REACTION OF 2,6-DI-tert-BUTYL-1,4-BENZOQUINONE DIAZIDE WITH DIAZOALKANES

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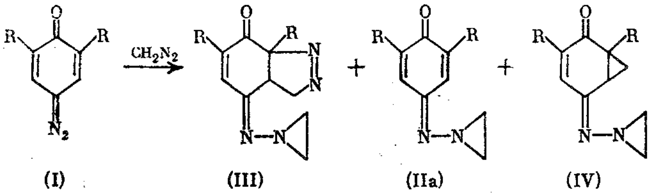
An analysis of the electronic structure of diazoalkanes [1, 2] has shown that the negative charge on these compounds is localized to a considerable degree on the carbon atom at the diazo group ($C-N_2$). Obviously, diazo alkanes can for this reason play the role of nucleophilic agents during azo coupling with 1,4-benzoquinonediazides. However, only one example of such a reaction is known: the reaction of diphenyldiazomethane with 2,6-dibromo-1,4-benzoquinone diazide forming a nonsymmetrical azine [3].

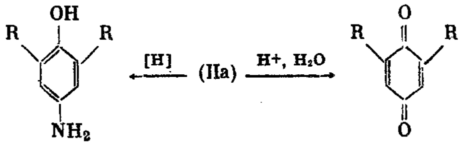
The azo coupling of 2,6-di-tert-butyl-1,4-benzoquinone diazide (I) with diazoalkanes [CH_2N_2, CH_3CHN_2, $C_6H_5CHN_2$, $(C_6H_5)_2CN_2$] was investigated in this paper and it was shown that the composition of the products is governed by the nucleophilic activity of the starting diazoalkanes and the reactivity of the azines formed. Thus when (I) was reacted with CH_2N_2, N-aminoaziridine hydrazone (IIa) was obtained as the principal reaction product with a 72.4% yield, instead of the expected azine (or its polymerization product). Besides (IIa), indazoline (III) (18.5%) and compound (IV) (4.6%) are formed:



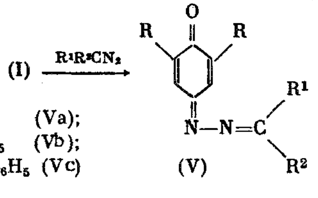
$R=C(CH_3)_3$

The yield of indazoline (III) increases with an increase in the duration of the reaction and amount of CH_2N_2 and also when the reaction is carried out in an ether medium. These facts indicate that (III) is a secondary product of the addition of CH_2N_2 to the multiple bond of the cyclohexadiene ring of hydrazone (IIa). In fact, the treatment of (IIa) with CH_2N_2 under similar conditions leads to product (III). The formation of compound (IV) is the result of the constriction of the pyrazoline ring in indazoline (III). This process, which is slow at room temperature (the conditions of the principal reaction), accelerates with heating. Thus when a solution of (III) was briefly heated in decane, (IV) was almost quantitatively formed. The structure of compounds (III) and (IV) was confirmed by spectral data and the results of their elemental analysis.

The structure of N-aminoaziridine (IIa) was confirmed by chemical conversions and spectral analysis. Acid hydrolysis of (IIa) yields 2,6-di-tert-butyl-1,4-benzoquinone, and hydrogenation over Pd is accompanied by the absorption of ~3 moles of H_2 and the formation of 4-amino-2,6-di-tert-butylphenol:



When quinone diazide (I) was reacted with diazoethane, phenyldiazomethane, and diphenyldiazomethane, the corresponding azines (V) were the only reaction products:



$R^1 = H$, $R^2 = CH_3$ (Va);
$R^1 = H$, $R^2 = C_6H_5$ (Vb);
$R^1 = C_6H_5$, $R^2 = C_6H_5$ (Vc)

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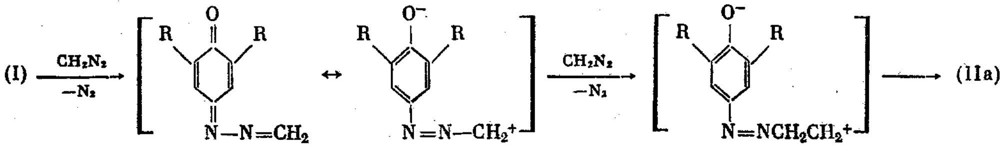
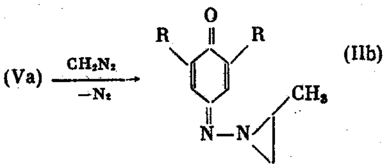
The azines were isolated chromatographically; the yield was 60-70%. Their structure was demonstrated by spectral data and counter synthesis, using, for example, the reaction between 2,6-di-tert-butyl-1,4-benzoquinone with benzophenone hydrazone.

