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ADDUCTS OF 2,5,6-TRICHLORO-3,4-PYRIDYNE WITH AROMATIC HYDROCARBONS

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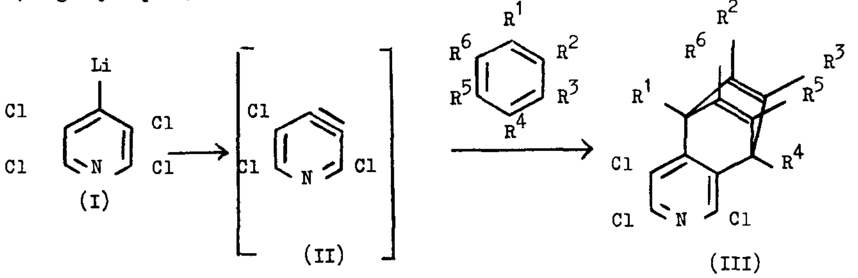
The recent report (1) that derivatives of 2,5,6-trifluoro-3,4-pyridyne could not be obtained by the decomposition of 2,3,5,6-tetrafluoro-4-pyridyl-lithium in the presence of furan and other aryne traps prompts us to publish the results of our experiments on related chloro-compounds.

Solutions containing mainly 2,3,5,6-tetrachloro-4-pyridyl-lithium (I) were prepared by the reaction of n-butyl-lithium with pentachloropyridine in diethyl ether (2). Hydrolysis of such solutions after heating at 80° for ¾ hr. gave 2,3,5,6-tetrachloropyridine, indicating that elimination of lithium chloride was slow under these conditions. However, when a large excess of benzene, mesitylene or durene was added, the ether distilled, and the solutions heated under reflux, adducts (III) of 2,5,6-trichloro-3,4-pyridyne (II) with the aromatic hydrocarbons were formed. Thus, durene gave a 25% yield of 4-aza-3,5,6-trichloro-9,10,11,12-tetramethyltricyclo$[6,2,2,0^{2,7}]$-dodeca-2(7),3,5,9,11-pentaene* (III: $R^1 = R^4 = H$, $R^2 = R^3 = R^5 = R^6 = CH_3$), m.p. 110-112°; mesitylene gave an 11% yield of 4-aza-3,5,6-trichloro-1,9,12-trimethyltricyclo-$[6,2,2,0^{2,7}]$-dodeca-2(7),3,5,9,11-pentaene (III: $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = R^6 = CH_3$) and/or the 8,10,11-trimethyl-isomer (III: $R^1 = R^3 = R^5 = CH_3$, $R^2 = R^4 = R^6 = H$), m.p. 110-113°; benzene gave a low yield (ca. 5%) of 4-aza-3,5,6-trichloro(-)tricyclo-$[6,2,2,0^{2,7}]$-dodeca-2(7),3,5,9,11-pentaene (III: $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$), m.p. 69-73° (slightly impure).



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* We use the system of nomenclature recommended by Heaney and Jablonski (3).

The structures of the adducts were established by their elemental analyses* and ^{1}H n.m.r. spectra, which are recorded in the Table.

Table

^{1}H n.m.r. spectra ($CDCl_3$).

Compound	τ	Number of protons	Splitting	Assignment
III: all R = H	3.05	4	multiplet	R^2,R^3,R^5,R^6
	4.61	2	multiplet	R^1,R^4
III: $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = R^6 = CH_3$ or isomer	3.97	2	quintet	R^3,R^5
	5.36	1	triplet	R^1
	7.87 8.02 8.04	9	unresolved singlets	R^2,R^4,R^6
III: $R^1 = R^4 = H$, $R^2 = R^3 = R^5 = R^6 = CH_3$	5.34	1	singlet	R^1,R^4
	5.49	1	singlet	
	8.19	12	singlet	R^2,R^3,R^5,R^6

It thus appears that 2,3,5,6-tetrachloro-4-pyridyl-lithium does eliminate lithium chloride to give a pyridyne intermediate analogous to the benzyne intermediates formed from pentafluorophenyl-lithium (4,5,6) and pentachlorophenyl-lithium (3), and that it is the tetrafluoropyridyl-lithium which is abnormal in its behaviour. However, the use of aryne traps other than furan may reveal the formation of trifluoro-pyridyne intermediates; when the tetrachloropyridyl-lithium compound (I) was kept at room temperature for one week, in the presence of furan, none of the expected adduct (or 1,3,4-trichloroisoquinoline) was obtained. Instead, the product was identified from its ^{1}H n.m.r.

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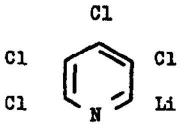
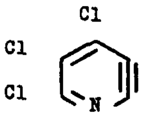
* Correct analyses were obtained for the mesitylene and durene adducts. We have not yet succeeded in obtaining the benzene adduct analytically pure.

spectrum (singlet, τ 2.83, of very low intensity), mass spectrum (M^+ 394 and 428) and elemental analysis, as a mixture of heptachloro- and octachloro-bipyridyls (of unknown orientation).

Attempts to characterise adducts of 4,5,6-trichloro-2,3-pyridyne (V) have so far been unsuccessful. Heating solutions of 3,4,5,6-tetrachloro-2-pyridyl-lithium (IV) (2) in the presence of durene, anthracene and N-methyl-pyrrole failed to yield identifiable products, although we have some evidence for the formation of a very small amount of an adduct of the 2,3-pyridyne (V) with mesitylene.



(IV)



(V)

The difference in behaviour between compounds (I) and (IV) could be due to reluctance of the 2-lithio-derivative to form the pyridyne (cf. ref. 7) or to low reactivity of the 2,3-pyridyne, once formed (cf. ref. 8). The possibility of formation of 3,4,5-trichloro-2,6-dehydropyridine *via* elimination of the chlorine atom in the 6-position must also be considered (cf. ref. 7).

References.

1. R. D. Chambers, F. G. Drakesmith, J. Hutchinson and W. K. R. Musgrave, Tetrahedron Letters, 1705 (1967).
2. J. D. Cook, B. J. Wakefield and C. J. Clayton, Chem. Comm., 150 (1967).
3. H. Heaney and J. M. Jablonski, Tetrahedron Letters, 4529 (1966).
4. P. L. Coe, R. Stephens and J. C. Tatlow, J. Chem. Soc., 3227 (1962).
5. J. P. N. Brewer and H. Heaney, Tetrahedron Letters, 4709 (1965).
6. D. D. Callander, P. L. Coe and J. C. Tatlow, Chem. Comm., 143 (1966).
7. T. Kauffmann, Angew. Chem., Intern. Edn., 4, 543 (1965).
8. H. L. Jones and D. L. Beveridge, Tetrahedron Letters, 1577 (1964).