bromoacetate) (3): mp 113–114°; ir ν_{max}^{KBr} 1740 cm^{-1}; nmr (10% $CDCl_3$) see text.

Anal. Calcd for $C_{10}H_{13}Br_3O_6$: C, 25.61; H, 2.79; Br, 51.12. Found: C, 25.54; H, 2.83; Br, 50.96.

Registry No.—**2**, 31446-54-5; **3**, 31446-55-6.

Protonation and Alkylation of Dianions Derived from 1,4-Diphenyl-1,4-di(1-naphthyl)butatriene, 2,5-Diphenyl-2,3,4-hexatriene, 1,1,4-Triphenyl-1,2,3-pentatriene, and 1,1-Diphenyl-4-methyl-1,2,3-pentatriene

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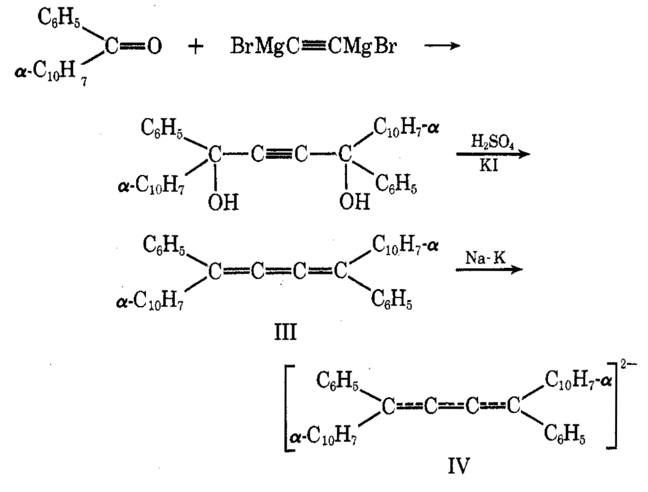
Received February 18, 1971

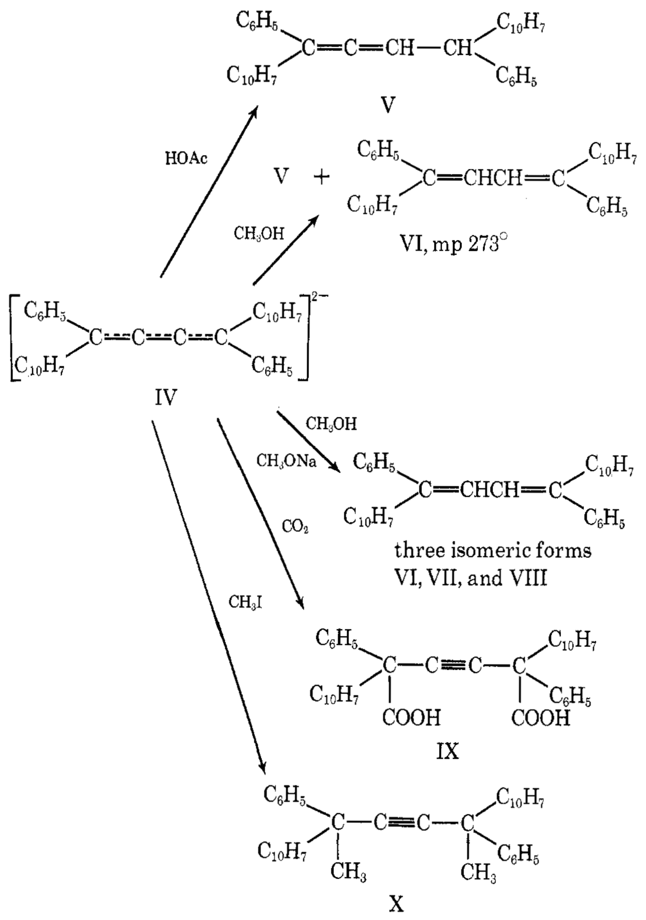
We have recently reported some of the reactions of dianions derived from 1,1,4,4-tetraphenylbutatriene[1] (I) and 1,4-bisbiphenylenebutatriene[2] (II). Both of these trienes are symmetrically substituted and their dianions are stabilized by considerable resonance energy. It was thought that a comparison of some reactions of dianions from less symmetrical butatrienes with reactions of the dianions derived from I and II would be of interest.

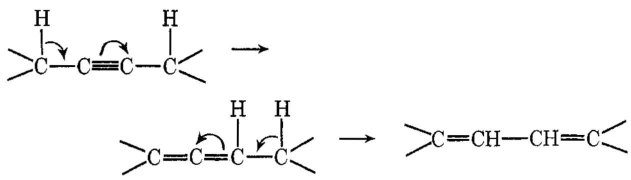
The first dianion which was studied was prepared according to the outline in Scheme I. 1,4-Diphenyl-1,4-di(1-naphthyl)butatriene (III) theoretically may exist in cis and trans forms. Attempts to chromatographically separate the isomers failed.[3] Our attempts to separate isomers also failed. From an examination of models, it would appear that steric interference would make the cis form less probable. The reactions of the dianion from III are shown in Scheme II. We believe that all of these additions involve the same initial step, namely, 1,4 addition. In the case of protonation, the 1,4-dihydro compound, which is kinetically favored, rearranges to the thermodynamically more stable 1,2-diene and finally to the even more stable conjugated diene. In the other cases, *i.e.*, carbonation and methylation, the required hydrogen for the prototropic changes is not present.

SCHEME I



SCHEME II





1,4-Diphenyl-1,4-di(1-naphthyl)-1,2-butadiene (V) possessed a characteristic[4] infrared absorption at 1950 cm^{-1}. The nmr spectrum consisted of an aromatic multiplet at δ 7.24, an olefinic doublet at δ 6.2 (1, J_{AB} = 6 Hz), and a tertiary proton doublet at δ 5.6 (1, J_{AB} = 6 Hz). The tertiary proton has been shifted downfield owing to deshielding by the aromatic rings.

