The hexane layer was drawn off and analyzed for contents of 2,6-di-tert-butylphenol and the ester (IV). The analyses were performed in a Tsvet-104 gas–liquid chromatograph with programmed heating (5% SE-30 by volume on Chromatone IV-W-AESD, column heating rate 11°C/min).

CONCLUSIONS

The alkylation of the lithium salt of 2,6-di-tert-butylphenol by methyl acrylate is a bimolecular process of nucleophilic addition at an activated double bond, which can be carried out in a "pseudocatalytic" regime by using a small excess of lithium phenolate.

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MECHANISM OF INTERACTION OF CYCLOHEXADIENONE CARBENES WITH DEUTEROBENZENE AND BENZENE

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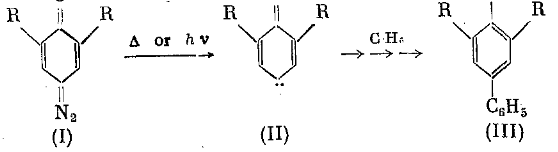
The interaction of electrophilic singlet carbenes with the aromatic ring usually begins with attack on the aromatic π-system by the carbene. The subsequent course of the reaction depends on the stability and the paths of conversion of the norcaradiene structure that is formed as an intermediate. Depending on the structure, two paths of norcaradiene transformation are possible: conversion to cycloheptatriene or aromatization to form products of formal implantation of the carbene in a C–H bond of the aromatic ring. The products of the latter type, arylphenols, are also formed by the interaction of cyclohexadienone carbenes with benzene derivatives [1]. It is natural to assume that cyclohexadienomylidenes will react with aromatic compounds in accordance with the generally accepted mechanism. In this case, however, attempts to register the formation of norcaradiene intermediates by chemical or spectral methods have been unsuccessful [2].

The present work has been aimed at spectral and kinetic investigation of the mechanism through which cyclohexadienone carbenes interact with aromatic compounds. As the reaction to be studied, we selected the thermal and photochemical decomposition of 2,6-di-tert-butyl-1,4-benzoquinonediazide (I) in a medium of benzene or deuterobenzene.

Through IR and PMR spectroscopic analysis of the reaction mixtures obtained at various degrees of thermolysis and photolysis of (I) in a benzene medium, it was shown that only two substances are present – the original quinonediazide (I) and 4-phenyl-2,6-di-tert-butylphenol (III). Evidently, the intermediate norcaradiene structure that is formed by the interaction of 3,5-di-tert-butyl-2,5-cyclohexadien-4-onylidene (II) with benzene is thermally unstable, and even at 25°C (conditions of photolysis) it is rapidly converted to the phenol (III). This is consistent with literature data on the thermal lability of cyclopropane spirane systems having a vinyl substituent on the three-membered ring [3].



Here and subsequently, R = $C(CH_3)_3$.

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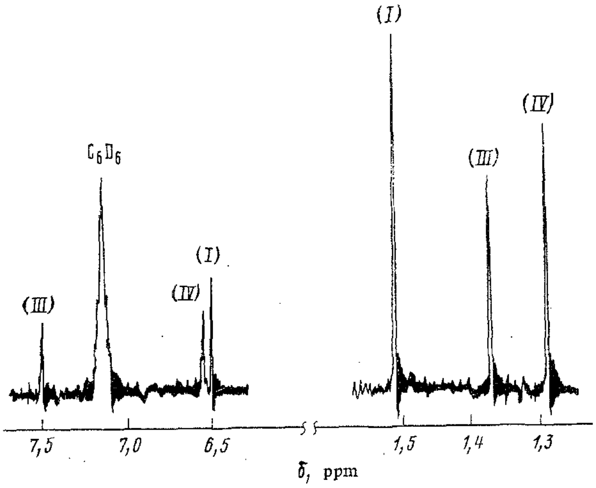

