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ORGANIC SYNTHESES BY MEANS OF METAL COMPLEXES—VII[1]

ONE STEP SYNTHESIS OF TRIARYLIMIDAZOLES AND TRIARYLIMIDAZOLINES FROM BENZYLAMINE DERIVATIVES AND CARBON TETRACHLORIDE

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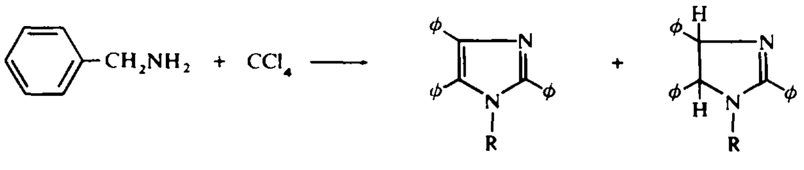
Abstract—Benzylamine and its derivatives react with carbon tetrachloride in the presence of a catalytic amount of metal carbonyls and their derivatives to form triarylimidazoles and triarylimidazolines.

IN THE previous paper, formation of benzamidine and various heterocyclic compounds by reaction of aniline and its derivatives with CCl_4 catalyzed by metal complexes was reported.[1] In these reactions, formation of free radicals from CCl_4 and metal complexes was assumed. The free radicals thus formed seem to be different from usual free radicals and hence unique synthetic reactions might be possible with them. Since these radicals may abstract hydrogen from an amino group or from the carbon attached to the amino group, somewhat different reactions are expected to occur with aliphatic amines in this system. For this reason, the reaction of benzylamine and its derivatives with CCl_4 in the presence of metal carbonyls and their derivatives was attempted. A unique cyclization reaction took place and triarylimidazoles and triarylimidazolines were formed.

RESULTS AND DISCUSSION

Benzylamine and CCl_4 were allowed to react in the presence of a catalytic amount of $Co_2(CO)_8$ at 150° for 16 hr in an autoclave under CO or N_2 pressure. The resultant mixture was separated by column chromatography. In addition to small amounts of benzaldehyde and dibenzylamine, four compounds, I, II, III and IV were isolated. Compound I was identified as 2,4,5-triphenylimidazole and compound II was found to be 1-benzyl-2,4,5-triphenylimidazole. As expected, II was converted into I by hydrogenolysis with Raney Ni catalyst.



I: R = $-H$

II: R = $-CH_2\phi$

III: R = $-H$

IV: R = $-CH_2\phi$

TABLE 1. REACTION OF BENZYLAMINE WITH CCl_4[a]

Cat.	Pressure (atm) CO	Pressure (atm) N_2	Reaction temp.	Reaction time (hr)	I	II	III·HCl	IV·HCl	dibenzylamine HCl
$Co_2(CO)_8$	50		150	16	6·00 g (26·1%)	1·75 g (7·6%)	4·75 g (18·2%)	1·20 g (18·2%)	4·64 g (16·9%)
$Co_2(CO)_8$	50		120	16	8·38 (36·4)	0	3·61 (13·8)	0	0[b]
$Co_2(CO)_8$		50	150	16	4·45 (19·4)	2·14 (9·5)	6·23 (23·9)	2·13 (8·6)	5·20 (19·0)
$Co_2(CO)_8$		50	150	5	0·73 (3·2)	0·68 (3·0)	11·68 (44·7)	1·93 (7·8)	4·43 (16·2)
$Co_2(CO)_8$		50	110	5	0	0	1·60	0	0[c]
$Mo(CO)_6$		50	150	16	0	0	0	10·23 (41·3)	12·34 (45·1)
$[CpMo(CO)_3]_2$		50	150	16	0	0	0	10·09 (40·9)	11·64 (42·4)

[a] The reaction was carried out with benzylamine (25·0 g). CCl_4 (25 ml). and catalyst (0·5 g). Yields are based on the benzylamine.

[b] Benzylamine hydrochloride (1·51 g) obtained.

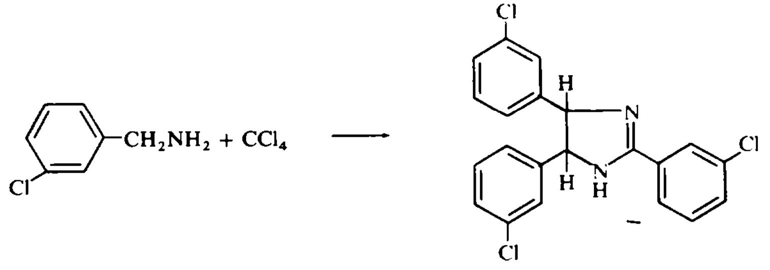
[c] Benzylidenebenzylamine (V) (9·98 g) and benzylamine hydrochloride (0·35 g) obtained.

