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# Hydrogenation Reactions of Some Spool-Shaped Acetylenes[1]

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The spool-shaped acetylenes bis(*p*-isopropylphenyl)acetylene (**1a**) and bis(*p*-*tert*-butylphenyl)acetylene (**1b**) have been synthesized and rigorously characterized. Their hydrogenation reactions have been studied. These acetylenes add hydrogen smoothly in solution, but at low pressures they do not add hydrogen on the metallic catalysts platinum, palladium, and nickel. This anomaly is explained in terms of the postulate that the isopropyl and tertiary butyl groups prevent the $C\equiv C$ group from resting flatly upon the catalyst. The simple structure of these molecules provides a crude estimate of the minimum critical distance of approach of the unsaturated moiety of the molecule to the surface of the metallic catalyst for effective hydrogenation.

In the homologous series of bis(*p*-alkylphenyl)acetylenes (**1**) the addition of hydrogen on a metallic catalyst occurs efficiently for these acetylenes, including the parent compound, diphenylacetylene,[2,3] and its dimethyl[4,5] and diethyl homologues.[6] The diisopropyl and di-*tert*-butyl homologues do not add hydrogen at pressures up to 3 atm and temperatures up to 60 °C. However, all of these acetylenes add hydrogen readily with active metal and acid in solution.[2–5,7] It is immediately apparent that the bulkiness of the freely rotating isopropyl and tertiary butyl groups might serve sterically to retard this catalytic hydrogenation by "lifting" the acetylenic moiety of the molecule up off the surface of the metallic catalyst to a distance which is greater than the required critical distance of approach that is necessary for effective hydrogenation. This paper reports a crude approximation of the magnitude of that distance.

This interpretation of the results here outlined can be valid only if these diisopropyl and di-*tert*-butyl homologues are indeed rigidly linear molecules. Furthermore, a claim that any acetylenes, which are otherwise so well-known to be quite reactive toward hydrogenation, indeed do not react under conditions here reported imposes the necessity for rigorous characterization.

The chemical evidence for the structural integrity of bis(*p*-isopropylphenyl)acetylene (**1a**) and bis(*p*-*tert*-butylphenyl)acetylene (**1b**) here presented is the syntheses of each of these species by several methods to produce the same compound. The hydration of these acetylenes to produce the corresponding ketones involves a mechanistic process which can hardly be sterically hindered by the bulky but remote alkyl groups. Such hydration attended by enol-to-ketone rearrangement is characteristic of acetylenes and is thus presented here as further chemical evidence for structural integrity. The physical evidence here presented is their NMR, IR, and Raman spectra.

## Syntheses and Structure Proofs

Scheme I outlines those methods which were used exclusively to synthesize bis(*p*-*tert*-butylphenyl)acetylene (**1b**). Schemes II and III outline the methods used to synthesize both bis(*p*-isopropylphenyl)acetylene (**1a**) and bis(*p*-*tert*-butylphenyl)acetylene (**1b**). Both of these acetylenes have been converted by hydration in the presence of $HgSO_4$ to their corresponding deoxybenzoins (**15**). These deoxybenzoins have also been synthesized from the corresponding benzoins (**10**). Because of the serious question regarding the possibility of poisoning the catalysts by traces of HgO and/or Hg unremoved from the acetylenes, care has been taken to use for these attempted catalytic reductions samples of acetylenes which were prepared by methods which did and did not involve the use of HgO. Synthesis of these acetylenes by the oxidative denitrification of the precursor dihydrazones **12** (Scheme II) with HgO was included as a part of the chemical evidence for proof of structure.

The absence of the band representing the $C\equiv C$ stretching frequency at 2200 cm$^{-1}$ in the infrared spectra of these two acetylenes and the appearance of a very intense polarized band at 2200 cm$^{-1}$ in their Raman spectra comprise significant evidence that the stretching mode of this bond in bis(*p*-isopropylphenyl)acetylene (**1a**) and in bis(*p*-*tert*-butylphenyl)acetylene (**1b**) is centrosymmetric.[8] This evidence and the chemical evidence for the nature of the bonding in these acetylenes strongly support the claim that these are linear molecules. If there is free rotation about the phenyl–alkanyl carbon bonds in their para positions these molecules are "spool shaped".

The structures of both **1a** and **1b** very probably belong to either the $C_{2h}$ or $C_{2v}$ point group, but the absence of the 2200-cm$^{-1}$ band in their infrared spectra and its presence in the Raman spectra of these acetylenes do not comprise absolute proof of the existence of a center of symmetry in these molecules in the crystalline state. The IR, Raman, and $^1$H NMR spectral data are presented in Table I. The complete vibrational analysis as well as $^{13}$C NMR analysis is under investigation[9] and will be reported later.

## Results and Discussion

Bis(*p*-isopropylphenyl)acetylene (**1a**) and bis(*p*-*tert*-butylphenyl)acetylene (**1b**) are reduced smoothly by dissolving active metals. They do not add hydrogen at low pressure (1–3 atm) on platinum, palladium, and nickel catalysts. This unusual lack of reactivity toward catalytic addition of hydrogen by an acetylene is here interpreted in the light of the steric inhibition of "proper" surface contact between the metallic catalyst and the acetylenic

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(1) Publication No. 117 from the Atlanta University Center Science Research Institute.

(2) E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948).

(3) B. S. Rabinovitch and F. S. Looney, *J. Am. Chem. Soc.*, **75**, 2652 (1953).

(4) M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1608 (1959).