Fig. 1

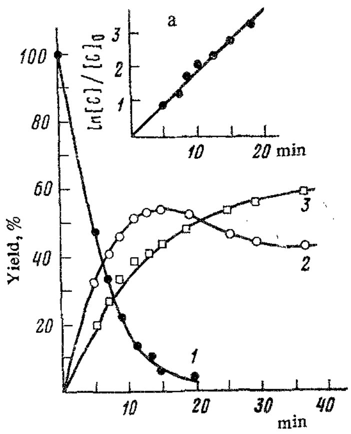

Fig. 2

Fig. 1. PMR spectrum of reaction mixture obtained by thermolysis of (I) in deuterobenzene medium for 15 min at 115°C (recorded at 25°C).

Fig. 2. Kinetics of consumption of (I) (1), conversion of (IV) (2), and accumulation of (III) (3) with time. Graph *a* is the anamorphosis of curve for consumption of (I). Thermolysis in deuterobenzene at 115°C.

More informative results were obtained by the thermolysis and photolysis of (I) in a deuterobenzene medium. The thermolysis of (I) in the NMR spectrometer resonator cavity showed that during the course of the reaction, a rather stable intermediate (IV) is formed, and this is gradually converted to the phenol (III). As can be seen from Fig. 1, in the spectrum of the mixture that had been thermolyzed at 115°C (spectrum recorded at 25°C), in addition to the signals from the (I) (1.51 and 6.50 ppm), phenol (III) (1.37 and 7.51 ppm), and deuterobenzene (7.15 ppm), two other signals are present, 1.29 and 6.55 ppm. The position of the downfield signal suggests that the intermediate (IV) that we have detected has the cyclohexadienone structure.

The concentration of (IV) in the reaction mixture depends on the thermolysis temperature, increasing with increasing temperature. For example, according to the PMR data, after 30 min of thermolysis at 90°C, the reaction mixture contains 46% (I), 44% (III), and 10% (IV); after thermolysis at 115°C, the respective contents are 0, 58%, and 42%. The kinetics of consumption of (I) and accumulation of (III) and (IV) at 115°C are shown in Fig. 2. An analysis of the curve for (I) shows that its consumption follows an exponential law with $k_1^{115°} = 2.61 \cdot 10^{-3}$ sec^{-1} ($k_1^{115°}$, recalculated from the Arrhenius relationship obtained by UV spectroscopy, is $2.42 \cdot 10^{-3}$ sec^{-1}). The kinetic curve for (IV) passes through a maximum.

The relationships we have noted are realized when a sequence of two reactions takes place, (I) $\xrightarrow{k_1}$ (IV) $\xrightarrow{k_2}$ (III) [4]. If this is the case, then, knowing the time required to reach the maximum concentration of (IV) (t_{max}) and the rate constant of the first stage of this process (k_1) (it is assumed that the carbene adds rapidly to the deuterobenzene), we can evaluate the rate constant of the reaction (IV) → (III), i.e., k_2. A graphical solution of the transcendental equation $t_{max} = (\ln k_2 - \ln k_1)/(k_2 - k_1)$ gives $k_2^{115°} = 1.5 \cdot 10^{-4}$ sec^{-1}.

This result indicates a high thermal stability of (IV). Nonetheless, attempts to isolate this compound in individual form were unsuccessful. In a chromatographic separation of the mixture on silica gel (TLC, hexane eluent), quantitative conversion of (IV) to (III) was observed. Crystallization from hexane gave only the quinonediazide (I). Repeated low-temperature crystallizations from hexane likewise fail to give the desired result. According to the PMR spectroscopic data, the crystalline sample that was obtained is a mixture of 60% (III) and 40% (IV). The IR spectrum of this mixture has a doublet in the 1620-1650 cm^{-1} region, which is evidence in favor of the cyclohexadienone structure for (IV). Here we must note that dissolution of the mixture in proton-donor solvents leads to rapid isomerization of (IV) to (III).

