

8.1–8.5, complex multiplet (2 H). Nitrile IVa gave  $n_D^{25}$  1.5240 (lit.<sup>23</sup>  $n_D^{25}$  1.5236).

**Preparation of Tricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7-dien-9-one (IVc).**—Pyridine (80 g, 1.0 mol) was slowly added to a solution of 121 g (0.58 mol) of phosphorus pentachloride in 700 ml of dry chloroform. To the resulting white suspension was added 64.8 g (0.388 mol) of nitrile IVa. Work-up after 36 hr of heating at reflux consisted of pouring onto ice, removing the aqueous layer, washing the aqueous phase twice with ether, washing the combined organic extracts with saturated sodium carbonate, and removing the solvent on a rotary evaporator. This treatment gives 88 g of dark liquid which was used without further purification. In a separate experiment, attempted distillation of the chloronitrile at 0.01 mm led to decomposition and loss of product. The 88 g of dark liquid described above was dissolved in 600 ml of DMSO, and to this was added a hot solution 66 g (1.0 mol) of 85% potassium hydroxide in 22 ml of water. After 24 hr the mixture was worked up as described for the purification of ketone IIc. After sublimation, 28.1 g (49.7% based on nitrile IVa) of ketone was obtained. The nmr spectrum exhibited bands at  $\tau$  3.80–4.42, complex multiplet (4 H); 6.9–7.5, broad absorption (4 H); 8.13 and 8.15, two doublets (1 H each). The ir showed absorptions at 1710 (C=O stretch) and 3060  $\text{cm}^{-1}$  (vinyl C—H stretch).

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{10}\text{O}$ : C, 82.16; H, 6.90. Found: C, 82.07; H, 6.96.

**8-Cyanotetracyclo[4.3.0.0<sup>2,4</sup>.0<sup>3,7</sup>]nonane (Va).**—Nitrile Va was prepared from freshly dried and distilled norbornadiene [bp 86–87° (693 mm)] and acrylonitrile [bp 74–75° (693 mm)]. The method of Shrauzer and Glockner<sup>24</sup> or Shrauzer and Eichler<sup>25</sup> was scaled up to preparative proportions. The latter method is more convenient for large-scale preparations if the acrylonitrile is added slowly rather than all at once as described.<sup>25</sup> Yields were 85–93% using centigram quantities.

**8-Cyano-8-chlorotetracyclo[4.3.0.0<sup>2,4</sup>.0<sup>3,7</sup>]nonane (Vb).**—A mixture of nitrile Va (494 g, 3.41 mol), 1000 ml of carbon tetrachloride, and phosphorus pentachloride (208 g, 1.00 mol) was heated at reflux in a vessel fitted with a stirrer, chlorine inlet, reflux condenser, and a gas bubbler. The chlorine inlet was placed between the flask and the condenser. There was a gradual evolution of hydrogen chloride, which after 24 hr becomes more sluggish. At this time chlorine gas was passed into the solution

(23) R. E. Benson and T. L. Cairns, *J. Amer. Chem. Soc.*, **72**, 5355 (1950).

(24) G. N. Schrauzer and P. Glockner, *Chem. Ber.*, **97**, 2451 (1964).

(25) G. N. Schrauzer and S. Eichler, *ibid.*, **95**, 2764 (1962).

to convert phosphorus trichloride to the pentachloride. This process was continued until no more HCl was evolved (about 3 days). The completeness of reaction can be conveniently checked by vpc or nmr (by following the disappearance of the absorption corresponding to hydrogen  $\alpha$  to nitrile). The cooled reaction mixture was poured onto 2.5 kg of ice and mixed until the ice melted. The two phases were allowed to separate (there may be an emulsion at this point which requires several hours to break up); the aqueous layer was extracted with carbon tetrachloride. The combined organic phases were washed once with water and then with 10% aqueous sodium carbonate until no more carbon dioxide was evolved. Simple distillation gives 463 g (76%) of oily chloronitrile: bp 89–94° (0.05–0.1 mm); ir,  $\nu_{\text{max}}$  at 3060, 2245  $\text{cm}^{-1}$ ; nmr, multiplets at  $\tau$  7.65–7.82 (2 H), 7.82–8.0 (3 H), 8.27–8.44 (2 H), 8.44–8.62 (1 H), 8.68–8.87 (2 H).