The 1,2-diene was also prepared by the reduction of the triene III with aluminum amalgam.[5] The diene prepared by this method was identical in every way with the sample obtained from the protonation of the dianion IV. A small amount of the conjugated diene, 1,4-diphenyl-1,4-di(1-naphthyl)-1,3-butadiene (VI), mp 273°, was also isolated. VI showed no allenic absorption at 1950 cm^{-1} and showed the usual conjugated absorption in the uv at 293 and 344 mμ. It was subse-

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[1] S. F. Sisenwine and A. R. Day, *J. Org. Chem.*, **32**, 1770 (1967).

[2] J. M. Edinger and A. R. Day, *ibid.*, **36**, 240 (1971).

[3] R. Kuhn and J. Jahn, *Chem. Ber.*, **86**, 759 (1953).

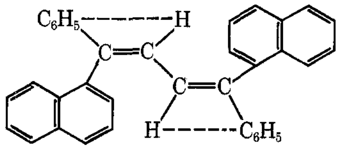
[4] J. H. Wotiz and D. E. Mancuso [*J. Org. Chem.*, **22**, 207, (1957)] examined 58 allenic compounds and concluded that the infrared band at 1950 cm^{-1} was characteristic of allene bonds.

[5] R. Kuhn and H. Fischer, *Chem. Ber.*, **94**, 3060 (1961).

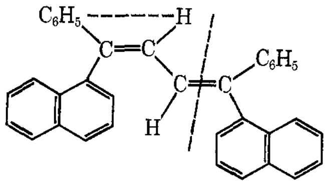
quently shown that V is easily rearranged to the 1,3-dienes by bases.

In an effort to prepare the conjugated diene in better yields, 1,4-diphenyl-1,4-di(1-naphthyl)butatriene (III) was reduced with zinc amalgam. Brand had previously reported that tetraphenylbutatriene, when reduced with zinc amalgam in amyl alcohol–acetic acid medium, gave the corresponding 1,3-diene.[6]

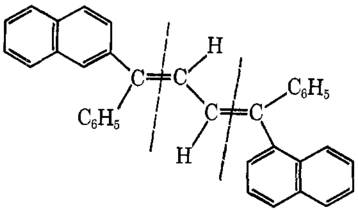
Reduction of III by this method gave two products melting at 259° (VII) and 194° (VIII) in contrast to the aluminum amalgam reduction which yielded a product melting at 273° (VI). None of these products showed an absorption at 1950 cm^{-1}, and the ultraviolet spectra were identical. Analyses and molecular weights for VI, VII, and VIII confirmed the belief that the three are geometric isomers. There should exist three forms, namely, *cis–cis*, *trans–trans*, and *cis–trans*. While all three forms have been isolated in pure form, we are reasonably certain only of the identity of the isomer melting at 194° (VIII).



VI or VII, cis-cis



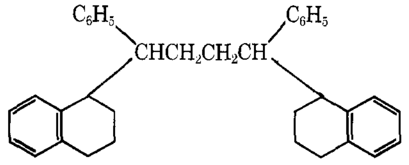
VIII, cis-trans



VI or VII, trans-trans

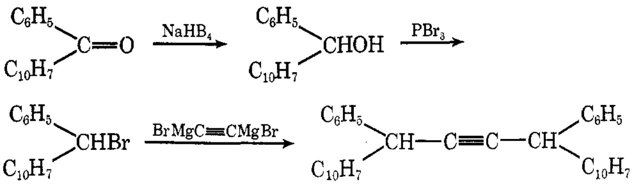
The nmr spectrum of VIII exhibited an aromatic multiplet at δ 7.7 (24) and an olefinic doublet at δ 6.1 (1, J_{AB} = 11 Hz). At first this spectrum appeared anomalous. However, on inspection of models it can be seen that the olefinic protons in VIII are not equivalent. The two protons split one another giving rise to an AB pattern one-half of which is visible in the spectrum. The other AB doublet presumably has merged with the aromatic multiplet and thus cannot be seen. These data best fit the cis–trans form. The isomer melting at 273° showed an aromatic multiplet at δ 7.35 (24) and an olefinic singlet at δ 6.6 (2), while the isomer melting at 259° showed an aromatic multiplet at δ 7.5 (24) and an olefinic singlet at δ 6.9 (2).

A mixture of the isomeric dienes VI, VII, and VIII was obtained when 1,4-diphenyl-1,4-di(1-naphthyl)-butatriene (III) was hydrogenated over Lindlar catalyst (lead-poisoned palladium). All three dienes as well as the triene were hydrogenated over 10% Pd/C to give 1,4-diphenyl-1,4-(1-naphthyl)butane (XI). The characteristic absorptions for a conjugated diene were missing in the uv spectrum for XI, and its nmr spectrum displayed an aromatic multiplet at δ 8.75 (24), a tertiary proton multiplet at δ 4.6 (2), and an unsymmetrical methylene proton triplet at δ 2.2 (4). The latter is probably a complex which is the result of splitting with the methine and aromatic protons. A small amount of a side product was isolated from the 10% Pd/C hydrogenation which was identified as 1,4-diphenyl-1,4-di[1-(1,2,3,4-tetrahydronaphthyl)]butane (XII).



XII

As a final check against confusing one of the dienes with 1,4-diphenyl-1,4-di(1-naphthyl)-2-butyne (XIII), another possible protonation product, the unknown 2-butyne, was synthesized by a procedure published by Wieland and Kloss.[7] The product (XIII) was actually a mixture (presumably of racemic and meso forms). This was not further studied since we were interested in absorption spectra only, and all fractions had the same spectra. For example, the nmr spectra displayed an aromatic multiplet at δ 7.5 (24) and a tertiary proton singlet at δ 5.5 (2). Hydrogenation of XIII over palladium gave the corresponding butane (XI).