Before leaving this matter, we will dwell on one fact that was observed in analyzing the PMR spectrum of reaction mixtures recorded at various temperatures (25-115°C). Data on the temperature dependence of the shifts of the ring hydrogen atoms for (I) and (IV) are presented in Table 1.

It can be seen that the position of the signal of the ring hydrogen atoms of (I) depends on the temperature, with a downfield shift of the signal as the temperature is raised. This phenomenon is evidently due to dissocia-

TABLE 1

Spectrum recording temperature, °C	δ, ppm	
	(I)	(IV)
25	6.50	6.55
95	6.58	6.55
115	6.63	6.55

tion of rather stable donor-acceptor complexes of the type [(I)...C_6D_6]. With complete breakup of the complexes, the magnitude of the shift of the ring hydrogen atoms (δ_0) should approach the value corresponding to the ring hydrogen atoms of (I) in CCl_4 solution, 7.01 ppm. When we take this value into account, and when we calculate the limiting value of the shift of the ring hydrogen atoms of (I) in its associate with C_6D_6 (δ_{comp}), we can use the equation given later in this article (see experimental section) to estimate the activation energy of monomolecular decomposition of the donor-acceptor complex [(I)...C_6D_6], which amounts to 2-4 kcal/mole with $p_z = 10^{13}$ sec^{-1}.

Extremely interesting data were obtained in the photolysis of (I) in deuterobenzene medium. An analysis of the PMR spectra of the photolyzed samples revealed the following facts:

1. The reaction mixtures contain, in addition to (I), (III), and (IV), one more intermediate substance (V) (singlet signals at 1.48 and 6.15 ppm). The position of the downfield signal is evidence in favor of the cyclohexadienone structure of the intermediate (V) (Fig. 3).

2. The intermediate (V) that was detected is unstable, and it is gradually converted to (IV) during the course of the photolysis. For example, according to the PMR data, after 6 min of photolysis, the reaction mixture contains 82% (I) and 18% (V), whereas after 18 min it contains 48% (I), 26% (IV), and 26% (V). At higher temperatures, the rate of conversion of (V) to (IV) is substantially higher. Apparently, the conversion of (V) to (IV) that is observed in the course of photolysis is a thermal process. Let us note that at 40°C, the rate constant of this process is approximately $3 \cdot 10^{-3}$ sec^{-1}. This corresponds in order of magnitude to the rate constant that we obtained previously for thermal isomerization of cyclopropane spirocyclohexadienones containing a vinyl substituent on the three-membered ring ($k^{40°} = 8.6 \cdot 10^{-3}$ sec^{-1} [3]).

3. In the PMR spectra of the reaction mixtures after the illumination was shut off, changes in the intensities of the ring hydrogen atoms of (I) were observed over a 30-40-sec period (the intensity increased), and also changes in intensity for the signals from the intermediate (V) (the intensity decreased) (Fig. 4). Such changes in the intensities of the signals from protons of the compounds converted in the course of photolysis from one to the other can be explained by longitudinal diffusion processes taking place in the sample after local illumination is turned off.* However, it must be kept in view that in the case of purely diffusional processes, the time for averaging of substance concentrations throughout the entire volume of the sample should amount to minutes or even tens of minutes. In our case, the process of relaxation of signal intensities from the ring hydrogen atoms of (I) and (V) proceeds in accordance with an exponential law with a characteristic time ~10 sec, practically coinciding with T_{1n} for the ring hydrogen atoms of (I) in the given solvent. This means that the changes we have observed in the PMR spectra are more logically explained from the standpoint of a true CIDNP effect.