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{10}\text{ClN}$ : C, 66.85; H, 5.61; N, 7.80. Found: C, 66.92; H, 6.13; N, 8.16.

**Preparation of Tetracyclo[4.3.0.0<sup>2,4</sup>.0<sup>3,7</sup>]nonan-8-one (Vc).**—Chloronitrile Vb (463 g, 2.58 mol) was dissolved in 2 l. of DMSO and the solution heated to 50°. A hot solution of 400 g of 85% potassium hydroxide in 120 g of water was slowly added. After stirring for 3 days at 50–60°, the dark reaction mixture was subjected to steam distillation. The distillate was saturated with sodium chloride and extracted with ether. The ether extracts were dried over magnesium sulfate, concentrated, and distilled to give 252 g (73%) of ketone, bp 69–70° (4 mm). In another experiment where the chloronitrile was not isolated the yield was 69.7% based on nitrile. The nmr spectrum showed multiplets centered at  $\tau$  7.48 (3 H), 7.78 (2 H), 8.40 (2 H), and a broad multiplet from 8.50 to 8.88 (3 H); ir had  $\nu_{\text{max}}$  at 3060 (cyclopropyl C—H stretch) and 1756  $\text{cm}^{-1}$  (carbonyl stretch). The ir and nmr spectra were identical with spectra of an authentic sample which were kindly supplied to us by Professor Alex Nickon.

**Registry No.**—Ic, 694-98-4; IIb, 6962-73-8; IIc, 2220-40-8; IIIa, 16282-02-3; IIIb, 16282-03-4; IIIc, 16282-04-5; IVc, 16282-05-6; Vb, 16282-06-7; Vc, 16282-07-8.

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## The Syntheses and Properties of Sterically Hindered Butadienes.

### A Modification of the Chugaev Reaction

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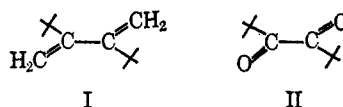
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The synthesis of 4,5-dimethylene-3,3,6,6-tetramethyl-1-thiacycloheptane (IV) was accomplished *via* a double Wittig reaction with 3,3,6,6-tetramethyl-1-thiacycloheptane-4,5-dione (III). The synthesis of 2,3-diisopropyl-1,3-butadiene (VIII) from 2,3-diisopropyl-1,4-butanediol (XI) was accomplished *via* a modification of the Chugaev reaction. The chemical and spectroscopic properties of 2,3-di-*t*-butyl-1,3-butadiene (I), of dienes IV and VIII, and of diketone III and dipivaloyl (II) are discussed. The heavily substituted butadienes I and IV are shown to be unusually unreactive.

Our interest in crowded molecules led to several unsuccessful attempts to synthesize 3,4-di-*t*-butylthiophene.<sup>1</sup> Ring-closure reactions of 2,3-di-*t*-butyl-1,3-butadiene (I), 2,3-di-*t*-butylsuccinic acid derivatives, or dipivaloyl (II) with suitable reagents were unsuccessful.<sup>1</sup> The lack of reactivity of these  $\alpha,\beta$ -di-*t*-butyl compounds in ring-closure reactions must be attributed to the bulky *t*-butyl groups. Spectroscopic evidence for an abnormal conformation in these  $\alpha,\beta$ -di-*t*-butyl

compounds was found for 2,3-di-*t*-butyl-1,3-butadiene (I).<sup>2</sup>



The ultraviolet absorption spectrum of the vapor of the butadiene I, taken at room temperature under

(1) Ae. de Groot, Ph.D. Thesis, Groningen, 1967.

(2) H. Wynberg, Ae. de Groot, and D. W. Davies, *Tetrahedron Lett.*, 1083 (1963).

