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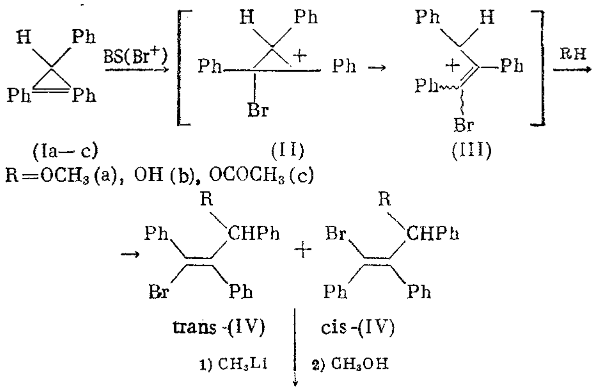
REACTIONS OF 1,2,3-TRIPHENYLCYCLOPROPENE WITH N-BROMOSUCCINIMIDE IN VARIOUS POLAR SOLVENTS

O. A. Nesmeyanova and G. A. Kudryavtseva

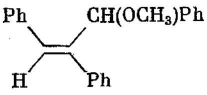
UDC 542.91:547.512:547.461.4

It is known that N-bromosuccinimide (BS) can take part in ionic reactions that are run in polar solvents, where it functions as a source of positive bromine ion [1]. In hydroxyl-containing solvents (alcohol or CH_3COOH in the presence of BS, compounds that contain C=C and C≡C multiple bonds add bromine ion and the anion from the solvent to give either bromo ethers [2] or dibromo ketals [3]. Olefins give bromohydrins in aqueous dimethoxyethane (DME) [4]. Diphenylcyclopropanes react under the same conditions to give bromine-containing addition products [5]. The C–C double and triple bonds behave differently in DMSO, which is capable of stabilizing the intermediately formed carbcation due to the formation of sulfoxonium ion. Olefins are brominated in anhydrous DMSO [6], while acetylene compounds are oxidized to α,α-diketones [6]; in water-containing DMSO the first give bromohydrins [1], whereas the second are brominated [6].

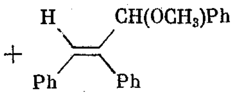
In the present paper we studied the reactions of BS with 1,2,3-triphenylcyclopropene (I) in methanol, CH_3COOH, aqueous DME, and anhydrous DMSO. By analogy with the reactions of BS at C–C multiple bonds it may be assumed that the first act when BS reacts with (I) will be the addition of Br^+ to give the cyclopropyl cation (II). Then it could be expected that either (II) will react with the solvent and form products that contain a three-membered ring, or that the ring will open, which leads to the formation of allylic ion (III), and reaction with the solvent at this step leads to the formation of linear reaction products. It proved that in all three hydroxyl-containing



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 234-237, January, 1977. Original article submitted July 9, 1976.



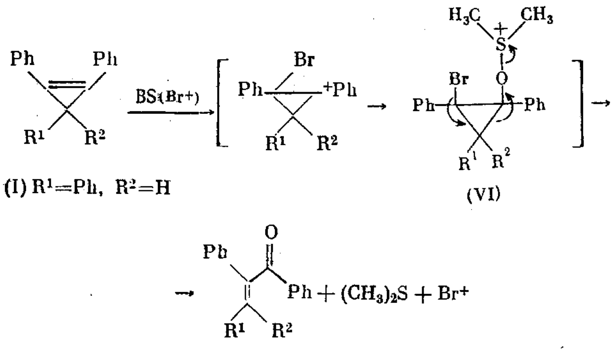
trans-(Va)



cis-(Va)

