9. S. E. Livingstone and J. H. Mayfield, Aust. J. Chem., <u>28</u>, No. 7, 1517 (1975). 10. D. Lloyd and D. R. Marshall, J. Chem. Soc., <u>2597</u> (1956).

TROPYLATION AND PYRYLATION OF SALTS OF ALIPHATIC MONO-, DI-, AND TRINITRO COMPOUNDS

A. A. Gakh and A. S. Kiselev

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We have studied the reactions of salts of nitroalkanes with tropylium and 2,6-diphenylpyrylium salts leading to products of C-tropylation and C-pyrylation of the corresponding anions. The only exception is the salt of cyano-dinitromethane, which is not tropylated. Splitting off of a HNO_2 molecule from the products of tropylation of nitroalkane anions to prepare nitrohepta-fulvenes was unsuccessful.

Reactions for the formation of new C-C bonds are the basis of synthetic organic chemistry. It is known that reactions of salts of nitroaliphatic compounds with activated aromatic and heteroaromatic compounds make it possible to prepare nitroalkylation products of aromatic substrates. In particular, reactions of pyridinium [1-4], quinolinium [5], acridinium [6], and some other azinium salts [7-9] with anions of various nitroalkanes have been well investigated. At the same time, such activated aromatic substrates as tropylium and pyrylium salts have practically not been studied in that respect. Known is the example of tropylation of 2-nitropropane [10], and also the reaction of 2,4,6-triphenylpyrylium salt with a salt of nitromethane, which yields 2,4,6-triphenylnitrobenzene through the ANRORC process [11].

We have studied the reaction of salts of dinitroaliphatic compounds, nitromethane, and trinitromethane with tropylium and 2,6-diphenylpyrylium salts with the purpose of examining the direction of tropylation and pyrylation in dependence of the structure of the anion.

It was found that water is the best medium to carry out the reaction. Mixing aqueous solutions of nitroalkane salts with aqueous solutions of tropylium fluoborate at ~20°C leads to momentary formation of a single reaction product that precipitates or separates out as an oil. The exception is nitromethane, of which the sodium salt on reaction with tropylium fluoborate in alcohol gives a mixture of two products (alcohol is taken instead of water because of the high basicity of the nitromethyl anion: $pK_a = 10.6$ [12]). The PMR, IR, and mass spectra, and also data of elemental analyses, show that all the compounds obtained, with the exception of (XI), are C-tropylation products of nitroalkane anions (Table 1):



During the study we found different behavior of anions of nitro- and dinitromethane, which can give mono- and ditropylated products: the anion of dinitromethane gives a single

