PHOTOCHEMISTRY OF ACETYLENE DERIVATIVES OF AROMATIC AMINES.

2. PHOTOLYSIS OF p-ETHYNYL- AND p-BUTADIYNYL-N,N-DIBENZYLANILINES AND p-DIMETHYLAMINOTOLANE IN THE PRESENCE OF CARBON TETRACHLORIDE AND OXYGEN

M. I. Bardamova and O. M. Usov

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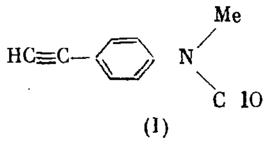
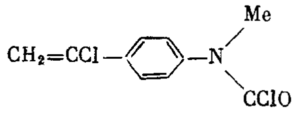
The radical-cations of alkynylanilines are formed during the photolysis of ethynylanilines substituted at the para position in the presence of carbon tetrachloride and oxygen. They undergo two types of reaction, i.e., ejection of the alkyl substituent from the amino group and addition of the H atom from the amine molecule or the Cl atom from the carbon tetrachloride to the triple bond of the radical-cation. In the radical-cation of p-butadiynyl-N,N-dibenzylaniline not only the N—Alk but also the N—Ar bond is cleaved. The mass spectra of the products from the photolysis of all the investigated alkynylarylamines were obtained and analyzed.

In [1] we showed that the irradiation of a solution of p-ethynyl-N,N-dimethylaniline (EDMA) with near UV light in carbon tetrachloride in the presence of oxygen leads to the formation of compounds (I-V) and a colored precipitate, consisting of an ionic compound with the supposed structure (VI).



(I)



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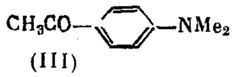

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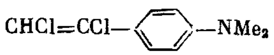

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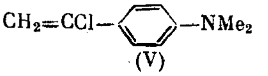

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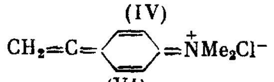

(VI)

The photochemical transformations of unsubstituted N,N-dimethylaniline in carbon tetrachloride lead to derivatives of di- and triphenylmethane, hydrazine, aminobenzylaniline, and also to p-dimethylaminobenzoic acid, Michler's ketone, etc. [2-4]. The difference in the structure of the products from the photolysis of EDMA is due to the effect of the accepting ethynyl group, which leads to redistribution of electron density both in the initial molecule and in the intermediate particles which are formed from it. This in turn must affect the dark reactions of the intermediates, directing them along a new pathway.

In the present work we compared the results from the photolysis of EDMA and p-ethynyl-N,N-dibenzylaniline (EDBA), p-butadynyl-N,N-dibenzylaniline (BDBA), and p-dimethylaminotolane (DMAT) with carbon tetrachloride in order to determine the effect of the structure of the molecule on its photochemical behavior. These and a number of other compounds with similar structure may prove important for silver-free photographic processes on account of their high photosensitivity in the solid phase, and for this reason it is necessary to investigate

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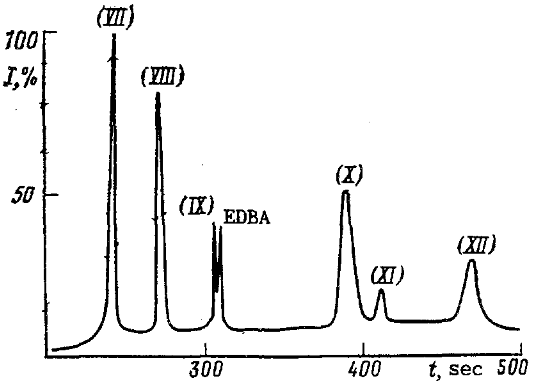
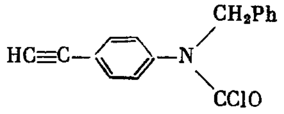


Fig. 1. Chromatogram of the irradiated solution of EDBA in acetonitrile (10 vol.% of carbon tetrachloride). The numbers of the peaks correspond to the numbers of the products (see the text and Table 1).

the primary photochemical reactions which involve their participation. Chromato-mass spectrometry (CMS) was used for separation and identification of the photolysis products.

