenylurea, the nonvolatile decomposition products were studied and an absorption band in the 3400-cm.$^{-1}$ region (probably due to N-H bonding, but possibly due to O-H bonding) was observed. The results are shown in Table III.

A more detailed study of the volatile decomposition products was made in the case of tetra-*n*-octylurea. By vapor phase chromatographic techniques, it was determined that 99 mole % of the volatile fragment consisted of 1-octene. The chromatogram was compared and found to be identical with a chromatogram obtained using a known, purified sample of 1-octene. Infrared analysis eliminated other isomeric octenes as possible products. The experimental evidence thus points to the existence of two primary decomposition products—namely, 1-alkenes and trisubstituted ureas.

The relative bond dissociation energies indicate that decomposition by a simple fission would be more likely to occur at an aliphatic-type C-C bond (83 kcal. per mole) than at an amide-type C-N bond (98 kcal. per mole) (*16*). However, there are two possible decomposition paths of lower energies which would favor cleavage of the C-N bond and give rise to the same decomposition products.

One possible degradative pathway might be through a "four-centric" transition state which may be represented by the following generalized equations:



A second mode of decomposition may involve a "quasi-six-membered ring" and be represented by the following generalized equation:

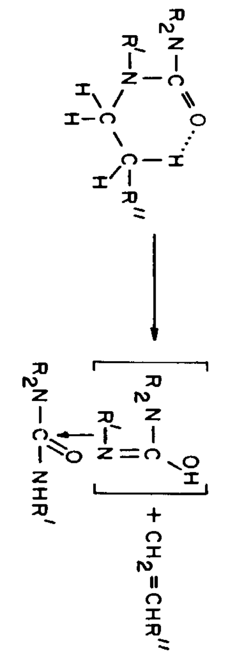


Table II. Intermediate

R_1R_2NY

Compd. No.	R_1	R_2	Y	Synthesis Method[a]	Yield %	B.P., °C./Mm. Hg[b]
I	$2\text{-}CH_3\text{-}4\text{-}C_6H_5O\text{-}C_6H_3$	H	H	B	27	186-90/13.0
II	$3\text{-}C_6H_5O\text{-}C_6H_4$	CH_3	H	E	89	189-96/10.3
III	$4\text{-}(CH_3)_3Si\text{-}C_6H_4$	C_6H_5	H	E	68	139-44/0.06
IV	$2,4\text{-}(CH_3)_2C_6H_3$	$4\text{-}C_6H_5O\text{-}C_6H_5$	H	E	78	196-98/0.05
V	$4\text{-}F\text{-}C_6H_4$	$2\text{-}CH_3\text{-}4\text{-}C_6H_5O\text{-}C_6H_3$	H	E	62	172-78/0.06
VI	$2,5\text{-}(CH_3)_2C_6H_3$	$3\text{-}C_6H_5O\text{-}C_6H_4$	H	E	55	180-81/0.18
VII	$4\text{-}CH_3\text{-}C_6H_4$	4′-*m*-terphenyl	H	E	89	. . .
VIII	$3\text{-}C_6H_5O\text{-}C_6H_4$	$4\text{-}C_6H_5O\text{-}C_6H_4$	H	E	88	226-33/0.06
