

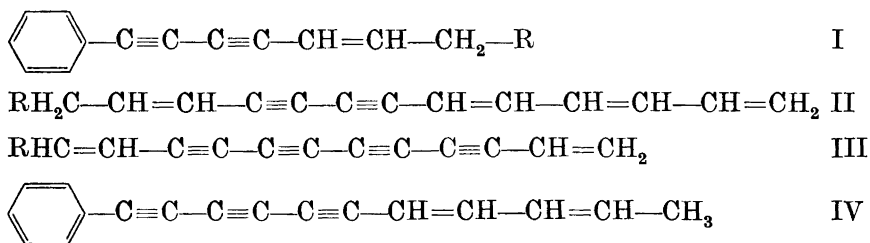
Studies Related to Naturally Occurring Acetylene Compounds. XXII* Correctional Studies on the Constitution of the Polyacetylenes of some Annual *Coreopsis* Species

JÖRGINE STENE SÖRENSEN and NILS ANDREAS SÖRENSEN

Institutt for Organisk Kjemi, Norges Tekniske Högskole, Trondheim, Norway

One of the polyacetylenes previously isolated from some annual *Coreopsis*-species and supposed to be 1-phenyl-undeca-1:3:5-triyne-7:9-diene (IV) is shown to be a mixture of trideca-1:3:11-triene-5:7:9-triyne (V, R = H), probably with *cis* configuration at the 3:4 double bond, and *trans*-1-phenyl-hepta-1:3-diyne-5-ene (I, R = H).

In the XVIIth Communication of this series J. Stene Sørensen and N. A. Sørensen¹ described the isolation of 4 new acetylenic compounds from some annual garden varieties of the genus *Coreopsis*, viz. *C. tinctoria* Nutt., *C. Drummondii* Torr. & Gray and *C. cardaminifolia* (D.C.) Torr & Gray. The 4 new acetylenic compounds were given the following constitutional formulas I, R = OCOCH₃, II, III, R = H, and IV.



The correctness of I, R = OCOCH₃ was proved by Bruun, Skattebøl and Sørensen² by the total synthesis, revealing that the configuration of the double bond is *trans*. II was shortly afterwards synthesised by Bohlmann³; this synthesis confirmed the supposition of Sørensen and Sørensen¹ that the configuration was all-*trans*.

* XXI Communication, cf. Festschrift Arthur Stoll, Basel 1957.

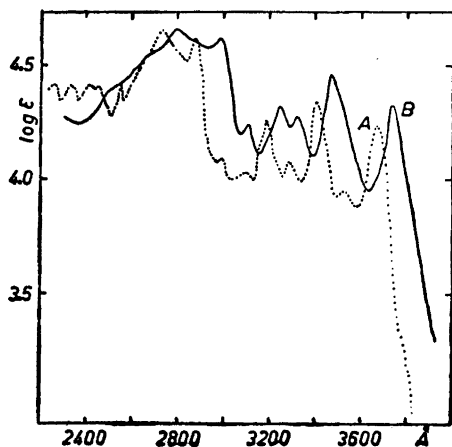


Fig. 1. Ultraviolet absorption of
A: "3650" Hydrocarbon supposed to be IV according to Sørensen *et al.*¹
B: *trans* IV, redrawn from Bohlmann *et al.*³

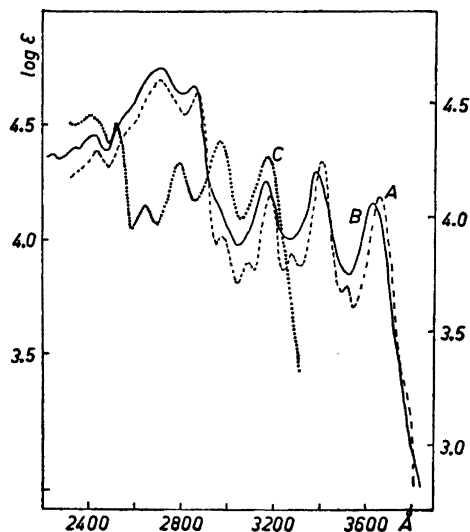


Fig. 2. Ultraviolet absorption in hexane of:
A. *cis* trideca-1:3:11-triene-5:7:9-triyn-
B. *trans* trideca-1:3:11-triene-5:7:9-
triyne
C. *trans* 1-phenyl-hepta-1:3-diyne-5-ene
(scale right side)

The hydrocarbon III, R = H was synthesised by Jones, Thompson and Whiting⁴ and turned out to be very similar but not identical with the so-called 3910-hydrocarbon from *Coreopsis* oils; Skattebøl⁵ synthesised both the *trans* and the *cis* isomers of the homologue III, R = CH₃. The *trans* compound turned out to be identical with the 3910-hydrocarbon, m.p. 43°C, which has a rather wide occurrence inside some tribes of the family *Compositae*. This brilliant synthetic work further established that the *cis* compound III, R = CH₃, undoubtedly also occurred in some chromatographic fractions from *Coreopsis* species measured by Sørensen and Sørensen¹ in the infrared.