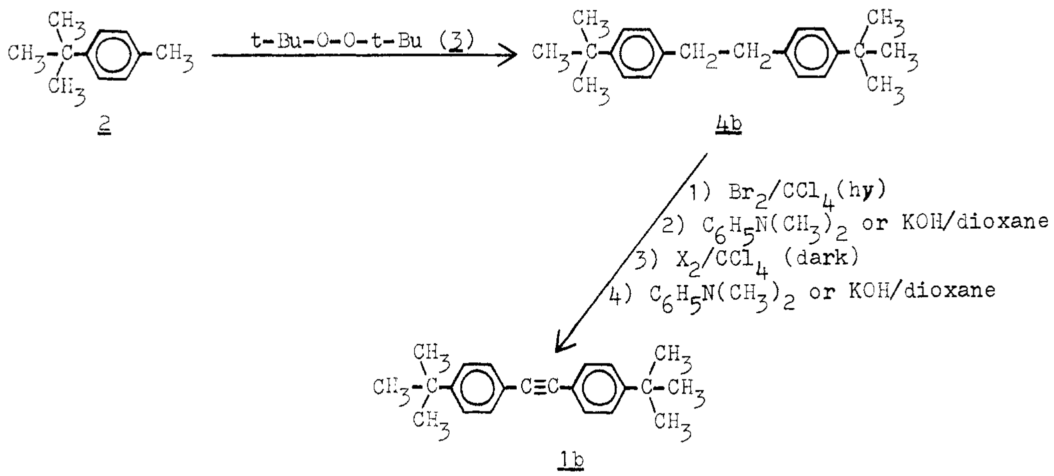
(5) H. Kunimoto, *Nippon Kagaku Zasshi*, **84**, 65 (1963).

(6) See the Experimental Section "Dehydrobromination of 21".

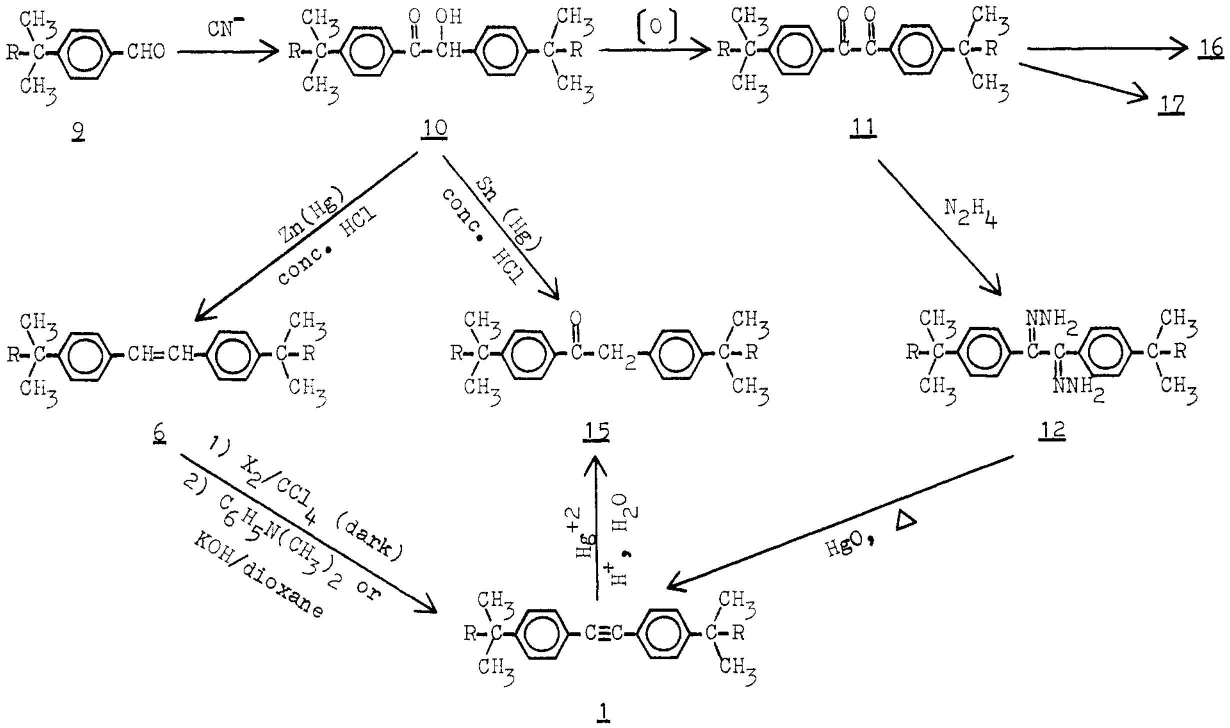
(7) G. H. Coleman, W. H. Holst, and R. D. Maxwell, *J. Am. Chem. Soc.*, **58**, 2310 (1936).

0022-3263/81/1946-4695$01.25/0

Scheme I. Synthesis of Bis(*p*-*tert*-butylphenyl)acetylene (1b)



Scheme II. Synthesis of Bis(*p*-isopropylphenyl)acetylene (1a) and Bis(*p*-*tert*-butylphenyl)acetylene (1b)[a]



[a] a, R = H; b, R = $CH_3$.

π system of the would-be hydrogen acceptor. That these molecules are both linear and symmetrical about the acetylenic bond is evident from spectroscopic studies.[8] The characteristic C≡C stretching frequency is absent in the infrared spectra and is pronouncedly present in the Raman spectra of both **1a** and **1b**. The chemical evidence presented here rigorously supports the indicated structures. Measurements made on a scale model indicate that the carbon nuclei of the upheld acetylenic group are 1.125 Å from the surface of the catalyst. The interpretation here presented suggests that for effective catalytic hydrogenation on metal surfaces unsaturated bonds must be structurally unencumbered to the extent that their critical atoms, the sp carbons of the acetylenes and presumably the $sp^2$ carbons of alkenes, may lie *closer than* 1.125 Å from the surface of the metallic catalyst. How much closer one cannot say at present, but these results seem to establish an upper limit.