IX	2-Naphthyl	$4\text{-}C_6H_5O\text{-}C_6H_4$	H	E	71	225-29/0.12
X	$3\text{-}(3\text{-}C_6H_5O\text{-}C_6H_4O)\text{-}C_6H_4$	$4\text{-}C_6H_5O\text{-}C_6H_4$	H	E	94	269-70/0.04
XI	$2\text{-}CH_3\text{-}4\text{-}C_6H_5O\text{-}C_6H_4$	H	$COCH_3$	C	63	. . .
XII	$3\text{-}(3\text{-}C_6H_5O\text{-}C_6H_4O)\text{-}C_6H_4$	H	$COCH_3$	C	84	234-39/0.15
XIII	$3\text{-}C_6H_5O\text{-}C_6H_4$	$COCH_3$	$COCH_3$	C	32	. . .
XIV	$3\text{-}C_6H_5O\text{-}C_6H_4$	CH_3	$COCH_3$	D	91	. . .
XV	$4\text{-}(CH_3)_3Si\text{-}C_6H_5$	C_6H_5	$COCH_3$	A	51	146-49/0.025
XVI	$3\text{-}CF_3\text{-}C_6H_4$	C_6H_5	$COCH_3$	A	65	118-21/0.01
XVII	$4\text{-}F\text{-}C_6H_4$	C_6H_5	$COCH_3$	A	76	141-44/0.08
XVIII	$4\text{-}C_6H_5\text{-}C_6H_4$	$4\text{-}C_6H_5\text{-}C_6H_4$	$COCH_3$	A	71	. . .
XIX	C_6H_5	3-Pyridyl	$COCH_3$	A	68	140-45/0.15
XX	$4\text{-}C_6H_5O\text{-}C_6H_4$	$2,4\text{-}(CH_3)_2C_6H_3$	$COCH_3$	A	82	210-17/0.07
XXI	$4\text{-}F\text{-}C_6H_4$	$2\text{-}CH_3\text{-}4\text{-}C_6H_5O\text{-}C_6H_4$	$COCH_3$	A	70	193-200/0.11
XXII	$2,5\text{-}(CH_3)_2C_6H_3$	$3\text{-}C_6H_5O\text{-}C_6H_4$	$COCH_3$	A	60	191-96/0.18
XXIII	4′-*m*-terphenyl	$4\text{-}CH_3C_6H_4$	$COCH_3$	A	39	242-49/0.08
XXIV	$4\text{-}C_6H_5OC_6H_4$	$3\text{-}C_6H_5OC_6H_4$	$COCH_3$	A	45	233-37/0.05
XXV	$4\text{-}C_6H_5O\text{-}C_6H_4$	2-Naphthyl	$COCH_3$	A	55	. . .
XXVI	$4\text{-}C_6H_5OC_6H_4$	$3\text{-}(3\text{-}C_6H_5O\text{-}C_6H_4O)\text{-}C_6H_4$	$COCH_3$	A	76	319-21/0.55
XXVII	$4\text{-}F\text{-}C_6H_4$	C_6H_5	COCl	F	92	. . .
XXVIII	$4\text{-}C_6H_5\text{-}C_6H_4$	$4\text{-}C_6H_5\text{-}C_6H_4$	COCl	F	87	. . .
XXIX	$2,4\text{-}(CH_3)_2C_6H_3$	$4\text{-}C_6H_5O\text{-}C_6H_4$	COCl	F	97	224-26/0.30
XXX	$4\text{-}C_6H_5O\text{-}C_6H_4$	C_6H_5	COCl	F	86	203-09/0.2
XXXI	CH_3	$4\text{-}CH_3C_6H_4$	COCl	F	74	. . .
XXXII	2-Naphthyl	$4\text{-}C_6H_5O\text{-}C_6H_4$	COCl	F	73	. . .
XXXIII	$3\text{-}C_6H_5O\text{-}C_6H_4$	$4\text{-}C_6H_5O\text{-}C_6H_4$	COCl	F	89	256-59/0.28

[a] Synthesis methods used. A. $R_1X + R_2NHCOCH_3 \longrightarrow R_1NR_2COCH_3$ (*19*). B. ArX + ArOH $\longrightarrow$ ArOAr (*3, 17*). C. $R_1R_2NH + (CH_3CO)_2O \longrightarrow R_1R_2NCOCH_3$. D. $R_1NCOCH_3Na + R_2I \longrightarrow R_1R_2NCOCH_3$ (*1*). E. $R_1R_2NCOCH_3 \xrightarrow{KOH}$

