Synthesis of Tetraallylmethane

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Tetraallylmethane has been synthesized by the following route: triallylcarbinol → triallylmethyl chloride → triallylmethylmagnesium chloride → tetraallylmethane *via* reaction with allyl bromide. Its stability is such that it can be kept for many months without polymerizing. An isomer of the tetraallylmethane is formed in the last step of the synthesis and is believed to be 4-allyl-4-vinyl-1,7-octadiene. It is presumed to be formed by the rearrangement of one homoallylic carbanion to an isomeric one through a cyclopropylmethyl carbanion intermediate.

We have prepared and characterized tetraallylmethane, an interesting olefin due to the tetrahedral symmetry about the quaternary central carbon atom. Although two syntheses were reported in a patent,[1] the yields were not stated and no evidence was included to support the assigned structure. The first synthesis involved the reaction of pentaerythritol tetrabromide with vinylmagnesium chloride in tetrahydrofuran solvent at 50°; the second involved the reaction of carbon tetrabromide with allylmagnesium bromide under Grignard conditions. We repeated the latter, but the only material obtained having approximately the right boiling range contained 25% bromine plus oxygen (*i.e.*, the analysis for carbon and hydrogen totalled 75%), and quantitative hydrogenation showed only two double bonds per molecular weight of $C_{13}H_{20}$. Our successful synthesis started with the known triallylcarbinol, which was converted successively into the triallylmethyl chloride and into the corresponding Grignard reagent, both of which are new compounds. The latter reacted with allyl bromide to yield a mixture of tetraallylmethane and an isomeric compound in a ratio of ~2:1.

Conversion of the triallylcarbinol into the chloride was noteworthy in that the reaction occurred relatively slowly (2 hr were required) with the usual concentrated hydrochloric acid–zinc chloride mixture at 0°, and that the triallylmethyl chloride was soluble in the concentrated hydrochloric acid. A striking array of dark red to deep purple colors was produced during this reaction. The colorless triallylmethyl chloride was isolated in 66% yield from the concentrated acid mixture by extraction with benzene followed by distillation. Attempts to prepare the chloride from the alcohol using concentrated hydrochloric acid alone were unsuccessful both at 0° (incomplete reaction). 25°, and steam bath temperature (where polymeric material was formed). The alcohol reacted incompletely with cold, concentrated hydrobromic acid, and only polymeric material was obtained by warming the alcohol with thionyl chloride.

Triallylmethyl chloride was converted into the Grignard reagent in 85% yield, using tetrahydrofuran as the solvent. The filtered Grignard solution was allowed to react at room temperature overnight with a threefold excess of allyl bromide; 5 hr was sufficient for the reaction to go to approximately 90% completion. The mechanism may be either SN2 or SN2′ with respect to the attack of the nucleophilic Grignard reagent on the allyl bromide; the same product results in either case. A tridecatetraene fraction was obtained in 34% yield based on triallylmethyl chloride. It consisted of two major components: two-thirds was tetraallylmethane and one-third was an isomer. Distillation through a spinning band column gave only incomplete separation. However, the two isomers could be separated by vpc using an 8-m diisodecyl phthalate column.

The tetraallylmethane fraction, obtained in 15% yield based on the starting triallylcarbinol, was characterized by elemental analysis, quantitative hydrogenation, and ir and nmr spectra. Tetraallylmethane appears to be quite stable insofar as samples could be kept for 1 year without noticable change. In contrast, the isomeric material polymerized under the same conditions. Most of the common oxidizing agents were used in attempts to convert the tetraallylmethane into methanetetraacetic acid, but only traces could be obtained.

Nmr Spectra.—Triallylcarbinol, triallylmethyl chloride, and tetraallylmethane all have nmr spectra typical of an allyl group. The outstanding features are a sharp doublet at about δ 2.2 (J = 7 Hz) due to the methylene group, and a sharp peak at δ 5.2 due to each of the terminal vinyl hydrogens coupling with the nonterminal vinyl hydrogen (J = 10 and 17 Hz) and two of these split peaks being superimposed. The other peaks due to the terminal vinyl hydrogens caused a poorly resolved quartet at δ 4.9. The splitting constant for the terminal vinyl hydrogens was 2 Hz. The nonterminal vinyl hydrogen showed up as a broad multiplet centered at δ 5.9.[2]

Structure of the Isomer.—The identical features of the spectra of allyl alcohol, triallylcarbinol, triallylmethyl chloride, and the final isolated tetraallylmethane (Figure 1) clearly show that no isomerized product is present in the triallylcarbinol or the triallylmethyl chloride, even though the formation of the latter presumably procceds through a triallylmethyl carbonium ion. It is in the final reaction step involving a homoallylic carbanion that the nmr spectrum of the product gives the first evidence (broad multiplet at δ 1.4) that an isomeric material is present.