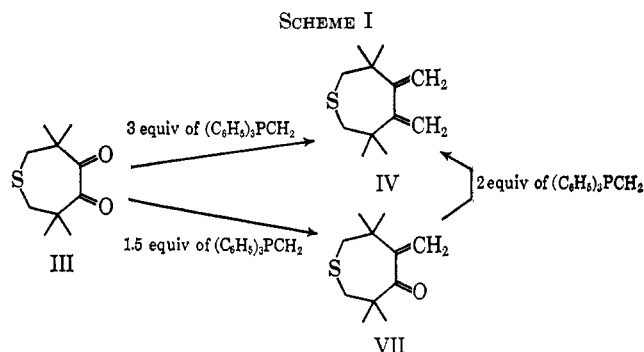
nitrogen, shows the absence of the typical dialkyldiene absorption maximum at 220 (vapor)  $\pm$  5  $m\mu$ .<sup>3</sup> Instead the spectrum of I shows a maximum near 185  $m\mu$  and a shoulder at 209  $m\mu$  which is characteristic of a substituted ethylene.<sup>4</sup> Molecular models show that a normal coplanar *cis* or *trans* conformation is sterically unlikely for diene I. An orthogonal conformation is clearly the favored one in this case. Leonard and Mader<sup>5</sup> studied the angle of twist about the intercarbonyl bond of  $\alpha$  diketones and assigned an angle  $\theta$  of 90–180° to dipivaloyl (II). An important difference between dipivaloyl and the butadiene I is the presence of the four vinyl protons in the butadiene. The hindrance between a proton at carbon atom 1 and the *t*-butyl group at carbon atom 3 prevents the coplanar *trans* conformation in the diene. This conformation is probably possible in the diketone.<sup>6</sup>

Bromination, hydrogenation, and ozonolysis reactions of I were investigated by Backer.<sup>7</sup> The latter<sup>7</sup> showed that diene I underwent no Diels–Alder reaction with sulfur dioxide or maleic anhydride. Our attempts to prepare 3,4-di-*t*-butylthiophene by heating the diene with sulfur were also unsuccessful. The relatively easy dealkylation of *t*-butylthiophene may well make any high-temperature route for the preparation of 3,4-di-*t*-butylthiophene impractical.<sup>8,9</sup> Huyser, Siegert, Sinnige, and Wynberg<sup>10</sup> showed that the diene I was unreactive in peroxide-induced free-radical reactions.

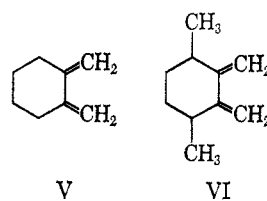
Dipivaloyl (II) does not react in ring-closure reactions. A Hinsberg thiophene synthesis with diethylthiodiacetate was unsuccessful.<sup>1</sup> In the literature unsuccessful ring-closure attempts of dipivaloyl to form 2,3-di-*t*-butylquinoxaline<sup>5</sup> and 4,5-di-*t*-butylimidazole<sup>11</sup> are mentioned. We developed a successful route to the last two *o*-di-*t*-butyl heteroaromatics using the cyclic diketone III as starting material for the ring-closure reactions.<sup>9</sup> In diketone III the two potential *t*-butyl groups are part of a ring and thus the carbonyl functions are kept in a favorable position for ring-closure reactions. However, the angle of twist  $\theta$  about the intercarbonyl bond in diketone III must also be about 90°,<sup>5</sup> as can be seen from molecular models of the diketone and from the longest wavelength absorption maximum in the ultraviolet spectrum [ $\lambda_{\max}$  333  $m\mu$  ( $\epsilon$  41.8)]. Comparison of the ultraviolet spectrum of diketone III with the spectra of the carbocyclic analogs of this diketone, prepared by Leonard and Mader,<sup>5</sup> shows that diketone III has the largest hypsochromic shift of the longest wavelength absorption maximum. This indicates that the interaction between the two carbonyl functions is minimal in diketone III, and the angle  $\theta$  between the two carbonyl functions in III must be about 90°.

The successful ring-closure reactions of diketone III in comparison with the unreactivity of dipivaloyl in this type of reaction prompted us to compare the behavior of diene IV with that of 2,3-di-*t*-butyl-1,3-butadiene (I).

Diene IV was prepared in 24–30% yield by reaction of diketone III with excess methylenetriphenylphosphorane in dimethyl sulfoxide as solvent<sup>12</sup> (Scheme I).