RESULTS AND DISCUSSION

In the present work we used acetonitrile containing 10 vol.% of carbon tetrachloride as solvent in order to avoid the formation of a precipitate insoluble in carbon tetrachloride. During the photolysis of EDBA in acetonitrile in the presence of carbon tetrachloride and atmospheric oxygen one of the main products was benzaldehyde, which was produced with a yield of ~40% (determined from the IR spectrum of the mixture). Its presence in such an amount did not make it possible to realize chromato-mass spectral analysis of the irradiated solution, since the benzaldehyde retained other products in the evaporator of the chromatograph. To remove the benzaldehyde we treated the solution with sodium bisulfite. The chromatogram of the mixture treated in this way is shown in Fig. 1, and the products were identified by analysis of their mass spectra (Table 1). The following products were found in the analyzed mixture: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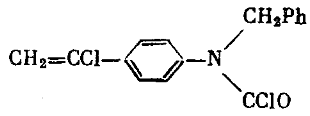
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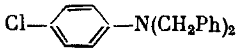
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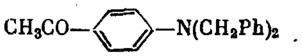
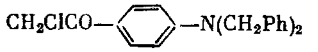

(X)


(XI)


(XII)

In addition, benzaldehyde and traces of EDBA were found. (We note that gaseous phosgene and hydrogen chloride were released from the solution during irradiation.)

As in the case of EDMA, irradiation of the mixture for a short time gave a single product, which can be regarded formally as the product from the addition of HCl to the triple bond of the initial acetylene [1] — in the present case p-dibenzylamino-α-chlorostyrene (XIII) (Table 1).

After distillation from a mixture of acetonitrile and carbon tetrachloride, washing of the residue with ether, and treatment with water, p-dibenzylamino-α-chloroacetophenone (XI) was isolated with a yield of up to 50%.

Thus, a significantly larger range of products is formed during the photolysis of EDBA than during the photolysis of EDMA. The formation of all the products from the photolysis of EDBA can be explained by modifying the reaction scheme proposed in [1] in the light of the fact that the solution contains oxygen and ~0.5% of water. In nonpolar solvents, as considered in [5], the excited amine molecule forms an exciplex with the carbon tetrachloride molecule, and its dissociation leads to the appearance of a radical pair, the transformation of which then takes place in

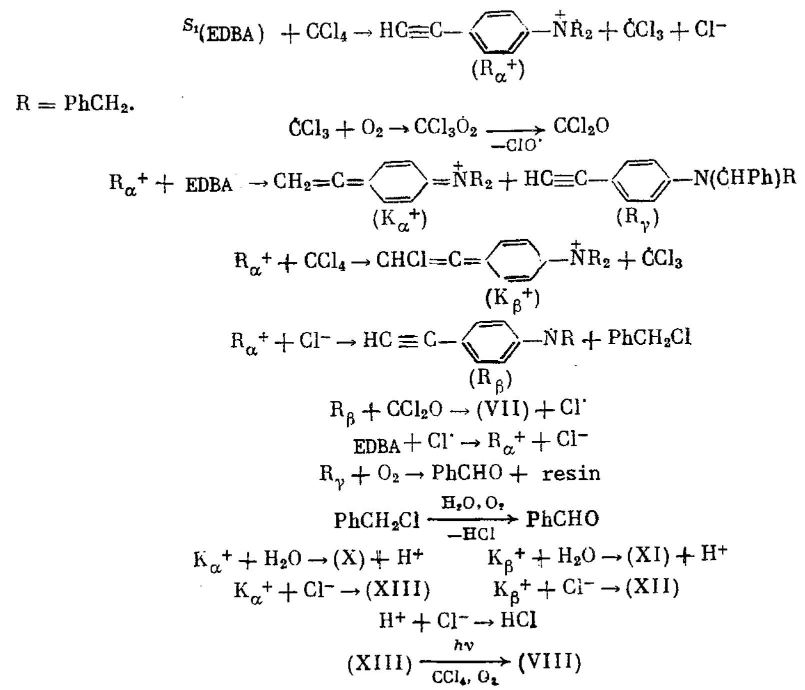
TABLE 1. Mass Spectra of the Products from Photolysis of EDBA