All of the analytical and spectral data for the isomeric compound are consistent with structure **4.** This could arise from the homoallylic carbanion (**1**) rearranging through a cyclopropylmethyl carbanion (**2**) to an isomeric homoallylic carbanion (**3**) which in turn would give **4,** 4-allyl-4-vinyl-1,7-octadiene.[3]

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[1] A. J. Mital and J. F. Jones, U. S. Patent 2,996,488 (1961).

[2] The nmr spectra were initially obtained by Dr. William McFarlane and we are deeply indebted to him for his interpretation. A detailed analysis of the spectra is in the M. S. thesis of R. J. Bianchi, University of Maryland, 1964.

[3] We are indebted to Dr. Paul Mazzocchi for this explanation of the formation of **4**. A review of many interesting examples of this rearrangement is in D. J. Cram's "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 215–217.

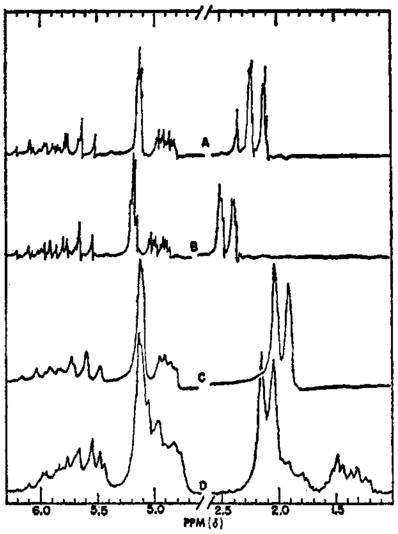
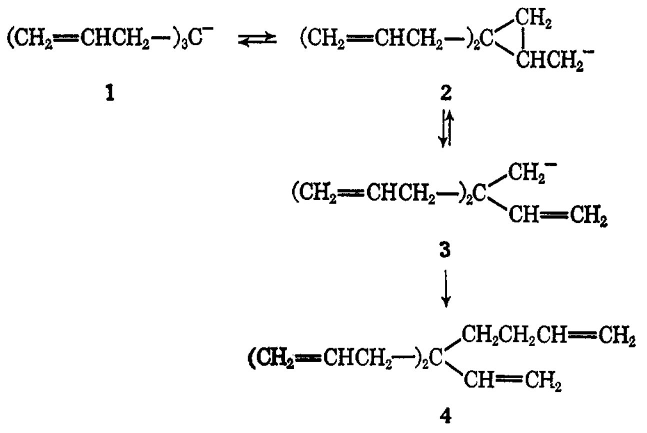


Figure 1.—Partial 60-Mc nmr spectra of (a) triallylcarbinol, (b) triallylmethyl chloride, (c) tetraallylmethane, and (d) isomer of tetraallylmethane; neat (tetramethylsilane, internal standard).



$$(CH_2{=}CHCH_2{-})_3C^- \rightleftharpoons (CH_2{=}CHCH_2{-})_2C\overset{CH_2}{\underset{CHCH_2^-}{|}}$$

1 2

$$(CH_2{=}CHCH_2{-})_2C\overset{CH_2^-}{\underset{CH{=}CH_2}{}}$$

3

$$(CH_2{=}CHCH_2{-})_2C\overset{CH_2CH_2CH{=}CH_2}{\underset{CH{=}CH_2}{}}$$

4

Examination of Fisher–Hirshcfelder models shows that there is no free rotation between the methylene groups in the butenyl chain of IV. These four hydrogens would accordingly appear in the nmr spectrum as an AA'BB' multiplet superimposed in part on the allylic doublet at δ 2.0, and this is what is observed.