XIII

Methylation of the dianion IV gave 2,5-diphenyl-2,5-di(1-naphthyl)-3-hexyne (XIV). Two isomers were obtained, mp 225° (75%) and mp 187–189° (3%). Presumably the higher melting isomer was the racemic form and the other the meso form. They had identical uv spectra and the nmr spectra were very similar.

Some work was also carried out on the protonation of the dianion from 1,4-diphenyl-1,4-di(1-naphthyl)-1,2-butadiene (V) and 1,4-diphenyl-1,4-di(1-naphthyl)-1,3-butadiene (VI). Both sources of the dianion gave the same end product. Protonation with acetic acid gave 1,4-diphenyl-1,4-di(1-naphthyl)-2-butene (XV). The ir spectrum showed a band at 975 cm^{-1} indicating a trans form. The nmr spectrum showed an aromatic multiplet at δ 7.45 (24), an olefin proton doublet at δ 5.85 (2, J = 4 Hz) and a tertiary proton doublet at δ 5.4 (2, J = 4 Hz).

The only significant difference noted between the reactions of the dianion IV from 1,4-diphenyl-1,4-di-(1-naphthyl)butatriene and the dianion derived from 1,4-bisbiphenylenebutatriene[2] was the difference in the protonation results with acetic acid. Dianion IV yielded only the 1,2-butadiene (X), whereas the dianion from 1,4-bisbiphenylenebutatriene gave only the corresponding 1,3-diene as the major product and the corresponding 2-butyne. There does not appear to be a satis-

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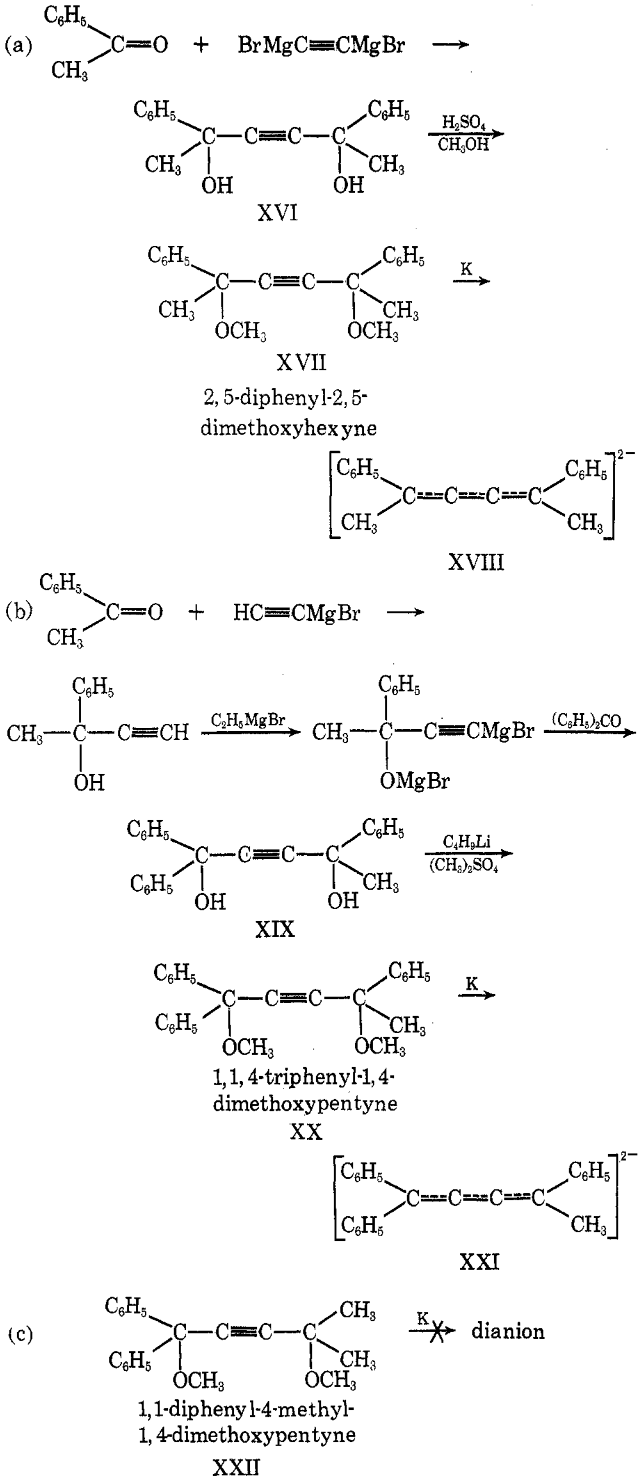
(6) K. Brand, *Chem. Ber.*, **54B**, 1987 (1921).

(7) H. Wieland and H. Kloss, *Justus Liebigs Ann. Chem.*, **470**, 201 (1929).

factory explanation for this difference at the present time. The fact that the 1,4-bisbiphenylenebutatriene dianion is more highly stabilized by resonance gives only a partial answer.

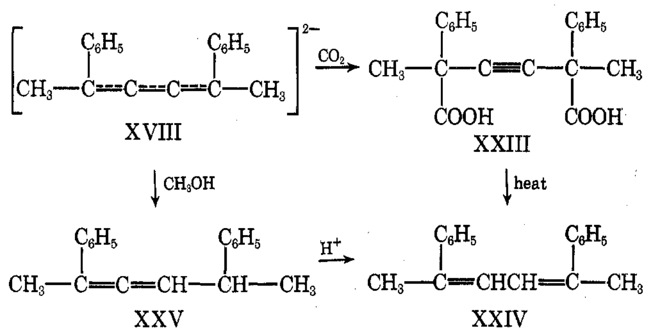
The fact that the least stabilized dianion permitted the ready isolation of the 1,2-diene prompted us to study the dianions of even less stabilized systems. For this purpose attempts were made to prepare the dianions of three tetrasubstituted butatrienes where one or two of the groups were methyl groups (Scheme III). 1,1-Diphenyl-4-methyl-1,4-dimethoxy-2-pentyne (XXII) was prepared by a method similar to that used for 1,1,4-triphenyl-1,4-dimethoxy-3-pentyne except that acetone was used as the starting materials. The dimethoxy compounds were used as the precursors of the dianions because of the relative instabilities of the corresponding butatrienes. Compound XXII apparently stopped with formation of the free-radical anion when treated with potassium.