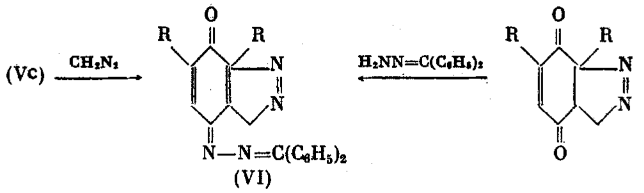
It follows from that discussed above that depending on the structure of the starting diazoalkane in the reaction with quinone diazide (I), either azines (V) or N-aminoaziridine hydrazones (IIa) are formed. It can be presumed that in the latter case, the reaction proceeds in two steps through the intermediate formation of the active azine:



The following factors should be important for converting the initially formed azines: electrophilic activity of the azines which govern the opportunity for the delocalization of the positive charge of the methylene unit with the participation of the substituents bonded to it, the shielding effects of the substituents, and the nucleophilicity of the diazoalkane (in the series chosen it is greatest for CH_2N_2). In fact, when CH_2N_2 reacts with azine (Va), the corresponding N-aminoaziridine hydrazone (IIb) is formed:



whereas azine (Vc) adds CH_2N_2 with the formation of (VI) under analogous conditions. Compound (VI) was also obtained by condensing benzophenone hydrazone with the appropriate quinone of the indazoline series:

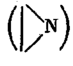


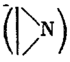
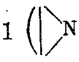
In conclusion, the characteristics of the PMR spectra of some of the compounds obtained should be dwelt on. The investigation of the change in shape of the PMR spectral signals of N-aminoaziridine hydrazone (IIa) on temperature showed that the singlet at 2.1 ppm from the protons of the methylene units is broadened with a decrease in temperature and is split into a doublet with its center at 2.1 ppm ($T_c = 0°C$, $\Delta G^{\neq} = 14.1$ kcal/mole). Similar investigations carried out with the N-aminoaziridine sample (III) yielded the following parameters: $T_c = 60°C$, $\Delta G^{\neq} = 16.75$ kcal/mole. The observed phenomenon and values for T_c and $\Delta G^{\neq}$ agree well with the proposals concerning the pyramidal stability of the nitrogen atom in the N-aminoaziridine hydrazones [4].

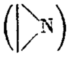
An analysis of the PMR spectra of azines (V) showed there are geometrical isomers in them which are characteristic for the azine series. One of the isomers for compound (Vb) was individually isolated. The splitting of the signals noted from the protons in the tert-butyl groups and the m protons of the quinoid ring is explained by their magnetic nonequivalency due to the steric configuration of the hydrazones (II) and azines (V).

EXPERIMENTAL

Reaction of 2,6-Di-tert-butyl-1,4-benzoquinone Diazide with CH_2N_2. To 1.16 g (0.005 mole) of (I) in 25 ml of methanol was added 25 ml of an ethereal solution of CH_2N_2 [from 2.06 g (0.02 mole) of nitrosomethylurea]. Within 1 day the solvent was distilled off in vacuo. Isolation was carried out by TLC on silica gel LL_{254} 5/40 μ (benzene–ether, 1 : 1).

2,6-Di-tert-butyl-4-(1-aziridine)imino-2,5-cyclohexadien-1-one (IIa). The yield of (IIa) was 0.94 g (72.4%), mp 52-54°C (from hexane). Found: C 73.88; H 9.31; N 10.78%; mol. wt. 260 (mass spectroscopically). $C_{16}H_{24}N_2O$. Calculated: C 73.80; H 9.29; N 10.70%; mol. wt. 260. UV spectrum: λ 295 nm, log ε 3.24. IR spectrum (ν, cm^{-1}): 2950 [$C(CH_3)_3$], 1635 (C=O, C=N), 1230 . PMR spectrum (δ, ppm): 1.22, 1.28 [$C(CH_3)_3$]; 2.10 (CH_2); 6.69, 7.53 (H_m).

6,7a-Di-tert-butyl-4-(1-aziridine)-7-oxo-3a,7a-dihydro-3H-indazoline (III). The yield of (III) was 0.28 g (18.5%), mp 84-85°C (from hexane). Found: C 68.10; H 8.80%; mol. wt. 302 (mass spectroscopically). $C_{17}H_{26}H_4O$. Calculated: C 67.51; H 8.67%; mol. wt. 302. UV spectrum: λ 272 nm, log ε 3.68. IR spectrum (ν, cm^{-1}): 2950 [$C(CH_3)_3$], 1665 (C=O, C=N), 1230 . PMR spectrum (δ, ppm): 1.19, 1.09 [$C(CH_3)_3$]; 2.01 ; 3.64 (CH); 5.14 (CH_2); 6.56 (=CH).