Product	Ion, M, *m/z* (*I*, %)
(VII)	$C_{16}H_{12}{}^{37}ClNO$ 271(10,2), $C_{16}H_{12}{}^{35}ClNO$ 269(22,4), $C_{16}H_{12}NO$ 234(4,9), $C_{15}H_{13}N$ 207(8,9), $C_{15}H_{12}N$ 206(4,9), $C_{15}H_{10}N$ 204(5,0), C_9H_5NO 143(89,7), C_8H_5N 115(15,0), C_8H_4N 114(5,4), C_8H_6 102(5,9), C_8H_5 101(20,4), C_7H_8 92(17,2), C_7H_7 91(100), C_7H_5 89(11,9), C_7H_4 88(10,0), C_6H_5 77(8,7), C_6H_3 75(16,3), C_5H_5 65(36.3), C_5H_3 63(18,8), C_5H_2 62(12,2), C_4H_3 51(20,0), C_4H_2 50(10,4), C_3H_3 39(18,8), C_3H_2 38(5,6)
(VIII)	$C_{16}H_{13}{}^{37}Cl_2NO$ 309(4,2), $C_{16}H_{13}{}^{35}Cl^{37}ClNO$ 307(9,3), $C_{16}H_{13}{}^{35}Cl_2NO$ 305(12,6), $C_{15}H_{12}{}^{37}ClN$ 243(1,4), $C_{15}H_{12}{}^{35}ClN$ 241(3,8), $C_9H_6{}^{37}ClNO$ 181(24,3), $C_9H_6{}^{35}ClNO$ 179(56,7), C_9H_6NO 144(31,9), C_8H_6N 116(11,9), C_8H_6 102(10,0), C_8H_5 101(9,3), C_7H_8 92(12,6), C_7H_7 91(100), C_7H_6 90(6,7), C_7H_5 89(12,9), C_6H_5 77(8,0), C_6H_4 76(4,9), C_6H_3 75(7,4), C_5H_5 65(26,8), C_5H_4 64(5,6), C_5H_3 63(15,0), C_2H_3NO 57(13,3), C_4H_3 51(13,9), C_4H_2 50(6,9), C_4H_3 39(14,7)
(IX)	$C_{20}H_{18}{}^{37}ClN$ 309(15,4), $C_{20}H_{18}{}^{35}ClN$ 307(34,4), $C_{14}H_{13}{}^{37}ClN$ 232(3,4), $C_{14}H_{13}{}^{35}ClN$ 230(9,6), $C_{13}H_{11}{}^{37}ClN$ 218(4,5), $C_{13}H_{10}{}^{37}ClN$ 217(6,1), $C_{13}H_{11}{}^{35}ClN$ 216(12,8), $C_{13}H_{10}{}^{35}ClN$ 215(10,4), $C_7H_5{}^{37}ClN$ 140(3,4), $C_7H_5{}^{35}ClN$ 138(7,6), $C_6H_4{}^{37}Cl$ 113(4,8), $C_6H_4{}^{35}Cl$ 111(12,1), C_7H_7 91(100), C_6H_5 77(6,6), C_6H_3 75(6,6), C_5H_5 65(19,6), C_4H_3 51(6,9), C_3H_3 39(7,9)
EDBA	$C_{22}H_{19}N$ 297(100), $C_{16}H_{14}N$ 220(17,1), $C_{15}H_{12}N$206(20,4), $C_{15}H_{11}N$ 205(23,7), $C_{15}H_{10}N$ 204(10,9), $C_{15}H_{12}$ 192(10,6), C_9H_6N 128(9,8), C_8H_5N 115(4,7), C_8H_5 101(15,2), C_7H_7 91(61,2), C_6H_5 77(5,5), C_5H_5 65(8,4), C_3H_3 39(2,7)
(X)	$C_{22}H_{21}$ 315(46,2), $C_{21}H_{18}N$ 300(8,4), $C_{16}H_{16}NO$ 238(10,1), $C_{15}H_{14}NO$ 224(16,7), $C_{15}H_{13}AO$ 223(5,0), $C_{14}H_{10}NO$ 208(8,1), $C_{13}H_{12}N$ 182(7,5), $C_3H_{11}N$ 181(5,8), $C_{13}H_{10}N$ 180(5,7), C_9H_8O 146(4,7), C_7H_4O 104(5,0), C_7H_8 92(16,3), C_7H_7 91(100), C_6H_5 77(9,9), C_5H_5 65(23,3), C_4H_3 51(7,9), C_2H_6N 43(14,8), C_3H_3 39(6,6)
(XI)	$C_{22}H_{20}{}^{37}ClNO$ 351(6,7), $C_{22}H_{20}{}^{35}ClNO$ 349(14,7), $C_{21}H_{18}N$ 300(27,3), $C_{16}H_{15}{}^{35}ClNO$ 272(1,5), $C_{15}H_{13}{}^{37}ClNO$ 260(0,9), $C_{15}H_{13}{}^{35}ClNO$ 258(2,5), $C_{14}H_{10}NO$ 208(7,1), C_7H_7 91(100), C_6H_5 77(8,4), C_5H_5 65(16,4), C_3H_3 39(6,5)
(XII)	$C_{22}H_{19}{}^{37}Cl_2N$ 371(3,3), $C_{22}H_{19}{}^{37}Cl^{35}ClN$ 369(22,1), $C_{22}H_{19}{}^{35}Cl_2N$ 367(28,7), $C_{22}H_{19}{}^{37}ClN$ 334(1,2), $C_{22}H_{19}{}^{35}ClN$ 332(2,8), $C_{16}H_{14}{}^{37}Cl^{35}ClN$ 292(3,4), $C_{16}H_{14}{}^{35}Cl_2N$ 290(4,9), $C_{15}H_{12}{}^{37}Cl_2N$ 280(0,6), $C_{15}H_{12}{}^{37}Cl^{35}ClN$ 278(6,3), $C_{15}H_{11}{}^{35}Cl_2N$ 275(7,1), $C_8H_5{}^{37}Cl$ 138(2,6), $C_8H_5{}^{35}Cl$ 136(7,5), C_8H_5 101(7,8), C_7H_7 91(100), C_6H_5 77(6,3), C_5H_5 65(17,9), C_4H_3 51(5,3), C_3H_3 39(6,0)
(XIII)	$C_{22}H_{20}{}^{37}ClN$ 335(19,8), $C_{22}H_{20}{}^{35}ClN$ 333(58,5), $C_{22}H_{20}N$ 298(10,8), $C_{22}H_{19}N$ 297(9,9), $C_{16}H_{15}{}^{37}ClN$ 258(3,7), $C_{16}H_{15}{}^{35}ClN$ 256(12,1), $C_{15}H_{13}{}^{37}ClN$ 244(5,1), $C_{15}H_{12}{}^{37}ClN$ 243(5,3), $C_{15}H_{13}{}^{35}ClN$ 242(14,6), $C_{15}H_{12}{}^{35}ClN$ 241(14,4), $C_{15}H_{12}N$ 206(12,4), C_8H_5 101(8,3), C_7H_7 91(100), C_6H_5 77(5,5), C_5H_5 65(7,4)