SCHEME III

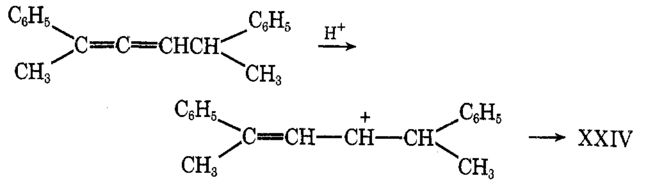


The reactions of the dianion XVIII are shown in Scheme IV. The ir spectrum for XXIII showed a strong carbonyl absorption at 1700 cm^{-1} and no absorption for allene bonds which would indicate 1,2 carbonation. Protonation of XVIII gave only the allene, 2,5-diphenyl-2,3-hexadiene (XXV). The diene gave a strong absorption at 1950 cm^{-1}. It was not isomerized by bases $(OCH_3)^-$ to the conjugated diene XXIV. 1,1,4,4-Tetraphenyl-1,2-butadiene was rapidly isomerized to the conjugated diene under similar circumstances.[1] However, the latter 1,2-diene $[(C_6H_5)_2C{=}C{=}CHCH(C_6H_5)_2]$ contains a benzhydryl hydrogen which is readily abstracted by the base to initiate the rearrangment to the more stable 1,1,4,4-tetraphenyl-1,3-butatriene. There is no benzhydryl hydrogen in XXV. The isomerization of XXV proceeded readily under acid conditions. The nature of the intermediate carbonium ion favors elimination of the C_1 hydrogen and the formation of the conjugated diene XXIV (Scheme V).

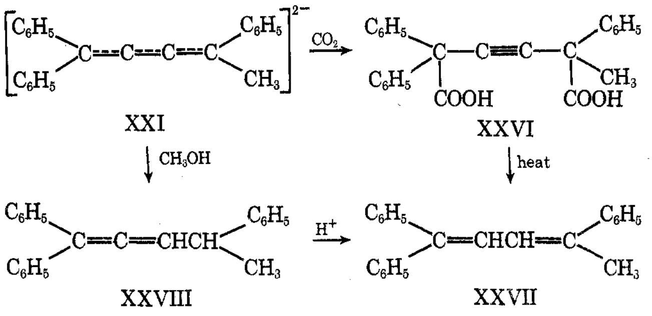
SCHEME IV



SCHEME V



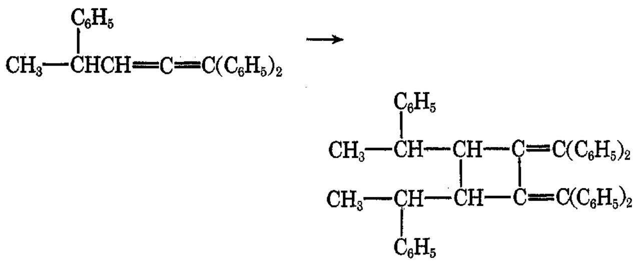
SCHEME VI



Anion XXI reacted very much like anion XVIII (Scheme VI). Compound XXVI showed a strong carboxyl absorption at 1700 cm^{-1} and no peak at 1950 cm^{-1}. The ir spectrum for XXVII showed no band at 1950 cm^{-1}, and its uv spectrum showed a characteristic absorption at 335 mμ (ϵ_{max} 32,000). The nmr spectrum showed an aromatic multiplet at δ 7.3 (15), an olefinic singlet at δ 7.0 (1, J = 1 cps), and an olefinic doublet at δ 2.2 (3, J = 1 cps). The ir spectrum of XXVIII showed a strong allene absorption at 1948 cm^{-1}. The nmr spectrum showed an aromatic multiplet at δ 7.0 (15), an allenic proton doublet at δ 5.79–5.69 (1), an aliphatic proton quintet at δ 3.53 (1), and a methyl proton doublet at δ 1.43–1.33. The fact that XXVIII is not isomerized to XXVII by bases (OCH_3^-) is strong evidence for the absence of the isomeric allene [$(C_6H_5)_2CHCH{=}C{=}C(C_6H_5)CH_3$], since the latter contains a benzhydryl hydrogen which would make it susceptible to base isomerization. XXVIII is readily isomerized to XXVII by acids.

Although 2,5-diphenyl-2,3-hexadiene (XXV) was relatively stable at 150°, 1,1,4-triphenyl-1,2-pentadiene (XXVIII) dimerized at this temperature to what appears to be 1,2-bis(diphenylmethylene)-3,4-bis(1-phenylethyl)cyclobutane (XXIX) (Scheme VII). This dimer had a uv absorption at 370 mμ (ϵ_{max} 15,000), and the nmr spectrum showed an aromatic multiplet at δ 6.81 (15), a cyclobutane proton singlet at δ 3.0 (1), an aliphatic proton multiplet at δ 2.47 (1), and a methyl proton doublet at δ 1.09–0.99 (3). The singlet at δ 3.0 is due to the cyclobutane proton which is at a 90° angle to the aliphatic proton. The multiplet at δ 2.73 should have been a quartet but the aliphatic proton is probably interacting with neighboring protons. The doublet at δ 1.09–0.99 is due to the methyl protons which are split by the aliphatic proton.