Diene IV is a perfectly stable, clear liquid [bp 78° (1.9 mm),  $n_D^{20}$  1.5135]. The ultraviolet absorption spectrum of diene IV shows no maximum above 185  $m\mu$ , clearly indicating that there is a complete lack of double-bond resonance in this diene. The angle of twist between the two double bonds must be about 90° (compare with diketone III). Thus the exocyclic diene IV and the open diene I show similar spectroscopic (and chemical, see below) behavior. However, the virtually fixed skew<sup>2</sup> conformation of diene I is clearly caused by steric interference between adjacent *t*-butyl groups and vinyl protons. A relatively rigid conformation of the seven-membered ring forces the two adjacent *exo*-methylene groups into an orthogonal position in diene IV, again causing the sharp hypsochromic shift in the absorption spectrum. 1,2-Dimethylenecyclohexane (V)<sup>13</sup> has abnormally low absorption in the ultraviolet spectrum [ $\lambda_{\max}$  220  $m\mu$  ( $\epsilon$  10,050)] and 3,6-dimethyl-1,2-dimethylenecyclohexane (VI) has an absorption maximum below 220  $m\mu$ .<sup>14</sup> Clearly the two



methyl groups in VI exhibit some influence on the coplanarity of the chromophore. The four methyl groups in 4,5-dimethylene-3,3,6,6-tetramethyl-1-thia-cycloheptane (IV) cause even greater rigidity of the molecule, as is shown by the nmr spectrum. This nmr spectrum shows two singlets at  $\tau$  8.90 and 8.73 at room temperature for the methyl protons, an AB multiplet for the 2 and 7 methylene protons, and an AB multiplet for the exocyclic methylene protons.<sup>15</sup> When the sample was warmed, the two singlets collapsed at 92° and the AB multiplet for the 2 and 7

(3) S. F. Mason, *Quart. Rev.*, **15**, 287 (1961).

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(5) N. J. Leonard and P. M. Mader, *J. Amer. Chem. Soc.*, **72**, 5388 (1950).

(6) E. L. Eliel and Sr. M. C. Knoeber, *ibid.*, **88**, 5347 (1966).

(7) H. J. Backer, *Rec. Trav. Chim.*, **58**, 643 (1939).

(8) H. Wynberg and U. E. Wiersum, *J. Org. Chem.*, **30**, 1058 (1965).

(9) Ae. de Groot and H. Wynberg, *ibid.*, **31**, 3954 (1966).

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(13) W. J. Bailey and H. R. Golden, *J. Amer. Chem. Soc.*, **75**, 4780 (1953).

(14) W. J. Bailey and R. L. Hudson, *ibid.*, **78**, 2806 (1956).

(15) The nmr spectrum of diketone III shows a singlet for the methyl protons at  $\tau$  8.75 and a singlet for the 2 and 7 methylene protons at  $\tau$  7.43 at room temperature. The differences in the nmr spectra at room temperature also indicate that in these cyclic compounds III and IV the vinyl protons in diene IV cause considerably more steric hindrance than the free electrons of the carbonyl functions in diketone III<sup>9</sup> [compare diene I and dipivaloyl (II)].

methylene protons did the same at 112°. Since this molecule (IV) gives two coalescence temperatures, it is very simple to calculate the flipping barrier. This turned out to be 8.3 kcal/mol.<sup>16</sup>

Diene IV gives no Diels–Alder adduct upon reaction with ethylacetylene dicarboxylate, tetracyanoethylene, thiofluorenone, or benzyne. Thus both dienes (I and IV) show complete lack of reactivity in these Diels–Alder reactions.

