DECARBONYLATION OF N-CARBAZOLYLACETYL CHLORIDE IN THE FRIEDEL-CRAFTS ACYLATION REACTION

B. I. Stepanov and V. F. Traven

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 2, pp. 369–371, 1967

UDC 547.572 + 547.759.32

Reaction products of N-carbazolylacetyl chloride under Friedel-Crafts reaction conditions include carbon monoxide, the reaction product from carbazole and formaldehyde (CF condensate), and carbazole. It is postulated that decarbonylation of N-carbazolylacetyl chloride involves intermediate formation of a N-carbazolylmethyl cation.

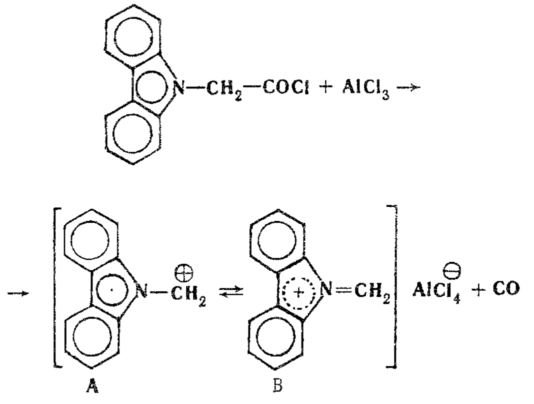
In attempting to effect cyclic condensation of N-carbazolylacetyl chloride, we have studied its reaction with aluminum chloride in benzene. It was found, however, that under these conditions the N-carbazolylacetyl chloride is decomposed with evolution of carbon monoxide.

Only one reaction equation is known for the decarbonylation of acid chlorides during Friedel-Crafts acylation, it being shown, for example, in the case of pivaloyl chloride [1] that the reaction is of the first order with respect to acid chloride, and of zero order with respect to the aromatic hydrocarbon. Thus the probability of decarbonylation of the acid chloride is determined by the conditions for distribution of the positive charge in the intermediately formed carbocation $R^{\oplus}$

$$\mathrm{R{-}COCl} + \mathrm{AlCl_3} \rightarrow \overset{\oplus}{\mathrm{R}} + \mathrm{CO} + \mathrm{Al}\overset{\ominus}{\mathrm{Cl}_4}$$

In full agreement with this equation are the instabilities of trialkyl-, triaryl-, and some aminoacetyl chlorides, and the stabilities of chlorides of normal fatty acids [2–4].

The splitting of the N-carbazolylacetyl chloride takes place independent of the aromatic hydrocarbon (no products of reaction with benzene are found), and as is assumed in the mechanism put forward above i.e., with formation of a N-carbazolylmethyl cation:



Distribution of the positive charge in the latter probably involves the π electrons of the carbazole ring system of the appropriate formula B (for example thin-layer chromatography shows that N-benzylcarbazole is not among the reaction products). The possibility of such stabilization of the N-carbazolylmethyl cation is also a cause of instability of N-carbazolylacetyl chloride in the Friedel-Crafts acylation reaction.

After hydrolysis of the reaction complex, there are isolated products of reaction of carbazole with formaldehyde, CF condensate (identified by IR spectrum infusibility, very low solubility in organic solvents [5]), yield 60%, and carbazole, yield 20%. N-Hydroxymethylcarbazole is not found among the reaction products [6], concentrated hydrochloric acid has been found [6] to convert it to CF condensate.

EXPERIMENTAL

N-Benzylcarbazole was prepared as described in [7]. After chromatographing and recrystallizing from EtOH, it had mp 116–116.5°; the literature [7] gives mp 114°.

N-Carbazolylacetic acid was prepared as described in [8]. After re-precipitating and then recrystallizing from EtOH, benzene, and EtOAc-$CHCl_3$ it had mp 184–184.5°. The literature gives mp 216°. Found: N 6.25; 6.38%; M 235; 225. Calculated for $C_{14}H_{11}NO_2$: N 6.22%; M 225. IR spectrum: intense CO (of the carboxyl group) absorption band at 1715 cm^{-1}, other bands at 1598, 1486, 1447, 1404, 1327, 1242, 1211, 1156, 921, 857, 749, 724, 700 cm^{-1}; no N-H valence vibrations absorption band (this band is found with carbazole, at 3410 cm^{-1}).

N-Carbazolylacetyl chloride. 3 g (0.013 mole) N-carbazolylacetic acid, 2 drops of pyridine, 5 ml (0.07 mole) $SOCl_2$, and 20 ml dry ether were stirred together for 15 min at 20°, and 30 min at 40°. The solution was decanted off, the solvent distilled off, the residue kept for 5 min at 1–2 mm pressure, to give N-carbazolylacetyl chloride $C_{14}H_{10}ClNO$ as pale yellow crystals, mp 115–117° (decomp). Heating the chloride with aniline in benzene gave a quantitative yield of N-carbazolylacetanilide, white needles mp 285.5–286° (ex xylene). Found: C 80.0; 80.2; H 5.35; 5.40; N 8.99; 9.07%. Calculated for $C_{20}H_{16}N_2O$: C 80.0; H 5.37; N 9.32%.