TABLE 2. Mass Spectra of the Products from Photolysis of BDBA and DMAT

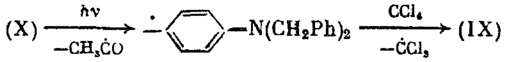
Product	Ion, M, *m/z* (*I*, %)
	Photolysis of BDBA
(XIV)	$C_{15}H_{14}{}^{37}ClNO$ 261(1,4), $C_{15}H_{14}{}^{35}ClNO$ 259(6,1), $C_{15}H_{14}NO$ 244(3,0), $C_{15}H_{13}NO$ 223(3,1), $C_8H_7{}^{37}ClNO$ 170(9,1), C_8H_7ClNO 168(24,3), $C_8H_7{}^{35}ClN$ 152(2,8) C_8H_6NO 132(12,1), $C_7H_6{}^{37}Cl$ 127(6,8), $C_7H_6{}^{35}Cl$ 125(18,6), C_8H_8N 104(4,9), C_7H_7 91(100), C_6H_5 77(7,3), C_5H_5 65(13,4), C_4H_3 51(5,2), C_3H_3 39(6,0)
(XV)	$C_{18}H_{12}{}^{37}ClNO$ 295(7,4), $C_{18}H_{12}{}^{35}ClNO$ 293(25,7), $C_{17}H_{12}N$ 230(2,6), $C_{17}H_{10}N$ 228(2,9), $C_{11}H_5NO$ 167(100), $C_{10}H_5N$ 139(7,8), $C_{10}H_5$ 125(8,2), C_8H_3 99(4,4), C_7H_7 91(89,8), C_6H_3 75(4,1), C_5H_5 65(11,6), C_4H_3 51(2,6), C_3H_3 39(1,9)
	Photolysis of DMAT
(XVI)	$C_{16}H_{17}NO$ 239(23,0), $C_9H_{11}NO$ 149(32,7), $C_9H_{10}NO$ 148(100), $C_8H_{10}N$ 120(9,9), C_8H_7O 119(8,5), C_8H_6O 118(5,0),C_7H_7N 105(14,6), C_7H_6N 104(10,0), C_7H_7 91,(16,5), C_5H_5N 79(9,4), C_5H_4N 78(8,4), C_6H_5 77(16,7), C_6H_4 76(4,7), C_5H_5 65(9,0), C_5H_3 63(5,6), C_4H_3 51(5,9), C_2H_5N 43(8,9), C_3H_3 39(7,6)
(XVII)	$C_{16}H_{16}{}^{37}ClN$ 259(23,4), $C_{16}H_{16}{}^{35}ClN$ 257(47,5), $C_{16}H_{16}N$ 222(86,8), $C_{16}H_{15}N$ 221(100), $C_{16}H_{14}N$ 220(66,9), $C_{15}H_{13}N$ 207(16,3), $C_{15}H_{12}N$ 206(29,4), $C_{15}H_{11}N$ 205(34,2), $C_{15}H_{10}N$ 204(12,9), $C_{14}H_{11}$ 179(14,8), $C_{14}H_{10}$ 178(38,3), $C_{14}H_9$ 177(24,1), $C_{14}H_8$ 176(27,9), $C_{13}H_9$ 165(9,3), $C_{12}H_8$ 152 (9,5), $C_{12}H_7$ 151(15,6), $C_{12}H_6$ 150(8,8), C_8H_6 102(22,5), C_7H_5 89(11,1), C_7H_4 88(15,4), C_6H_5 77(9,7), C_6H_4 76(9,4), C_6H_3 75(9,8), C_5H_3 63(8,5), C_4H_3 51(11,0), C_4H_2 50(6,4), C_2H_4N 42(13,7), C_3H_3 39(9,1)