The fact that we have found CIDNP in the photodecomposition of (I) in deuterobenzene is extremely noteworthy. The appearance of polarization on the ring hydrogen atoms of (I) may come from two sources: reversible fixation of nitrogen by the carbene (II) or the consecutive photophysical processes shown below:

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*As a matter of fact, with local photolysis of a sample close to the zone of action of the receiver coil of the spectrometer in the absence of any vertical displacement in this particular part of the specimen, we should observe a decrease in the concentration of (I) (drop in signal intensity) and an increase in the concentration of (V) (increase in signal intensity) due to the occurrence of the photoreaction. When the light is turned off, then as a consequence of diffusional averaging of the concentrations of (I) and (V) throughout the entire volume of the sample, we should observe the reverse changes in intensities of the signals of (I) and (V) ("false CIDNP" effect).

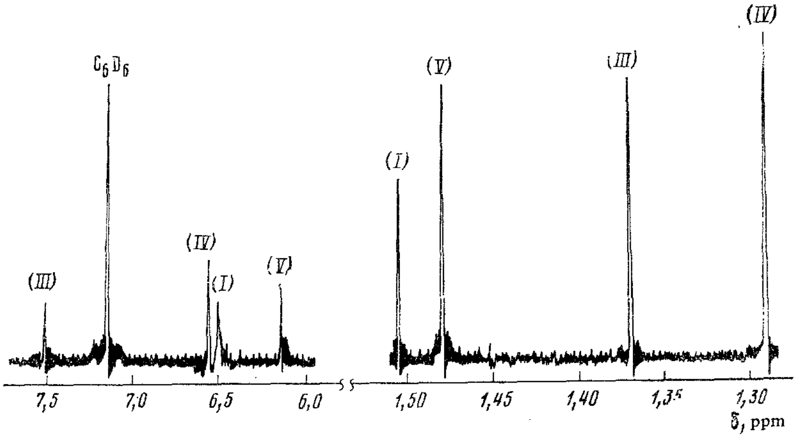


Fig. 3

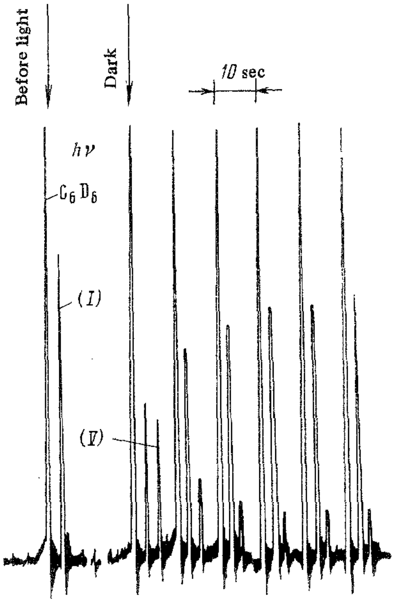
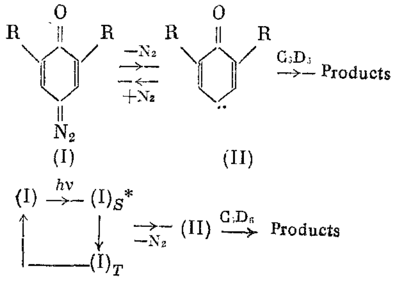


Fig. 4

Fig. 3. PMR spectrum of reaction mixture obtained by photolysis of (I) for 15 min in deuterobenzene medium (25°C).

Fig. 4. Timewise changes in signal intensities for ring hydrogen atoms of (I) and (V) after illumination is shut off.



The second path of generation of CIDNP is the more probable. Here, polarization should arise at the expense of nuclear-spin-dependent selective occupation and destruction of electron-nuclear magnetic sublevels of triplet-excited molecules of (I), with allowance for mixing of S−T states of the hyperfine interaction [5]. In contrast to the triplet mechanism that has been examined in detail in the literature [6], the CIDNP in our case is observed on the nuclei of molecules that have undergone a dual selective intercombination transition ($S_1^* \rightarrow T$, $T \rightarrow S_0$). Apparently, competition of the chemical reaction of monomolecular decomposition of (I) in the S_1^* state and deactivation of (I) by means of two consecutive intercombination transitions, the rate of which depends also on the net nuclear spin, effects a selection of (I) according to the orientations of nuclear spins, enriching the (I) in molecules with ring hydrogen atoms with spins directed along the field.