Experimental Section

All melting and boiling points are corrected. The ir spectra were recorded on a Beckman IR-5 except for those of tetraallylmethane and the isomer which were recorded on a Beckman IR-8; the liquids were measured as films between sodium chloride plates. The nmr spectra were recorded on a Varian A-60, using tetramethylsilane as the internal standard. An F & M Model 300 vapor phase chromatograph was used for the vpc analyses. Other analyses are by Dr. Franz J. Kasler.

Triallylmethyl Chloride.—Triallylcarbinol was prepared from allylmagnesium bromide and ethyl carbonate.[4] It was converted into the chloride by stirring 46 g (0.3 mol) at ice-bath temperature with 169 g (0.7 mol of acid) of Lucas reagent prepared by mixing equimolar amounts of anhydrous zinc chloride and concentrated hydrochloric acid. After 20 min, the ice bath was removed and the mixture was stirred for another 2 hr. When 100 ml of benzene was added and the mixture was stirred for 5 min, two layers separated. After the acid layer was reextracted with benzene, the combined benzene extracts were dried overnight with anhydrous magnesium sulfate and filtered. Small portions of magnesium sulfate and anhydrous sodium bicarbonate were then added until there was no detectable odor of hydrogen chloride. On distillation through a short fractionating column, there was obtained 30 g (59%) of triallylmethyl chloride: bp 69–70° (9 mm); $n^{25}D$ 1.4725; ir 3025, 2900, 1850, 1640, 1430, 1310, 1290, 1270, 1240, 1145, 1030, 1000, 970, 920, 855, 830, and 660 cm^{-1}; nmr (neat) δ 5.9 (m, 3, =CH–), 5.2 (sharp singlet, 3, one-half $H_2C{=}$, see Discussion), 5.0 (m, 3, J = 2 and 17 Hz, one-half $H_2C{=}$), 2.50 (d, 6, J = 7 Hz, $-CH_2-$).

Anal. Calcd for $C_{10}H_{15}Cl$: C, 70.38; H, 8.85; Cl, 20.77. Found: C, 70.75; H, 8.87; Cl, 20.40.

Triallylmethylmagnesium Chloride.—A 500-ml three-necked flask was charged with 18 g of magnesium turnings, and a crystal of iodine was added and sublimed onto the magnesium with a small flame. After the flask had cooled, 15 ml of tetrahydrofuran was added, the mixture was heated to 50°, and 1 ml of triallylmethyl chloride together with a few drops of methyl iodide were added. The reaction started shortly thereafter and an ice bath was temporarily required to control the temperature. Finally, a heating mantle was used to maintain the temperature at the refluxing point. An additional 40 g (total of 0.24 mol) of triallylmethyl chloride dissolved in 165 ml of tetrahydrofuran was added dropwise over a period of 6 hr while the reaction was maintained at reflux temperature. Refluxing was continued for an additional 1.5 hr, and the mixture was then allowed to stand overnight. An acidimetric titration, using Gilman's method,[5] indicated an 85% yield of the Grignard reagent. The latter was placed in a narrow-mouth funnel containing a medium-porosity sintered glass plate, and was filtered under nitrogen pressure into a dropping funnel for use in the next reaction.

Tetraallylmethane.—The triallylmethylmagnesium chloride reagent (0.2 mol) was added over a 4-hr period under an atmosphere of nitrogen to 81 g (0.67 mol) of allyl bromide dissolved in 60 ml of tetrahydrofuran while the reaction mixture was cooled to 15°. The reaction was followed by testing qualitatively for the presence of Grignard reagent with Michler's ketone. (The usual iodometric procedure could not be used because of the addition of iodine to the double bonds, and the acidimetric titration failed because of rapid hydrolysis of the excess allyl bromide.) The reaction was also followed by decomposing a sample with acid and analyzing the hydrocarbon mixture by vpc using a diisodecyl phthalate column. Four hours after the last addition of the Grignard reagent, the size of the major peak indicated that the reaction was complete. After standing overnight, the reaction mixture was decomposed with dilute hydrochloric acid and the hydrocarbon mixture was extracted with ether and washed with water. Distillation gave 19.7 g of crude tetraallylmethane, bp 102–108° (25 mm). Following a steam distillation, the material was distilled using a 60-cm spinning band column and the fractions obtained are listed in Table I.

