shifts in water suggests that the last methylene group (corresponding to peak E) is fully exposed to solvent in the micelle. T_1 measurements in D_2O–H_2O mixtures provide some evidence for a partial immobilization of water molecules between the polyethoxy chains on a micelle.

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Radical Ions of *tert*-Butylphenylacetylene. Mechanism of Their Unconventional Dimerization and Structures of the Four Isomeric Protonated Dimers

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Abstract: The reduction of *tert*-butylphenylacetylene in THF by metallic potassium at −70° yields radical anions of that hydrocarbon which, under those conditions, undergo an unconventional dimerization. The dimers result from the addition of one radical anion to the para position of the phenyl group of another. Such a reaction yields dimeric dianions of quinonoid structure possessing a labile H atom on the quinonoid ring. Subsequent protonation or deuteration resulting from the addition of H_2O or D_2O produces four isomeric para-substituted benzene derivatives having the labile ring H replaced by another H (or D) atom on the α carbon, *viz.*, the hydrocarbons IH, IIH, IIIH, and IVH. The four isomers were separated and identified by their nmr and mass spectra, their structure being confirmed by ozonolysis. The mechanism of this dimerization was elucidated. In addition to the dimers, a small amount of carbanions $Ph\bar{C}{=}CH(t\text{-}Bu)$ is formed through the protonation of the dianions of *tert*-butylphenylacetylene by THF. These yield on the addition of H_2O or D_2O the respective β-*tert*-butylstyrenes. The reduction performed at room temperature mainly yields a completely protonated benzyl-type carbanion, *viz.*, $Ph\bar{C}H\cdot CH_2(t\text{-}Bu)$; *i.e.*, the protonation by THF becomes the dominant reaction.

It has been reported elsewhere[1] that the low temperature (*ca.* −80°) reduction of *tert*-butylphenylacetylene (BPA) by potassium results in the formation of its radical anion, $BPA\cdot^-$. Its esr spectrum is exceedingly simple; it consists of a doublet, $a = 7.15$ G, resulting from the coupling to para proton, split into triplets, $a = 2.8$ G, presumably arising from the coupling to the ortho protons. The narrow width of that spectrum, about 13 G only, implies that about 50% of the spin density is localized in the C≡C system. The fate of these radical ions, when kept at *ca.* −70° in prolonged contact with potassium, is elucidated in the present communication. The products of the reaction were isolated and identified. They arise from protonation by the solvent of the dianions (BPA^{2-}) formed by further reduction of $BPA\cdot^-$ and from an unconventional dimerization of the radical ions resulting in the precursors of four distinct dimers, all of which were isolated and identified.

Low-Temperature Reduction of *tert*-Butylphenylacetylene

About 2×10^{-2} *M* tetrahydrofuran solution of *tert*-butylphenylacetylene,[2] cooled to *ca.* −70°, was contacted with a freshly prepared potassium mirror kept at the same temperature. The reduction, performed in an all glass, vacuum tight apparatus, proceeded for about 6 hr. The resulting reddish solution, after being decanted from the mirror, was divided into two approximately equal portions. One of them was protonated with deaerated water while the other deuterated with D_2O; thereafter each solution was acidified. All of these operations were performed under vacuum, keeping the reagents at −70°.

The acidified solutions were warmed up to room temperature and the solvent was distilled off under vacuum. The residue was three times extracted with 5 ml of hexane and once with benzene. The combined extracts were freed from the solvents by vacuum distillation and then fractionated on a preparative gas chromatographic column (20% Carbowax on Chromosorb G). The separation was clearcut and eventually two monomeric and four dimeric fractions were collected.

Identification of the Monomeric Products of Low-Temperature Reduction

The monomeric products were unambiguously identified as the unreacted *tert*-butylphenylacetylene and

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[1] G. Levin, H. D. Connor, P. Caluwe, and M. Szwarc, submitted for publication.

[2] Prepared according to the method of B. S. Kupin and A. A. Petrov, *Zh. Obshch. Khim.*, 31, 2958 (1961).

