work-up afforded 6.0 g (70%) of vpc-pure α-*n*-butylphenylacetonitrile, bp 105–106° (4.5 mm) [lit.[13] bp 152–155° (20 mm)].

Also, disodio phenylcyanoacetate (0.05 mole) was benzylated with 6.33 g (0.05 mole) of benzyl chloride. Subsequent work-up and distillation afforded 1.75 g (17%) of vpc-pure α-benzylphenylacetonitrile, bp 145–146° (2 mm) [lit.[12] bp 134–135° (0.5 mm)]. The melting point (57–58°) was not depressed on admixture with an authentic sample.[12]

α-Alkylphenylacetamides (II).—These compounds were prepared by the method described previously[5] by employing 0.25 mole of phenylacetamide and 0.5 mole of sodium amide in 300 ml of anhydrous liquid ammonia.[10] After 30 min, the resulting brown-green suspension containing disodiophenylacetamide (0.25 mole) was treated during 10 min with a solution of 0.25 mole of the appropriate alkyl halide in 50 ml of ethyl ether. The reaction mixture was stirred for 15 min, then neutralized by the addition of 30 g of solid ammonium chloride. After the liquid ammonia had evaporated, hydrolysis and work-up were performed as before.[5] One recrystallization from ethanol afforded 41.5 g (87%) of the pure α-*n*-butyl- and 36.6 g (65%) of the pure α-benzylphenylacetamides, mp, mmp 97–98° and 132.5–133.5°, respectively. Several recrystallizations of the α-methyl derivative from aqueous ethanol and finally from benzene–hexane were required to afford 8.2 g (22%) of product, mp 95–96° (lit.[14] mp 91–92°).

Dehydrations of II (Method B).—To a solution of 3.725 g (0.025 mole) of α-methylphenylacetamide in 50.8 ml of anhydrous THF was added under nitrogen at room temperature during 3 min, 50.8 ml (0.0813 mole) of 1.6 *M* *n*-butyllithium in hexane.[8] The reaction was exothermic (64°), and the solution turned yellow, then orange as the second and third equivalents of the reagent were added, respectively. After refluxing for 2 hr, the reaction mixture was cooled to 0° by an ice bath and then hydrolyzed by the dropwise addition of 100 ml of 3 *N* hydrochloric acid. The layers were separated and the aqueous layer was extracted with three 50-ml portions of ethyl ether.[11] After drying (magnesium sulfate) and removal of the solvent, distillation afforded 2.5 g (77%) of pure α-methylphenylacetonitrile, bp 90–91° (5.5 mm).[12]

Similarly, 9.55 g (0.05 mole) of α-*n*-butylphenylacetamide dissolved in 101.6 ml of anhydrous THF was treated with 101.6 ml (0.1625 mole) of 1.6 *M* *n*-butyllithium in hexane[8] added during 7 min. Subsequent work-up and distillation afforded 7.35 g (85%) of vpc-pure α-*n*-butylphenylacetonitrile, bp 105–106° (4.5 mm).[13]

Also, a similar dehydration effected on a THF solution of 11.25 g (0.05 mole) of α-benzylphenylacetamide afforded 7.9 g (76%) of vpc-pure α-benzylphenylacetonitrile, bp 145–146° (2 mm).[12] The melting point (57–58°) was not depressed on admixture with an authentic sample.[12]

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[13] L. H. Baldinger and J. A. Nieuwland, *ibid.*, **55**, 2851 (1933).

[14] H. Janssen, *Ann.*, **250**, 125 (1888).

Selective Hydrogenolysis. Dehalogenation in the Presence of N-Benzyl Linkage

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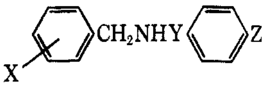
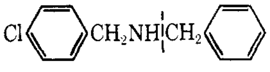
In a previous report on the attempted hydrogenolysis of N-benzyl 1-(4-chlorophenyl)-2-aminopropane (A) to obtain 1-(4-chlorophenyl)-2-aminopropane it was found that dehalogenation was the preferred reaction.[1] It seemed worthwhile to investigate the hydrogenation of some related chloro-N-benzylphenylalkylamines, where the halogen was on either ring, to learn whether dehalogenation would be a general reaction. Compounds of the following type were studied



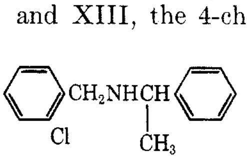
where X = 2- or 4-Cl; Y = CH_2, $CH(CH_3)$, or CH_2CH_2; Z = H or Cl. In one instance X = H, Y = CH_2CH_2, and Z = Cl.