several directions. In a polar solvent, where the formation of the exciplex is less characteristic (see [6]), electron transfer takes place directly from the excited state of the arylamine:



Among the products from the photolysis of EDBA we detected a significant number of compounds containing a chlorine atom at the terminal carbon atom of the previous triple bond, and this was not observed during the photolysis of EDMA. In [1] it was shown that a cation K_α^+, which accumulates in the precipitate in nonpolar solvents, is formed during the photolysis of EDMA. The chlorine-containing cation K_α^+ evidently appears in the same way and is then converted into (XI) and (XII). The reason for the preferential formation of K_β^+ and not K_α^+ may be the steric factors due to the presence of the bulky benzyl substituents at the amino group, which hinder attack on the CH_2 group of EDBA by the radical-cation R_α^+. At the same time the removal of the Cl from carbon tetrachloride does not depend on steric factors. In addition, the rate of the various stages of the reaction must also be affected by the solvation of the intermediate charged particles by the polar acetonitrile molecules.

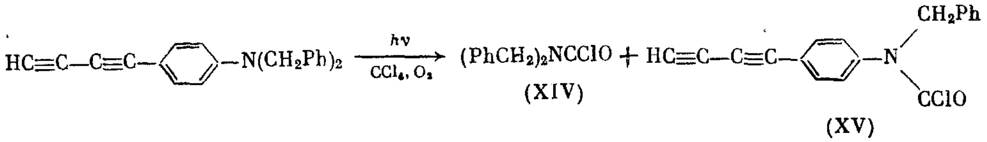
The formation of a small amount of p-chloro-N,N-dibenzylaniline (IX) can only be explained as the result of photolysis of the acetyl derivatives of dibenzylaniline (X) and (XI). They undergo dissociation of type I according to Norrish, giving the dibenzylaminophenyl radical, which changes into (IX):



Although it is atypical of acylbenzenes [7], such α-cleavage can take place under the influence of the dibenzylamino group. The possibility of preliminary electron phototransfer to the carbon tetrachloride is not excluded. It is clear that direct substitution of the ethynyl group by the Cl atom is unlikely.

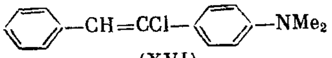
The absence of the substituted styrene (XIII) among the products of the photoreaction after prolonged irradiation demonstrates its high photochemical activity; reactions which lead finally to the carbamoyl chloride (VIII) take place during excitation. With regard to the formation of the styrene (XIII) itself it should be noted that another path to this formation is possible in addition to the photochemical path. In [8] it was shown that the amino group in p-ethynylanilines activates the triple bond so much that it acquires the ability to add hydrogen halides even in the absence of the usual catalysts [salts of Cu(I) or Hg(II)] under conditions which exclude protonation of the amino group. Protonation is impossible at the low concentration of HCl formed during photolysis.