Bohlmann⁶ described the synthesis of the *trans* isomer of IV. Although there was some similarity in the ultraviolet spectra, synthetic *trans* IV was undoubtedly different from the compound occurring in the flowering parts of the investigated annual *Coreopsis* species, *cf.* Fig. 1. Bohlmann put forward the hypothesis that the naturally occurring compound might be one of the possible *cis* isomers. This, however, was unlikely since the synthetic *trans* isomer has the ultraviolet absorption maxima about 65 Å at longer wavelengths than the natural compound, whereas *cis* polyen-ynic isomers mostly absorb at longer wavelengths than their corresponding *trans* isomers⁷.

I—III were solids which could be purified by recrystallisation; IV, however, was a liquid the homogeneity of which was difficult to guarantee. Sørensen and Sørensen¹ recorded some difficulties in their experimental work; thus

the perhydrogenation product, which should be 1-phenyl-*n*-undecane could not be brought to correct melting point, -5°C , although the melting point obtained, -8 to -6.5°C , came very close to that of the best synthetic preparation of 1-phenyl-*n*-undecane which Sørensen and Sørensen were able to synthesise and no clear-cut m.p. depression could be observed.

That in reality the constitution of the perhydrogenation product was completely misinterpreted became clear when Dr. A. J. P. Martin most kindly investigated a melting point sample of the perhydrogenation product in his vapour fractometer. According to a personal report from Dr. Martin the perhydrogenation product contained at least two products one of which might possibly be *n*-tridecane. Thus the constitution of the compound supposed to be IV had to be reinvestigated.

The characteristic double maxima in the longwaved band group of this compound, *cf.* Fig. 1, were taken by Sørensen and Sørensen as an indication of the occurrence of a mixture of compounds. However, all chromatographic fractions from the different garden varieties showed the same relative intensity of the main and subsidiary maxima, a very improbable happening with a mixture of compounds.

By the reinvestigations these double maxima in ultraviolet were again taken as the analytical mark, but every effort to obtain an alteration in the relative intensities by taking narrower cuts in the chromatographic fractions were again without success.

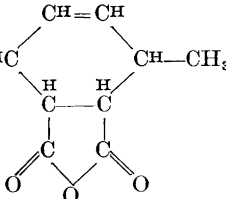
The picture remained unchanged when the chromatographic cuts were made still narrower; elution with 2—4 % benzene in petroleum ether taking 5—20 fractions at each concentration. When, however, these fractions with conform long-wave band group in the ultraviolet region simultaneously were investigated in the infrared region characteristic definite differences emerged. The characteristic phenyl-peaks at 1 494, 753 and 686 cm^{-1} changed in intensity relative to the acetylenic one at 2 200 cm^{-1} and a characteristic peak at 775 cm^{-1} .

Reinspection of the ultraviolet spectra then revealed that the fractions with the most intensive phenyl peaks in the infrared had some extra ultraviolet bands at 3 180 and 2 970 ÅU. With these experimental facts well established repeated chromatography on deactivated alumina finally led to a separation of this part of the flower oil into two components of constant properties. Both could be crystallised. Recrystallisation seemed rather unsuccessful however, as a method of separation, possibly because of mixed crystals. Both components were very readily soluble in most solvents which of course hampered purification of small amounts of substance by recrystallisation.

Fig. 2. gives the ultraviolet spectra of the 2 compounds. As will be seen the main component still has the characteristic double maxima in the long-wave band group. Fig. 3, which gives the infrared spectra, reveals that the most long-wave chromophore belongs to a compound containing no phenyl group, whereas the minor component with first maximum in ultraviolet at 3 180 Å obviously is a phenyl compound.

With the tedious separation of the two components achieved constitutional work could again be started.

Table 1. Ultraviolet absorption maxima of ene-triynes and phenyl-triynes (Å).