Similar results have been reported by other workers, and a recent review of this general phenomenon is given by Freifelder.[10a] Over metallic catalyst 4,4,7,7-tetramethylocta-2,5-diyne, $(CH_3)_3CC{\equiv}CC(CH_3)_2C{\equiv}CCH_3$, adds hydrogen selectively at the less hindered acetylenic group, and the resulting double bond is also selectively reduced.[10b] Note, however, that di-*tert*-butylacetylene adds hydrogen over Raney nickel at 40 lbs/sq in.[10c] It is difficult to rationalize this last fact except to assert that in the case of the disubstituted tolans here reported the phenyl groups may also be a factor contributing to the anomaly. Indeed, phenyl groups are electron sinks, and this effect combined with the positive inductive effects of the methyl groups may account for the difference. The $^{13}C$ NMR studies[9]

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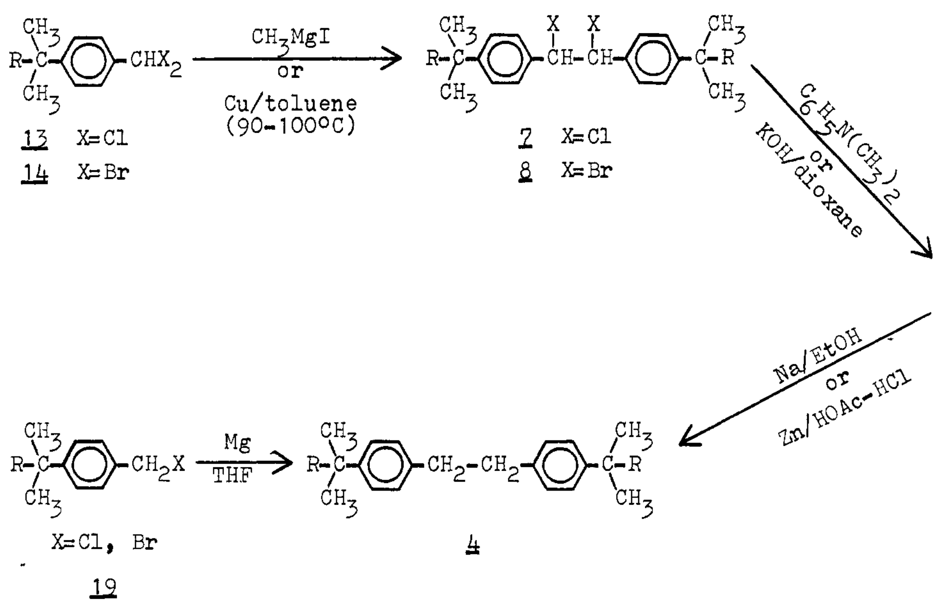
(8) See the mutual exclusion rule: E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955, p 246; E. Herzberg, "Infrared and Raman Spectra", Van Nostrand, Princeton, NJ, 1966, p 256; G. W. King, "Spectroscopy and Molecular Structure", Holt, Rinehart, and Winston, Inc., New York, 1964, p 366.

(9) J. Perkins, R. Sullivan, G. Y. Han, and H. C. McBay, unpublished data.

Scheme III. Syntheses of Bis(*p*-alkylphenyl)acetylenes 1a,b[a]



[a] a, R = H; b, R = $CH_3$.

Table I. Selected Spectral Data of Hydrocarbons, Benzoins, Benzils, and Deoxybenzoins