Compounds III and IV were hydrochlorides and converted to amines with Na_2CO_3. From their physical data, III was identified as 2,4,5-triphenyl-2-imidazoline and IV was 1-benzyl-2,4,5-triphenyl-2-imidazoline. III and IV have two more hydrogens than I and II, respectively.

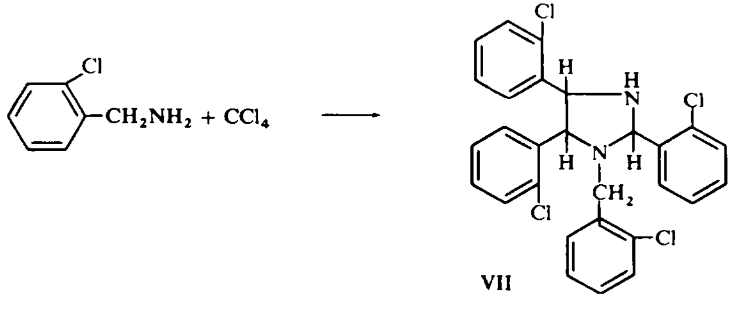
Thus the reaction of benzylamine with CCl_4 gives imidazole and imidazoline and their N-benzylated products. When $Mo(CO)_6$ and $[C_5H_5Mo(CO)_3]_2$ were used as catalyst, the products were benzylimidazoline and dibenzylamine, and no imidazole was obtained. Results of the reactions of benzylamine under different conditions are shown in Table I. By careful treatment of the reaction mixture, benzylidenebenzylamine (V) was isolated. Benzaldehyde was certainly formed by hydrolysis of V during chromatography. No attempts at optimization of conditions were made in the present investigation, but it is felt that yields could probably be improved.

As can be seen from Table 1, product distribution is dependent on reaction conditions. At temperatures below 120°, II, IV and dibenzylamine were not formed, indicating that these benzylated products were formed by reaction of I and III with benzylamine with liberation of NH_3 at high temperature. When the reaction time was shortened, the amount of III increased relative to that of I. At lower temperatures and shorter times, V was obtained as a major product, suggesting that it is an intermediate in imidazole ring formation.

The reactions of *m*- and *o*-chlorobenzylamines were carried out to determine the effect of substituents on the reaction. Interestingly, the product from *m*-chlorobenzylamine was 2,4,5-tris(*m*-chlorophenyl)-2-imidazoline (VI) (12·2%) and the corresponding imidazole derivative was not obtained. Furthermore, the product from *o*-chlorobenzylamine was neither an imidazole nor an imidazoline, but was 1-(*o*-chlorobenzyl)-2,4,5-tris(*o*-chlorophenyl)imidazoline (VII) (52·3%).



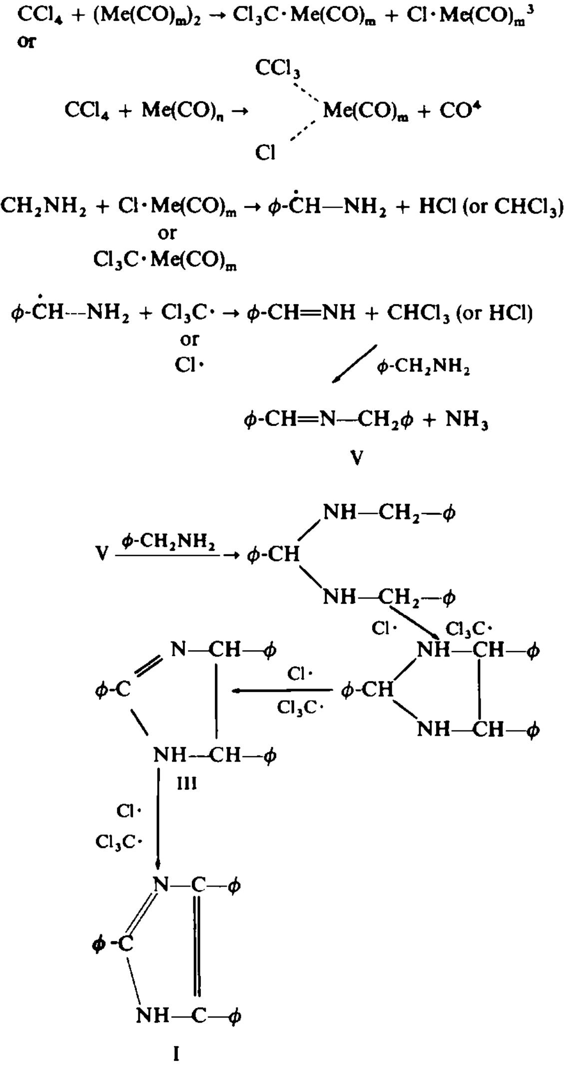
VI



VII

In general, imidazolidines are not stable to hydrolysis due to an N—C—N type structure in the molecule. However, due to the strong steric hindrance of *o*-chlorophenyl group, VII was isolated as a stable compound even after treatment with base and chromatography. Thus the hindrance by chlorine in the *ortho* position inhibits hydrogen abstraction from the initially cyclized product and only a saturated imidazolidine ring was obtained. The effect was less when chlorine was in the *meta* position and partial dehydrogenation to form an imidazoline took place. These results indicate that formation of imidazoles proceeds *via* stepwise dehydrogenation of the initially formed imidazolidine ring.