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Come	Found , %			PMR spectrum,		TD
pound	Calculated			δ, ppm	Mass spectrum, m/z	IK Spectrum
<u> </u>	н	C	N	(CDC1 ₃)		
(11)	4,16	48,86	<u>14,44</u> 14,32	4,15 qu (1H, C^2), 5,47 t (2H, C^3 , C^8), 5,83 d (111, C^1) 6,51m (2H, C^4 , C^7), 6,78 m (2H, C^5 , C^6)	M+, 196 [M+-NO ₂], 150 [M+-HNO ₂], 149	704s, 738, 792, 858, 1238, 1328s, 1380, 1404, 1574 vs, 2850, 3026
(111)	2,98 2,91	<u>39,32</u> 39,83	<u>17,86</u> 17,78	3.07 t (1H. C ⁴), 5.37 m (2H, C ² , C ⁷), 6.64 m (2H, C ³ , C ⁶), 6.84 m (2H, C ⁴ , C ⁵)	$[M^+-HNO_2], 195$ $[M^+-2NO_2+H], 150$ $[M^+-2NO_2-2H], 149$	696°s, 738, 792s, 858, 1118, 1146, 1194, 1226, 1234's.br, 1362's.br, 1592'vs, 2872, 3018
(IV)	<u>4,54</u> <u>4,50</u>	48,98	<u>10,52</u> 10,45	1,22 t (3H, CH_3), 4,08 q (2H, CH_2), 3,12 t (1H, C^1), 5,06 m (2H, C^2 , C^7), 6,57 t (2H, C^3 , C^6), 6,76 m (2H, C^4 , C^5)		724 s, 750s, 782, 1058s, 1104, 1144, 1352, 1462, 1582 vs, 1598, 1788 s, 2992, 3008
(V)	<u>4,08</u> 4,03	45.92 45,98	<u>11,42</u> 11,38	2.73 t (2H, C ¹), 4.46 s (4H, CH ₂ *), 4.68 s (2H, CH ₂), 5.38 qu(4H, C ² , C ⁷), 6.36 t (4H, C ³ , C ⁶), 6.83 t (4H, C ⁴ , C ⁵)		722 s, 748 s, 766, 798, 828, 876, 1054 s, 1090, 1126, 1176, 1334, 1362, 1458, 1576 vs, 1592 s, 2916, 2984, 3008
(VI)	4,68	51,37 51,42	<u>13.51</u> 13,48	2.31 s (3H, CH ₃), 2.72 t (1H, C ¹), 5.27 m (2H, C ² , C ⁷), 6.35 m (2H, C ³ , C ⁶), 6,78 m (2H, C ⁴ , C ⁵)	M ⁺ , 211 [M ⁺ -HNO ₂], 164 [M ⁺ -HNO ₂ -H], 163	702 vs, 738s, 792, 858, 1098, 1232, 1246, 1346 vs, 1358 s. 1386s. 1444 s, 1572 vs, 2884, 3018
(VII) *				1.58 d'(2H, C ¹), 2.98 m (1H, C ²), 5.31 m (2H, C ³ C ⁸), 6.32 m (2H, C ⁴ , C ⁷), 6.67 m (2H, C ⁵ , C ⁶)		
(VIII)	<u>3,81</u> <u>3,84</u>	63,94 63,88	8,43 8,47	4.20 q(1H, C ³), 5.17 d(2H, C ² , C ⁴), 5,76 d (1H, CH(NO ₂) ₂), 7.52 m (phenyl ring)	$\begin{array}{c} M^+, \ 338 \\ [M^+-NO_2], \ 292 \\ [M^+-HNO_2], \ 291 \\ [M^+-CH(NO_2)_2], \ 233 \end{array}$	648s,752 vs, 776,1024. 1056,1112, 1216 s.1256, 1288s,1320, 1336s,1448, 1496s,1512, 1568 vs, 1640,1680, 3016s
(IX)	4,80 4,88	66,76 66,68	<u>8,22</u> 8,09	2.16 m (3H, CH ₃), 4,66 t (1H, C ³), 5.34 d (2H, C ² , C ⁴), 7,4 m (phenyl ring)	$\begin{array}{c} M^+, \ 352 \\ [M^+-HNO_2], \ 305 \\ [M^+-HNO_2-H], \ 304 \\ [M^+-CH_3C(NO_2)_2], \\ (233) \end{array}$	694, 768, 844, 1108, 1288 br 1332, 1388, 1446, 1496, 1562 vs, 1688, 3092 br

TABLE 1. Spectral Data of the Prepared Compounds

Com- pound	Found Calculated , %			PMR spectrum, ^δ , PPm (CDCl ₃)	Mass spectrum, m/z	IR spectrum, v.cm ⁻¹
	н	С	N			
(X)	<u>1,46</u> 1,70	64,98 64,77	8,26 7,98	Unstable		684 s. 720, 764 vs, 794 s, 998, 1116 s, 1156 s. 1214 s, 1294 br, 1384. 1446 vs, 1472, 1486. 1506 vs, 1518; 1536, 1580 vs, 1602, 1682. 2908 br, 3060 br
(XI)				8,76 s (7H) (in CD ₃ CN)		748, 850, 867, 11545, 1226, 1268 s, 1280, 1426, 1476 vs, 1492 vs, 2218 s, 3026, 3038

TABLE 1 (continued)

*The reaction mixture contains product (VIIa), ratio (VII): (VIIa) = 3:1.

product while the reaction of the nitromethane anion leads to a mixture of mono- and ditropylation products (VII) and (VIIa):



That is probably explained not only by different nucleophilicity of anions of nitro- and dinitromethane [13] but also by a difference in reaction conditions. Product (II) precipitates as it is formed because the reaction is carried out in water, which excludes the possibility of further tropylation. In the case of carrying out the reaction of (I) with nitromethane in alcohol, further tropylation of the nitromethane anion is possible.