| compd | IR, $cm^{-1}$ (assignment) | Raman, $cm^{-1}$ (assignment) | $^1H$ NMR, $\delta$ (assignment) |
|---|---|---|---|
| 1a | 2995-3120 (Ar CH), 2830-2940 (CH), 1620-1660 (C=C) | 3036-3069 (Ar CH), 2863-2965 (CH), 2200-2216 (C≡C), 1599-1604 (C=C), 1493-1498 (C—C) | 1.24 [d, $C(CH_3)_2$, 12 H, $J$ = 7 Hz], 2.89 (m, CH, 2 H, $J$ = 7 Hz), 7.02-7.61 (Ar, 8 H) |
| 1b | 2950-3120 (Ar CH), 2880-2930 (CH), 1570-1615 (C=C) | 3020-3064 (Ar CH), 2863-2965 (CH), 2218 (C≡C), 1600-1604 (C=C), 1493-1506 (C—C) | 1.31 [s, $C(CH_3)_3$, 18 H], 7.25-7.44 (Ar, 8 H) |
| 4a | 2980-3115 (Ar CH), 2860-2960 (CH), 1570-1620 (C=C) | | 1.28 [d, $C(CH_3)_2$, 12 H, $J$ = 7 Hz], 2.88 (m, CH, 2 H, $J$ = 7 Hz), 2.90 (s, $CH_2$, 4 H), 7.24 (s, Ar, 8 H) |
| 4b | 2950-3180 (Ar CH), 2860-2930 (CH), 1505-1565 (C=C) | | 1.32 [s, $C(CH_3)_3$, 18 H], 2.95 (s, $CH_2$, 4 H), 7.12-7.53 (Ar, 8 H) |
| 6a | 2975-3100 (Ar CH), 2880-2945 (CH), 1560-1610 (C=C) | | 1.27 [d, $C(CH_3)_2$, 12 H, $J$ = 7 Hz], 2.93 (m, CH, 2 H, $J$ = 7 Hz), 7.07 (s, CH=, 2 H), 7.11-7.63 (Ar, 8 H) |
| 6b | 2950-3120 (Ar CH), 2860-2945 (CH), 1570-1620 (C=C) | | 1.28 [s, $C(CH_3)_3$, 18 H], 6.80 (s, CH=, 2 H), 7.13 (s, Ar, 8 H) |
| 10a | 3020-3100 (Ar CH), 2865-2985 (CH), 1580-1620 (C=C), 3425 (OH), 1675 (C=O) | | 1.04-1.41 [dd, $C(CH_3)_2$, 12 H, $J$ = 7 Hz], 2.52-3.19 (m, CH, 2 H, $J$ = 7 Hz), 4.59 (OH), 5.96 (s, CH-O, 1 H), 7.01-8.21 (m, Ar, 8 H) |
| 10b | 3540 (OH), 1665 (C=O), 2950-3120 (Ar CH), 2880-2940 (CH), 1570-1615 (C=C) | | 1.29 [s, $C(CH_3)_3$, 18 H], 4.51 (s, OH), 5.94 (s, CH-O, 1 H), 7.28-8.10 (Ar, 8 H) |
| 11a | 3050-3100 (Ar CH), 2860-2980 (CH), 1668 (C=O), 1663 (C=O), 1578-1600 (C=C) | | 1.30 [d, $C(CH_3)_2$, 12 H, $J$ = 7 Hz], 2.92 (m, CH, 2 H, $J$ = Hz), 6.86-8.29 (Ar, 8 H) |
| 11b | 2960-3120 (Ar CH), 2860-2960 (CH), 1680 (C=O), 1565-1615 (C=C) | | 1.30 [s, $C(CH_3)_3$, 18 H], 7.38-8.02 (Ar, 8 H) |
| 15a | 3000-3120 (Ar CH), 2870-2950 (CH), 1680 (C=O), 1520-1620 (C=C) | | 1.13 [d, $C(CH_3)_2$, 12 H, $J$ = 7 Hz], 2.80 (m, CH, 2 H, $J$ = 7 Hz), 4.13 (s, $CH_2$, 2 H), 7.02-8.06 (Ar, 8 H) |
| 15b | 2960-3080 (Ar CH), 2860-2940 (CH), 1680 (C=O), 1560-1600 (C=C) | | 1.32 [s, $C(CH_3)_3$, 9 H], 1.38 [s, $C(CH_3)_3$, 9 H], 4.28 (s, $CH_2$, 2 H), 7.28-7.65 (Ar, 8 H) |

now in progress may provide a basis for better understanding.

If the interpretation of this phenomenon in terms of the simple steric requirement is valid, then it must follow that *tert*-butyl groups should be at least as effective as isopropyl groups, if not more so, at this steric retardation and hence at prohibiting the catalytic reduction. This test has been performed on the homologous bis(*p*-*tert*-butylphenyl)acetylene (**1b**), and the results are the same as with the isopropyl derivative. Furthermore, the unsubstituted diphenylacetylene,[2,3] bis(*p*-methylphenyl)acetylene,[4,5] and bis(*p*-ethylphenyl)acetylene (**20**)[6] do add hydrogen under these conditions on metallic catalysts. Although we have

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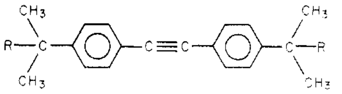
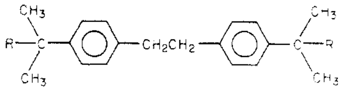
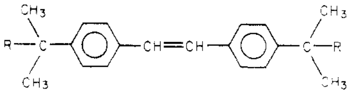
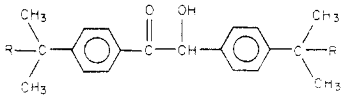
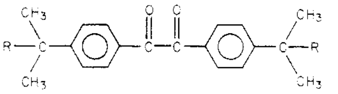
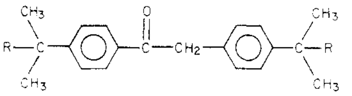
(10) (a) M. Freifelder, "Practical Catalytic Hydrogenation", Wiley-Interscience, New York, 1971, p 112; (b) A. I. Zakharova and G. D. Il'ina, *Zh. Obshch. Khim.*, **34**, 1389 (1964); (c) G. F. Hennion and T. F. Babigan, Jr., *J. Am. Chem. Soc.*, **68**, 1202 (1946).

Table II. Substituted Hydrocarbons, Benzoins, Deoxybenzoins, and Benzils[a]

| structure | compd[b] | mp, °C (solvent, appearance) | formula |
|---|---|---|---|
|  | 1a | 125-126 (EtOH, colorless plates) | $C_{20}H_{22}$ |
| | 1b | 177-178 (EtOH, colorless plates) | $C_{22}H_{26}$ |
|  | 4a | 56-58[12,13] (EtOH, colorless plates) | $C_{20}H_{26}$ |
| | 4b | 151-152[14-17] (EtOH, colorless flakes) | $C_{22}H_{30}$ |
|  | 6a | 129-130[18,19] (hexane, colorless plates) | $C_{20}H_{24}$ |
| | 6b | 179-180 (hexane, colorless plates) | $C_{22}H_{28}$ |
|  | 10a | 99-101[20] (EtOH, colorless crystals) | $C_{20}H_{24}O_2$ |
| | 10b | 156-158[21] (EtOH, colorless crystals) | $C_{22}H_{28}O_2$ |
|  | 11a | 78-79[22] (hexane, yellow crystals) | $C_{20}H_{22}O_2$ |
| | 11b | 101-102[21] (hexane, yellow crystals) | $C_{22}H_{26}O_2$ |
|  | 15a | 46-48 (MeOH, colorless needles) | $C_{20}H_{24}O$ |
| | 15b | 99-100 (hexane, colorless needles) | $C_{22}H_{28}O$ |

[a] Satisfactory combustion analytical data for C and H (±0.3%) have been provided for these compounds. [b] a, R = H; b, R = $CH_3$.

no rate constants for these hydrogenations, it was observed that the diethyl homologue adds hydrogen catalytically at a rate which is significantly slower than the former two acetylenes under similar conditions.