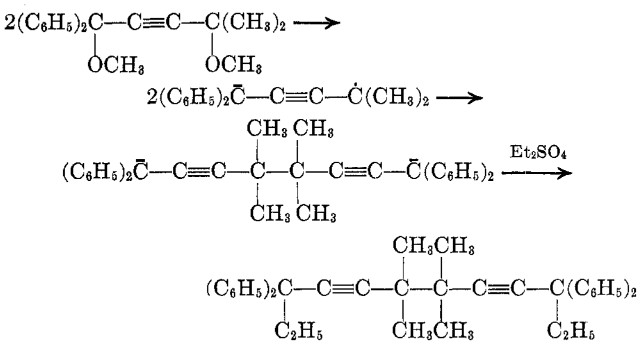
Scheme VII



XXIX

To this point the dianions prepared had at least one phenyl group attached to each of the terminal carbon atoms of the original butatriene. The dianion corresponding to 1,1-diphenyl-4-methyl-1,2,3-pentatriene has only methyl groups attached to the one carbon atom. Because of the absence of stabilizing phenyl groups at this position, it was of interest to see if a stable dianion could be prepared. The corresponding dimethoxy compound 1,1-diphenyl-4-methyl-1,4-dimethoxypentyne (XXII) was treated with excess potassium in the usual way. Diethyl sulfate was then added at a low temperature. Only one product could be isolated from the reaction mixture. Analytical and spectral data have shown this compound to be 3,3,10,10-tetraphenyl-6,6,7,7-tetramethyl-4,8-dodecadiyne (XXX) (Scheme VIII). The ir spectrum of XXX showed absorptions for phenyl, methyl, and ethyl groups but no other characteristic absorptions. This ruled out the possibility of allenic structures and other olefinic structures that absorb in the ir. The nmr spectrum showed an aromatic multiplet at δ 7.6–7.2 (10), a methylene proton quartet at δ 2.3–2.2 (2), a methyl proton singlet at δ 1.4 (6), and a methyl proton triplet at δ 0.90 (3). The anion radical, in this case, is much more reactive than the ones made in our previous studies and dimerizes rapidly to form the stable dianion of the dimer which is then ethylated. The anion radical is thus similar in reactivity to the anion radical of 1,1-diphenylethylene.[8]

Scheme VIII



XXX

Experimental Section

All melting points were determined with a Thomas-Hoover capillary melting point apparatus. The ir spectra were measured on a Perkin-Elmer 521 recording spectrophotometer using KBr disks, Nujol mull, or thin films on NaCl disks. The uv spectra were determined on a Cary 14 spectrophotometer using 1-cm quartz cells. Nmr spectra were measured at 60 Hz on a Varian Associates Model A-60A spectrophotometer with the tetramethylsilane as an internal standard. Esr spectra were measured on a Varian E-3 spectrophotometer.

1,4-Diphenyl-1,4-di(1-naphthyl)butatriene (III).—1,2-Diphenyl-1,4-di(1-naphthyl)-1,4-butynediol[3] was converted to the butatriene III by the sulfuric acid–iodide method,[9] yield 67%, mp 236–237°.

1,4-Diphenyl-1,4-di(1-naphthyl)-1,4-dimethoxy-2-butyne.—This dimethyl ether was prepared in poor yield from the diol[3] by treatment with methanol and sulfuric acid, yield 11%, mp 189–190° (from ethanol). The low yield was probably due to rearrangement.

Anal. Calcd for $C_{38}H_{30}O_2$: C, 87.99; H, 5.83. Found: C, 87.87; H, 5.94.

Dianion from 1,4-Diphenyl-1,4-di(1-naphthyl)butatriene (III).—This dianion was prepared by the method published previously.[2] The solution was stirred for 12 hr during which time the color of the solution changed from a red color to a deep green and the esr signal had disappeared. The solution was stirred for an additional 2–3 hr.

1,4-Diphenyl-1,4-di(1-naphthyl)-2-butyne-1,4-dicarboxylic Acid (IX).—The dianion solution prepared from 2.739 g (0.006 mol) of III was poured over Dry Ice. The mixture was allowed to come to room temperature and the solvent was evaporated. The reddish solid was shaken with water and ether, and after the layers had separated (12 hr) the water layer was removed and acidified with hydrochloric acid. The tan precipitate was extracted with ether and the extract dried ($MgSO_4$). The ether was evaporated and the resulting solid was extracted with hot carbon tetrachloride. The insoluble residue was washed with carbon tetrachloride and then with water leaving a colorless solid: yield 12%; mp 314° (with evolution of CO_2); ir (KBr) 3060–2800 (broad), 1685 (s), 1270 (s), 800 (s), 775 (s), 700 cm^{-1} (s).

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[8] W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, **463**, 1 (1928).

[9] J. Wolinski, *Rocz. Chem.*, **29**, 23 (1955).

Anal. Calcd for $C_{38}H_{26}O_4$: C, 83.50; H, 4.80; O, 11.70. Found: C, 83.32; H, 4.96; O, 11.80 (by actual analysis).

Protonation of Dianion IV with Acetic Acid. Preparation of 1,4-Diphenyl-1,4-di(1-naphthyl)-1,2-butadiene (V).—The dianion solution from 3.2 g (0.007 mol) of III was cooled in Dry Ice-acetone and 10 ml of acetic was added. Instant decolorization occurred. The solution was stirred for 0.5 hr and allowed to come to room temperature. The solvent was removed under reduced pressure and the residual brown oil was crystallized from methanol. The product was recrystallized from acetone, colorless crystals, yield 77%, mp 180–181°.

Anal. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol wt, 458. Found: C, 94.14; H, 5.74; mol wt, 442 (Rast method).

The solid that did not dissolve in the hot acetone proved to be pure 1,4-diphenyl-1,4-di(1-naphthyl)-1,3-butadiene (VI), yield 3%, mp 273°.

