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OXIDATION OF DERIVATIVES OF 1,4-DIHYDROPYRIDINE BY TETRANITROMETHANE

V. A. Kaminskii and V. S. Pavlova

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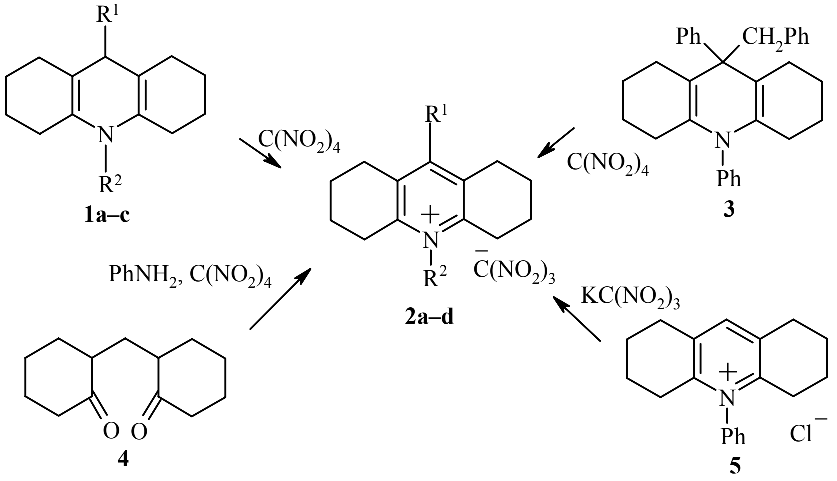
Tetranitromethane displays oxidative properties to some degree. Examples are known of aromatization of dihydroaromatic compounds when treated with it [1], but data are lacking on aromatization of dihydroheteroaromatic compounds when treated with tetranitromethane.

We have established that the products of reaction between alicyclic 1,5-diketones and primary amines, namely tricyclic derivatives of 1,4-dihydropyridine **1a-c**, which do not contain electron-acceptor groups, easily react with tetranitromethane in ether to form pyridinium nitroformates **2a-c.**



1, 2 a $R^1 = R^2 = Ph$; **b** $R^1 = Ph$, $R^2 =$ *cyclo*-C_6H_{11}; **c** $R^1 = H$, $R^2 = CH_2Ph$; **d** $R^1 = H$, $R^2 = Ph$

When 4,4-disubstituted dihydropyridine **3** is treated with tetranitromethane, oxidative elimination of the benzyl group occurs and nitroformate **2a** is formed. We have shown that it is possible to synthesize pyridinium nitroformates directly from 1,5-diketones: upon reaction of the alicyclic 1,5-diketone **4** with aniline in the presence of tetranitromethane, the pyridinium nitroformate **2d** is formed, which is also obtained by an alternate synthesis from pyridinium chloride **5** and the potassium salt of trinitromethane.

A dihydropyridine that contains electron-acceptor groups, namely 3,5-dicarboethoxy-2,6-dimethyl-1,4-dihydropyridine, is not oxidized by tetranitromethane.

Far Eastern State University, Vladivostok 690600, Russia; e-mail: kamin@chem.dvgu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 558-559, April, 2001. Original article submitted July 6, 2000.

9,10-Diphenyl-1,2,3,4,5,6,7,8-octahydroacridinium nitroformate (2a). Yield 83%; mp 176-178°C (2-propanol). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, *J*, Hz: 1.69-1.81 (8H, m, 2-, 3-, 6-, 7-H); 2.49 (4H, t, *J* = 6, 4- ,5-H); 2.56 (4H, t, *J* = 6, 1-, 8-H); 7.23 (2H, dd, J_o = 8, J_m = 1.7, Ar-H); 7.46-7.56 (6H, m, Ar-H); 7.66-7.73 (3H, m, Ar-H). IR spectrum (CH$_2$Cl$_2$), ν, cm^{-1}: 1372, 1537 (NO$_2$). Found, %: C 63.32; H 5.44; N 11.23. $C_{26}H_{26}N_4O_6$. Calculated, %: C 63.67; H 5.31; N 11.43.

10-Cyclohexyl-9-phenyl-1,2,3,4,5,6,7,8-octahydroacridinium Nitroformate (2b). Yield 91%; mp 170-171°C (benzene). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, *J*, Hz: 2.45 (8H, t, *J* = 6, 2-, 3-, 6-, 7-H); 3.19 (4H, t, *J* = 6, 4-, 5-H); 3.33 (4H, t, *J* = 6, 1-, 8-H); 5.02 (1H, td, N$^+$–CH); 7.11 (2H, d, *J* = 8, Ar-H); 7.44-7.55 (3H, m, Ar-H). IR spectrum (CH$_2$Cl$_2$), ν, cm^{-1}: 1373, 1536 (NO$_2$). Found, %: C 62.77; H 6.63; N 11.16. $C_{26}H_{32}N_4O_6$. Calculated, %: C 62.90; H 6.45; N 11.29.

10-Benzyl-1,2,3,4,5,6,7,8-octahydroacridinium Nitroformate (2c). Yield 52%; mp 108-109°C (2-propanol). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, *J*, Hz: 1.88 (8H, m, 2-, 3-, 6-, 7-H); 2.93-3.01 (8H, m, 1-, 4-, 5-, 8-H); 5.79 (2H, s, N$^+$–CH$_2$–Ph); 6.85 (2H, dd, J_o = 8, J_m = 2, Ar–H); 7.36-7.42 (3H, m, Ar–H); 7.85 (1H, s, 9-H). IR spectrum (CH$_2$Cl$_2$), ν, cm^{-1}: 1374, 1537 (NO$_2$). Found, %: C 59.11; H 5.66; N 13.33. $C_{21}H_{24}N_4O_6$. Calculated, %: C 58.87; H 5.61; N 13.08.

10-Phenyl-1,2,3,4,5,6,7,8-octahydroacridinium nitroformate (2d). Yield 41% (from diketone **4**), 69% (from compound **5**); mp 159-160°C (2-propanol). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, *J*, Hz: 1.84 (8H, q, 2-, 3-, 6-, 7-H); 2.51 (4H, br. s, 4-, 5-H); 2.98 (4H, br. s, 1-, 8-H); 7.50 (3H, m, Ar-H); 7.69 (2H, d, *J* = 8); 7.93 (1H, s, 9-H). IR spectrum (CH$_2$Cl$_2$), ν, cm^{-1}: 1374, 1537 (NO$_2$). Found, %: C 57.80; H 5.48; N 13.29. $C_{20}H_{22}N_4O_6$. Calculated, %: C 57.97; H 5.31; N 13.53.

REFERENCES

1. A. T. Nielsen, *Nitrocarbons*, New York (1995), p. 73.