## Experimental Section

All melting points and boiling points are uncorrected. NMR spectra were recorded in $CDCl_3$ or neat on a Varian Model A-60A or EM-360 spectrometer. Chemical shifts ($\delta$) refers to parts per million downfield from $Me_4Si$ as an internal reference. IR spectra were measured on a Perkin-Elmer Model 137 or Beckman Model IR 9 spectrometer, while Raman spectra were measured on a Spex Ramalog-5 spectrometer. Excitation was provided by a coherent-radiation CR-3 argon-ion laser using 5145-Å radiation. All solvents used were spectral grade and were anhydrous or purified and dried prior to use. The irradiations used in bromination were all carried out with a 300-W sunlamp at 2 in. from the reaction flask. All the compounds prepared from different methods were identified by direct comparison of their NMR, IR, and melting and boiling point data. Elemental analyses and molecular weight determinations were performed by Clark Microanalytical Laboratory or by Galbraith Laboratories, Inc. A Parr hydrogenator at a 45 psi pressure was used for catalytic hydrogenation. Except for 1,2-dichloro-1,2-bis(*p*-isopropylphenyl)ethane (**7a**), 1,2-dibromo-1,2-bis(*p*-*tert*-butylphenyl)ethane (**8b**), 4-*tert*-butylbenzaldehyde (**9b**), 4-*tert*-butylbenzal chloride (**13b**), 4-*tert*-butylbenzal bromide (**14b**), bis(*p*-ethylphenyl)acetylene (**20**), 1,2-dibromo-1,2-bis(*p*-ethylphenyl)ethane (**21**), and *p,p'*-diethylstilbene (**22**), the spectral data of the compounds prepared are summarized in Table I and their melting points are presented in Table II. Quinoxalines of **11**, bis(2,4-dinitrophenylhydrazones) of **11**, and 2,4-dinitrophenylhydrazones of **15** were prepared in the standard manners,[11] and the data are summarized in Table III.

**1,2-Bis(*p*-*tert*-butylphenyl)ethane (4b).** A liquid sample of 400 g (2.70 mol) of 4-*tert*-butyltoluene (**2**) was heated to 145 °C in an oil bath. To this hot liquid was added dropwise beneath its surface[23] a solution of 50 g (0.34 mol) of di-*tert*-butyl peroxide (**3**) in 100 g (0.68 mol) of 4-*tert*-butyltoluene (**2**). After all the peroxide was added, the temperature of the resulting solution was raised to 155–180 °C and remained at this range for 4 h. At this point, the evolution of methane, one of the products, had subsided. After the volatile products, acetone and *tert*-butyl alcohol, had been removed, the reaction mixture was then distilled under reduced pressure. After the mixture cooled, 79.4 g (80%) of **4b** was obtained. Recrystallization from 95% ethanol gave colorless plates melting at 150–151 °C.[14-17] Compound **4b** was also obtained in high yield from the noncatalytic reduction of the corresponding acetylene (**1b**) and the reduction (catalytic and noncatalytic) of the substituted stilbene **6b**. The melting points of the mixtures of the products from the different methods showed no depressions.

**1,2-Bis(*p*-alkylphenyl)ethane (4) through Grignard Reaction.**[12,14] Compounds **4** were obtained in 50–75% yield from 0.24 mol of 4-alkylbenzyl halides (**19**), 0.12 mol of magnesium turnings, and 3 drops of methyl iodide in 300 mL of THF. Compounds **4** were also obtained from the reduction of either the corresponding acetylenes (**1**) or stilbenes (**6**) in high yield (see Table II for physical constants).

***p,p'*-Di-*tert*-butylstilbene (6b).** 1-Bromo-1,2-bis(*p*-*tert*-butylphenyl)ethane (**5**) obtained from monobromination under irradiation at room temperature of 30 g (0.102 mol) of 1,2-bis(*p*-*tert*-butylphenyl)ethane (**4b**) was dissolved in 1000 mL of *N,N*-dimethylaniline and refluxed for 24 h (or refluxed 4 h with 6.6 g of KOH in 1000 mL of dioxane). The yield was 60–70%.

***p,p'*-Dialkylstilbene (6) through Reduction of the Corresponding Benzoins (10).**[24] Compounds **6** were obtained in 40–45% yields from 3 mmol of **10**, zinc amalgam (from 1.3 g of zinc dust, 0.4 g of $HgCl_2$, and 4 mL of water), and 4 mL of concentrated HCl in 40 mL of 95% ethanol for 6 h at 0–5 °C. When the reaction mixture was held at room temperature overnight before being worked up, compounds **4** were obtained in 60–65% yields (see Table II for physical constants). Compounds **6** were also obtained from the corresponding alkylbenzene and chloroacetaldehyde diethyl acetyl by following the procedure reported by Sieber.[19]

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[11] L. F. Fieser and K. L. Williamson, "Organic Experiments", 3rd ed., D. C. Heath Co., Boston, MA, 1975, pp 133, 265.