Preparation of the intermediate Schiff bases was relatively simple. The amine and aldehyde were dissolved in benzene and heated under reduced pressure until the elimination of water was complete. In most instances the residue was distilled (see Table I). The resulting Schiff bases were hydrogenated in the presence of platinum on carbon. This catalyst was chosen because it had been reported that it was ineffective for dehalogenation.[2] No dehalogenation was found to have taken place. The resulting secondary amines are listed in Table II.

The amines were hydrogenated in acidic medium to eliminate the effect of the basic nitrogen on dehalogenation. Acetic acid appeared to be the best medium for the reaction because of fewer solubility difficulties. A 5–10% ratio of 5% palladium on carbon was used as catalyst. As can be seen from Table III dehalogenation was the preferred reaction. The reduction of 4-chlorodibenzylamine (IX) was of particular interest in view of the work of Baltzly and Buck who studied the effect of substitution on the strength of the N-benzyl linkage.[3] They found that when the tertiary amine, N-methyl-4-chlorodibenzylamine, as the hydrochloride salt, was subjected to hydrogenation in the presence of palladized charcoal they obtained 4-chlorobenzylmethylamine. In contrast, under the conditions used in this work hydrogenolysis of IX showed that dehalogenation to dibenzylamine (E) was certainly the major reaction. It is difficult to say whether cleavage took place in the manner described by Baltzly and that



4-chlorobenzylamine was further dehalogenated or whether the amount of benzylamine resulted from further hydrogenolysis of dibenzylamine (E). However, in order to eliminate possible effect of solvent two other experiments were carried out. In one, IX as hydrochloride salt was hydrogenated in methanol according to the method of Baltzly and Buck, in a second run the base was reduced in the same solvent. The results of chromatography, 76.5% of dibenzylamine, 15.1% of IX, 91.9% dibenzylamine, and 7.4% of IX, respectively, suggest that the debenzylation noted in acetic acid solution was a secondary reaction. In the reduction of XII and XIII, the 4-chloro analog, the



presence of α-methylbenzylamine (H) probably resulted from further debenzylation of α-methyldibenzylamine (I).

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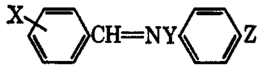
[1] M. Freifelder, Y. H. Ng, and P. F. Helgren, *J. Med. Chem.*, **7**, 381 (1964).

[2] R. Baltzly, *J. Am. Chem. Soc.*, **74**, 4586 (1952).

[3] R. Baltzly and J. S. Buck, *ibid.*, **65**, 1984 (1943).

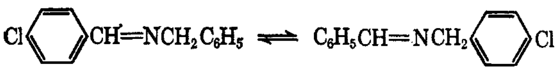
TABLE I

SCHIFF BASES



Compd	X	Z	Y	Yield, %	Bp, °C (mm)	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
I[a]	4-Cl	H	CH_2	55	169–170 (1.6)	$C_{14}H_{12}ClN$	73.19	5.26	6.09	73.26	5.20	6.27
II	2-Cl	H	CH_2CH_2	79	175–178[b] (3.0–3.3)	$C_{15}H_{14}ClN$	73.91	5.79	5.74	73.65	5.82	5.80
III	4-Cl	H	CH_2CH_2	83.5	180[c] (2.0)	$C_{15}H_{14}ClN$[d]	73.91	5.79	5.74	73.82	6.11	6.09
IV	2-Cl	H	$CH(CH_3)$	67	165[c] (2.5)	$C_{15}H_{14}ClN$	73.91	5.79	5.74	73.96	5.91	5.73
V	4-Cl	H	$CH(CH_3)$	78	170[c] (3.0)	$C_{15}H_{14}ClN$	73.91	5.79	5.74	73.66	5.81	5.73
VI	2-Cl	Cl	CH_2CH_2	86.5	[e]	$C_{15}H_{13}Cl_2N$	64.76	4.70	5.03	64.87	4.67	4.89
VII	4-Cl	Cl	CH_2CH_2	93.5	[f]	$C_{15}H_{13}Cl_2N$[g]	64.76	4.70	5.03	64.53	4.71	4.80
VIII	H	Cl	CH_2CH_2	89	164–165[h]	$C_{15}H_{14}ClN$	73.91	5.79	5.74	73.65	5.78	6.08