Compounds

n^t_D	d^t_4	Recryst. Solvents[c]	M.P., ° C.	Molecular Formula		MR $_D$[d]	Analysis	
							C	H
1.6122^{25}	1.0953^{60}	5	70–71	$C_{13}H_{13}NO$	Calcd.	62.26	...	...
					Found	63.25	...	...
1.6047^{26}	1.1046^{25}	...	...	$C_{13}H_{13}NO$	Calcd.	60.95	...	...
					Found	62.09	...	...
...	...	5	40–42	$C_{15}H_{19}SiN$	...	...	...	...
					...	...	...	...
1.6286^{25}	1.1070^{25}	...	...	$C_{20}H_{19}NO$	Calcd.	89.97	...	...
					Found	92.52	...	...
1.6120^{26}	1.1760^{63}	5, 8	116.5–18.5	$C_{19}H_{16}NOF$	Calcd.	85.37	...	...
					Found	86.70	...	...
1.6315^{20}	1.1127^{25}	...	...	$C_{20}H_{19}NO$	Calcd.	89.97	...	...
					Found	92.69	...	...
...	...	2, 7	142–44	$C_{25}H_{21}N$	Calcd.	...	89.51	6.31
					Found	...	89.69	6.45
1.6582^{25}	1.1990^{40}	...	...	$C_{24}H_{19}NO_2$	Calcd.	106.87	...	...
					Found	108.47	...	...
...	...	...	98.5–101.5	$C_{22}H_{17}NO$	...	...	...	...
					...	...	...	...
1.6483^{50}	1.2145^{50}	...	...	$C_{30}H_{23}NO_3$	Calcd.	133.03	...	...
					Found	133.51	...	...
...	...	5	124–28	$C_{15}H_{15}NO_2$	...	...	...	...
					...	...	...	...
...	...	2 + 4	69–71	$C_{20}H_{17}NO_3$	...	...	...	...
...	...	6	98–100	$C_{16}H_{15}NO_3$	Calcd.	...	71.36	5.64[e]
					Found	...	71.49	5.66
...	...	2	64.0–65.5	$C_{15}H_{15}NO_2$	Calcd.	...	...	...
					Found	...	...	...
1.6076^{25}	1.1209^{25}	...	...	$C_{17}H_{21}SiNO$	Calcd.	87.56	...	...
					Found	87.39	...	...
1.5422^{20}	1.2187^{33}	5, 6	117–18	$C_{15}H_{12}NOF_3$	Calcd.	71.76	...	...
					Found	72.13	...	...
1.5724^{20}	1.1647^{25}	...	115–17.5	$C_{13}H_{12}NOF$	Calcd.	64.01	...	...
					Found	64.80	...	...
...	...	...	173.5–75.5	$C_{26}H_{21}NO$	...	...	...	...
					...	...	...	...
...	...	...	47.5–50.0	$C_{13}H_{12}N_2O$	...	...	...	...
					...	...	...	...
...	...	2	91.0–93.5	$C_{22}H_{21}NO_2$	...	...	...	...
					...	...	...	...
...	...	5	95–98	$C_{21}H_{18}NO_2F$	Calcd.	...	75.21	5.41
					Found	...	75.22	5.15
1.600^{35}	1.048^{94}	...	...	$C_{22}H_{21}NO_2$	Calcd.	99.40	...	...
					Found	102.62	...	...
...	...	2	180–82	$C_{27}H_{29}NO$	...	...	...	...
					...	...	...	...
1.6215^{30}	1.2018^{90}	...	...	$C_{26}H_{21}NO_3$	Calcd.	116.30	78.97	5.35
					Found	115.52	79.00	5.13
...	...	...	102–04	$C_{24}H_{19}NO$	...	...	...	...
					...	...	...	...
...	...	...	...	$C_{32}H_{25}NO_4$	...	...	...	...
					...	...	...	...
...	...	2	86–89	$C_{13}H_9NOClF$	...	...	...	...
					...	...	...	...
...	...	2	165–67	$C_{25}H_{18}NOCl$	...	...	...	...
					...	...	...	...
1.6082^{25}	1.1805^{100}	...	...	$C_{21}H_{18}NOCl$	Calcd.	99.61	...	...
					Found	103.05	...	...
...	...	1	105–08	$C_{18}H_{14}NO_2Cl$	...	...	...	...
					...	...	...	...
...	...	6	75–77	$C_9H_{10}NOCl$	Calcd.	...	58.86	5.49
					Found	...	58.80	5.40
...	...	2 + 5	139.5–42	$C_{23}H_{18}NO_2Cl$	...	...	...	...
					...	...	...	...
1.6177^{25}	1.2460^{82}	2 + 5	88.5–91.0	$C_{25}H_{18}NO_3Cl$	Calcd.	116.51	...	...
					Found	116.89	...	...