$\text{I}_3\text{C}-(\text{C}\equiv\text{C}-)_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_3^9$	3 286	3 081	2 890	2 725	2 577	2 425	2 310
$\text{I}_3\text{C}-\text{CH}=\text{CH}-(\text{C}\equiv\text{C}-)_3-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_3^8$	3 300	3 085	2 895	2 730	2 580	2 422	2 305
$\text{I}_3\text{C}-(\text{C}\equiv\text{C}-)_3-\text{CH}=\text{CH}-\text{CH}_2\text{OC}_2\text{H}_5^{10}$	3 295	3 080	2 890	2 725	2 578	2 410	2 300
$\text{I}_3\text{C}-(\text{C}\equiv\text{C}-)_3-\text{CH}=\text{CH}-\text{CH}_2-\text{COOH}^{10}$	3 300	3 090	2 900	2 730	2 570	2 435	2 335
${}^1_6\text{H}_5-(\text{C}\equiv\text{C}-)_3-\text{CH}_3^{11}$	3 309	3 097	2 908	2 735	2 590	2 504	2 380
${}^1_6\text{H}_5-(\text{C}\equiv\text{C}-)_3-\text{C}_2\text{H}_5^2$	3 315	3 100	2 905	2 735	2 595	2 510	2 387
${}^1_6\text{H}_5-(\text{C}\equiv\text{C}-)_3-\text{HC}$ 	3 335	3 125	2 935	2 767	—	2 545	2408*

* in ether

The hydrocarbon with the first maximum at 3 670 Å could be crystallised from petroleum ether and showed m.p. 50.5—56°C. By the catalytical hydrogenation 8.25 moles of hydrogen were taken up. The perhydrocompound crystallised readily in the refrigerator m.p. —7°. *n*-Tridecane has m.p. —6.5 to —6°, a 1:1 mixture showed no depression. The infrared spectrum was in every detail identical with that of *n*-tridecane. Although normal paraffins higher than *n*-decane show nearly identical infrared spectra the identity of the perhydrogenation product and *n*-tridecane should be well established.

Sørensen and Sørensen¹ obtained in very small yield an adduct with maleic anhydride from what they supposed to be 1-phenyl-undeca-1:3:5-triyn-7:9-diene IV. The yield was too small for elementary analysis, the m.p. was given as 146°C and the adduct was characterised by a U.V. spectrum which came very close to that of 1-phenyl-octa-1:3:5-triyn-7:9-diene.

It turned out that this adduct belongs to the aliphatic hydrocarbon with the characteristic double maxima. From the pure hydrocarbon the yield was appreciably higher, but still low.

The fact which was overlooked by Sørensen and Sørensen was that the spectra of phenyl-triynes and ene-triynes are very similar, especially in the long-wave band group. The main difference is a small displacement of the first sharp maximum of the short-wave band group. As will be seen from Table 1 where some characteristic examples are collected, the phenyl triynes have this maximum some 90 Å at longer wave-lengths.

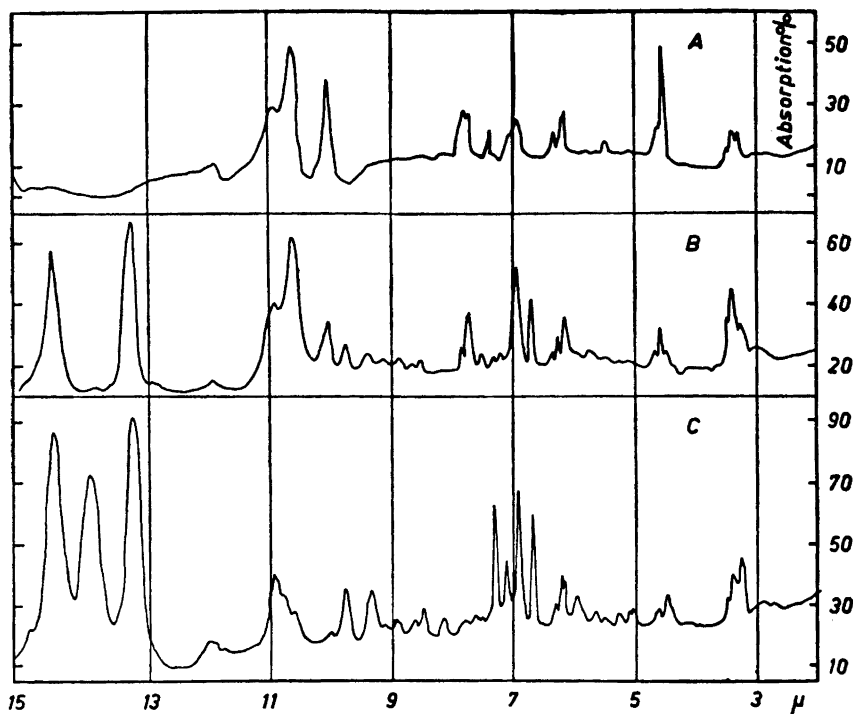


Fig. 3. Infrared absorption of:

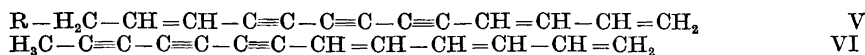
- A. trideca-1:3:11-triene-5:7:9-triyne in CHCl_3 , $c = 10.6\%$, $l = 0.05$ mm.
 B. *trans* 1-phenyl-hepta-1:3-diyne-5-ene liq.
 C. *cis* 1-phenyl-hepta-1:3-diyne-5-ene liq.