[a] Described as existing in equilibrium



mp 34 and 36–37°: C. W. Shoppee, *J. Chem. Soc.*, 1225 (1931). [b] Solidified, mp 41–42°. [c] Solidified after distillation. [d] *Anal.* Calcd for chlorine: Cl, 14.54. Found: Cl, 14.65. [e] Isolated as a solid, mp 60.5–62.5° from hexane. [f] Isolated as a solid, mp 93–94°, from hexane. [g] *Anal.* Calcd for chlorine: Cl, 25.51. Found: Cl, 25.31. [h] Solidified, recrystallized from hexane for analysis mp 52°.

TABLE II

HALOBENZYLARALKYLAMINES

Compd	X	Y	Y	Yield, %	Bp, °C (mm)	Mp, °C	Formula Base	Formula Hydrochloride	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
IX	4-Cl	H	CH_2	50	191–193[a] (10)									
X	2-Cl	H	CH_2CH_2	90.5	173 (5.5)		$C_{15}H_{16}ClN$		73.30	6.56	5.70	73.40	6.78	5.85
						174.5		$C_{15}H_{17}Cl_2N$	63.83	6.07	4.96	63.80	6.13	5.16
XI	4-Cl	H	CH_2CH_2	91	183[b] (4.8)		$C_{15}H_{16}ClN$		73.30	6.56	5.70	73.52	6.63	5.50
						251[c]		$C_{15}H_{17}Cl_2N$	63.83	6.07	4.96	64.01	5.80	4.87
XII	2-Cl	H	$CH(CH_3)$	77	162–165 (4.0)		$C_{15}H_{16}ClN$		73.30	6.56	5.70	73.33	6.57	5.57
						179.5–180.5		$C_{15}H_{17}Cl_2N$	63.83	6.07	4.96	64.00	6.19	4.97
XIII	4-Cl	H	$CH(CH_3)$	86.8[d]	166 (3.8)		$C_{15}H_{16}ClN$		73.30	6.56	5.70	73.19	6.60	5.80
						188		$C_{15}H_{17}Cl_2N$	63.83	6.07	4.96	64.00	6.05	5.15
XIV	2-Cl	Cl	CH_2CH_2	72	170–175 (1.0–1.3)		$C_{15}H_{15}Cl_2N$		64.29	5.39	5.00	64.59	5.52	4.75
						198–199		$C_{15}H_{16}Cl_3N$	56.88	5.09	4.42	56.94	4.96	4.44
XV	4-Cl	Cl	CH_2CH_2	90	[e]		$C_{15}H_{15}Cl_2N$		64.29	5.39	5.00	64.49	5.36	4.75
						242		$C_{15}H_{16}Cl_3N$	56.88	5.09	4.42	57.14	5.18	4.42
XVI	H	Cl	CH_2CH_2	83	177–182 (2.5–3.0)		$C_{15}H_{16}ClN$		73.30	6.56	5.70	73.06	6.51	5.83
						242		$C_{15}H_{17}Cl_2N$	63.83	6.07	4.96	63.60	5.90	5.07

[a] J. von Braun, M. Kuhn, and J. Weismantel [*Ann.*, **449**, 249 (1926)], who prepared this compound from 4-chlorobenzylamine and benzyl chloride, give 195–196° (13 mm). [b] Material solidified. [c] S. L. Shapiro, V. A. Parrino, and L. Freeman [*J. Am. Chem. Soc.*, **81**, 3728 (1959)] prepared XI from N-(4-chlorobenzoyl)-2-phenethylamine by $LiAlH_4$ reduction. They identified the salt by melting point only, 260°. [d] After reduction of V a sample of the solution was submitted for ionic halogen. The result showed that dehalogenation was insignificant, 0.25%. [e] Solid, mp 62–63°, from hexane.