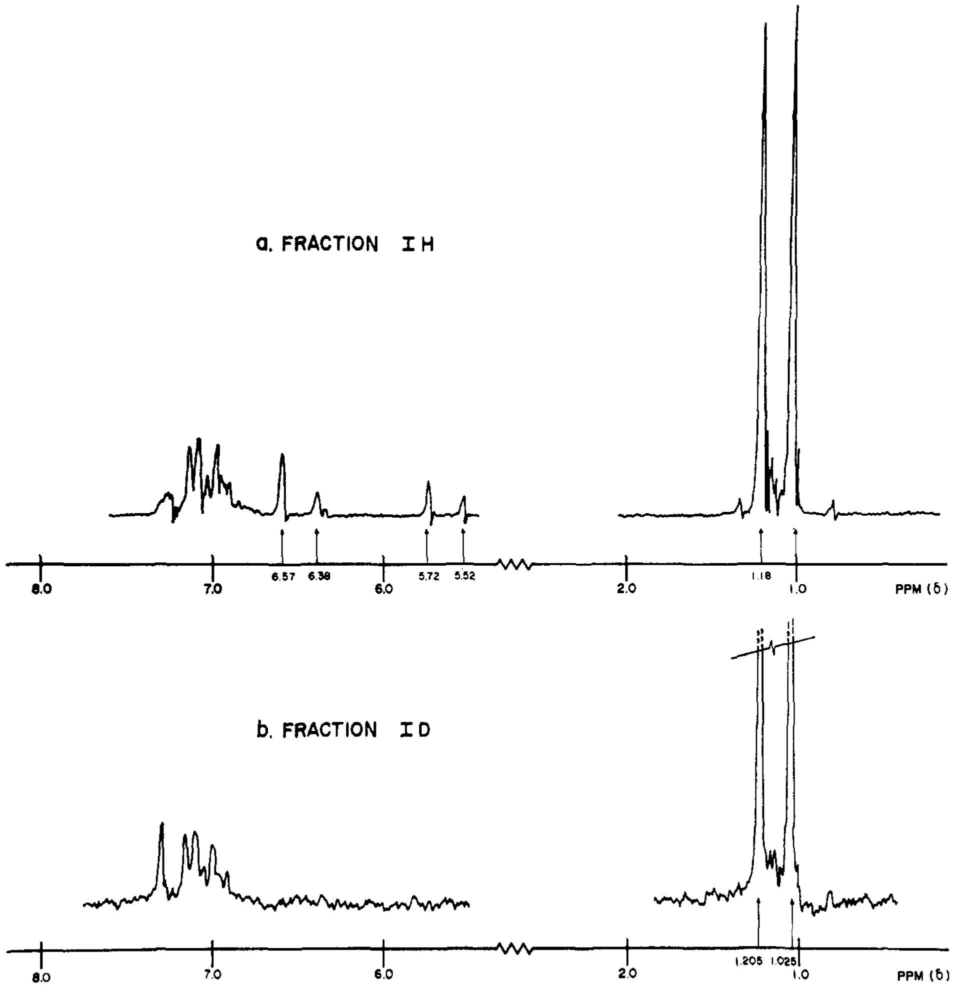

Figure 1. Nmr spectra of protonated and deuterated fraction I of the dimer.

trans-β-*tert*-butylstyrene. The evidence was provided by their retention time on gas chromatographic column and by their nmr and mass spectra. The nmr spectrum of the latter hydrocarbon in $CDCl_3$ shows a multiplet centered at δ 7.32 (5) attributed to the aromatic protons, a singlet, δ 6.27 (2), due to the olefinic protons that accidentally have the same chemical shift, and a sharp peak, δ 1.10 (9), due to the *tert*-butyl protons. Such is the pattern of the nmr spectrum of an independently prepared sample of *trans*-β-*tert*-butylstyrene and it has been previously reported by Seyferth and Singh.[3]

$Ph \cdot CH:CH \cdot C^{+}(CH_3)_2$ (*m/e* 145) is the most abundant ion in the mass spectrum of the styrene produced through protonation. Its abundance is about 3 times as high as that of the molecular ion (*m/e* 160) or the tropylium ion (*m/e* 91).

The styrene resulting from deuteration of the reduction products revealed in its mass spectrum the ions of *m/e* 92, 146, and 161, indicative of the α-monodeuterated *tert*-butylstyrene. No evidence of the dideuteriostyrenes could be found. We conclude, therefore, that $BPA \cdot^{-}$ radical ions are protonated by the solvent or, more likely, reduced further to the BPA^{2-} dianions which in turn are protonated by THF. This yields the $Ph \cdot \bar{C}:CH(t\text{-}Bu)$ carbanions and the latter form $Ph \cdot CD:CH(t\text{-}Bu)$ on the addition of D_2O. Thus the mechanism of β-*tert*-butylstyrene formation is elucidated.

However, the ions of *m/e* 91, 145, and 160 also appear in the mass spectrum of the deuterated product. Since the abundance of the ions of *m/e* 90, 144, and 159 in the mass spectrum of $Ph \cdot CH:CH(t\text{-}Bu)$ is exceedingly low, one concludes that some of the $Ph \cdot \bar{C}:CH(t\text{-}Bu)$ carbanions are protonated prior to the addition of D_2O, either by the solvent or by some acidic product of the dimerization.