In order to determine the effect of the structure of the acetylene substituent on the photochemical behavior of the ethynylanilines we conducted the photolysis of p-butadiynyl-N,N-dibenzylaniline (BDBA) under the same conditions. Here an unexpected result was obtained. It was found that cleavage not only of the N—Alk bond but also of the N—Ar bond is possible during the photooxidation of ethynylanilines, as shown by the presence of N,N-dibenzylcarbamoyl chloride (XIV) among the products.

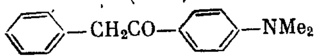


The ease with which the N—C bond is cleaved in ethynylanilines forces us to conclude that the presence of the accepting ethynyl substituents facilitates the process. The substituent at the N atom is eliminated in the form of a carbocation. It is known that dialkylanilines are practically nonphotoactive in the absence of electron acceptors, but the formation of a small amount of the monoalkylaniline is observed during irradiation in the presence of carbon tetrachloride [3, 4]. On the other hand, it was shown in [9] that the photolysis of a solution of p-dimethylamino-p′-nitrotolane without the addition of acceptors gives a large amount of p-methylamino-p′-nitrotolane (yield 67%). In this system intramolecular electron transfer from the amino to the nitro group occurs during photoexcitation, and the appearance of a large positive charge at the amino group gives rise to elimination of the alkyl group in the form of a cation. In BDBA the positive charge at the amino group in the radical-cation is evidently increased in comparison with the radical-cation of EDBA, since the butadiynyl group is a stronger acceptor than ethynyl. This leads to weakening of the N—Ar bond. The second product from the photolysis of BDBA, i.e., butadiynyl (XV) (Table 2), is similar to the corresponding carbamoyl chlorides (I) and (VII) formed from the arylalkylaminyl radicals during irradiation of EDMA and EDBA.

We also conducted the photolysis of p-dimethylaminotolane (DMAT) in acetonitrile with carbon tetrachloride. The obtained mixture is not amenable to chromato-mass spectral analysis on account of the low volatility of the products. The products were separated by preparative TLC and identified by elemental analysis and IR and NMR spectroscopy. Their mass spectra were obtained with direct injection into the mass spectrometer (Table 2). The photolysis of DMAT takes place similarly to the phototransformations of the other alkynylanilines examined above with the formation of the products (XVI) and (XVIII).



(XVI)



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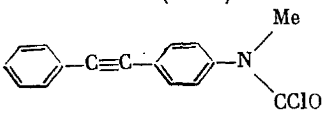

(XVIII)

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EXPERIMENTAL

The electron-impact mass spectra were recorded on an LKB-2091 chromato-mass spectrometer (SE-30, column length 40 m, column temperature 20-280°C, 16 deg/min, injection chamber 310°C) and on a "Jeol JMS-DX 303" mass spectrometer linked to a "Jeol GCG06" gas chromatograph (0.32 mm x 25 m column, methylsilicone, column temperature 200-280°C, 16 deg/min, injection chamber 300°C). The conditions for the mass spectra in both cases were as follows: 70 eV, accelerating potential 3 kV, ion current 300 μA, scan rate 1 $\sec^{-1}$. The IR spectra were recorded on a UR-20 spectrophotometer. The PMR spectra were recorded on a "Jeol FX 90Q" NMR spectrometer. Except where indicated otherwise, the IR spectra were recorded in chloroform and the NMR spectra in trideuteroacetonitrile.

Photolysis was conducted by means of a DRSh-500 mercury lamp as described in [1].