The mixtures were analyzed by vpc using a 2-m diisodecyl phthalate column. The total of 10.4 g of tetraallylmethane in the various fractions corresponds to a 30% yield based on the Grignard reagent or a 15% yield based on the starting triallylcarbinol. Data on the 90% tetraallylmethane–10% isomer fractions are as follows: $n^{25}D$ 1.4726; ir and nmr same as pure tetraallylmethane separated by vpc (see below). A quantitative hydrogenation of 79 mg of the sample resulted in the absorption of 42 ml of hydrogen at 23° (762 mm), equivalent to 3.92 double bonds per mole of $C_{13}H_{20}$.

Anal. Calcd for $C_{13}H_{20}$: C, 88.58; H, 11.42. Found: C, 88.79; H, 11.20.

Data on the 50% tetraallylmethane–50% isomer fraction are as follows: $n^{25}D$ 1.4712; for spectra, see data below on pure isomer fraction separated by vpc. A quantitative hydrogenation of 81 mg of the sample resulted in the absorption of 46 ml of hydrogen at 23° (760 mm), equivalent to 4.08 double bonds per mole of $C_{13}H_{20}$.

TABLE I

FRACTIONATION OF CRUDE TETRAALLYLMETHANE

Fraction	Amount, g	Bp (mm), °C	Ratio, tetraalylmethane/isomer
1	1.4	82 (14)	1:1
2	3.3	84.5–85.5 (13)	1:1
3	1.4	86.5–88 (12)	4:1
4	5.7	88–88.5 (12.5)	8:1
Residue	2.2		9:1

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[4] M. P. Dreyfuss, *J. Org. Chem.*, **28**, 3269 (1963).

[5] H. Gilman, E. A. Zoellner, and E. B. Dickey, *J. Amer. Chem. Soc.*, **51**, 1576 (1929).

Anal. Calcd for $C_{13}H_{20}$: C, 88.58; H, 11.42. Found: C, 88.85; H, 11.70.

The two isomers were separated by vpc using an 8-m 10% diisodecyl phthalate on 60–80 mesh silanized diatomaceous earth column (Diatoport S). Data on tetraallylmethane are as follows: ir 3068, 3000, 2980, 2840, 1638, 1440, 1410, 989, 905, and 850 cm^{-1}; nmr (neat) δ 5.8 (m, 4, =CH–), 5.13 (sharp singlet, 4, one-half H_2C=, see Discussion), 4.87 (q, 4, J = 2 and 17 Hz, one half H_2C=), and 1.98 (d, 8, J = 7 Hz, $-CH_2-$). Data on the isomeric compound (believed to be 4-allyl-4-vinyl-1,7-octadiene) are as follows: ir 3068, 3000, 2980, 2920, 2845, 1638, 1450–1430, 1410, 989, and 905 cm^{-1}. The nmr spectrum was similar to that of tetraallylmethane except for the following: the singlet at δ 5.13 and the quartet at 4.87 merged to give an eight-proton multiplet from 5.2 to 4.8; the sharp doublet at 1.98 now accounted for only six protons including a one proton shoulder from 2.0 to 1.7; and there was a two-proton multiplet from 1.7 to 1.2.

Registry No.—Tetraallylmethane, 19255-02-8; triallylmethyl chloride, 19255-03-9; **4**, 19255-04-0.

Negatively Substituted Acetylenes. II.[1] Cycloaddition Reactions with Styrenes

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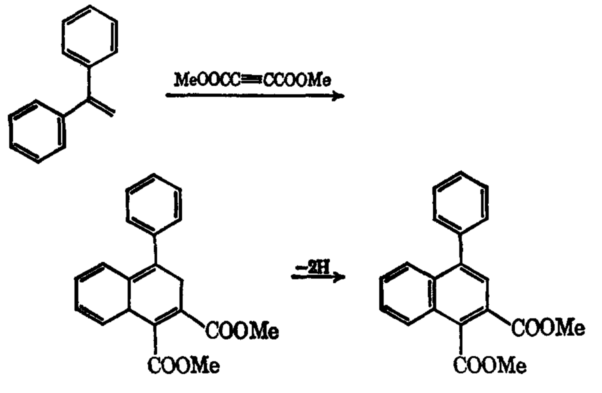
Activated acetylenes, such as dicyanoacetylene, acetylenedicarboxylic ester, and benzyne, react with styrenes to give 1:2 adducts of type **2** by a sequence of Diels-Alder addition and ene reaction. Unlike in previously reported additions of this nature, the styrene, and not the acetylene, acts as the enophile in the second step. From the reactions of dicyanoacetylene and benzyne with styrene, mixtures of *threo* and *erythro* adducts have been isolated, resulting from exoid and endoid attack by the styrene in the ene reaction. The fact that no β-phenylethyldihydronaphthalenes (*e.g.*, **22**) could be detected among the products indicates that in the transition state of the second-step ene reaction, hydrogen transfer has proceeded to a larger extent than carbon–carbon bond formation. The scope of these reactions is discussed.