Considering that $S^* \rightarrow T$ transitions are determined mainly by nuclear spins, we can estimate the lower limit of effectiveness of deactivation of excited molecules of (I) in comparison with their decomposition to the cyclohexadienone carbene (II) and nitrogen. The original experimental data are as follows: light flux W $\sim 10^{15}$ quanta/sec, photoexcitation efficiency 1, number of molecules in illuminated zone n $\sim 10^{18}$, K ~ 0.5, $T_{1n} \sim 10$ sec.

Since in 10 sec (time of recording spectrum) the signal of (I) decreases by approximately one-half, the number of deactivated molecules, for which the nuclear spins are oriented against H_0, must be comparable to the difference in populations of the nuclear levels at thermal equilibrium. Consequently, the fraction of molecules that have undergone $S_1^* \rightarrow T$ and $T \rightarrow S_0$ transitions is equal in order of magnitude to $\frac{1}{2}\exp(t/T_{1n}) \cdot 10^{18} \cdot 10^{-6} \simeq 10^{12}$. If the total number of molecules of (I) excited in 10 sec amounts to 10^{16}, then the fraction of mole-

TABLE 2

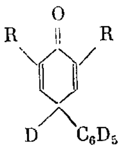
Compound	Δδ, ppm†	
	expt.	calc.
(III)	+0,30	+(0,5–0,7)
(IV)	–0,46	–(0,3–0,6)
(V)	–0,86	–(0,5–0,9)

†Relative to (I) in CCl_4, δ 7.01 ppm.

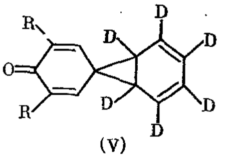
cules of (I) that have undergone $S_1^* \rightarrow T \rightarrow S_0$ transitions is $\approx 10^{-4}$, i.e., ~0.01% of the photoexcited molecules of (I).

The spectral data obtained in the thermolysis and photolysis of (I) in C_6D_6 medium, along with the chemical properties of the intermediates (IV) and (V), allow us to draw certain conclusions as to their structure and the mechanism of interaction of cyclohexadienone carbenes with aromatic compounds.

The chemical properties (sensitivity to proton-donor solvents and thermal stability) of the intermediates (IV) and (V) provide grounds for ascribing the following structures to these compounds:



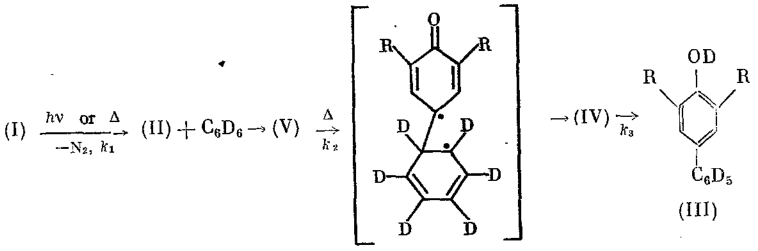
(IV)



(V)

Such a structure of the intermediates is also supported by a comparison of experimental and calculated* values for the shift of the signals from the ring hydrogen atoms of (III)-(V) (Δδ) relative to the signal of (I) in CCl_4. As can be seen from the data of Table 2, qualitative estimates of the shifts of these compounds give a satisfactory reflection of the actual sequence of location of signals from the ring hydrogen atoms in the spectrum.

In conclusion, let us dwell on the mechanism of the interaction of cyclohexadienone carbenes with aromatic compounds. In accordance with the material set forth above, the thermal and photochemical decomposition of (I) in C_6D_6 medium can be represented by the following sequence of reactions:



Regardless of the method of generation of the carbene (II), when it interacts with C_6D_6, the norcaradiene (V) is formed, and when this compound is subjected to heat, it passes through the stage of biradical generation and is converted to (IV). The (IV) undergoes a dienone–phenol rearrangement, giving the final phenol (III). The absence of signals from (V) in the PMR spectra of the reaction mixtures obtained in the thermolysis of (I) is logical; it reflects the fact that the rate of the reaction (V) → (IV) is substantially lower than the rate for the sequence of reactions (I) → (II) → (V).