Synthesis of p-Butadiynyl-N,N-dibenzylaniline (BDBA). A mixture of 4 g (10 mmoles) of p-(5-methyl-5-hydroxy-1,3-hexadiynyl)-N,N-dibenzylaniline [10] and 2.7 g (50 mmoles) of powdered potassium hydroxide in 100 ml of absolute benzene was stirred at 70°C for 15-30 min. The reaction was monitored by TLC (Silufol, ether). The mixture was filtered through a thin layer of aluminum oxide and evaporated at reduced pressure. Hexane was added (100 ml), and the product was applied to a column of aluminum oxide (of II Brockman activity) and diluted first with hexane and then with benzene. White crystals separated from the hexane fraction. They were filtered off and dried under vacuum; mp 131-132°C. A product containing a yellow impurity was isolated from the benzene fraction; mp 129-131°C. The overall yield was 2.5 g (70%). Found %: C 89.49; H 5.89; N 4.34. $C_{24}H_{19}N$. Calculated %: C 89.68; H 5.96; N 4.36. IR spectrum (carbon tetrachloride, ν, cm^{-1}): 2220 (C≡CC≡C), 3320 (≡CH). PMR spectrum (δ, ppm): 2.87 s (≡CH), 4.77 s ($2CH_2$), 6.77 d and 7.30 d (J = 9.02 Hz, p-C_6H_4), 7.32 s ($2C_6H_5$).

p-Ethynyl-N,N-dibenzylaniline (EDBA) was obtained by the same method from p-(3-methyl-3-hydroxy-1-butynyl)-N,N-dibenzylaniline [11] with absolute toluene as solvent at 80°C. The yield was 90%; mp 111-112° see [11].

Synthesis of p-Dimethylaminotolane (DMAT). To a mixture of 33 g (137 mmoles) of p-iodo-N,N-dimethylaniline, 0.4 g of $Pd(PPh_3)_2Cl_2$, and 0.4 g of cuprous iodide in 400 ml of triethylamine in a stream of argon, while stirring over 5 min, we added dropwise 15 ml (150 mmoles) of phenylacetylene in 15 ml of triethylamine. The mixture was kept at 60°C for 20 min. After cooling the reaction mixture was diluted with 1.5 liters of water, and the crude product was filtered off in the form of a brownish-green precipitate. After drying in air the precipitate was dissolved in benzene and passed through a thin layer of aluminum oxide. After evaporation of the eluate and recrystallization from benzene we obtained 28.5 g (94%) of the product in the form of a white crystalline powder; mp 109-110°. Found %: C 86.82; H 6.79; N 6.26. $C_{16}H_{35}N$. Calculated %: C 86.84; H 6.83; N 6.33. IR spectrum (carbon tetrachloride, ν, cm^{-1}): 2225 (C≡C). PMR spectrum [$CCl_4/CDCl_3$ (1:1), δ, ppm]: 2.98 s ($2CH_3$), 6.63 d and 7.44 d (J = 8.82 Hz, p-C_6H_4), 7.27-7.47 m (C_6H_5).

Photolysis of EDBA. A solution of 5 g of EDBA and 10 ml of carbon tetrachloride in 80 ml of acetonitrile was exposed in 10-ml portions. The thickness of the absorbing layer was ~3 mm. After irradiation of each portion for 1 h (the portions were combined, the solvents were removed on a rotary evaporator, and ether and benzene (~50 ml of each) were added to the solid residue. The obtained suspension was filtered, and the ether—benzene extract was washed with a concentrated solution of sodium bisulfite and with water, dried over sodium sulfate, and submitted to chromato-mass spectral analysis. The residue was washed on the filter with water, dissolved in chloroform, and passed through a column of silica gel. After removal of the chloroform the residue was recrystallized from acetone. We isolated 2.3 g of white crystals of (XI); mp 182-183°C. Found %: C 75.24; H 5.98; N 4.30. $C_{22}H_{20}ClHO$. Calculated %: C 75.50; H 5.76; N 4.00. IR spectrum (ν, cm^{-1}): 1670 (C=O). PMR spectrum (δ, ppm): 4.79 s (CH_2Cl), 4.89 s ($2CH_2Ph$), 6.82 d and 7.80 d (J = 9.23 Hz, p-C_6H_4), 7.34 s ($2C_6H_5$).

To obtain the mass spectra of (XIII) we used one of the portions of the solution which had been irradiated for 10 min.

The BDBA (0.4 g) was irradiated similarly in 20 ml of acetonitrile containing 10% of carbon tetrachloride. Strong resin formation occurred, and before chromato-mass spectral analysis the solution was passed through a thin layer of aluminum oxide.