Reaction of N-carbazolylacetyl chloride with aluminum chloride. A flask was fitted with mercury-sealed stirrer, dropping funnel, reflux condenser with bubbler (40–50 ml/min) for argon, and vent for gaseous reaction products. 0.71 g (0.0053 mole) $AlCl_3$ and 30 ml benzene were added, the mixture held at 5–7°, and 1.29 g (0.0053 mole) acid chloride in 40 ml benzene added. The whole was then stirred for 50 min more, and the reaction products poured onto ice plus HCl. The precipitate was filtered off, and washed with water, when compound I was obtained. The organic layer of the filtrate was washed with water, the solvent distilled off, the residue treated with 2% NaOH, the mixture filtered, and the filtrate acidified to give N-carbazolylacetic acid, yield 0.3 g (25%). The NaOH-insoluble reaction product was dried, and along with compound I, exhaustively extracted with benzene. The extract was chromatographed on Al_2O_3, using benzene, when carbazole was isolated, yield 0.18 g (20%), mp 236–238° (ex xylene). Undepressed mixed mp with authentic carbazole. The residue remaining after extraction was CF condensate, an infusible amorphous powder (when heated above 360° it gradually charred) of very low solubility in organic solvents (pyridine, nitrobenzene, aniline, etc). There was N-H valence vibrations absorption band [5]. Yield of CF condensate 0.42 g (60% on the acid chloride decomposed, as calculated on the fragment $C_{12}H_8NCH_2$). The gas mixture collected during the reaction was analyzed with a VTI-2 gas analyzer, yield of CO 84.2 ml (NTP), 71%.

IR spectra were recorded with a IKS-14 spectrophotometer: a) for the 3600–3100 cm^{-1} and 2000–700 cm^{-1} regions a vaseline mull was used (LiF and NaCl prisms), in the 3100–2800 cm^{-1} region, tablets with KBr (LiF prism).

REFERENCES

1. M. E. Grundy, E. Rothstein, and Wei-Hwa Hsu, J. Chem. Soc., 4558, 1956.
2. E. Rothstein and R. W. Saville, J. Chem. Soc., 1950, 1949.
3. N. O. V. Sonntag, Chem. Rev., 52, 251, 1953.
4. C. Mannich and R. Kuphal, Ber., 45, 314, 1912.
5. V. F. Traven, V. A. Plakhov, and B. I. Stepanov, KhGS [Chemistry of Heterocyclic Compounds], 1967 (in press).
6. V. F. Traven, V. A. Smrchek, and B. I. Stepanov, KhGS [Chemistry of Heterocyclic Compounds], 1967 (in press).
7. B. Levy, Mon., 33, 177, 1912.
8. S. I. Omel'chenko, Z. V. Pushkareva, and S. G. Bogomolov, ZhOKh, 27, 3220, 1952.

25 October 1965

Mendeleev Moscow Chemical
Engineering Institute

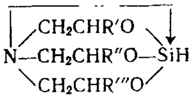
ATRANES

XI. 1-Hydrosilatranes*

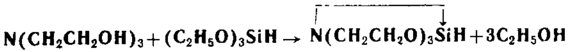
G. I. Zelchan and M. G. Voronkov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 2, 371–373, 1967

UDC 542.95 + 546.287+547.89

A new and original method of synthesizing difficultly accessible 1-hydrosilatranes  $N(CH_2CHR'O)(CH_2CHR''O)(CH_2CHR'''O)SiH$, is developed. It is based on transesterification of the appropriate boratranes in the presence of aluminum alkoxide catalyst. The method is used to prepare four compounds of the type stated, only one of which (R'=R"=R'''=H) was previously known.

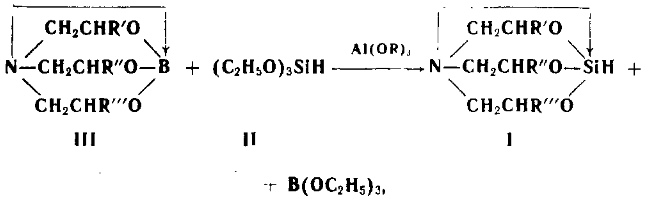
Up to the present the only known representative of 1-hydrosilatranes with a Si—H bond, is silatrane itself (Ia), which was prepared by reacting triethanolamine with triethoxysilane (II) [2]:



$$N(CH_2CH_2OH)_3+\underset{II}{(C_2H_5O)_3SiH}\rightarrow \underset{Ia}{N(CH_2CH_2O)_3SiH}+3C_2H_5OH$$

However this reaction, for which the reaction conditions are not given in the literature, is complicated by side reaction of the triethanolamine with the Si—H bond, resulting in quite a low yield of Ia (22%) [3].

We have developed a quite new and original method of preparing silatrane and its C-derivatives containing the Si—H bond [4, 5]. It is based on the aluminum alkoxide-catalyzed transesterification of the readily accessible corresponding boratranes (III) [6] by triethoxysilane (II), the equation being



---

* For Part X see [1].