A reaction of diketone III with 1.5 equiv of methylenetriphenylphosphorane gives the methylene ketone VII (60–70%) (Scheme I). Reaction of VII with more phosphorane yields diene IV. The ultraviolet absorption spectrum of VII shows only one maximum at  $\lambda$  300 m $\mu$  ( $\epsilon$  40), again indicating the absence of resonance between the methylene and the carbonyl group. The ultraviolet spectra of the exocyclic cyclohexanedienes V and VI indicate diminished resonance between the double bonds but Diels–Alder adducts of these dienes can be obtained.<sup>14</sup> Since in the dienes I and IV there is a complete lack of resonance between the double bonds and no Diels–Alder adducts could be obtained, it appeared interesting to study the spectroscopic and chemical properties of 2,3-diisopropyl-1,3-butadiene (VIII). We expected that the steric hindrance in diene VIII would be intermediate between the hindrance in dienes V and VI, on the one hand, and dienes I and IV, on the other hand. Diene VIII was not known in the literature and several routes for its preparation were tried. A double Wittig reaction on 2,5-dimethyl-3,4-hexanedione analogous to the preparation of diene IV was unsuccessful.<sup>17</sup> 2,3-Diisopropyl-1,3-butadiene (VIII) was prepared *via* the route shown in Scheme II. Kolbe electrolysis of monoester IX gave 2,3-diisopropylsuccinic acid diethyl ester (X).<sup>18</sup> Reduction of diester X with lithium aluminum

hydride gave diol XI in 90% yield. The dehydration of this diol to diene VIII was accomplished by pyrolysis of the dixanthate XII (Chugaev reaction).<sup>19</sup>

The utility of the Chugaev reaction is dependent upon the ease of formation and purification of the xanthate. The most commonly encountered difficulty in the preparation of xanthates is formation of the metal salt of the alcohol.

Reaction of diol XI with potassium in xylene gave only 5–10% yield of the dixanthate XII in a slow, heterogeneous reaction. A major improvement was made by using dimethyl sulfoxide as solvent and dimethyl sulfoxide carbanion as the stronger base. In an equilibrium reaction the bisalcoholate of diol XI is formed rapidly; the reaction remains homogeneous since the salt stays in solution.

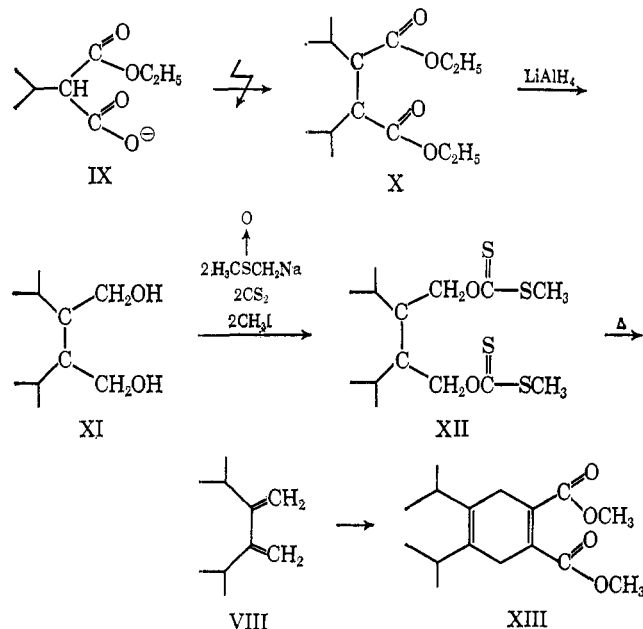
Addition of carbon disulfide and methyl iodide results in the formation of the dixanthate XII in 50–60% yield.<sup>20</sup> The pyrolysis of dixanthate XII was performed in a normal distillation apparatus. At atmospheric pressure and 225–250° bath temperature, 2,3-diisopropyl-1,3-butadiene (VIII) was obtained in 60% yield. The ultraviolet spectrum of diene VIII shows a maximum at  $\lambda$  223 m $\mu$  ( $\epsilon$  6180); this maximum occurs at slightly lower wavelength than predicted for a dialkyl-substituted butadiene ( $227 \pm 5$  m $\mu$ ),<sup>21</sup> but the deviation is small. 2,3-Diisopropyl-1,3-butadiene (VIII) does give a Diels–Alder adduct with acetylenedicarboxylic acid dimethyl ester. These data indicate that the behavior of the diisopropylbutadiene VIII is more like that of a normal butadiene. Steric hindrance increases rapidly when *t*-butyl groups are substituted for isopropyl groups. From this work and from that of others<sup>22</sup> it is clear that substantial steric hindrance must be present before the chemical and physical properties of substituted butadienes are materially affected.