Identification of the Dimeric Products of Low-Temperature Reduction

The protonation as well as the deuteration yielded dimeric products which were separated on a Carbowax column into four fractions denoted as IH, IIH, IIIH, and IVH and ID, IID, IIID, and IVD, respectively. All the fractions resulting from the protonated dimers yielded in the mass spectrograph the molecular ions of *m/e* 318 and their 319 satellites; the satellite's relative abundance conformed to the normal isotopic composition. Ions of higher mass were not observed. Mass 318 is expected for the products of protonation of the conventional $BPA \cdot^{-}$ dimers, *e.g.*

$$2BPA\cdot^{-} \longrightarrow Ph\cdot\bar{C}:C(t\text{-}Bu)C(t\text{-}Bu):\bar{C}Ph \xrightarrow{+2H^{+}} PhCH:C(t\text{-}Bu)C(t\text{-}Bu):CHPh$$

Surprisingly, all the fractions derived from the deu-

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[3] D. Seyferth and G. Singh, *J. Amer. Chem. Soc.*, **87**, 4156 (1965).

terated products yield in the mass spectrograph ions of *m/e* 321 in addition to those of *m/e* 320 and 319. Typically, the 320 ions were the most abundant, those of *m/e* 321 somewhat less, while the abundance of 319 ions was very low (~10% of 320). The deuteration of the conventional dimeric dianions should yield hydrocarbons of mass 320. The formation of hydrocarbons of mass 321 requires either the occurrence of H–D exchange *during* the deuteration process or the formation of some trinegative ions by formal loss of proton, *e.g.*, loss of an H atom coupled with electron transfer to the resulting radical followed by deuteration.

The nmr spectra of the dimeric fractions manifest again the complexity of the dimerization process. Figure 1a gives the nmr spectrum of the IH fraction. The multiplet around δ 7.0 is attributed to aromatic protons; the four lines at δ 6.57, 6.38, 5.72, and 5.52 are assigned to olefinic protons and the two sharp lines at δ 1.00 and 1.18 to two *different* *t*-Bu groups. The integration gives the ratios: 9 aromatic, 3 olefinic, and 9 *t*-Bu protons. None of the olefinic protons appear in the spectrum of the deuterated fraction, ID, whereas the lines of *tert*-butyl protons and the aromatic multiplet remain virtually unaffected (compare Figures 1a and 1b).

The lines at δ 1.00 and 5.52, 5.72, 6.38, and 6.57 appearing in the nmr spectrum of the IH fraction closely coincide with those found in the nmr spectrum of *cis*-β-*tert*-butylstyrene. The spectrum of an independently prepared sample of the latter hydrocarbon (see also ref 3) shows *t*-Bu protons at δ 0.98 (9) and an AB pattern (J = 13 cps) at δ 5.50, 5.71, 6.35, and 6.55 due to two olefinic protons. (The third olefinic proton of the IH hydrocarbon also absorbs at 6.57; *i.e.*, this line coincides with the last one of the AB pattern.) In addition the aromatic protons yield a sharp line at δ 7.23 (5). It seems, therefore, that a fragment of the IH dimer has the structure of *cis*-β-*tert*-butylstyrene; *i.e.*, it involves a phenyl ring and a *t*-Bu group attached in cis configuration to a CH=CH group.

The nmr spectrum of the IIH fraction is shown in Figure 2a. Here the two distinct *t*-Bu groups are represented by two sharp lines at δ 1.00 (9) and 1.13 (9); the olefinic protons give rise to two lines at δ 6.35 (2) and 6.46 (1) and the aromatic protons to one unresolved peak at δ 7.29 (9). The lines of the aromatic and *t*-Bu protons appear in the same locations in the spectrum of the deuterated fraction, IID, as in IIH, but those of the olefinic protons are again lacking; only a residual bump is seen at δ ~6.35 (see Figure 2b).

The lines appearing at δ 1.13 and 6.35 closely resemble those corresponding to the *t*-Bu and olefinic protons of *trans*-β-*tert*-butylstyrene (see the data given in the preceding discussion of the monomeric products), and this suggests that a fragment containing a phenyl ring and a *tert*-butyl group, both linked in trans configuration to the CH=CH group, forms a part of the IIH dimer.

The nmr spectrum of the IIIH fraction is shown in Figure 3. It seems again that a fragment of this hydrocarbon consists of a phenyl ring and a *tert*-butyl group attached in trans configuration to a C=C bond. The two degenerate protons resonate at δ 6.35, like those of the IIH hydrocarbon, but the third olefinic proton is different. It absorbs at δ 6.61, resembling thus its counterpart in the IH fraction (δ 6.57). The protons of the two distinct *tert*-butyl groups absorb at δ 1.18 and 1.14. The latter resonance again coincides with that assigned to the protons of one of the *tert*-butyl groups of the IIH hydrocarbon (δ 1.13), while the former coincides with its counterpart in the IH hydrocarbon (δ 1.18). Moreover, the aromatic multiplets of the IIIH and IH hydrocarbons seem to be similar.