solvents the reaction went with opening of the ring and the formation in 65-95% yield (based on the NMR data) of compounds with the structure of (IV). The structure of the obtained compounds was established on the basis of the elemental analysis, NMR, UV, and mass-spectral results. The structure of compound (IVa, R = OCH_3) was confirmed by the reduction to 3-methoxy-1,2,3-triphenyl-1-propene (Va) [7]. The position of the bromine in the vinylic, and not in the allylic position, was confirmed by the inertness of (IVa) toward $AgNO_3$. Analysis of the NMR spectra of the reaction mixtures made it possible to conclude that the (IV) compounds represent a mixture of the cis and trans isomers. The signals in the region, characteristic for the methylene protons of the benzyl group, are represented in the spectra of compounds (IVa) and (IVb) by pairs of singlets with a different integral intensity; in the case of (IVc) the benzyl downfield singlet falls in the aromatic region, whose integral intensity is high. By applying the data given in [8, 9] it proved possible to assign the upfield signals of the benzyl protons, which have a high integral intensity, to the isomers with a trans arrangement of the phenyl groups relative to the double bond, and the downfield signals to the cis isomers. This was confirmed by an inversion of the integral intensity of the upfield and downfield signals of the methylene protons of the benzyl group, which occurs in the stereospecific reduction of the vinylic bromine in (IVa) when going to (Va). Such inversion would not be observed with a cis arrangement of the phenyl groups in the (IV) compounds. From this it follows that the studied reaction is stereoselective and leads to the predominant formation of the trans-isomers of (IV). As a result, in the above studied hydroxyl-containing solvents the reaction actually goes by a scheme that is general for C–C multiple bonds, with the formation of bromo ethers. Its distinguishing feature consists in the fact that the cyclopropyl cation is converted to the allyl cation and the addition of the anion occurs at this stage.

It is interesting to compare the presented data with the behavior of (I) in the presence of BS in anhydrous DMSO as the medium. Previously we had shown [10] that the bromo ether is not formed in this case, and instead (I) is oxidized to a mixture of the cis- and trans-α-phenylchalcones (VII). By analogy with the mechanism for the oxidation of acetylenes under such conditions [6], we proposed a scheme of the reaction mechanism that includes the intermediate formation of sulfoxonium ion (VI). According to the scheme, the



(I) R^1=Ph, R^2=H

(VI)

(VII a,b) R^1=Ph, R^2=H (a); R^2=H, R^2=Ph (b)

similarity in the behavior of acetylenes and (I) can be explained by the fact that in both systems the intermediately formed ion (VI) (in contrast to the cation obtained from olefins) has quite labile electrons and is capable of being stabilized by their transfer to the oxygen, which leads to the formation of the carbonyl group and the elimination of dimethyl sulfide.

EXPERIMENTAL

The melting points were determined on a Kofler instrument. The IR spectra were taken on a UR-10 instrument as KBr pellets, and the UV spectra were taken on a Specord UV-VIS instrument in alcohol solution. The NMR spectra were recorded on a Varian DA-60-IL instrument in CCl_4 solution relative to HMDS (δ scale), and the mass spectra were recorded on a Varian MAT instrument. The GLC analysis was run on a Pye-104 instrument equipped with a flame-ionization detector, and using a 0.4 × 120 cm glass column packed with 3% SE-30 deposited on Gasochrome Z, 100-200 mesh, at 225°C, and argon as the carrier gas.

N-Bromosuccinimide (BS) was recrystallized from water, dried in vacuo over P_2O_5, and the amount of active bromine (95%) was determined iodometrically. The DMSO was dried by successive vacuum-distillation over CaH_2 and 4-Å molecular sieves.

General Experimental Procedure. To a suspension of 0.001 mole of (I) in 5-7 ml of solvent was added 0.0015 mole of BS (0.003 mole in the case of DMSO), the mixture was stirred in the dark for 10 h at ~20°, poured into cold water, neutralized, washed with water, and extracted with ether. The extract was dried over Na_2SO_4, the solvent was distilled off, and the residue was recrystallized.

1-Bromo-3-methoxy-1,2,3-triphenyl-1-propene (IVa). The reaction was run in dry methanol and nearly all of the product precipitated. The yield of (IVa) (based on GLC) was 95%. NMR spectrum of reaction mixture: 3.32 s (OCH_3, 3H); 5.12 and 5.35 s (CHPh, 1H) in a 7 : 1 ratio; 7.0-7.7 m (Ph, 15H). Recrystallized of the mixed isomers from alcohol gave the trans-(IVa), mp 87.5-88.0°. Found: C 69.30; H 5.23; Br 21.06%. $C_{22}H_{19}OBr$. Calculated: C 69.65; H 5.05; Br 21.08%. Ultraviolet spectrum (λ_{max}, nm (log ε)): 227(18100), 263(5050). Mass spectrum (m/e, rel. %): 378,380 (M^+), 299(32), 267(9), 121(100), 105(10), 70(20), 91(10).