## Experimental Section

Infrared spectra were determined in carbon tetrachloride, in potassium bromide disks or neat on a Perkin-Elmer Infracord Model 137 or on a Unicam SP 200. Ultraviolet spectra were recorded on a Zeiss spectrophotometer, Model P.M.Q. II, the solvents are indicated. Nuclear magnetic resonance (nmr) spectra were taken on a Varian A-60 spectrometer with tetramethylsilane as internal standard and are reported in  $\tau$  values (parts per million). The solvents used are indicated. Melting points and boiling points are uncorrected. Microanalyses were performed by the Analytical Department of this laboratory under the supervision of Mr. W. M. Hazenberg.

**3,3,6,6-Tetramethyl-4,5-dimethylene-1-thiacycloheptane (IV).**—A dispersion of 7.2 g (0.15 mol) of sodium hydride (as a 50% dispersion in mineral oil) was washed twice with 25 ml of sodium-dried pentane in a nitrogen atmosphere to remove the mineral oil. Then 150 ml of dimethyl sulfoxide (dried and distilled from calcium hydride) was added *via* a syringe, and the mixture was heated at 70–75° for 45 min. The resulting solution was cooled to room temperature, and 54 g (0.15 mol) of methyltriphenylphosphonium bromide in 150 ml of dimethyl sulfoxide was added *via* a syringe. The dark red solution of the ylide was stirred at room temperature for 15 min and then 10 g (0.05 mol) of diketone III in 25 ml of dimethyl sulfoxide was added over a

SCHEME II



IX gave 2,3-diisopropylsuccinic acid diethyl ester (X).<sup>18</sup> Reduction of diester X with lithium aluminum

(16) We thank Dr. S. van der Werf for the performance of the nmr experiments and calculations.

(17) 2,3-Di-*t*-butyl-1,3-butadiene (I) could not be prepared by a double Wittig reaction with dipivaloyl (II). A double Wittig reaction with benzil gave 2,3-diphenyl-1,3-butadiene in 15% yield. The double Wittig reaction is thus of limited use in the preparation of dienes from  $\alpha$  diketones.

(18) L. Ebersson, *Acta Chim. Scand.*, **13**, 40 (1959).

(19) R. Nace, *Org. Reactions*, **12**, 57 (1962).

(20) Cholesterol and *n*-octanol also gave the corresponding xanthates rapidly and in 90% yield. The general usefulness of this improved method for making xanthates is being investigated further.

(21) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 196.

(22) G. Vogel, *Chem. Ind. (London)*, 1954 (1964).

period of 15 min. The reaction mixture was stirred at 45° for 20 hr and then poured into 300 ml of ice-water. The aqueous phase was filtered and extracted thoroughly with pentane. The pentane fractions were combined and washed with 100 ml of a 1:1 water-dimethyl sulfoxide solution and then with 200 ml of a saturated sodium chloride solution. The pentane solution was dried over sodium sulfate and then concentrated to a volume of about 20 ml. The solution was subjected to chromatography using 50 g of neutral aluminum oxide (activity grade 1) to remove all of the triphenylphosphine oxide. Elution with pentane and evaporation of the solvent gave a residue. Distillation gave 3.0 g (30%) of colorless diene IV: bp 78° (1.9 mm);  $n_D^{20}$  1.5135; ir spectrum (neat), absorptions at 3100 and 1620  $\text{cm}^{-1}$ ; nmr spectrum (20% in carbon tetrachloride), two singlets at  $\tau$  8.90 and 8.73 (methyl protons), AB multiplet centered on 7.64 (ring methylene protons), AB multiplet at 5.35 and 5.07 (vinyl protons).

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{20}\text{S}$  (196.35): C, 73.40; H, 10.26; S, 16.34. Found: C, 73.7, 73.7; H, 10.2, 10.2; S, 16.1, 16.1.