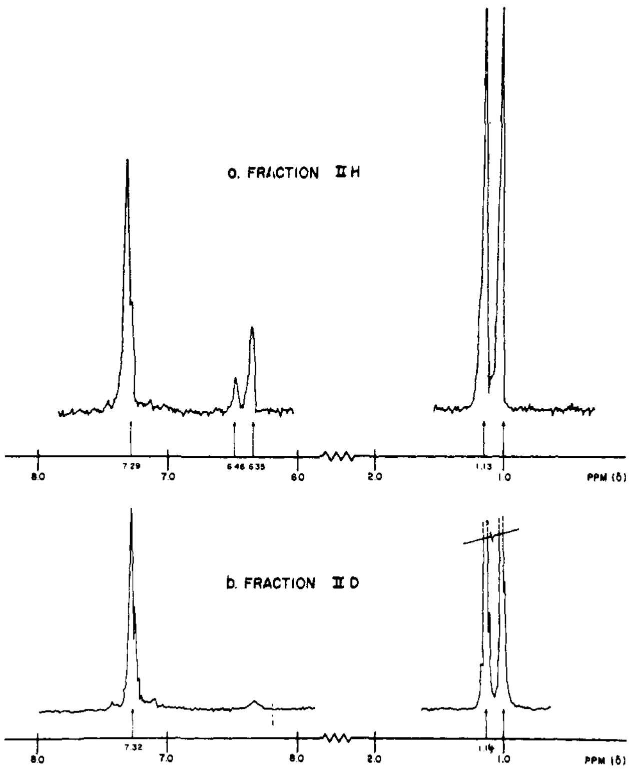


Figure 2. Nmr spectra of protonated and deuterated fraction II of the dimer.

Finally, the nmr spectrum of the IVH fraction, depicted in Figure 4, is unique in exhibiting *two identical tert*-butyl groups. Their protons resonate at δ 1.00 (18), like those of one of the *tert*-butyl groups of IH and IIH fractions. The characteristic AB pattern of the cis olefinic protons, seen in the spectra of the IH hydrocarbon and *cis*-β-*tert*-butylstyrene, is clearly discerned in the spectrum of IVH, *viz.*, δ 5.53, 5.73, 6.37, and 6.59 (compared with δ 5.52, 5.72, 6.38, and 6.57). Hence, a fragment of IVH, like IH, has the configuration of *cis*-β-*tert*-butylstyrene. However, the third olefinic proton, resonating at δ 6.48, is similar to its counterpart in the IIH fraction (δ 6.46). Also, the aromatic protons (δ 7.30 and 7.17, total of 9) resemble somewhat those of the IIH hydrocarbon (δ 7.29).

As in the previous fractions, the olefinic protons do not appear in the nmr spectra of the deuterated materials.

Mechanism of Dimerization

Two striking results of our studies call for explanation. (1) Some of the dimeric products of deuteration have mass 321, although the protonation always yields hydrocarbons of mass 318 corresponding to that of simple dimers having a C=C—C=C skeleton. (2) The nmr spectra of protonated dimers reveal the presence of three olefinic and nine aromatic protons, while the simple protonated dimers of BPA$\cdot^-$ radicals, *i.e.*, butadiene derivatives, have only two olefinic but ten aromatic protons.