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*It is assumed that the main contribution to the change in shifts of ring hydrogen atoms close to the substituent in (III)-(V) is that of the nature of the substituent (magnetic anisotropy of multiple bonds) at the C^4 atom of the cyclohexadienone or aromatic ring. Approximate calculations of Δδ were performed by the procedure of [7], using the general equation of McConnel [8].

EXPERIMENTAL

The following materials were used in the experiments: deterobenzene with 99% content of isotope; benzene for UV spectroscopy. The 2,6-di-tert-butyl-1,4-benzoquinonediazide was crystallized from heptane (purity monitored on Silufol UV-254).

The experiments were performed in XL-100, BC-487C, and NX-90ER NMR spectrometers, with HMDS standard. The pickups of the last two spectrometers were modified so that light could be supplied through a quartz light guide, directly within the pickup in the region of the receiver coil. The illumination was accomplished through a 0.5-mm wall. The light source was a DRSh-500 lamp equipped with a BS-8 light filter.

The limiting value $\delta_{\mathrm{comp}} = \delta_0 - \Delta\delta_{\mathrm{max}} = 6.3$ ppm was obtained by calculation, following [7], of the value $\Delta\delta_{\mathrm{max}} \simeq 0.75$ ppm, on the assumption that $\rho_H \geq 2.1$ Å, $Z_H \simeq 3.5$ Å.

The activation energy of monomolecular decomposition of the donor-acceptor complex $[(\mathrm{I})\ldots C_6D_6]$ was estimated in accordance with Eq. (1).

For a given temperature, the shift of the ring hydrogen atoms of (I) in C_6D_6 solution is $\delta = \delta_0[1 - [\tau \cdot (\tau + \tau_g)^{-1}]] + \delta_{\mathrm{comp}}[\tau/(\tau + \tau_g)]$, where τ and τ_g are the characteristic lifetimes of the complexed and uncomplexed molecules of (I). Since for a monomolecular reaction $k = \tau^{-1} = pZe \exp(-E/RT)$, then, in view of the above, we have

$$\frac{\delta - \delta_{\mathrm{comp}}}{(\delta_0 - \delta)\,\tau_g} = pZe^{-E/RT}. \tag{1}$$

With $[C_6D_6] \gg [(\mathrm{I})]$, $\tau_g = 1/f$, where $f \approx 10^{13}$ sec^{-1} is the frequency of particle collisions in the liquid.

CONCLUSIONS

1. It has been shown by means of PMR spectroscopy that the cyclohexadienone carbene generated by thermolysis or photolysis of 2,6-di-tert-butyl-1,4-benzoquinonediazide interacts with aromatic compounds to form a noncaradiene derivative, which, under the reaction conditions, is isomerized thermally to the 4-aryl-2,5-cyclohexadienone. The latter is converted to the 4-arylphenol as a result of a dienone–phenol rearrangement.

2. It is believed that the CIDNP that has been found for the ring hydrogen atoms of the quinonediazide and the norcaradiene derivative arises because of a nuclear-spin-dependent intercombination $S_1^* * T$ transition; qualitative evidence is presented in favor of this assumption. An estimate has been made of the lower limit of effectiveness for deactivation of excited molecules of the quinonediazide in comparison with its decomposition to nitrogen and the cyclohexadienone carbene.

3. The kinetic parameters have been determined for the thermal decomposition of 2,6-di-tert-butyl-1,4-benzoquinonediazide in deuterobenzene medium, the isomerization of the norcaradiene derivative to the 4-aryl-2,5-cyclohexadienone, and the dienone–phenol rearrangement of the latter.

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