The vinyl group and one of the aromatic double bonds of styrene form a diene system that is potentially capable of undergoing the Diels–Alder reaction. Although this possibility was foreseen at an early stage, examples of such additions are not so numerous as might be expected because of the tendency of styrenes to polymerize and copolymerize under the reaction conditions required. As a rule, only very reactive dienophiles will give nonpolymeric products in acceptable yields. The initial 1:1 adducts usually cannot be isolated; they either aromatize to give derivatives of dihydro- or tetrahydronaphthalene as exemplified in eq 1,[2,3] or add a second molecule of the dienophile. This second addition can either be another Diels–Alder reaction (*e.g.*, eq 2[4,5]), an ene reaction[6] as shown in



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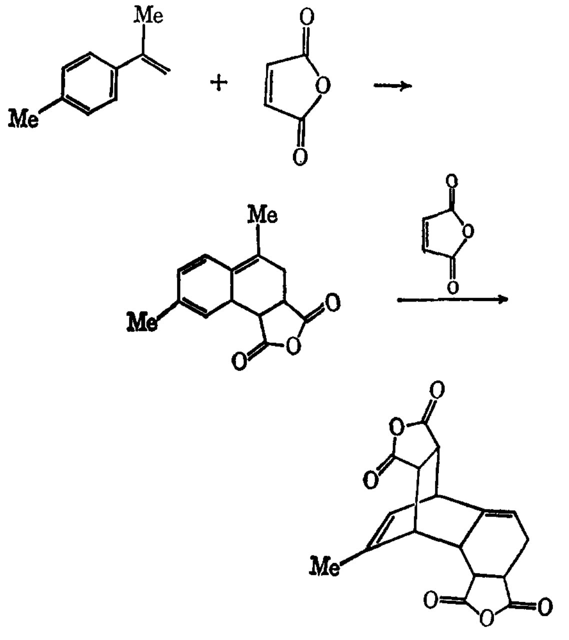

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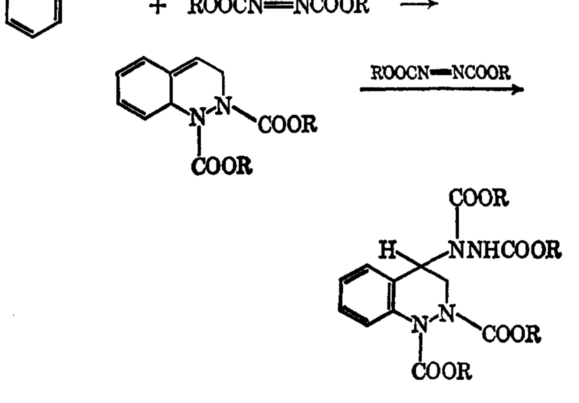

(3)

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[1] E. Ciganek and C. G. Krespan, *J. Org. Chem.*, **33**, 541 (1968) is considered to be paper I in this series.

[2] K. Alder, F. Pascher, and H. Vagt, *Ber.*, **75**, 1501 (1942).

[3] For reviews of the Diels-Alder addition, see A. S. Onishchenko, "Diene Synthesis," English translation, D. Davey, New York, N. Y., 1964; J. Sauer, *Angew. Chem.*, **78**, 233 (1966).

[4] This type of addition was first observed by T. Wagner-Jauregg, *Ber.*, **63**, 3213 (1930); *Ann. Chem.*, **491**, 1 (1931). The example of eq 2 is from ref 5.

[5] J. Hukki, *Acta. Chem. Scand.*, **5**, 31 (1951).

[6] For a brief review of the ene reaction see W. R. Roth, *Chimia* (*Aarau*), **20**, 229 (1966).