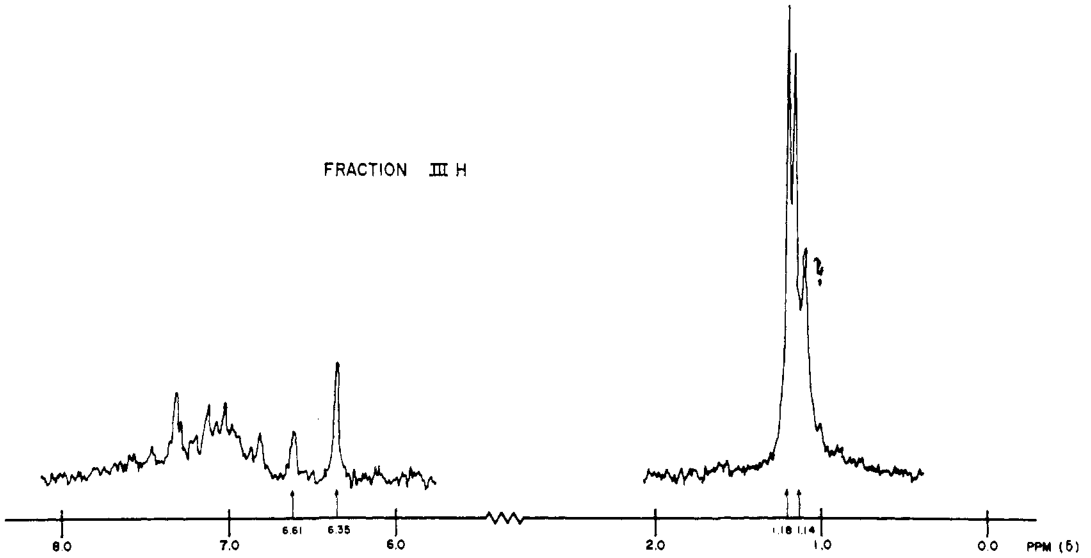
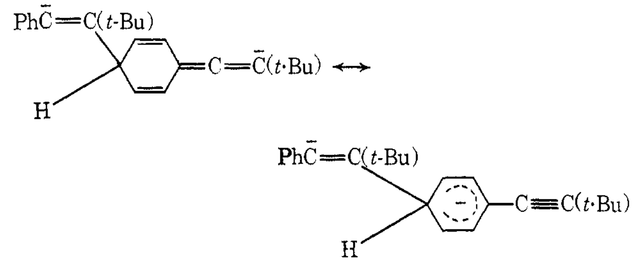


Figure 3. Nmr spectrum of protonated fraction III of the dimer.

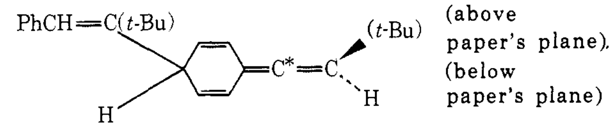
Apparently the steric hindrance caused by the bulkiness of the substituents impedes the simple mode of dimerization. Instead, one BPA·⁻ radical anion adds to the phenyl group of another, presumably in the para position. This yields a dianion such as



or its isomers with negative charge partially localized on the =C̄(t-Bu) end group. Such an addition resembles those observed in the triphenylmethyl system where the conventional dimerization is again impeded by the bulkiness of the substituents and consequently reactions on para positions of phenyl groups become eminent.[4]

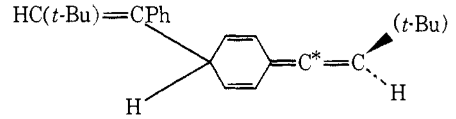
It is plausible to expect that as the BPA·⁻ radical ion adds to a phenyl group of another radical it acquires trans configuration in order to minimize steric strain. On protonation (or deuteration) of the terminal carbanions the resulting configuration becomes irreversibly established. (We assume that this carbanion, or rather its ion pair, maintains its configuration at low temperature.) However, since either end of the radical may participate in the bonding process, hydrocarbon I as well as I′ may be formed.

The formerly aromatic, odd hydrogen atom has to be lost in some subsequent reaction. Initially its relief as a proton is impeded by the negative charge of the dimer. However, when the protonation resulting from the addition of H_2O or D_2O destroys the negative charges, that proton becomes quite acidic. Its eventual transfer to some base, *e.g.*, OH^-, seems to take place simultaneously with the protonation, or deuteration, of the starred carbon atom; *i.e.*, it is a push-pull reaction which restores the aromaticity of the quinonoid ring.



I

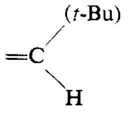
or



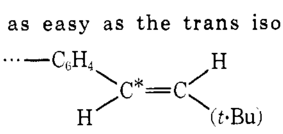
I′

Thus, a hydrocarbon of mass 318 is formed when H_2O was added to the system, but the addition of D_2O may yield a hydrocarbon of mass 321. The proposed mechanism accounts, therefore, for the mass spectroscopic observations and explains the presence of three olefinic and nine aromatic protons in the dimers.[5]

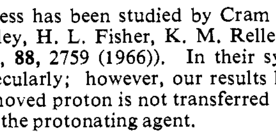
The plane of the



group attached to the starred carbon of the acidic hydrocarbon I or I′ is perpendicular to the plane of the quinonoid system. Probably this geometry is still retained in the transition state of the concerted reaction in which a proton adds to the starred carbon atom while the acidic H is removed. Hence, such an addition may occur as well from above the quinonoid plane as from below. This accounts then for another puzzling observation, namely, the cis isomer; *i.e.*



may be formed as easy as the trans isomer



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[4] (a) C. S. Marvel, W. I. Rieger, and M. B. Müller, *J. Amer. Chem. Soc.*, **61**, 2769 (1939); (b) C. S. Marvel, M. B. Müller, C. H. Himel, and J. Kaplan, *ibid.*, **61**, 2771 (1939).