1-Bromo-3-hydroxy-1,2,3-triphenyl-1-propene (IVb). The reaction was run in 80% DME. After the usual workup the obtained compound was recrystallized from alcohol and dried in vacuo over P_2O_5. Found: C 68.61; H 4.79; Br 21.88%. $C_{21}H_{17}OBr$. Calculated: C 69.04; H 4.70; Br 22.07%. NMR spectrum of mixture: 5.5 and 6.3 s (PhCH, 1H) in a ratio ranging from 4.5 : 1 to 6 : 1; 6.5-7.5 m (Ph, 15H). Ultraviolet spectrum (λ_{max} (log ε)): 227(18300), 260(5400). Mass spectrum (m/e, rel. %): 364,366 (M^+, 5), 285(50), 178(100), 105(50), 107(32).

1-Bromo-3-acetoxy-1,2,3-triphenyl-1-propene (IVc). The reaction was run in 80% CH_3COOH. According to the NMR spectrum, the reaction mixture analyzed ~75% of (IVc) and ~20% of (IVb). The isolated (IVc) was recrystallized from alcohol. Found: C 67.61; H 5.00; Br 20.14%. $C_{23}H_{19}O_2Br$. Calculated: C 67.80; H 4.71; Br 20.14%. NMR spectrum: 1.89 s ($OCOCH_3$, 3H); 6.60 s (CHPh, 1H); 7.18-7.70 m (Ph, 15H). Ultraviolet spectrum (λ_{max}, nm (log ε)): 227(18200), 262(6400). Infrared spectrum (ν, cm^{-1}): 1230 (C–O), 1750 (C=O). Mass spectrum (m/e, rel. %): 346,348 (M^+, 10), 267(100), 252(15), 189(15).

Reaction of (IVa) with $AgNO_3$. To a solution of 0.23 g of (IVa) in 10 ml of acetone was added an aqueous solution of 0.25 g of $AgNO_3$ and the mixture was let stand overnight in the dark. A precipitate of AgBr failed to deposit; 0.22 g of (IVa) was recovered.

Reduction of (IVa) to (Va). With stirring, to a suspension of 0.12 g of (IVa) in ether was added in an argon atmosphere 2.0 ml of a 1 N ether solution of CH_3Li. The mixture was heated for 15 min, cooled in ice, and decomposed with methanol. GLC analysis disclosed the absence of the starting (IVa) in the mixture and the presence of two peaks: 93% of trans-(IVa) and 7% of cis-(Va). NMR spectrum: 3.37 and 3.42 s (OCH_3, 3H); 4.9 and 5.55 s (CHPh, 1H), in a 6 : 1 ratio [7].

α-Phenylchalcones trans-(VIIa) and cis-(VIIb). The reaction was run in anhydrous DMSO. Heating up of the mixture and the liberation of $(CH_3)_2S$ were observed here. Analysis of the reaction mixture by GLC and UV spectroscopy gave a (VIIb):(VIIa) ratio = 15:85. Recrystallization from alcohol led to the isolation of (VIIa), mp 103°. Found: C 88.96; H 5.92%. $C_{21}H_{16}O$. Calculated: C 88.73; H 5.63%. Infrared spectrum: 1655 (C=O). Ultraviolet spectrum (λ_{max}, nm (log ε)): 255(17400), 300(15500). Mass spectrum (m/e, rel. %): 284 (M^+, 61), 205(12), 178(37), 105(100), 77(48).

CONCLUSIONS

A study was made of the reactions of 1,2,3-triphenylcyclopropene with N-bromosuccinimide in alcohol, acetic acid, aqueous DME, and also anhydrous DMSO. The direction and stereochemistry of these reactions were established.