[12] T. Nakajma, *Yakugaku Zashi*, **82**, 1278 (1962).

[13] E. C. Leonard, Jr., *J. Org. Chem.*, **27**, 1921 (1962).

[14] J. H. Gardner and P. Borgstrom, *J. Am. Chem. Soc.*, **51**, 3375 (1929).

[15] R. L. Huang and O. K. Yeo, *J. Chem. Soc.*, 3190 (1959).

[16] D. Bellus and K. Schaffner, *Helv. Chim. Acta*, **52**, 1010 (1969).

[17] M. Tashiro, T. Yamato, and G. Fukata, *J. Org. Chem.*, **43**, 1413 (1978).

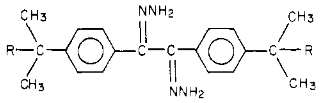
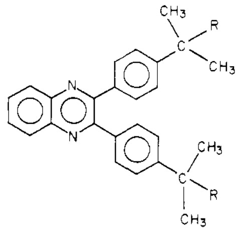
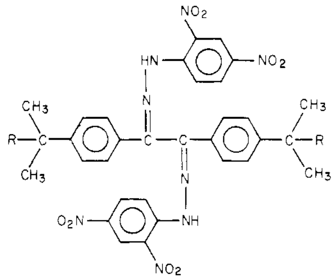
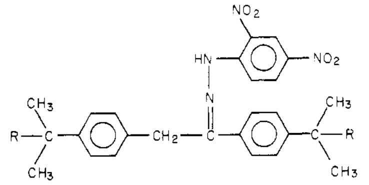
[18] I. I. Lapkin and G. Ya. Zinnatullina, *Zh. Obshch. Khim.*, **39**, 1132 (1969).

[19] R. H. Sieber, *Justus Liebigs Ann. Chem.*, **730**, 31 (1969).

[20] O. Widman, *Ber.*, **14**, 609 (1881).

[21] H. Kwart and M. M. Baevsky, *J. Am. Chem. Soc.*, **80**, 580 (1958).

Table III. Hydrazones, Quinoxalines, and 2,4-Dinitrophenylhydrazones[a]

| structure | compd[b] | mp, °C (solvent, appearance) | formula |
|---|---|---|---|
|  | **12a** | 190 dec (*i*-PrOH, colorless crystals) | $C_{20}H_{26}N_4$ |
| | **12b** | 220 dec (toluene, colorless crystals) | $C_{22}H_{30}N_4$ |
|  | **16a** | 160-161 (EtOH, yellow crystals) | $C_{26}H_{26}N_2$ |
| | **16b** | 208-210 (*i*-PrOH, yellow crystals) | $C_{28}H_{30}N_2$ |
|  | **17a** | 234-235 (EtOH, orange crystals) | $C_{32}H_{30}N_8O_8$ |
| | **17b** | 300 (EtOAc-MeOH, orange needles) | $C_{34}H_{34}N_8O_8$ |
|  | **18a** | 168-169 (EtOH, orange crystals) | $C_{26}H_{28}N_4O_4$ |
| | **18b** | 194-195 (EtOAc-MeOH, red orange crystals) | $C_{28}H_{32}N_4O_4$ |

[a] Satisfactory analytical data for C, H, and N (±0.3%) have been provided for these compounds. [b] **a**, R = H; **b**, R = $CH_3$.

**4-*tert*-Butylbenzal Bromide (14b).** Compound **14b**, lachrymatory needles from pentane melting at 41–42 °C [bp 208–211 °C (4 mm)], was obtained in 78% yield from 0.13 mol of 4-*tert*-butyltoluene (**2**) and 0.26 mol of bromine under irradiation: NMR δ 0.96 [s, $C(CH_3)_3$, 9 H], 6.45 (s, $CHBr_2$, 1 H), 7.11–7.24 (d, Ar protons, 4 H). Anal. Calcd for $C_{11}H_{14}Br_2$: C, 43.14; H, 4.58; Br, 52.29. Found: C, 43.24; H, 4.55; Br, 52.18.

**4-*tert*-Butylbenzaldehyde (9b).** Compound **9b** was prepared from 4-*tert*-butylbenzal bromide (**14b**) by following the procedure of Coleman and Honeywell:[25] yield 60–70%; bp 128–129 °C (3.5 mm);[26] NMR δ 0.96 [s, $C(CH_3)_3$, 9 H], 6.88–7.40 (dd, Ar protons, 4 H), 9.12 (s, CHO, 1 H).

**4-*tert*-Butylbenzal Chloride (13b).** To a stirred solution of 31.2 g (0.193 mol) of 4-*tert*-butylbenzaldehyde (**9b**) in 500 mL of ligroin (bp 94 °C) was added slowly a slurry of 80 g (0.385 mol) of $PCl_5$ in 250 mL of ligroin. The mixture was stirred at room temperature for 24 h. After removal of solvent, the residue was distilled to give **13b**: bp 145–146 °C (3 mm); yield 80–90%; NMR δ 0.93 [s, $C(CH_3)_3$, 9 H], 6.44 (s, $CHCl_2$, 1 H), 7.13–7.30 (d, Ar protons, 4 H). Anal. Calcd for $C_{11}H_{14}Cl_2$: Cl, 32.72. Found: Cl, 32.80.

**4,4′-Dialkylbenzoins (10),**[11,27] **4,4′-dialkylbenzils (11),**[11] **and 4,4′-dialkylbenzil dihydrazones (12)**[28] were prepared by following the standard methods (see Tables II and III for physical constants).