Anal. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72. Found: C, 94.17, H, 5.78.

Zinc-Amalgam Reduction of 1,4-Diphenyl-1,4-di(1-naphthyl)-butatriene (III). Preparation of 1,4-Diphenyl-1,4-di(1-naphthyl)-1,3-butadiene (VII, Mp 259°) and 1,4-Diphenyl-1,4-di(1-naphthyl)-1,3-butadiene (VIII, Mp 194°).—The zinc-amalgam reduction method reported by Brand[6] for the reduction of tetraphenylbutatriene was used for the reduction of III. After the required refluxing, the mixture was filtered. The solid was extracted with carbon disulfide and water, and the carbon disulfide layer was washed with water and dried ($CaCl_2$). The solvent was removed under reduced pressure and the residual colored solid was washed with a little cold methanol followed by a small amount of cold acetone. The product was recrystallized from acetone: yield 50%; mp 259°; nmr, aromatic multiplet at δ 8.0–7.0 (24), olefinic singlet at δ 6.9 (2).

Anal. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol wt, 458. Found: C, 94.12; H, 5.92; mol wt, 455 (Rast method).

The original filtrate from the zinc-amalgam reduction, on further evaporation under reduced pressure, gave another colorless, crystalline 1,3-diene IX. It was dissolved in hot acetone and filtered while hot to remove a small amount of isomer VII. On cooling, isomer VIII crystallized, yield 34%, mp 194°.

Anal. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol wt, 458. Found: C, 94.37; H, 5.61; mol wt, 451 (Rast method).

The nmr spectrum was practically identical with that of VIII.

Catalytic Reduction of 1,4-Diphenyl-1,4-(1-naphthyl)butatriene (III) with Lindlar Catalyst.—Compound III (2.02 g, 0.0044 mol) and 4.7 g of Lindlar catalyst[10] in 150 ml of tetrahydrofuran were hydrogenated at 45 psi for 7 hr. The mixture was filtered and the solvent removed *in vacuo*. The solid was refluxed with acetone and filtered. The insoluble residue proved to be the conjugated diene, mp 259° (VII), yield 15.2%. Fractional evaporation of the acetone filtrate gave isomers VI (9%) and VIII (15.4%). Extended fractionation would increase the yields. The overall crude yield was nearly 100°.

Catalytic Hydrogenation of III with 10% Pd on Carbon. Preparation of 1,4-Diphenyl-1,4-di(1-naphthyl)butane (XI).—The hydrogenation was carried out at 45 psi for 28 hr in ethanol solution. At the end of 7 and 14 hr a small amount of fresh catalyst was added. The mixture was cooled and filtered, and the solvent was evaporated under reduced pressure to yield a negligible amount of an oil. The original precipitate was extracted with hot ethanol and the alcohol evaporated to give colorless crystals which were crystallized from ethanol, yield 47%, mp 160°.

Anal. Calcd for $C_{36}H_{30}$: C, 93.46; H, 6.54. Found: C, 93.42; H, 6.54.

Protonation of the Dianion IV from III with Methanol.—The procedure was the same as with the protonation with acetic acid. Decolorization of the dianion solution occurred more slowly. The 1,2-butadiene (V) was the main product. However, when V was recrystallized from acetone, a small residue proved to be the isomeric diene VI, mp 273°.

Preparation of 1,4-Diphenyl-1,4-di(1-naphthyl)-2-butyne (XIII).—Phenyl-1-naphthylcarbinyl bromide[11] (34.2 g, 0.115 mol) in 75 ml of benzene was added slowly to an ether solution of acetylenedimagnesium bromide (0.225 mol). After the addition, the solution was refluxed for 4 hr and then cooled and poured into 500 ml of 2*N* hydrochloric acid and ice. The mixture was extracted with ether and the ether extract dried ($MgSO_4$). The ether was evaporated and the residual oil taken up in a minimum amount of petroleum ether (bp 60–110°). On standing at 3°, white crystals separated which were recrystallized from petroleum ether: yield 38%; mp 148–160°; nmr, aromatic multiplet at δ 8.0–7.0 (24) and a tertiary proton singlet at δ 5.65 (2). This product was probably a mixture of meso and racemic forms.

Anal. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72. Found: C, 94.17; H, 5.83;

A small amount of one of the isomers was obtained by repeated recrystallization from acetone, mp 178–179.5°.

Anal. Found: C, 94.22; H, 5.67.

Catalytic Hydrogenation of 1,4-Diphenyl-1,4-di(1-naphthyl)-2-butyne (XIII) over 10% Pd on Carbon.—Catalytic hydrogenation (45 psi) in acetic acid gave both 1,4-diphenyl-1,4-di(1-naphthyl)-butane (XI) and 1,4-diphenyl-1,4-di[1-(1,2,3,4-tetrahydronaphthyl)]butane (XII). Their identities were established by analyses, melting points, and spectral studies.

Methylation of Dianion IV from III. Preparation of 2,5-Diphenyl-2,5-di(1-naphthyl)-3-hexyne (XIV).—Methyl iodide (10 ml) was added to the dianion solution prepared from 3.2 g (0.007 mol) of III at Dry Ice-acetone temperature. The mixture was stirred for 30 min and filtered, and the solvent was evaporated under reduced pressure. The resulting crystals were washed with a small amount of hot ethanol and dried, yield 74%, mp 225°.

Anal. Calcd for $C_{38}H_{30}$: C, 93.79; H, 6.21. Found: C, 93.72; H, 6.23.

An isomer was isolated in small amounts from the ethanol extract by evaporation, mp 187–189°.

Anal. Calcd for $C_{38}H_{30}$: C, 93.79; H, 6.21. Found: C, 93.79; H, 6.19.