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ELECTRONIC ABSORPTION SPECTRA OF SOME ORGANOBIMETALLIC COMPOUNDS

G. A. Domrachev and V. T. Bychkov

UDC 543.422.27:547.1'13

The physical properties of organobimetallic compounds of type $[(C_2H_5)_3E]_2M$, where M = Cd, Hg, and E = Si, Ge, have received little study. Only the IR spectra of some of them have been taken [1]. The electronic absorption spectra of compounds of this type and of some other organometallic compounds (I)-(XI) were studied in the present paper. The long-wave absorption maxima and the values of the logarithms of the extinction coefficients of the studied compounds are given in Table 1.

As can be seen from the presented data, the insertion of the mercury atom into (VI), i.e., the transition to (IX), is accompanied by the formation of a new long-wave maximum (335 nm). A similar picture is also observed for (VII), where the insertion of the mercury atom leads to the appearance of a new band in the spectrum with a maximum at 368 nm (X) [2]. A similar strong bathochromic shift occurs when going from (II) and (I) to their germanium analogs (X) and (XI).

When analyzing the reasons for this phenomenon it is necessary to take into account the singular properties of the Group IIB metals when compared with other nontransition metals. The Zn, Cd, and Hg atoms are the end members of the corresponding d series of transition metals. The filling of the d shell up to 10 electrons ends in them, and when compared with other nontransition metals this shell is located shallowly. Its participation in the formation of the C–Hg bond is clearly manifested on the example of $(CH_3)_2Hg$. Thus, if we start with the ionization potentials (IP) of the CH_3 radical and mercury (respectively), 9.8 and 10.4 eV) [3], then the bonding orbital of the $(CH_3)_2Hg$ molecule should lie below 10 eV. However, the experimental data give values of 9.3 and 11.7 eV for the energies of the bonding orbitals [4]. This increase in the energy of one of the bonding orbitals is caused by the ejection of these orbitals by the closed mercury d^{10} shell. Due to the ability of the d^{10} orbitals to take part in bond formation the Group IIB metals are called post-transition. The authors of [5-8] discuss some of the properties of the compounds of these metals from this standpoint. In [9], where the UV spectra of the complexes of $(C_2H_5)Zn$ with α,α'-bipyridyl (α,α'-Bipy) and o-phenanthroline (o-Phen) are studied, the long-wave shift of the absorption maxima is also explained by the interaction of the d^{10} electrons of zinc with the p orbitals of the ligand.

However, the closure of the d^{10} shell for the Group IIIB metals and, as a consequence of this, the high IP of these electrons in R_2M compounds, lead to the situation that the participation of the d^{10} electrons in bond formation is realized only in special cases. Thus, in the complex of $(C_2H_5)_2Zn$ with α,α'-Bipy, due to complex formation, the δ^+ on the Zn atom is decreased, which facilitates a decrease in the IP of the d^{10} electrons. We will mention that the IP value is strongly dependent on the charge on the metal atom. For example, the IP of the d^{10} electrons in $(CH_3)_2Hg$ is equal to 16 eV [4], whereas in the Hg^{++} ion it is equal to 34 eV [10]. At the same time, the possibility of the d^{10} electrons of zinc coupling with the p orbitals of the ligand also facilitates their involvement in bond formation. This is an important factor, since a decrease in only the δ^+ on the metal atom is not always sufficient so that the d^{10} electrons can take part in bonding. For example, in the complex of $(C_2H_5)_2Zn$ with N,N,N',N'-tetramethylethylenediamine, which, in contrast to α,α-Bipy, is only a σ donor and consequently is incapable of π-bonding, the participation of the d^{10} electrons in bond formation is much less than in the case of α,α'-Bipy [9].

As a result, these two factors, namely a shift of the electron density of the ligand to the vacant p orbitals of the metal, which decreases the IP of the d^{10} electrons, and the presence of orbitals in the ligands that are

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Institute of Chemistry, Academy of Sciences of the USSR, Gorki. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 237-239, January, 1977. Original article submitted July 12, 1976.