**1,2-Dihalo-1,2-bis(*p*-alkylphenyl)ethanes (7 or 8). Method A. Halogenation of *p*,*p*′-Dialkylstilbene (6).** Dihalide **7** or **8** was obtained in 90–95% from 28.4 mmol of **6** and 28.4 mmol of halogen in $CCl_4$ under cold, dark conditions. Compound **8b**, 1,2-dibromo-1,2-bis(*p*-*tert*-butylphenyl)ethane, was obtained in quantitative yield: mp 222–223.5 °C dec (heptane); NMR δ 1.28 [s, $C(CH_3)_3$, 18 H], 5.52 (s, CHBr, 2 H), 7.42 (Ar protons, 8 H). Anal. Calcd for $C_{20}H_{24}Br_2$: Br, 35.40. Found: Br, 35.57.

**Method B. Grignard Reaction.**[29] Dihalide **7** or **8** was obtained in 20–30% yield from 20.9 mmol of magnesium turnings, 20.9 mmol of methyl iodide, and 14.8 mmol of 4-alkylbenzal halide **13** or **14** in ether. Compound **7a**, 1,2-dichloro-1,2-bis(*p*-isopropylphenyl)ethane, was thus obtained in 25% yield and melted at 188–189 °C (95% EtOH). Anal. Calcd for $C_{20}H_{24}Cl_2$: Cl, 21.19. Found: Cl, 21.16.

**Method C. Coupling Reaction.**[30] A mixture of 16.3 mmol of copper powder, 16.3 mmol of 4-alkylbenzal halide **13** or **14**, and 100 mL of toluene was heated at 95–100 °C for 24 h. The critical nature of the temperature control is here important. At 5 °C below this range one gets no reaction. At 5 °C above this range one obtains only gunks. The yield was 40–50%. Compound **7b**, 1,2-dichloro-1,2-bis(*p*-*tert*-butylphenyl)ethane, was obtained in 45% yield and melted at 228 °C (95% EtOH) with decomposition. Anal. Calcd for $C_{22}H_{28}Cl_2$: Cl, 19.56. Found: Cl, 19.80.

**Bis(*p*-isopropylphenyl)acetylene (1a) and Bis(*p*-*tert*-butylphenyl)acetylene (1b). Method A. Oxidative Denitrification.**[28] Compounds **1** were obtained in 80–90% yields from a mixture of 5.7 mmol of 4,4′-dialkylbenzil dihydrazone (**12**) and 3.5 g of mercuric oxide in 150 mL of *m*-xylene under refluxing (see Table II for physical constants).

**Method B. Dehydrohalogenation of Dihalide 7 or 8.** A solution of 26.5 mmol of compound **7** or **8** in 200 mL of *N*,*N*-

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dimethylaniline (or refluxed with 3.7 g of KOH in 500 mL of dioxane) was refluxed for 24 h. The yield was 85–90%.

**1,2-Dibromo-1,2-bis(*p*-ethylphenyl)ethane (21).** Compound **21** was prepared in the standard manner by using *p,p'*-diethylstilbene (**22**)[19] and Br$_2$ in CCl$_4$ under cold, dark conditions. The yield was quantitative. The needles thus obtained melted at 175.5–177 °C dec (EtOH): NMR $\delta$ 1.26 (t, CH$_3$, 6 H, $J$ = 7 Hz), 2.72 (q, CH$_2$, 4 H, $J$ = 7 Hz), 7.40 (Ar protons, 8 H). Anal. Calcd for C$_{18}$H$_{20}$Br$_2$: Br, 40.40. Found: Br, 40.22.

**Dehydrobromination of 21.** A mixture of 1.68 g (4.24 mmol) of **21** and 50 mL of 43% KOH in 95% ethanol was stirred and refluxed for 24 h. After the mixture was worked up, the crude product was recrystallized from methanol to give colorless crystals of 1,2-bis(*p*-ethylphenyl)acetylene (**20**): mp 69–70 °C;[7] 90% yield; NMR $\delta$ 1.23 (t, CH$_3$, 6 H, $J$ = 7 Hz), 2.69 (q, CH$_2$, 4 H, $J$ = 7 Hz), 7.22 (dd, Ar protons, 8 H). This dehydrobromination temperature seemed critical. When **21** was refluxed with *N,N*-dimethylaniline, one obtained only the debrominated product, *p,p'*-diethylstilbene (**22**): NMR $\delta$ 1.23 (t, CH$_3$, 6 H, $J$ = 7 Hz), 2.63 (q, CH$_2$, 4 H, $J$ = 7 Hz), 7.04 (s, CH=CH, 2 H), 7.12–7.60 (dd, Ar protons, 8 H).

**Hydration[31] of Bis(*p*-isopropylphenyl)acetylene (1a) and Bis(*p*-*tert*-butylphenyl)acetylene (1b).** A mixture of 0.5 g of bis(*p*-alkylphenyl)acetylene (**1a** or **1b**), 10 mL of glacial acetic acid, 0.05 g of mercuric sulfate, and 2 g of concentrated sulfuric acid was stirred and refluxed for 20 min. Then, 40 mL of water was added slowly and the mixture refluxed for 2 h. After the mixture was worked up, 4,4'-dialkyldeoxybenzoin (**15**) was obtained in 85–92% yield (see Table II for physical constants).

**4,4'-Dialkyldeoxybenzoins (15).**[32,33] To a stirred mixture of 0.5 g of 4,4'-dialkylbenzoin (**10**), tin amalgam (from 0.33 g of tin, 0.0524 g of mercuric chloride, and 10 mL of water), and 10 mL of 95% ethanol was added 1 mL of concentrated HCl slowly. The resulting mixture was then refluxed for 3 days. The corresponding **15** was obtained in 70–90% yield after the mixture was worked up. The melting point of the mixture of compound **15** thus obtained and the hydration product of bis(*p*-alkylphenyl)acetylene (**1**) showed no depression (see Table II for physical constants).