**3,3,6,6-Tetramethyl-4-methylene-1-thiacycloheptane-5-one (VII).**—To 0.1 mol of methylenetriphenylphosphorane in 200 ml of dimethyl sulfoxide was added 14.5 g (0.07 mol) of diketone III in 35 ml of dimethyl sulfoxide at room temperature (for details, see diene IV). The reaction mixture was stirred at 45° for 2.5 hr and then poured into 300 ml of ice-water. The reaction mixture was worked up as described for diene IV. The yield of methylene ketone VII was 9.2 g (63%): bp 60° (0.5 mm); mp 40.5–41°; ir spectrum (neat), absorptions at 1680 and 1610  $\text{cm}^{-1}$ ; nmr spectrum (10% in carbon tetrachloride), two singlets at  $\tau$  8.80 and 8.83 (methyl protons), two singlets at 7.53 and 7.47 (ring methylene protons), two singlets at 5.28 and 4.98 (vinyl protons); uv spectrum (in 96% ethanol),  $\lambda_{\text{max}}$  300  $\text{m}\mu$  ( $\epsilon$  40).

*Anal.* Calcd for  $\text{C}_{11}\text{H}_{18}\text{OS}$  (198.33): C, 66.61; H, 9.15; S, 16.16. Found: C, 66.7, 66.7; H, 9.2, 9.2; S, 16.2, 16.2.

**2,3-Diphenyl-1,3-butadiene.**—To 0.13 mol of methylene triphenylphosphorane in 225 ml of dimethyl sulfoxide was added 9.25 g (0.044 mol) of benzil in 30 ml of dimethyl sulfoxide in 10 min at room temperature. The reaction mixture was stirred for 3 hr in a nitrogen atmosphere at room temperature and then poured into 300 ml of ice-water. The reaction mixture was worked up as described for diene IV. The yield of 2,3-diphenyl-1,3-butadiene was 1.5 g (15%): mp 45–46° (lit.<sup>23</sup> mp 46–47°); nmr spectrum (20% in carbon tetrachloride), two doublets at  $\tau$  5.23 and 5.45 (vinyl protons), multiplet centered on 2.21 (aromatic protons).

**$\alpha,\alpha'$ -Diisopropylsuccinic Acid Diethyl Ester (X).**—A mixture of *d,l* and meso  $\alpha,\alpha'$ -diisopropylsuccinic acid diethyl ester (X) was obtained as described by Ebersson.<sup>18</sup> The yield of diester X, bp 134–136° (15 mm),  $n_D^{20}$  1.4345, was 60% [lit. bp 125–127° (11 mm),  $n_D^{20}$  1.4350<sup>18</sup>].

**2,3-Diisopropyl-1,4-butanediol (XI).**—A solution of 60 g (0.23 mol) of diester X in 200 ml of dry ether was added to a suspension of 11.4 g (0.30 mol) of lithium aluminum hydride in 200 ml of dry ether. The reaction mixture was refluxed for 1 hour after all the diester was added. The reaction products were hydrolyzed by careful addition of water and of a dilute solution of hydrochloric acid in water. The ether layer was separated, and the water layer was extracted with ether. The combined ether fractions were washed with water and dried over potassium carbonate. The ether was evaporated, and the residue was distilled *in vacuo*. The yield of diol XI, bp 109–110° (0.4 mm), was 36 g (90%). Analytically pure diol XI, mp 78–83°, was obtained by crystallization from petroleum ether (bp 60–80°): ir spectrum (neat), absorption at 3350  $\text{cm}^{-1}$ ; nmr spectrum

(10% in deuteriomethanol), two doublets at  $\tau$  9.13 and 9.03 and at 9.07 and 8.95 (methyl protons), multiplet from 8.0 to 8.8 (tertiary protons), doublet at 6.38 and 6.32 (methylene protons).

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{22}\text{O}_2$  (174.18): C, 68.95; H, 12.68. Found: C, 69.2, 68.8; H, 12.4, 12.5.