1,3-Di-tert-butyl-5-(1-aziridine)iminobicyclo[4.1.0]hept-3-en-2-one (IV). The yield of (IV) was 0.063 g (4.6%), mp 81-83°C (from hexane). Found: C 74.27; H 9.29%; mol. wt. 274 (mass spectroscopically). $C_{17}H_{26}N_2O$. Calculated: C 74.41; H 9.55%; mol. wt. 274. UV spectrum: λ 272 nm, log ε 3.88. IR spectrum (ν, cm^{-1}): 2950 [$C(CH_3)_3$], 1640 (C=O, C=N), 1230 .

Thermolysis of (III). A solution of 0.15 g (0.0005 mole) of (III) in 10 ml of n-decane was heated to 150°C and maintained there for 5 min. The isolation was carried out by the method described above. The yield of (IV) was 0.12 g (88.1%).

Hydrolysis of (IIa). To 0.30 g (0.0012 mole) of (IIa) in 15 ml of aqueous acetone was added several drops of 20% H_2SO_4; the mixture was boiled for 3 h. A total of 0.09 g (35.2%) of 2,6-di-tert-butyl-1,4-benzoquinone, mp 67-68°C [5] was isolated.

Reduction of (IIa). A solution of 0.7 g (0.003 mole) of (IIa) in alcohol was hydrogenated with H_2 over Pd black at ~25°C and atmospheric pressure. A total of 0.175 liter (0.007 mole) of H_2 was absorbed. 2,6-Di-tert-butyl-4-aminophenol, 0.57 g (0.0026 mole), mp 106-107°C [6], was isolated.

2,6-Di-tert-butyl-4-ethylidenehydrazono-2,5-cyclohexadien-1-one (Va). Into a solution of 1.16 g (0.005 mole) of (I) in 25 ml of ether was poured 25 ml of an ethereal solution of diazoethane [from 2.34 g (0.02 mole) of nitrosoethylurea]. Within 2 days the solvent was evaporated in vacuo. The remainder was dissolved in hexane. When frozen (dry ice), yellow crystals precipitated out. Yield (Va) 0.87 g (66.9%), mp 78-79°C (from hexane). Found: C 74.03; H 9.27%; mol. wt. 260 (mass spectroscopically). $C_{16}H_{24}N_2O$. Calculated: C 73.81; H 9.29%; mol. wt. 260. UV spectrum: λ 308 nm, log ε 4.48. IR spectrum (ν, cm^{-1}): 2950 [$C(CH_3)_3$], 1635 (C=O, C=N). PMR spectrum (δ, ppm): 1.28, 1.31 [$C(CH_3)_3$]; 1.94, 2.17 (CH_3), 6.90, 6.92, 7.23, 7.60 (H_m); 7.23, 7.88 (CH).

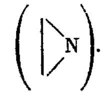
2,6-Di-tert-butyl-4-benzylidenehydrazono-2,5-cyclohexadien-1-one (Vb). To a solution of 0.58 g (0.0025 mole) of (I) in 10 ml of ether was added 12.5 ml of an ethereal solution of phenyldiazomethane [from 2.0 g (0.011 mole) of nitrosobenzylurea]. Within 2 days the solvent was evaporated in vacuo. Unreacted (I) and the side products of the reaction were separated by TLC on silica gel LL_{254} 5/40 μ (benzene–hexane, 1:1). Yield of (Vb) 0.56 g (70.0%), mp 102-103°C (from hexane). Found: C 78.30; H 8.12%; mol. wt. 322 (mass spectroscopically) $C_{21}H_{26}N_2O$. Calculated: C 78.27; H 8.07%; mol. wt. 322. UV spectrum: λ 356 nm, log ε 4.62. IR spectrum (ν, cm^{-1}): 2950 [$C(CH_3)_3$], 1630 (C=O, C=N). PMR spectrum (δ, ppm): 1.18, 1.32 [$C(CH_3)_3$]; 7.02, 7.80 (H_m); 7.52, 7.65 (C_6H_5): 7.17, 8.47 (CH).

2,6-Di-tert-butyl-4-benzophenolidenehydrazono-2,5-cyclohexadien-1-one (Vc). A) This compound was obtained similarly from 0.58 g (0.0025 mole) of (I) and 1.9 g (0.01 mole) of diphenyldiazomethane. The yield of (Vc) was 0.51 g (61.0%), mp 127-128°C (from hexane). Found: C 81.34; H 7.21; N 6.90%. $C_{27}H_{30}N_2O$. Calculated: C 81.33; H 7.58; N 7.03%. UV spectrum: λ 360 nm, log ε 4.43. IR spectrum (ν, cm^{-1}): 2950 [$C(CH_3)_3$], 1640 (C=O, C=N). PMR spectrum (δ, ppm): 1.18, 1.21 [$C(CH_3)_3$]; 7.35 (C_6H_5), 6.78, ≈7, 7.50, 7.66 (H_m).