**Reduction of Bis(*p*-isopropylphenyl)acetylene (1a) and Bis(*p*-*tert*-butylphenyl)acetylene (1b). Method A. Catalytic Hydrogenation.** In a low-pressure Parr apparatus operating at 45 psi was hydrogenated a solution of 0.2 g of compound **1a** or **1b** in 150 mL of isopropyl alcohol for 3 h at 60 °C by using 0.05 g of platinum black (0.5 g of 10% palladium on charcoal, 1 g of 5% platinum asbestos, and 0.5 g of W-2 Raney Ni were used in different experiments as the catalysts). The recovery of compound **1** was quantitative after the workup. Upon reclamation, these catalysts were still pyrophoric. In selected cases, samples from the same batch of catalysts were used successfully to reduce stilbene and *m*-bromocinnamic acid.

**Method B. Chemical Reduction.** A stirred mixture of 0.2 g of compound **1**, 25 mL of benzene, and 0.30 g of sodium was added dropwise 25 mL of absolute ethanol and the mixture allowed to stand overnight at room temperature (or refluxed with 0.9 g of zinc dust in a mixture of 25 mL of acetic acid and 5 mL of concentrated HCl for 24 h). Bis(*p*-alkylphenyl)ethane (**4**), the reduced product, was obtained.

**Catalytic Hydrogenation of Bis(*p*-ethylphenyl)acetylene (20).** Compound **20** (0.20 g) dissolved in 150 mL of 95% ethanol was hydrogenated for 6 h at 60 °C with 0.05 g of 10% palladium on charcoal as the catalyst in a Parr hydrogenator under a 45-psi pressure. After the mixture was worked up, it was found through NMR spectral analysis that the white crystals obtained were a mixture of compound **20** and the reduced product, *p,p'*-diethylstilbene (**22**).

**Registry No. 1a**, 79135-52-7; **1b**, 61440-86-6; **2**, 98-51-1; **3**, 110-05-4; **4a**, 5789-33-3; **4b**, 22927-07-7; **5**, 79135-53-8; **6a**, 23429-40-5; **6b**, 79135-54-9; **7a**, 79135-55-0; **7b**, 79135-56-1; **8b**, 79135-57-2; **9b**, 939-97-9; **10a**, 5623-24-5; **10b**, 77387-64-5; **11a**, 79135-58-3; **11b**, 76471-78-8; **12a**, 79152-62-8; **12b**, 79135-59-4; **13b**, 79135-60-7; **14b**, 75966-32-4; **15a**, 79135-61-8; **15b**, 79135-62-9; **16a**, 79135-63-0; **16b**, 79135-64-1; **17a**, 79135-65-2; **17b**, 79135-66-3; **18a**, 79135-67-4; **18b**, 79135-68-5; **20**, 79135-69-6; **21**, 79135-70-9; **22**, 25347-49-3.

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# Photobenzidine Rearrangements. 7. Disproportionation and Recombination of *N*-Methylarylamino Radicals in the Photodecomposition of 1,4-Bis(*p*-cyanophenyl)-1,4-dimethyl-2-tetrazene and Other 2-Tetrazenes[1,2,†]

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The photochemical decomposition of 1,4-bis(*p*-cyanophenyl)-1,4-dimethyl-2-tetrazene (**1c**) in 1,2-dimethoxyethane (DME) was studied in detail. It was deduced that *N*-methyl-*p*-cyanoanilino radicals are formed and undergo three reactions: recombination into 1,2-bis(*p*-cyanophenyl)-1,2-dimethylhydrazine (**2c**, 21%), disproportionation (70%) into *N*-methyl-*p*-cyanoaniline (**3c**) and *N*-methylene-*p*-cyanoaniline (**4c**), and hydrogen atom abstraction (7%). A small amount of a *p*-semidine is thought to be formed also. These deductions were made from quantitative high-pressure LC measurements of yields of **2c**, **3c**, *p*-cyanoaniline (**5c**), and formaldehyde, the last two products arising from hydrolysis of **4c**. Quantitative measurement of the conversion of **4c** into **3c** by hydrogenation and by trapping of radicals with butyl mercaptan was also used. Approximately 10% of **2c** is formed in a solvent cage. Disproportionation also appears to occur within the cage. Less detailed studies were carried out with 1,4-diphenyl-1,4-dimethyl-2-tetrazene (**1d**) and 1,4-bis(*p*-bromophenyl)-1,4-dimethyl-2-tetrazene (**1e**). Decomposition of **1d** led to 40% of *N,N'*-dimethyldiphenylhydrazine (**2d**, 10% in cage) and 40% of disproportionation products. The remaining 20% of the **1d** is thought to form a *p*-semidine (*N,N'*-dimethyl-*N*-phenyl-1,4-benzenediamine) and the dibenzocarbazole related to it. Radicals from the decomposition of **1e** led to 37% of 1,2-bis(*p*-bromophenyl)-1,2-dimethylhydrazine (**2e**, 10% in cage), 47% of disproportionation, and 16% of hydrogen atom abstraction.

1,4-Dialkyl-1,4-diaryl-2-tetrazenes undergo singlet-state photochemical conversion into *N,N'*-dialkylhydrazoarenes.[3,4] A second major product is the *N*-alkylarylamine. Recently we were able to show with **1a** (X = Me) and **1b**

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