**Dixanthate of 2,3-Diisopropyl-1,4-butanediol (XII).**—A solution of 5.3 g (0.11 mol) of methylsulfinylsodium in 150 ml of dimethyl sulfoxide was obtained as described for diene IV. To this solution was added at room temperature 8.7 g (0.05 mol) of diol XI in 25 ml of dimethyl sulfoxide. The reaction mixture was stirred for 1 hr and then 9.2 g (0.12 mol) of carbon disulfide in 25 ml of dimethyl sulfoxide was added. The temperature of the reaction mixture was kept below 45° by external cooling. After 1 hr 17 g (0.12 mol) of methyl iodide in 25 ml of dimethyl sulfoxide was added. The reaction mixture was stirred for 1 hr and then poured into 300 ml of ice-water. The water solution was extracted with pentane; the pentane fractions were washed with a small portion of water and dried over sodium sulfate. The pentane was evaporated, and the residue was crystallized from ethanol. The yield of dixanthate XII, mp 82–84°, was 8.8–10.6 g (50–60%): nmr spectrum (10% in carbon tetrachloride), two doublets at  $\tau$  8.90, 9.00 and 9.00, 9.10 (methyl protons), multiplet at 7.9–8.25 (tertiary protons), singlet at 7.45 (sulfur methyl protons), and a doublet at 5.40 and 5.32 (methylene protons).

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{26}\text{O}_2\text{S}_4$  (354.63): C, 47.41; H, 7.39; S, 36.17. Found: C, 47.9, 47.5; H, 7.5, 7.5; S, 35.3, 35.7.

**2,3-Diisopropyl-1,3-butadiene (VIII).**—In a Claisen flask 4.5 g (0.013 mol) of dixanthate XII was slowly heated to 230° (bath temperature). The bath temperature was kept at 230–250° until no more gas evolution was observed. The distillate was dissolved in pentane and treated with a dilute solution of mercuric chloride in ethanol. The alcoholic solution was filtered, and 100 ml of water was added. The water solution was extracted with pentane. The pentane solution was washed with water and dried over sodium sulfate. The solvent was evaporated, and the residue was distilled at atmospheric pressure. The yield of diene VIII, bp 140°,  $n_D^{20}$  1.4405, was 1.1 g (60%). An analytical sample was obtained by means of preparative glpc (F & M 810, 4 ft, 75°): ir spectrum (neat, 0.1-mm cell), absorptions at 3080, 1625, and 1600  $\text{cm}^{-1}$ ; nmr spectrum (10% in carbon tetrachloride), doublet at  $\tau$  9.00 and 8.90 (methyl protons), heptet centered on 7.63 (tertiary protons), two doublets at 5.08, 5.10 and 5.17, 5.19 (vinyl protons); uv spectrum (in isoctane),  $\lambda_{\text{max}}$  223  $\text{m}\mu$  ( $\epsilon$  6180).

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{18}$ : C, 86.88; H, 13.12. Found: C, 86.8, 87.0; H, 13.0, 13.1.

**1,2-Dicarbomethoxy-4,5-diisopropyl-1,4-cyclohexadiene (XIII).**—A solution of 600 mg (4.35 mmol) of diisopropylbutadiene VIII and 618 mg (4.35 mmol) of acetylenedicarboxylic acid dimethyl ester in 10 ml of benzene was refluxed for 5 hr. The solvent was evaporated, and the residue was recrystallized from petroleum ether (bp 40–60°). The yield of adduct XIII, mp 97–100° (Kofler blok), was 720 mg (60%): ir spectrum (KBr disk), absorptions at 1710 and 1650  $\text{cm}^{-1}$ ; nmr spectrum (10% in deuterioacetone), doublet at  $\tau$  9.05 and 8.93 (methyl protons), singlet at 7.07 (methylene protons), singlet at 6.27 (ester methyl protons).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{24}\text{O}_4$  (280.35): C, 68.55; H, 8.63. Found: C, 68.3, 68.3; H, 8.5, 8.6.

**Registry No.**—IV, 16134-09-1; VII, 16134-10-4; VIII, 16134-06-8; XI, 16134-07-9; XII, 16170-26-6; XIII, 16134-08-0; 2,3-diphenyl-1,3-butadiene, 2548-47-2.

(23) C. F. H. Allen, C. G. Eliot, and A. Bell, *Can. J. Res.*, **17B**, 75 (1939); *Chem. Abstr.*, **33**, 6284 (1939).