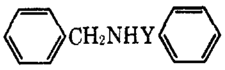
TABLE III

HYDROGENATION OF AMINES IN TABLE II

Compd	Products of reduction,[a] % B	C	D	E	F	G	H	I	J	K	L	M	N
IX	29.0	16.5	4.5	50.0									
IX[b]	15.1	4.0[c]		76.5									
IX[d]	7.4	1.0		91.7									
X	6.5				0.8	92.7							
XI	9.6				4.25	86.1							
XII	4.4						9.5	76.0					
XIII	23.5						9.15	67.3					
XIV	15.0				1.0	11.5			3.5	[e]	[e]		
XV	52.8[f]					17.0			0.2			[g]	[g]
XVI	6.0				2.7	90.3			1.0				

[a] B, starting amine; C, benzylamine; D, 4-chlorobenzylamine; E, dibenzylamine; F, phenethylamine; G, N-benzylphenethylamine; H, α-methylbenzylamine; I, α-methyldibenzylamine; J, 4-chlorophenethylamine; K, N-benzyl 4-chlorophenethylamine; L, N-(2-chlorobenzyl)phenethylamine; M, N-(4-chlorobenzyl)phenethylamine; N, N-benzyl-4-chlorophenethylamine. [b] Hydrogenation of hydrochloride salt in methyl alcohol. [c] About 4% of toluene was detected. [d] Hydrogenation of base in methyl alcohol. [e] Separation of the two components could not be effected. The total amounts to 69%. From the broad peak in the chromatograph it is assumed both K and L are present. [f] Uptake stopped at about 75% of the expected amount of hydrogen. The poor solubility of the salt of XV is probably responsible. [g] The two components, M and N (30%), were also difficult to separate by gas–liquid partition chromatography. It is assumed that both are present.

From an analysis of the results in Table III it appears in the reduction of compounds of the type



where Y is an aliphatic chain and chlorine is attached to either or both rings, that dehalogenation should be the expected reaction. Debenzylation which may accompany loss of halogen probably is a secondary reaction which takes place after dehalogenation.

Experimental Section[4]

The following is typical of the preparation of the Schiff bases. The ensuing reduction of III to XI is an example of the procedure used to obtain the secondary amines listed in Table II.

N-(4-Chlorobenzylidene)-2-phenethylamine (III).—4-Chlorobenzaldehyde (42.15 g, 0.3 mole), from an unopened bottle or freshly distilled, was added to a solution of 36.3 g (0.3 mole) of 2-phenethylamine in 200 ml of thiophene-free benzene. In a few minutes the solution became cloudy and globules of water began to appear. The mixture was heated and concentrated under reduced pressure until the removal of water was complete (about 1 hr). The residue was then distilled or recrystallized from a suitable solvent.

N-(4-Chlorobenzyl)-2-phenethylamine (XI).—A solution of 0.3 mole of III in 200 ml of 95% ethyl alcohol was hydrogenated in the presence of 3.0 g of 5% platinum on carbon[5] at room temperature and 2-atm pressure. After uptake of hydrogen was complete (less than 2 hr), the solution was filtered from the catalyst and the catalyst was washed with alcohol. After concentration of the filtrates the residue was fractionated (see Table II for results).

The amines listed absorbed carbon dioxide and had to be analyzed shortly after distillation.

Hydrogenolyses of the Bases in Table II.—The reduction of XI is a typical example. A solution of 24.55 g (0.1 mole) of XI in 150 ml of glacial acetic acid was hydrogenated in the presence of 2.5 g of 5% palladium on activated carbon[5] under 2.5 atm of pressure. Uptake of hydrogen was fairly rapid but slowed down at 75%. At this point the reaction was warmed to dissolve precipitated material. Uptake for 1 equiv was complete in about 3 hr. In most reductions a considerable amount of precipitate was present. It was necessary to heat the reaction mixture, filter hot, and extract the precipitate and catalyst further with hot aqueous or 95% alcohol. The combined filtrates were concentrated under reduced pressure. The residue was suspended in water and the mixtue was stirred and made strongly basic with 40–50% sodium hydroxide solution. In some instances it was necessary to warm the mixture to completely convert the salt to base. After cooling, the mixture was thoroughly extracted with benzene and dried over anhydrous magnesium sulfate. After removal of the drying agent the solution was concentrated. A sample of the oily or sometimes solid residue was submitted for chromatographic analysis.