These results allow us to propose the following mechanism for the reaction of benzylamine with CCl_4 catalyzed by metal carbonyls and their derivatives. Free radical species coordinated to metal complexes are first formed as shown below.



$$CCl_4 + (Me(CO)_m)_2 \rightarrow Cl_3C\cdot Me(CO)_m + Cl\cdot Me(CO)_m$$ [3]

or

$$CCl_4 + Me(CO)_n \rightarrow (CCl_3)(Cl)Me(CO)_m + CO$$ [4]

$$\phi\text{-}CH_2NH_2 + Cl\cdot Me(CO)_m \text{ (or } Cl_3C\cdot Me(CO)_m) \rightarrow \phi\text{-}\dot{C}H\text{—}NH_2 + HCl \text{ (or } CHCl_3)$$

$$\phi\text{-}\dot{C}H\text{—}NH_2 + Cl_3C\cdot \text{ (or } Cl\cdot) \rightarrow \phi\text{-}CH\text{=}NH + CHCl_3 \text{ (or } HCl)$$

$$\phi\text{-}CH\text{=}NH \xrightarrow{\phi\text{-}CH_2NH_2} \phi\text{-}CH\text{=}N\text{—}CH_2\phi + NH_3$$

V

$$V \xrightarrow{\phi\text{-}CH_2NH_2} \phi\text{-}CH(NH\text{—}CH_2\text{—}\phi)_2$$

These then abstract hydrogen from benzylamine to give V, which was actually isolated under mild reaction conditions. V reacts with another molecule of benzylamine, and cyclization of the product takes place by hydrogen abstraction to give the imidazolidine ring. Once this ring is formed, stepwise dehydrogenation follows to give an imidazoline and finally the imidazole. It is reasonable that the imidazoline is obtained under mild conditions or short reaction times.

The nature of the first step, namely formation of radical species by the reaction of CCl_4 with metal carbonyl complexes is not clear. Reactions of benzylamine with CCl_4 have been reported,[2] and the products described were benzylamine hydrochloride, dibenzylurea and benzylidenebenzylamine. No heterocyclic compound was formed. Therefore, interaction or coordination of the intermediate species with metallic species probably plays an important role for these selective multistep cyclization reaction. However, it is difficult to define the role of the metal complexes and no effort has been made to incorporate the metallic species in the mechanism depicted.

EXPERIMENTAL

Reaction of benzylamine. Benzylamine (25·0 g), CCl_4 (25 ml) and $Co_2(CO)_8$ (0·5 g) were mixed in a glass vessel equipped with a gas inlet capillary, placed in an autocalve. CO was introduced (50 atm) and the reaction carried out at 150° for 16 hr with shaking. The mixture was a green solid, which upon washing with acetone, gave NH_4Cl and dibenzylamine hydrochloride (4·64 g) as insoluble products. The acetone solution was evaporated and the residue subjected to column chromatography (silica gel) and eluted with $CHCl_3$. At first ϕ-CHO (0·35 g) was eluted, followed by 1-benzyl-2,4,5-triphenylimidazole (II) (1·75 g). Then 2,4,5 triphenylimidazole (I) (6·0 g). Further elution with $CHCl_3$ acetone, gave hydrochlorides of 1-benzyl-2,4,5 triphenylimidazoline (IV) (1·20 g) and 2,4,5-triphenylimidazoline (III) (4·75 g). The hydrochlorides were made free by Na_2CO_3.

2,4,5-Triphenylimidazole (I), m.p. 275°. (Found: C, 84·82; H, 5·68; N, 9·64; MW, 297 (acetone). $C_{21}H_{16}N_2$ requires: C, 85·11; H, 5·44; N, 9·45%, MW, 296). IR (KBr, cm^{-1}): 3000, 1600, 770, 695.

1-Benzyl-2,4,5-triphenylimidazole (II), m.p. 164°. (Found: C, 86·92; H, 5·96; N, 7·36; MW, 388 (acetone). $C_{28}H_{22}N_2$ requires: C, 87·01; H, 5·74; N, 7·25%, MW, 386). IR (KBr, cm^{-1}): 3030, 1600, 775, 760, 700. NMR (τ): 4·83 (2H, singlet), 2·1–3·3 (20 H).

dl-2,4,5-Triphenylimidazoline (III), m.p. 201–203°. (Found: C, 84·29; H, 6·06; N, 9·38; MW, 302 (acetone). $C_{21}H_{18}N_2$ requires: C, 84·53; H, 6·08; N, 9·39; MW, 298). IR (KBr, cm^{-1}): 3130, 3000, 1600, 1570, 755, 695. NMR (τ): 5·15 (2H), 2–2·7 (15 H).