Protonation of the Dianion from 1,4-Diphenyl-1,4-di(1-naphthyl)-1,2-butadiene (V). Preparation of 1,4-Diphenyl-1,4-di(1-naphthyl)-2-butene (XV).—The dianion was prepared in the usual manner from 2.1096 g of V and 0.4736 g of Na–K. Acetic acid (10 ml) was added to the solution cooled in Dry Ice-acetone. The mixture was stirred for 15 min, allowed to come to room temperature, and filtered. The solvent was evaporated under reduced pressure, leaving an oil which was taken up in ether. The ether extract was washed with water and dried ($MgSO_4$). The ether was evaporated and the resulting solid was extracted with ethanol. The residue was dried, yield 62%, mp 211–214°.

Anal. Calcd for $C_{36}H_{28}$: C, 93.87; H, 6.13. Found: C, 93.77; H, 6.31.

2,5-Diphenyl-3-hexyne-2,5-diol (XVI).[12]—Both the α and β forms were obtained in almost equal yields, 28–35% (70–75% overall): α form, mp 163°; β form, mp 125–126°.

2,5-Diphenyl-2,5-dimethoxy-3-hexyne (XVII).—Both diols gave good yields of the same dimethyl ether. The diol XVI was dissolved in 250 ml of warm methanol and to this solution was added 2 g of concentrated sulfuric acid in 20 ml of methanol. After 24 hr, the crystals were removed and washed with methanol, ammonium hydroxide, and again with methanol. The product was recrystallized from methanol, yield 85%, mp 76°; the ir spectrum showed no hydroxyl absorption.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48. Found: C, 81.60; H, 7.60.

1,1,4-Triphenyl-2-pentyne-1,4-diol (XIX).—The published synthesis of this compound[13] gave a yield of 64%. The product was recrystallized from benzene-cyclohexane, mp 124°.

1,1,4-Triphenyl-1,4-dimethoxy-2-pentyne (XX).—Over a period of 45 min a solution of 32.8 g (0.01 mol) of XIX in 250 ml of dry ether was added, under nitrogen, to 133 ml (0.2 mol) of a 15% butyllithium solution in hexane. The temperature was kept at 20°. At the end of the addition, the blue color had disappeared and the lithium salt had precipitated. Dimethyl sulfate (26 g, 0.22 mol) in 100 ml of dry ether was gradually added to the mixture at 5–10° and the mixture was stirred for 24 hr. A 0.5 *M* solution of sodium methoxide in methanol (100 ml) was added to destroy an excess dimethyl sulfate. The solution was washed with water and the ethane-hexane layer was dried ($MgSO_4$). The solvent was removed under reduced pressure and the residual oil was crystallized from methanol. The product was recrystallized from methanol, yield 69%, mp 54°. The ir spectrum had the characteristic methoxy absorption at 2825 cm^{-1} but no hydroxyl absorption.

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Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.27; H, 6.74. Found: C, 84.15; H, 6.60.

1,1-Diphenyl-4-methyl-2-pentyne-1,4-diol.—This diol was prepared by the method of Babayan,[14] yield 76%, mp 115°.

1,1-Diphenyl-4-methyl-1,4-dimethoxy-2-pentyne (XXII).—XXII was prepared by the procedure used for XX. Instead of crystallizing the residual oil from methanol, it was distilled *in vacuo*, yield 64%, bp 138–142° (0.55 mm), $n^{22}D$ 1.5495; the ir spectrum showed the methoxy absorption at 2825 cm^{-1}.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48. Found: C, 81.55; H, 7.41.

2,5-Diphenyl-3-hexyne-2,5-dicarboxylic Acid (XXIII).—2,5-Diphenyl-2,5-dimethoxy-3-hexyne (XVII) (5.88 g, 0.02 mol) was added to 200 ml of dry tetrahydrofuran, and 3.2 g (0.082 g-atom) of potassium was added under nitrogen. After stirring for 24 hr the dark solution was poured onto Dry Ice. The Dry Ice was allowed to evaporate and *tert*-butyl alcohol was added to destroy the excess potassium. The mixture was poured into water and the solution acidified with hydrochloric acid. The solution was extracted with ether and the extract was dried ($MgSO_4$). After removing the ether, the residue was recrystallized from carbon tetrachloride, yield 69%, mp 224° dec.

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.53; H, 5.59. Found: C, 74.34; H, 5.68.

Decarboxylation of XXIII to 2,5-Diphenyl-2,4-hexadiene (XXIV).—Compound XXIII (1.61 g) was heated at 225° until the evolution of carbon dioxide had ceased. The residue was recrystallized from 95% ethyl alcohol, yield 68%, mp 138°; uv ($CHCl_3$) 317 mμ (ϵ 34,100). These values agreed with literature values.[15]

Protonation of the Dianion XVIII Corresponding to 2,5-Diphenyl-2,3,4-hexatriene. Preparation of 2,5-Diphenyl-2,3-hexadiene (XXV).—To a dianion solution prepared from 5.88 g (0.02 mol) of 2,5-diphenyl-2,5-dimethoxyhexyne-3 (XVII) and 3.2 g (0.082 g-atom) of potassium in 200 ml of tetrahydrofuran was added an excess of methanol at −20°. The solution was poured into water, and the resulting oil was separated, taken up in ether, and dried ($MgSO_4$). After removing the ether, the viscous oil was transferred to an alumina column with the aid of a little petroleum ether (bp 70–110°). The column was eluted with 500 ml of petroleum ether. The movement of the allene band was followed by the yellow color of the band and its fluorescence when irradiated with a uv lamp. Evaporation of the solvent gave the pure allene as a yellow oil, yield 48%; the uv spectrum showed the absence of any conjugated diene.

Anal. Calcd for $C_{18}H_{18}$: C, 92.30; H, 7.70; mol wt, 234. Found: C, 92.12; H, 7.82; mol wt, 242 (Rast method).