The only exception is the reaction of tropylium fluoborate with the anion of cyanodinitromethane, which gives the tropylium salt of cyanodinitromethane, which is poorly soluble in water, and not the tropylation product:



In our opinion, that result may be explained by the extremely low nucleophilicity of the cyanodinitromethane anion ($pK_a = -5.6$ [14]).

It may be assumed that the reaction of the tropylium cation with other anions that have low nucleophilicity (for example, the trinitromethane anion, $pK_a = 0$ [13]) should be reversible to some degree. However, we failed to record the presence of the tropylium cation in solutions of tropylation products (II)-(VI). Apparently, even in the case of derivative (III) the equilibrium is practically completely shifted to the side of the tropylated covalent form.

Like the tropylium cation, the 2,6-diphenylpyrylium cation is capable of heterylating polynitroalkanes at the carbon atom. The reaction proceeds instantaneously on mixing aqueous solutions of the reagents; the pyrylation product, which is poorly soluble in water, precipitates and is formed in a yield that is close to quantitative.



In contrast to tropylation products (II)-(VI), compounds (VIII)-(X) are not very stable and on storing they rapidly become resinous. However, we could ascertain that 2,6-diphenyl-pyrylium adds to the nitroalkyl moiety at the 4-position (see Table 1).

We attempted to prepare nitroheptafulvenes according to the scheme proposed in the literature for cyanoheptafulvens [15]:



However, that method proved to be inapplicable to the synthesis of nitroheptafulvenes. Thus, refluxing (VII) in toluene leads only to resinification. Also attempts to eliminate HNO_2 from compounds (II)-(VI) were unsuccessful:



With UV irradiation, addition of nitrogen oxides, heating in polar solvents (DMF), and treatment with bases, the splitting off of HNO_2 did not take place. More rigid conditions lead to resinification and the absorption band at $\lambda_{max} = 400$ nm, which is characteristic of heptafulvenes, was not present in the spectra of the reaction mixtures.

The easiness of formation of tropylium derivatives of nitroalkanes, the unambiguity, the purity, and the high yield of tropylation products make it possible to propose that reaction for the isolation and identification of nitroalkane salts.

Thus, tropylation products (II)-(VII) have in the PMR spectrum (CDCl₃) characteristic groups of signals of the tropylidene system: a triplet (H^1) and three multiplets related to the proton pairs H^2-H^7 , H^3-H^6 , and H^4-H^5 . In addition to these signals, the PMR spectrum contains characteristic signals of the protons that are present in the nitroalkane part of the compound.

All the tropylation products are easily separated by TLC in the case that they are simultaneously present in the solution (eluent hexane-ether, 2:1) and are detected by the UV luminescence indicator.

EXPERIMENTAL

The PMR spectra were recorded at 20°C on a Bruker WM-250 spectrometer operating at 200.12 MHz. Mass spectra were taken on a Varian MAT CH-6 mass spectrometer and IR spectra on a Specord 75-IR spectrometer. The proceeding of the reaction was checked by TLC on Silufol UV-254 plates, eluent hexane-ether, 2:1.

Tropylium fluoroborate was prepared according to [16]. As starting compound for that synthesis we used tropylidene of the firm Aldrich, purity 90%, bp 116-117°C, n_D^{20} 1.5190, d = 0.888. 2,6-Diphenylpyrylium hydrosulfate was prepared by method [17], and nitroalkane salts by the following methods: $K^{+-}C(NO_2)_3$ [18], $Na^{+-}CH(NO_2)_2$ [19], $NH_4^{+-}C(NO_2)_2CH_3$ [20], $K^{+-}C(NO_2)_2COOEt$ [21], and $K^{+-}C(NO_2)_2CN$ [22]. The sodium salt of nitromethane was prepared

by adding dropwise in the cold a solution of nitromethane in absolute alcohol to a solution of sodium ethylate and was used without isolation.