[5] A similar process has been studied by Cram and his coworkers (D. J. Cram, F. Willey, H. L. Fisher, K. M. Relles, and D. A. Scott, *J. Amer. Chem. Soc.*, **88**, 2759 (1966)). In their system the proton is transferred intramolecularly; however, our results leave no doubt that in our system the removed proton is not transferred but exchanged for a proton arriving from the protonating agent.

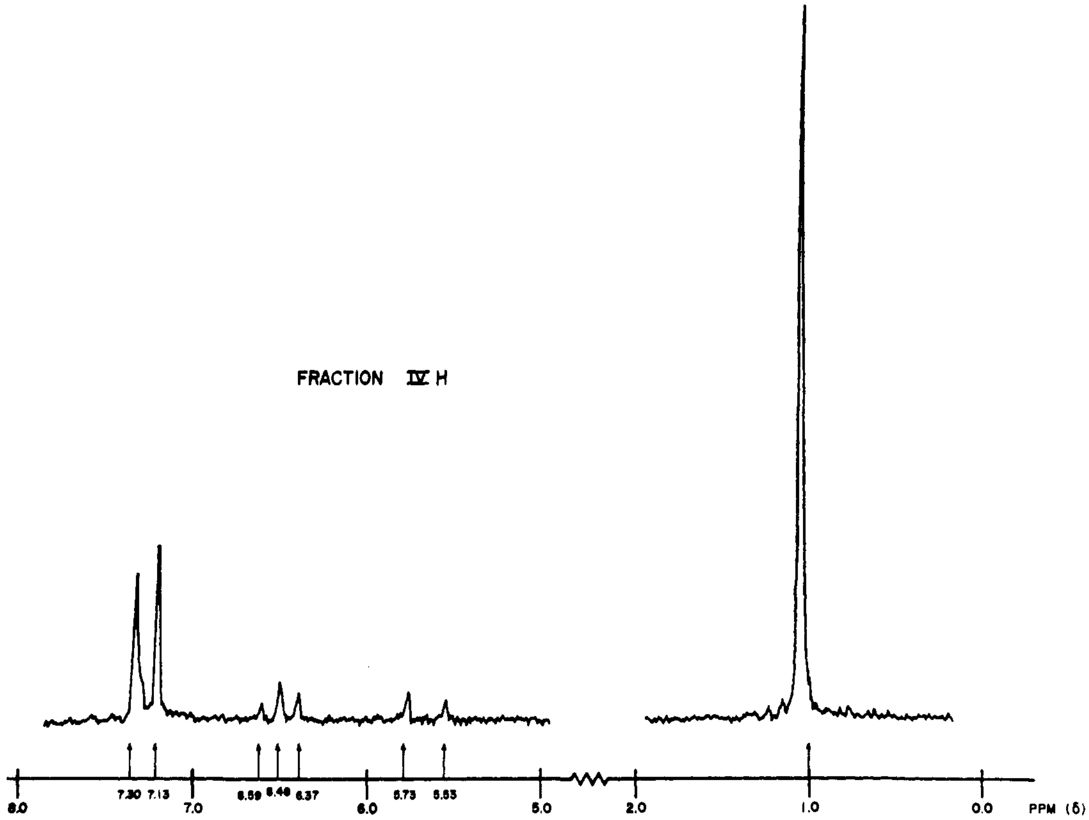
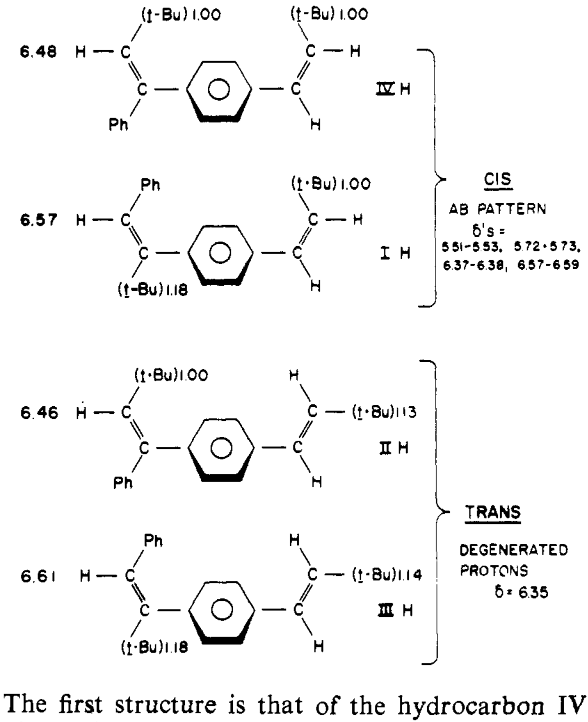


Figure 4. Nmr spectrum of protonated fraction IV of the dimer.

although the steric strain is much greater in the former than in the latter compound.