Isomerization of 2,5-Diphenyl-2,3-hexadiene (XXV) to 2,5-Diphenyl-2,4-hexadiene (XXIV).—XXV (1 g) was refluxed with 50 g of methanol containing 1 g of concentrated sulfuric acid for 2 hr. The solution was partially evaporated and cooled. The resulting product was recrystallized from ethanol, yield 60%, mp 138°, uv ($CHCl_3$) 320 mμ (ϵ 34,100).

1,1,4-Triphenyl-2-pentyne-1,4-dicarboxylic acid (XXVI).—A dianion solution prepared from 7.12 g (0.02 mol) of 1,1,4-triphenyl-1,4-dimethoxy-2-pentyne (XX) and 3.2 g (0.082 g-atom) of potassium, in 200 ml of tetrahydrofuran, was poured onto Dry Ice. The resulting solution was worked up as in the preparation of the diacid XXIII. The product was recrystallized from chloroform–cyclohexane, yield 64%, mp 194° dec.

Anal. Calcd for $C_{25}H_{20}O_4$: C, 76.71; H, 5.39. Found: C, 76.90; H, 5.49.

Decarboxylation of XXVI to 1,1,4-Triphenyl-1,3-pentadiene (XXVII).—Compound XXVI (1.92 g) was heated at 200° until the evolution of carbon dioxide had ceased. The residue was recrystallized from ethanol–water, yield 42%, mp 121–122°.

Anal. Calcd for $C_{23}H_{20}$: C, 93.24; H, 6.76. Found: C, 93.05; H, 6.87.

Protonation of Dianion XXI. Preparation of 1,1,4-Triphenyl-1,2-pentadiene (XXVIII).—To an anion solution prepared from 1,1,4-triphenyl-1,4-dimethoxy-2-pentyne (XX), prepared in the usual manner, was added an excess of methanol at −20°. The reaction mixture was worked up by the procedure used for XXV. A yellow oil was obtained after column chromatography, yield 55%.

Anal. Calcd for $C_{23}H_{20}$: C, 93.24; H, 6.76. Found: C, 93.11; H, 6.87.

Dimerization of 1,1,4-Triphenyl-1,2-pentadiene (XXVIII) to 1,2-Bis(diphenylmethylene)-3,4-bis(1-phenylethyl)cyclobutane (XXIX).—One gram of the allene XXVIII was heated at 150° for 2 hr. The residue was dissolved in acetone and precipitated by the addition of ethanol. The product was recrystallized from chloroform–methanol, yellow crystals, yield 39%, mp 197°.

Anal. Calcd for $C_{46}H_{40}$: C, 93.24; H, 6.76; mol wt, 592. Found: C, 93.41; H, 6.92; mol wt, 576 (Rast method).

Isomerization of 1,1,4-Triphenyl-1,2-pentadiene (XXVIII) to 1,1,4-Triphenyl-1,3-pentadiene (XXVI).—XXVII (1 g) was refluxed in 50 ml of ethanol containing 5 ml of concentrated sulfuric acid for 3 hr. On cooling, an oil separated which was crystallized from methanol–water and recrystallized from methanol–water, yield 34%, mp 121–122°.

Attempted Preparation of a Dianion Corresponding to 1,1-Diphenyl-4-methyl-1,2,3-pentatriene. Ethylation of the Resulting Solution to Form 3,3,10,10-Tetraphenyl-6,6,7,7-tetramethyl-4,8-dodecadiyne (XXX).—To a solution prepared from 5.88 g (0.02 mol) of 1,1-diphenyl-4-methyl-1,4-dimethoxy-2-pentyne (XXII) and 3.2 g (0.082 g-atom) of potassium was added 15.4 g (0.1 mol) of diethyl sulfate at 0°. After 30 min, methanol was gradually added to destroy the excess potassium, and the mixture was then poured into water. The oil which separated was taken up in ether, washed with water, and dried ($MgSO_4$). After the ether was removed, the residue was recrystallized from methanol, yield 50%, mp 154°.

Anal. Calcd for $C_{40}H_{42}$: C, 91.95; H, 8.05; mol wt, 522. Found: C, 91.76; H, 8.18; mol wt, 501 (Rast method).

Registry No.—III, 31382-35-1; IV, 12537-75-6; V, 31382-36-2; VI, 31382-37-3; VII, 31382-38-4; VIII, 31382-39-5; IX, 31382-40-8; XI, 31382-41-9; *rac*-XIII, 31382-42-0; *meso*-XIII, 31382-43-1; *rac*-XIV, 31382-44-2; *meso*-XIV, 31382-45-3; XV, 31382-46-4; XVI, 6289-26-5; XVII, 31382-48-6; XVIII, 12537-72-3; XIX, 2979-97-7; XX, 31382-49-7; XXI, 12537-74-5; XXII, 31382-50-0; XXIII, 31428-89-4; XXIV, 16819-47-9; XXV, 31382-52-2; XXVI, 31382-53-3; XXVII, 31382-54-4; XXVIII, 31382-55-5; XXIX, 31382-56-6; XXX, 31382-57-7; 1,1-diphenyl-4-methyl-1,2,3-pentatriene dianion, 12537-73-4; 1,4-diphenyl-1,4-di(1-naphthyl)-1,4-dimethoxy-2-butyne, 31382-58-8.

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Isomerization of Fluorenone Anil *N*-Oxide to *N*-Phenylphenanthridone by Photochemical and Mass Spectral Pathways

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In an earlier note[2] it was suggested that in the isomerization of 2-phenylisatogen to 2-phenyl-4*H*-3,1-benzoxazin-4-one there was similar behavior in both the photolytic and the mass spectral pathways. The nitrone–amide rearrangement has been discussed in terms of a photochemical–mass spectral analogy.[3] A common oxaziridine intermediate was proposed for both 2-phenylisatogen and 2-phenyl-4*H*-3,1-benzoxazin-4-one in their mass spectral fragmentations.[2]

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