α-trichloromethylcarbinol), α-trichloromethylcarbinol acetate, and 2-substituted 1,1-dichloroolefin. The best procedure for the dechloroacetoxylation by the action of zinc powder in a mixture of acetic acid and ether.

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NEW STABLE NITROXYL RADICALS FROM HYDROGENATED QUINOLINES

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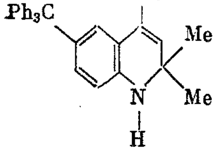
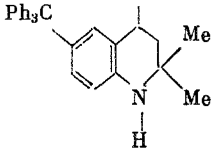
The EPR spectra of the nitroxyl radicals of 2,2,4-trimethyl-substituted hydrogenated quinolines have been described by various workers [1-5]. However, all the nitroxyl radicals of this type proved metastable and none could be isolated as a pure compound. Bulky substituents in the para position relative to the nitroxy group hinder recombination and subsequent disproportionation of the aromatic nitroxyl radicals [2, 3] and, thus, enhance the stability of these radicals.

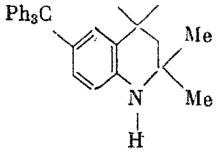
In the present work, we synthesized new derivatives of 2,2,4-trimethyl-substituted hydrogenated quinolines containing a bulky triphenylmethyl group in the aromatic ring and the oxidation of these derivatives to the corresponding nitroxyl radicals. The alkylation substituted dihydro- and tetrahydroquinolines by triphenylcarbinol in acetic acid gave (I)-(III). We should note that the alkylation proceeds selectively with the formation of good yields of only 6-substituted hydrogenated quinolines. The structures of (I)-(III) were supported by IR and PMR spectroscopy and mass spectrometry. The IR spectra of these compounds show signals characteristic of bands for 2,2,4-trimethyl-substituted hydrogenated quinoline at 3980 (NH), 3060 and 3030 (arom. CH), 2950 (CH_3), and 1595 cm^{-1} (quinoline ring). The spectrum for (I) also has a band at 1625 cm^{-1} (C=C). In comparison with the PMR spectra of the starting compounds, the spectra of (I)-(III) lack peaks for the protons at position 6 at 6.4-6.5 ppm and signals appear for the 15 protons of the triphenylmethyl group at 7.10-7.17 ppm. In addition to the molecular ion peaks, the mass spectra of these compounds show peaks for the $[M - CH_3]^+$, $[M - CH_3 - C_6H_5]^+$, and $[Ph_3C]^+$ ions.



(I)



(II)



(III)

Lenin Komsomol Voronezh State University. Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimichesksya, No. 12, pp. 2870-2873, December, 1988. Original article submitted April 13, 1988.

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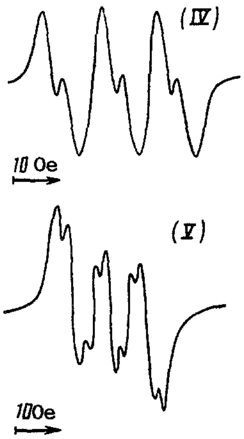
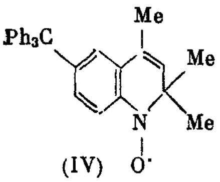
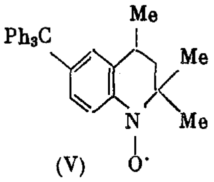
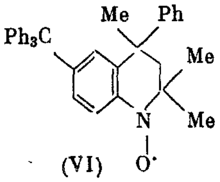


Fig. 1. EPR spectra of nitroxyl radicals (IV) and (V).


(IV)


(V)


(VI)

The oxidation of (I)-(III) was carried out using hydrogen peroxide in methanol in the presence of Na_2WO_4. Quinoline derivative III was also oxidized by meta-chloroperbenzoic acid in chloroform. The corresponding nitroxyl radicals (IV)-(VI) were isolated as pure compounds. Radicals (IV)-(VI) are crystalline compounds ranging in color from bright red to dark cherry red with sharp melting points. These products are significantly more stable than previously identified nitroxyl radicals of this class and remain unchanged upon storage at least for one year both in the crystalline state and in solution.

The EPR spectrum of (IV), which is completely identical to the spectrum of (VI), consists of six lines (triplet of doublets) with coupling constants a_N = 11.2 and a_{H^8} = 2.8 Oe. Figure 1 shows the nature of the observed splittings for (IV). This figure also gives the EPR spectrum of (V), in which nine lines are seen (triplet of triplets), a_N = 11.2 and a_{H^8} = a_{H^4} = 2.8 Oe. The EPR spectra indicate that the triphenylmethyl group in (IV)-(VI) is found at C_6 since there is no splitting due to H^6.

EXPERIMENTAL

The monitoring of the reaction course and the identification of the products obtained were carried out using thin-layer chromatography on Silufol UV-254 plates using 3:1 benzene–CCl_4 as the eluent. Iodine vapor was used as the developer. The IR spectra were taken for KBr pellets on a UR-20 spectrometer. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz in $CDCl_3$ using TMS as the internal standard. The mass spectra were taken on a Ribermag R10-10C chromato-mass spectrometer with direct sample inlet into the ion source and 70 eV ionizing voltage. The EPR spectra were taken on an EPR-2V spectrometer of the Institute of Chemical Physics.