Photolysis of DMAT. A 2.6-g sample of DMAT in 200 ml of acetonitrile containing 10% of carbon tetrachloride was irradiated by a similar method. The solvent was removed, and the solid residue was washed with 100 ml of boiling benzene. Of the 3.2 g of residue the insoluble part amounted to 0.3 g. The extract which had been evaporated to a small volume was applied to a column of aluminum oxide, and 0.2 g of DMAT was eluted with hexane. The product was then eluted with benzene, which was evaporated to a small volume, and the solution was applied to a plate with silica gel and chromatographed with a 1:1 mixture of benzene and hexane. The mixture was separated into three fractions, which were collected and extracted with ether. From the upper fraction after recrystallization from ether we obtained 0.76 g of a mixture of the E and Z isomers of p-dimethylamino-α-chlorostilbene (XVI). Found %: C 74.76; H 6.08; Cl 13.58. $C_{16}H_{16}ClN$. Calculated %: C 74.55; H 6.22; Cl 13.79. PMR spectrum (δ, ppm): 3.07 s ($2CH_3$, Z), 3.10 s ($2CH_3$, E), 6.79 s (=CH—, E), 7.17 s (=CH—, Z), 6.84-7.86 (aromatic, E and Z). The E/Z ratio was 1:3.

β-Dimethylamino-p-dehydrobenzoin (XVII) (0.6 g) was isolated from the second fraction. Found %: C 80.15; H 7.48. $C_{16}H_{17}NO$. Calculated %: C 80.30; H 7.16. IR spectrum ($\tilde{\nu}$, cm^{-1}): 1670 (C=O). PMR spectrum (δ, ppm): 3.13 s ($2CH_3$), 4.30 s (CH_2), 6.83 d and 7.80 d (J = 9.10 Hz, p-C_6H_4), 7.39 m (C_6H_5).

From the last fraction we isolated 1.1 g of N-methyl-N-chloroformyl-p-aminotolane (XVIII). Found %: C 71.22; H 4.54; Cl 13.35. $C_{16}H_{12}ClNO$. Calculated %: C 71.24; H 4.48; Cl 13.14. IR spectrum (CCl_4, $\tilde{\nu}$, cm^{-1}): 1680 and 1760 (N—C=O), 2225 (C≡C). PMR spectrum (δ, ppm): 3.44 s (CH_3), 7.40-7.73 (p-C_6H_4 and C_6H_5).

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FLUORINATED 3,6-DI-TERT-BUTYL-o-BENZOQUINONES

G. A. Abakumov, L. G. Abakumova, V. K. Cherkasov,
and V. I. Nevodchikov

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New fluorine-containing 3,6-di-tert-butyl-o-benzoquinones have been synthesized. In the EPR spectra the ^{19}F *hyperfine coupling constant of the corresponding semiquinones was shown to be highly dependent on the metal, its surrounding ligand, and the solvent.*

Synthesis of new sterically hindered o-benzoquinones is of great interest since the synthesis conditions, electronic and molecular structure, and chemical behavior of o-benzosemiquinone (SQ) complexes of transition elements depend essentially on the oxidation power of the o-quinones which are starting reagents for synthesis of these substances.

In this work the following new fluorine-containing derivatives of 3,6-di-tert-butyl-o-benzoquinone were synthesized by double displacement of chlorine using KF by the method of [1]: 3,6-di-tert-butyl-4-fluoro-o-benzoquinone (3,6-t-Bu-4-F-Q) (I), 3,6-di-tert-butyl-4-fluoro-5-chloro-o-benzoquinone (3,6-t-Bu-4-F-5-Cl-Q) (II), 3,6-di-tert-butyl-4,5-fluoro-o-benzoquinone (3,6-t-Bu-4,5-F-Q) (III). As starting compounds chlorinated 3,6-di-tert-butyl-o-benzoquinones obtained by us [2] were used. Reactions were carried out in refluxing acetonitrile. Fluorination of 3,6-t-Bu-4,5-Cl-Q proceeds in several steps

$$3,6\text{-}t\text{-Bu-4,5-Cl-Q} \xrightarrow[-\text{KCl}]{\text{KF}} (\text{II}) \xrightarrow[-\text{KCl}]{\text{KF}} (\text{III})$$

Isolation of mixed quinone (II) is difficult because in the reaction mixture all three o-quinones are present.

Quinones (I) and (III) are solid crystalline substances stable in air as solids as well as in solution. The electronic spectrum of (I) and (III) contains typical o-benzoquinone absorption bands in the UV- and visible ranges. For (I) $\nu_1 = 25{,}600$, $\nu_2 = 21{,}400$ cm^{-1}; for (III) $\nu_1 = 26{,}800$, $\nu_2 = 23{,}000$ cm^{-1}. Comparison of the frequency of the long-wave-

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