1-Benzyl-dl-2,4,5-triphenylimidazoline (IV), m.p. 110–112°. (Found: C, 86·67; H, 6·30; N, 7·41; MW, 380 ($CHCl_3$). $C_{28}H_{24}N_2$ requires: C, 86·56; H, 6·23; N, 7·21%, MW, 388). IR (KBr, cm^{-1}): 3000, 2900, 1600, 1570, 760, 700. NMR (τ): 6·07 (1H, d); 5·63 (1H, d), 5·30 (1H, d), 4·95 (1H, d), 2·0–3·2 (20 H).

The reaction was carried out under N_2 at 110° for 5 hr. The product was treated with acetone, acetone evaporated and the residue distilled to give benzylamine (5·49 g, 46–48°/3 mm) and N-benzylidenbenzylamine (V) (9·98 g, 126–127°/3 mm). From the residue, III·HCl (1·60 g) was obtained. V was identified by the following data.

N-Benzylidenebenzylamine. (Found: C, 86·08; H, 6·57; N, 7·09; MW, 198 ($CHCl_3$). $C_{14}H_{13}N$ requires: C, 86·11; H, 6·71; N, 7·18; MW, 195). IR (cm^{-1}): 1645 (—C=N—), 755, 695.

Hydrogenation of II. II (0·6 g) was mixed with Raney Ni (0·3 g) in MeOH (50 ml) and the hydrogenation was carried out in an autoclave under H_2 pressure (93 atm) at room temp. for 18.hr. I (0·38 g) was obtained as crystals.

Reaction of o-*chlorobenzylamine with* CCl_4. *o*-Chlorobenzylamine (25·0 g), CCl_4 (25 ml) and $Co_2(CO)_8$ (0·5 g) were allowed to react under CO at 150° for 16 hr. The product was extracted with acetone, evaporated and the residue was subjected to chromatography to give 1-(*o*-chlorobenzyl)-2,4,5-tris(*o*-chlorophenyl) imidazolidine (VII) (6·40 g) and N,N'-bis(*o*-chlorobenzyl) urea (1·11 g). The acetone insoluble part was washed with Na_2CO_3 solution and Et_2O. 1-(*o*-Chlorobenzyl)-2,4,5-tris(*o*-chlorophenyl) imidazolidine (VII) (4·03 g) was obtained as solid. From the ethereal solution, 1-(*o*-chlorobenzyl)-2,4,5-tris(*o*-chlorophenyl)-imidazolidine (VII) (1·02 g) was obtained as crystals. Also *o*-chlorobenzylamine (1·53 g) was recovered.

1-(*o*-Chlorobenzyl)-2.4.5-tris(*o*-chlorophenyl) imidazolidine. m.p. 162–164°. (Found: C. 63·75; H. 4·17; N. 5·31; Cl. 27·07; MW. 536 ($CHCl_3$). $C_{28}H_{22}N_2Cl_4$ requires: C. 63·63; H. 4·17; N. 26·96%. MW. 528). IR (KBr. cm^{-1}): 3350. 750. NMR (τ): 1·7–3·1 (16H). 4·45 (1H. d). 4·97 (1H. d). 5·48 (1H. d). 6·15 (2H. s). 7·75 (1H).

m-Chlorobenzylamine (25·0 g) was reacted similarly and 2.4.5-tris(*m*-chlorophenyl-2-imidazoline (VI) (2·88 g) obtained. m.p. 258°. (Found: C. 62·78; H. 3·49; N. 6·93; Cl. 26·62; MW. 399 (acetone). $C_{21}H_{15}N_2Cl_3$ requires: C. 62·76; H. 3·74; N. 6·97; Cl. 26·53%. MW. 401).

REFERENCES

[1] Part VI: Y. Mori and J. Tsuji, (in press).

[2] [a] M. Pesez and J. Bartos. *Bull. Soc. Chim. France* 1122 (1963)
[b] T. G. Bonner and R. A. Hancock. *Chem. & Ind.* 267 (1965)
[c] M. Asscher. *Ibid.*. 1430 (1965)

[3] R. Ercoli. E. Santambrogo and G. T. Casagrands. *Chim. Ind. Milan* **44**. 1344 (1962)

[4] [a] C. H. Bamford. G. C. Eastmond and D. Writtle. *J. Organometal. Chem.* **17**. 33 (1969)
[b] W. Strohmeier and P. Hartmann. *Z. Naturforsch.* **19b**. 882 (1964)