B) To a solution of 1.1 g (0.005 mole) of 2,6-di-tert-butyl-1,4-benzoquinone in 50 ml of methanol was added 0.98 g (0.005 mole) of a methanolic solution of benzophenone hydrazone. Within 1 day the precipitated crystals were isolated. The yield of (Vc) was 1.52 g (76.5%), mp 127-128°C.

6,7a-Di-tert-butyl-4-benzophenolidenehydrazono-7-oxo-3a,7a-dihydro-3H-indazoline (VI). A) To a solution of 3.98 g (0.01 mole) of (Vc) in 25 ml of ether was added 25 ml of an ethereal solution of CH_2N_2. Within 2 days the solvent was evaporated off in vacuo. The yield of (VI) was 3.2 g (72.7%), mp 155-157°C (from hexane). Found: C 76.18; H 7.40; N 12.41%. $C_{28}H_{32}N_4O$. Calculated: C 76.33; H 7.32; N 12.72%. UV spectrum: λ 325 nm, log ε 4.08. IR spectrum (ν, cm^{-1}): 2950 [$C(CH_3)_3$], 1675 (C=O, C=N).

B) To a solution of 1.3 g (0.005 mole) of 6,7a-di-tert-butyl-4,7-dioxo-3a,7a-dihydro-3H-indazoline in 50 ml of methanol was added 0.98 g (0.005 mole) of a methanolic solution of benzophenone hydrazone. Within two days the crystalline precipitate was separated out. The yield of (VII) was 1.5 g (68.3%), mp 155-157°C.

2,6-Di-tert-butyl-4-(2 methyl-1-aziridine)imino-2,5-cyclohexadien-1-one (IIb). To a solution of 0.52 g (0.002 mole) of (Va) in 10 ml of ether was added 12.5 ml of an ethereal solution of CH_2N_2. Within 2 days the solvent was evaporated in vacuo. Unreacted (Va) and the side products were separated by TLC on silica gel LL_{254} 5/40 μ, $CHCl_3$. The yield of (IIb) was 0.18 g (32.7%), mp 44-46°C (from methanol). Found: C 74.83; H 9.49%. $C_{17}H_{26}N_2O$. Calculated: C 74.41; H 9.55%. UV spectrum: λ 300 nm, log ε 4.30. IR spectrum (ν, cm^{-1}): 2950 [$C(CH_3)_3$], 1630 (C=O, C=N), 1230 .

CONCLUSIONS

1. The reaction of 2,6-di-tert-butyl-1,4-benzoquinonediazide with diazoalkanes leads to the corresponding azines or N-aminoaziridine hydrazones, the reaction products of azines with dialkanes.

2. The route described for forming the N-aminoaziridine derivatives can serve as a preparative method for their synthesis.

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AN UNUSUAL CLEAVAGE OF MIXED ANHYDRIDES OF α-HYDROHEXAFLUOROISOBUTYRIC ACID BY THE ACTION OF TERTIARY AMINES

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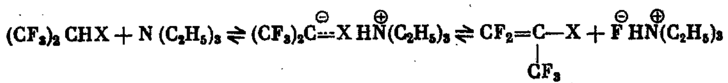
Compounds of type (I) in the presence of tertiary amines form a system in equilibrium, which may be shifted in favor of the various products [(I), (II), and (III)] depending on the nature of the residue X [1-3]:



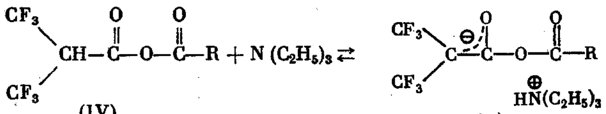
$$(CF_3)_2CHX + N(C_2H_5)_3 \rightleftharpoons (CF_3)_2\overset{\ominus}{C}{\cdots}X\,H\overset{\oplus}{N}(C_2H_5)_3 \rightleftharpoons CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}X + \overset{\ominus}{F}\,H\overset{\oplus}{N}(C_2H_5)_3$$

(I) (II) (III)

X = COF(a), CN, COOR, $CONR_2$, CF_3

Such systems are more or less stable under ordinary conditions but undergo further conversion upon heating or the action of a third component [1, 2].

The adduct (IIa) is mainly obtained from the acid fluoride of α-hydrohexafluoroisobutyric acid (Ia). It might be thought that the corresponding adducts (V) containing the mesomeric fluorocarbanion would form in the reaction of anhydrides (IV) with tertiary amines:



(IV) (V)

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