R_1R_2NH; F. $R_1R_2NH \xrightarrow{COCl_2} R_1R_2NCOCl$ (*15*). See experimental for examples of methods A and F. [b] Boiling point in ° C. at pressure specified in mm. of Hg. [c] Recrystallization solvents. 1 = abs. ethanol; 2 = Skellysolve B; 3 = chloroform; 4 = ether; 5 = 95% ethanol; 6 = toluene; 7 = acetone; 8 = benzene. [d] Molar refraction values of Warrick, (*18*). [e] Nitrogen analysis. Calcd. = 5.20; found = 5.31.

Table III. Infrared Spectra of Tetrasubstituted Ureas and Their Thermal Decomposition Products

Table I Compound No.	Material	Remarks
I	Tetra-*n*-hexylurea Volatile decomposition products	C=O at 1,655 cm.$^{-1}$ (s); $(CH_2)_{>4}$ at 730 cm.$^{-1}$ (s) $>CH=CH_2$ masked; N-H or O-H at 3,350 cm.$^{-1}$ (s)
II	Tetrakis (2-ethylhexyl) urea Volatile decomposition products	C=O at 1.655 cm.$^{-1}$ (s); $(CH_2)_{>4}$ at 730 cm.$^{-1}$ (s) $>CH=CH_2$ at 1,650 cm.$^{-1}$ (m); N-H or O-H = none
IV	Tetra-*n*-octylurea Volatile decomposition products^a	C=O at 1,660 cm.$^{-1}$ (s); $(CH_2)_{>4}$ at 720 cm.$^{-1}$ (s) $>CH=CH_2$ at 1,650 cm.$^{-1}$ (m); N-H or O-H = none
V	Tetra-*n*-decylurea Volatile decomposition products	C=O at 1,660 cm.$^{-1}$ (s); $(CH_2)_{>4}$ at 725 cm.$^{-1}$ (s) $>CH=CH_2$ at 1,645 cm.$^{-1}$ (m); N-H or O-H = none
X	Benzyltriphenylurea Volatile decomposition products Nonvolatile decomposition products	C=O at 1,680 cm.$^{-1}$ (s); $>CH=CH_2$ masked; N-H or O-H at 3,400 cm.$^{-1}$ (s) N-H or O-H at 3,400 cm.$^{-1}$ (m); band at 1,680 cm.$^{-1}$ broadened and decreasing intensity

^{a}Spectrum matches spectrum of 1-octene (does not match spectra of other octenes). (s) and (m) refer to strong and medium band intensity.

The final step in the degradation process is the rapid decomposition of the trisubstituted urea into an isocyanate and a secondary amine:

$$R_2N-\overset{\overset{O}{\|}}{C}-\overset{H}{N}-R' \rightleftharpoons R'NCO+R_2NH$$

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The Synthesis of 3-Nitro-o-terphenyl and Acyl Derivatives of 3- and 4-Amino-o-terphenyl

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The synthesis of 3-nitro-o-terphenyl is reported. Acyl derivatives of 3-amino-o-terphenyl and 4-amino-o-terphenyl have been prepared.

ALTHOUGH five isomeric mono-nitro-*o*-terphenyls are possible, to date only three have been reported (*1, 2, 4*). Direct nitration of *o*-terphenyl yields the 4-nitro isomer; however, preparation of 3-nitro-*o*-terphenyl by this method is not feasible. The synthetic route employed during the course of this work involved the nitration of 4-acetamido-*o*-terphenyl yielding 3-nitro-4-acetamido-*o*-terphenyl. Subsequent removal of the acetamido group gave the desired 3-nitro-*o*-terphenyl.

Most of the derivatives reported for 4-amino-*o*-terphenyl have been of an unusual nature or have been oils that crystallized slowly. (*1,3*). During the course of the work,