In a few experiments the reductions were run in 90–95% alcohol containing 3 molar equiv of hydrochloric acid. Work-up was essentially the same. However when hydrochloric acid was used heavy precipitation took place immediately upon the addition of it to the solution before reduction.

In the hydrogenation of 4-chlorodibenzylamine hydrochloride in methanol the material did not dissolve completely. When uptake of hydrogen was interrupted at 2 equiv some water was added to dissolve the precipitate. After removal of catalyst the solution was made strongly basic with sodium hydroxide and then submitted for chromatographic analysis. In the reduction of the base precipitation occurred as reduction proceeded. The same procedure was followed to get results of chromatography.

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[4] Microanalyses were carried out by Mr. O. F. Kolsto and Mr. V. Rauschel and their associates. Chromatography (glpc) of the products of reduction were run by Mr. P. F. Helgren with known standards. The author is grateful to these men. The unit was an F and M Model 810-29 equipped with a thermal conductivity detector. Column, 4 ft, silicone SE 30, 10% on Anakrom A, 80–90 mesh; temperature, 250° (injector), 240° (detector); carrier, helium, 80 cc/min.

[5] Available from Engelhard Industries, Newark, N. J.

The Reaction of Cyanomethylenephosphoranes with Carbon Disulfide

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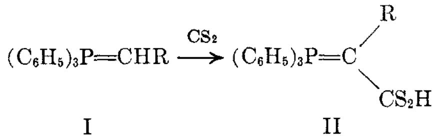
Received May 31, 1966

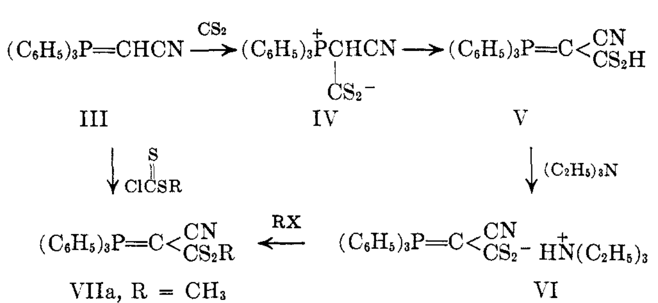
Although methylenephosphoranes have been studied extensively in recent years, little is known about the reaction of these compounds with carbon disulfide.[1] The only recorded examples involve disubstituted methylenetriphenylphosphoranes which are reported to give the Wittig products, namely, thioketenes and triphenylphosphine sulfide. Diphenylmethylenetriphenylphosphorane, for example, is converted to polymeric diphenylthioketene,[2] and fluorenylidenetriphenylphosphorane gives the corresponding dimeric thioketene.[3]

The present report deals with the reaction of carbon disulfide with monosubstituted methylenephosphoranes (I) to give the dithiocarboxylic acids (II). When



phosphoranes of type I in which R = CO_2CH_3, $CO_2C_2H_5$, $\overset{\text{O}}{\overset{\|}{\text{C}}}C_6H_5$, $C_6H_3(NO_2)_2$-2,4 were treated with excess carbon disulfide at room temperature for 24 hr, no reaction occurred. In the case where R = C_6H_5, reaction was immediate and complete under similar conditions; however, the only identifiable product was triphenylphosphine sulfide, indicating that a Wittig-type reaction had occurred. In no case was dithiocarboxylic acid II detected.

In contrast, cyanomethylenetriphenylphosphorane (III) gave a 98% yield of the dithiocarboxylic acid V. Presumably, the reaction proceeds *via* the zwitterion IV which then tautomerizes to V. Compound V dissolves readily in 0.1 *N* aqueous sodium hydroxide solution and is regenerated quantitatively on acidification with dilute hydrochloric acid. The infrared spectrum of V exhibits a sharp, strong band at 2200 cm^{-1}, characteristic for a conjugated nitrile function.



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[1] A. Maercker, *Org. Reactions*, **14**, 385 (1965).

[2] H. Staudinger, G. Rathsam, and F. Kjelsberg, *Helv. Chim. Acta*, **3**, 853 (1920).

[3] A. Schönberg, E. Frese, and K.-H. Brosowski, *Chem. Ber.*, **95**, 3077 (1962).