<u>General Method for Carrying Out the Reaction of Nitroalkane Salts with Tropylium and</u> 2,6-Diphenylpyrylium Cations. To an aqueous solution of 0.01 mole of tropylium fluoroborate or 2,6-diphenylpyrylium hydrosulfate is added dropwise with stirring a solution of 0.012 mole of nitroalkane salt. The obtained precipitate or oil is extracted with $CHCl_3$, dried over MgSO₄, and the solvent is evaporated to dryness. Yields of products (II)-(VI) and (VIII)-(X) are quantitative. Spectral data of the prepared compounds are summarized in Table 1.

<u>Reaction of Tropylium Fluoroborate with the Sodium Salt of Nitromethane</u>. To a solution of 1.77 g (0.01 mole) of tropylium fluoroborate in absolute ethanol is added dropwise an alcoholic solution of 1 g (0.012 mole) of the sodium salt of nitromethane. The solution obtained is evaporated to dryness, the residue is dissolved in $CDCl_3$, and analyzed by PMR spectroscopy. The total yield of products (VII) and (VIIa) is 92%, the ratio (VII)/(VIIa) is 3:1.

LITERATURE CITED

- 1. H. Ahlbrecht and F. Krohnke, Liebigs Ann., 704, 133 (1967).
- 2. J. A. Zoltiewics, L. S. Helmick, and J. K. O'Halloran, J. Org. Chem., <u>41</u>, No. 8, 1308 (1976).
- 3. F. Krohnke, K. Ellegant, and E. Bertram, Liebigs Ann., 600, 176 (1956).
- 4. A. A. Onishchenko, T. V. Ternikova, O. A. Luk'yanov, and V. A. Tartakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2342 (1975).
- 5. H. Ahlbrecht and F. Krohnke, Liebigs Ann., 717, 96 (1968).
- 6. R. H. Tress and W. E. McEwen, J. Am. Chem. Soc., 76, No. 2, 580 (1954).
- 7. S. W. H. Damji, C. A. Fyfe, D. Smith, and F. J. Sharom, J. Org. Chem., <u>44</u>, No. 11, 1761 (1979).
- 8. W. Kiel, F. Krohnke, and G. Schneider, Liebigs Ann., 766, 45 (1972).
- 9. C. A. Fyfe and D. Smith, J. Org. Chem., <u>38</u>, No. 10, 1778 (1973).
- 10. M. Berson, J. Am. Chem. Soc., 83, No. 9, 2137 (1961).
- 11. K. Dimroth, G. Brauninger, and G. Neubauer, Chem. Ber., <u>90</u>, No. 8, 1634 (1957).
- 12. A. J. Gordon and R. A. Ford, A Chemist's Companion. A Handbook of Practical Data, Techniques, and References, Wiley-Interscience, New York (1973).
- 13. R. H. Boud, J. Am. Chem. Soc., 83, No. 20, 4288 (1961).
- 14. R. G. Pearson and R. L. Dillon, J. Am. Chem. Soc., 75, No. 5, 2439 (1953).
- 15. M. Oda and Y. Kitanare, J. Chem. Soc., Chem. Commun., No. 7, 352 (1969).
- 16. M. E. Vol'pin, I. S. Akhrem, and D. N. Kursanov, Zh. Org. Khim., <u>29</u>, No. 12, 2855 (1959).
- 17. G. N. Dorofeenko and S. M. Luk'yanov, Zh. Vses. Khim. Ova., <u>13</u>, No. 5, 597 (1968).
- M. Shch. L'vova, V. I. Slovetskii, and A. A. Fainzil'berg, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 649 (1966).
- 19. F. Bogardt, A. Seeler, and P. Noble, J. Org. Chem., <u>31</u>, No. 9, 2806 (1966).
- V. I. Slovetskii, A. F. Toshcheva, A. A. Fainzil'berg, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1054 (1968).
- 21. I. V. Tselinskii and V. K. Krylov, Zh. Org. Khim., 9, No. 12, 2474 (1973).
- 22. C. Parker, Tetrahedron, <u>17</u>, No. 1, 109 (1962).