In conclusion, the following four dimers are formed in this dimerization.



The first structure is that of the hydrocarbon IVH. Both *tert*-butyl groups are identical and their protons resonate at δ 1.00, like the *tert*-butyl protons of *cis*-β-*tert*-butylstyrene (δ 0.98). Also the AB pattern of the *cis* olefinic protons, characteristic for *cis*-β-*tert*-butylstyrene, appears in the nmr spectrum of IVH. Hence, the absorbance at δ 6.48 has to be attributed to the third olefinic proton located on the left-side C=C double bond, the configuration around it being now uniquely determined as shown above.

The second structure is that of the hydrocarbon IH. The *cis* configuration of its right-side moiety is confirmed by the absorbance of the protons of one of the *tert*-butyl groups (δ 1.00) and by the AB pattern of its olefinic protons. The second *tert*-butyl group, protons of which resonate at δ 1.18, has to be located on the carbon atom adjacent to the central phenyl group, provided our assumed trans configuration of the added BPA$\cdot^-$ moiety is correct. This assumption gains support from the observed frequency of absorption of the third olefinic proton, δ 6.57. The proposed configuration around the left-side C=C bond resembles more that of *cis*-stilbene than *trans*-β-*tert*-butylstyrene,[6] and indeed the protons of *cis*-stilbene resonate at δ 6.57.

The third structure is that of the hydrocarbon IIH. The configuration around the left-side C=C bond is the same as in the first structure—protons of the *tert*-butyl group resonate again at δ 1.00 and the odd olefinic proton absorbs at δ 6.46 as compared with 6.48 observed in IVH. However, the configuration around the right-side C=C bond is clearly the same as in *trans*-β-*tert*-butylstyrene, two degenerate protons absorbing at δ 6.35 and the protons of the respective *tert*-butyl group at δ 1.13.

Finally, the last structure is that of the hydrocarbon IIIH. The *trans*-β-*tert*-butylstyrene configuration is obviously indicated by the absorbance at δ 1.14 and 6.35, and the identity of the structures around the left-

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[6] In *trans*-β-*tert*-butylstyrene the phenyl group and C=C bond are coplanar. This cannot be the case in the structure discussed above.

side C=C bond in IIIH and IH is demonstrated by the resonance of *tert*-butyl protons at δ 1.18 and by that of the odd olefinic proton. Its absorbance is slightly shifted downfield to δ 6.61 while that of its counterpart in IH and in *cis*-stilbene is at δ 6.57. This slight discrepancy is not considered to be serious.

The position of the resonance of the odd olefinic proton in the first and third structures calls for some comments. There is a claim[7] that such a proton, *i.e.*, =CH—(*tert*-Bu) should absorb at δ 5.52. This is true for *cis*-β-*tert*-butylstyrene where the phenyl group *cannot be* coplanar with the C=C bond, but not for the trans isomer, the relevant proton of which resonates at δ 6.35. Inspection of the models shows that in the first and third structures, as in *trans*-β-*tert*-butylstyrene, one of the phenyl groups may be coplanar with the C=C bond; hence, the proton in question should behave more like the olefinic proton of *trans*-β-*tert*-butylstyrene.

Additional Evidence for the Proposed Structures of the Dimers

Further evidence confirming the proposed structure of the dimers was obtained by investigating the products of their ozonolysis followed by reduction with triphenylphosphine.[8] The ozonolysis was performed with the dimer IH. Gas chromatographic separation of the products yielded pivalaldehyde $(CH_3)_3CCHO$, benzaldehyde, and a compound yielding molecular ion, *m/e* 190, conforming to the expected keto aldehyde, $(t\text{-Bu})\cdot CO\cdot C_6H_4\cdot CHO$. The identity of the latter is verified by the pattern of its mass spectrum. The most abundant were the ions *m/e* 133, 134, and 57. The latter corresponds to $(t\text{-Bu})^+$, while the former arise from the molecular ions through loss of the *t*-Bu group or isobutene, respectively. The ions $CHO\cdot C_6H_4\cdot CO^+$ (*m/e* 133) and $CHO\cdot C_6H_4CHO^+$ (*m/e* 134) easily lose CO yielding the ions $CHO\cdot C_6H_4^+$ (*m/e* 105) and $CHO\cdot C_6H_5^+$ (*m/e* 106), both equally abundant and clearly discerned in the spectrum. Finally, the anticipated ion $(t\text{-Bu})\cdot CO\cdot C_6H_4^+$ (*m/e* 161) is definitely observed, although its abundance is very low (~1%).