2,2,4-Trimethyl-6-triphenylmethyl-1,2-dihydroquinoline (I). A solution of 17.3 g (0.1 mole) 2,2,4-trimethyl-1,2-dihydroquinoline and 26 g (0.1 mole) triphenylcarbinol in 200 ml acetic acid was heated at reflux for 5 h. Then the reaction mixture was poured into water and neutralized with saturated aqueous sodium carbonate. The precipitate was filtered, washed with water, dried, and crystallized from 2-propanol to give 32 g (77%) (I), mp 171-172°C. Found: C 89.39; H 7.19; N 3.49%, molec. mass 415 (mass spectrometry). $C_{31}H_{28}N$. Calculated: C 89.6; H 7.03; N 3.37%, molec. mass 415.584. PMR spectrum (δ, ppm): 1.31 s (6H, $C(CH_3)_2$), 1.74 s (3H, 4-CH_3), 4.27 s (1H, NH), 5.21 s (1H, C=CH), 6.7-6.9 m (3H, arom.), 7.16 s (15H, CPh_3).

2,2,4-Trimethyl-6-triphenylmethyl-1,2,3,4-tetrahydroquinoline (II). This was obtained under analogous conditions from 3.5 g (0.02 mole) 2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline and 5.2 g (0.02 mole) triphenylcarbinol. The yield was 5.1 g (61%), mp 198-199°C. Found: C 89.02, H 7.59, N 3.18%, molec. mass 417 (mass spectrometry). $C_{31}H_{31}N$. Calculated: C 89.16; H 7.48; N 3.36%, molec. mass 417.6. PMR spectrum (δ, ppm): 1.11, 1.21 two s (2 × 3H, $C(CH_3)_2$), 1.49 d (3H, 4-CH_3), 1.66 d (2H, 3-CH_2), 2.78 m (1H, 4-CH), 4.28 s (1H, NH), 6.6-6.8 m (3H, arom.), 7.17 s (15H, CPh_3).

2,2,4-Trimethyl-4-phenyl-6-triphenylmethyl-1,2,3,4-tetrahydroquinoline (III). This was obtained by analogy from 2,2,4-trimethyl-4-phenyl-1,2,3,4-tetrahydroquinoline in 65% yield, mp 117-118°C. Found: C 90.38; H 7.03; N 2.95%, molec. mass 493 (mass spectrometry). $C_{37}H_{35}N$. Calculated: C 90.02; H 7.15; N 2.84%, molec. mass 493.699. PMR spectrum (δ, ppm): 0.90, 1.03 two s [2 × 3H, $C(CH_3)_2$], 1.30 s (3H, 4-CH_3), 2,26 q (2H, 3-CH_2), 4.17 s (1H, NH), 4.17 s (1H, NH), 6.7-7.3 m (8H, arom.), 7.10 s (15H, CPh_3).

2,2,4-Trimethyl-6-triphenylmethyl-1,2-dihydroquinoline 1-Oxide (IV). A sample of 1 g (I) was dissolved in 100 ml methanol and 0.8 g Na_2WO_4 and 0.5 ml 30% H_2O_2 were added. The reaction mixture was heated at reflux for 8 h. Methanol was distilled off at reduced pressure. Water was added to the residue, which was extracted with chloroform, dried, and subjected to chromatography on a column packed with grade-II alumina with benzene as the eluent. The first colored fraction with $R_f = 0.54$ was collected. The eluent was evaporated at reduced pressure and the dry residue was crystallized from hexane to give 0.55 g (53%) (IV), mp 174-176°C. Found: C 86.35; H 6.63; N 3.46%, molec. mass 430 (mass spectrometry). $C_{31}H_{28}NO$. Calculated: C 86.44; H 6.55; N 3.25%; molec. mass 430.52.

2,2,4-Trimethyl-6-triphenylmethyl-1,2,3,4-tetrahydroquinoline 1-Oxide (V). This was obtained by analogy in 60% yield, mp 172-173°C. Found: C 85.72; H 6.65; N 3.28%; molec. mass 432 (mass spectrometry). $C_{31}H_{30}NO$. Calculated: C 86.04; H 6.99; N 3.24%; molec. mass 432.6.

2,2,4-Trimethyl-4-phenyl-6-triphenylmethyl-1, 2,3,4-tetrahydroquinoline 1-Oxide (VI). This was obtained by analogy and also by the oxidation of (III) by m-chloroperbenzoic acid in chloroform at 0°C and subsequent separation on a column packed with alumina using chloroform as the eluent, $R_f = 0.66$. The yield was 64%, mp 204-206°C. Found: C 86.72; H 6.36; N 2.61%; molec. mass 508 (mass spectrometry). $C_{37}H_{34}NO$. Calculated: C 87.06; H 6.74; N 2.75%; molec. mass 508.686.

CONCLUSIONS

Syntheses were reported for 6-triphenylmethyl derivatives of 2,2,4-trimethyl-1,2-dihydroquinolines and 2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines as well as 4-phenol-1,2,3,4-tetrahydroquinoline. The oxidation of these compounds by H_2O_2 in the presence of Na_2WO_4 and also by m-chloroperbenzoic acid gave nitroxyl radicals, whose structures were supported by EPR spectroscopy.

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