A linear dimer $(t\text{-Bu})\cdot CH{=}C(Ph){-}C(Ph){=}CH(t\text{-Bu})$ has been recently described and identified by Eisch and Amtmann.[7] However, neither benzaldehyde nor a compound of mass 190 could result from its ozonolysis. Its linear isomer, *viz.*, $(t\text{-Bu})\cdot CH{=}CH(Ph)\cdot CH(t\text{-Bu}){=}CH(Ph)$, not reported in the literature, could give the products of ozonolysis observed by us, *viz.*, $(CH_3)_3C\cdot CHO$, $Ph\cdot CHO$, and a diketone $(t\text{-Bu})\cdot CO\cdot CO\cdot Ph$ isomeric with the keto aldehyde $(t\text{-Bu})\cdot CO\cdot C_6H_4\cdot CHO$. But, the mass pattern of this diketone should be different from the observed one. The fragmentation of the α-diketones is reported to be simple[9]—resulting predominantly from fission of the -CO-CO- bond. Moreover, this α-diketone cannot yield an ion of *m/e* 161.

In conclusion, the structures of the dimers are well established and subsequently the proposed mechanism of dimerization of *tert*-butylphenylacetylene seems to be well justified.

Acknowledgment. The financial support of thes- studies by the National Science Foundation is gratefully acknowledged. We thank also Professor Milton Silverstein for his help in the ozonolysis experiments. The mass spectrometer was purchased through a special grant of the National Science Foundation.

Appendix

Although $BPA\cdot^-$ radical anions mainly dimerize at −70° (dimers represented 80–90% of all the products), protonation by solvent also takes place to some extent under those conditions. The protonation was limited to the formation of $Ph\bar{C}{=}CH(t\text{-Bu})$ carbanions and partially to its further protonation, since $PhCH{=}CH(t\text{-Bu})$ formed prior to the addition of D_2O amounted to about 30% of $PhCD{=}CH(t\text{-Bu})$.

The situation is basically different at ambient temperature. Reduction performed at room temperature, under conditions otherwise identical with those described earlier, led to $PhCH_2CH_2(t\text{-Bu})$ as the main reaction product. The reduced solution was divided again into two portions, one being treated with H_2O, the other with D_2O. Gas chromatography of the products led to 12 fractions, the first accounting for about 85% of all the material, while the minor products, collected in the remaining 11 fractions, were all of comparable abundance.

Mass and nmr spectroscopy proved that the first fraction consisted of $PhCH_2CH_2(t\text{-Bu})$ when the products quenched by H_2O were fractioned. However, the products quenched by D_2O resulted in $PhCHD\cdot CH_2(t\text{-Bu})$. Hence, at room temperature the protonation by solvent followed by the electron transfer leads to a series of reactions such, *e.g.*, as

$$BPA\cdot^- \longrightarrow BPA^{2-} \longrightarrow Ph\bar{C}{=}CH(t\text{-Bu}) \longrightarrow PhCH{=}CH(t\text{-Bu})$$

$$PhCH{=}CH(t\text{-Bu}) + e^- \longrightarrow [PhCH{=}CH(t\text{-Bu})]\cdot^-, \text{etc.} \longrightarrow Ph\bar{C}H\cdot CH_2(t\text{-Bu})$$

The last carbanion *is not* protonated by THF, even at room temperature, and yields the observed products when reacted with H_2O or D_2O.

The third fraction consisted of β-*tert*-butylstyrene which contained only about 15% of $PhCHD{=}CH(t\text{-Bu})$ when D_2O was used as a quencher. Hence, $Ph\bar{C}{=}CH(t\text{-Bu})$ is protonated by THF when formed at ambient temperature. We may recall that a brief contact of BPA solution with potassium at room temperature yields *tert*-butylstyrene radical anion which was identified by its esr spectrum.[1] Such radical anion rapidly disappears at room temperature but its solution is stable at −60°. This observation corroborates with our findings.

Reduction by potassium of the independently prepared *tert*-butylstyrene[3] performed at room temperature led to the formation of the ethane derivative, $PhCH_2CH_2(t\text{-Bu})$. No dimers were found, suggesting that dimerization of the styrene radical ions is negligible.

In conclusion, it is found that the protonations are greatly retarded at lower temperatures, making the dimerization a predominant reaction at −70°. However, at ambient temperatures the protonation proceeds much faster than dimerization and becomes the major reaction in our system.

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(7) J. Eisch and R. Amtmann, *J. Org. Chem.*, 37, 3410 (1972).
(8) M. Beroza, *Accounts Chem. Res.*, 3, 36 (1970).
(9) W. Reusch and C. Djerassi, *Tetrahedron*, 2893 (1967).