The maleic anhydride adduct isolated by Sørensen and Sørensen from the "3 650"-hydrocarbon has the strongest band at $2\ 450\ \text{Å}$ and so Bohlmann⁶ was correct in his suggestion that the adduct had originated from an other poly-yne-diene present in the fraction. As Table 1 demonstrates the adduct belongs to the ene-triyne class.

The hydrogenation experiments and the properties of the dien-adducts reveal that the hydrocarbon is a *n*-trideca-triene-triyne. So it is the missing link between the *n*-trideca-tetra-yne-diene (II, $\text{R} = \text{CH}_3$) isolated from the root part of the annual *Coreopsis* species and the *n*-trideca-diyne-tetraene II ($\text{R} = \text{H}$) isolated from their leaves.

The infrared spectrum, *cf.* Fig. 3, gives clear indication ($1\ 840\ \text{cm}^{-1}$) of a vinyl group in the triene-triyne.

The ultraviolet spectrum of the maleic anhydride adduct further gives the information that the acetylenic bonds are conjugated; it remains then only 2 possible formulas for a *n*-trideca-triene-triyne, *viz* V, $\text{R} = \text{H}$, and VI.



Of these possibilities V, R = H, should be the correct one for the following reasons. From *Carlina vulgaris* Sørensen and Sørensen¹² isolated an acetate for which they deduced formula V, R = OCOCH₃. Bohlmann¹³ has synthesised the *trans* isomer of this 1-acetoxy-*n*-trideca-2:10:12-triene-4:6:8-triayne which differed from the *Carlina* acetate but gave the same anhydride adduct. Bohlmann concluded that the *Carlina* acetate differs in having *cis* configuration at C₁₀₋₁₁.

These *cis* and *trans* 1-acetoxy-trideca-triene-triaynes (V, R = OCOCH₃) show ultraviolet spectra conform with our triene-triayne-hydrocarbon which definitely points to V, R = H, as the correct formula. V, R = H is just the 9:10-dihydro-compound of III, R = CH₃ and the 5:6-dehydro-compound of II, R = H. Finally the choice between V, R = H and VI has been supported by synthetic work, which, because of some interesting side-reactions, will be described in a separate communication.

As to the configuration of the *n*-deca-triene-triayne from *Coreopsis* species an accidental observation gave valuable hints. A chromatographic fraction of nearly pure triene-triayne was so small that both ultraviolet and infrared spectra had to be taken on the same sample. Accidentally the infrared spectrum was recorded first. Surprisingly the subsequent ultraviolet spectrum demonstrated remarkable changes. As Fig. 2 demonstrates, the long-wave group has lost the characteristic double maxima, at the same time the main maxima have moved about 40 Å towards shorter wave-lengths.

This spectral difference relative to the nearest fractions indicated that a *cis-trans* isomerisation had taken place during the infrared measurement. It was not further investigated if the transformation was due to heat alone or to traces of HCl in the solvent chloroform. Instead the *cis-trans* isomerisation was achieved in the usual way through action of light in the presence of traces of iodine in spectral hexane.

As mentioned above⁷ it is usual in polyenyne that the *cis* isomers absorb at somewhat longer wave-lengths than the *trans* isomers; in the known pair of spectra of *cis-trans* isomers the spectra have, however, been very nearly conform. Therefore the characteristic double maxima in the naturally occurring *cis* isomer of V, R = H, might be due to special constitutional details. We find it reasonable to suppose that the *cis-trans* isomerism occurs at least at the C₃₋₄ double bond. Assuming that a conjugated molecule tends to exist in a planar conformation, if at all possible, inspection of models, *cf.* Fig. 4, revealed that the 3-*cis-n*-trideca-1:3:11-triene-5:7:9-triayne may exist in two planar conformations of rather different molecular shape. Synthetically it should be possible to provide spectra of model compounds which might elucidate whether the double maxima are due to a coexistence of these two rotational isomers.

The second, phenyl-containing component was difficult to purify because of low crystallising power and high solubility in all solvents. The purest fraction obtained had m.p. 25—27°.

The ultraviolet spectrum of this fraction showed great similarity with the 1-phenylhepta-1:3-diyn-5-en-7-ol acetate isolated from all parts of the investigated annual *Coreopsis* species. For this reason we guessed on the structure 1-phenylhepta-1:3-diyn-5-ene (I, R = H) and tested this hypothesis by

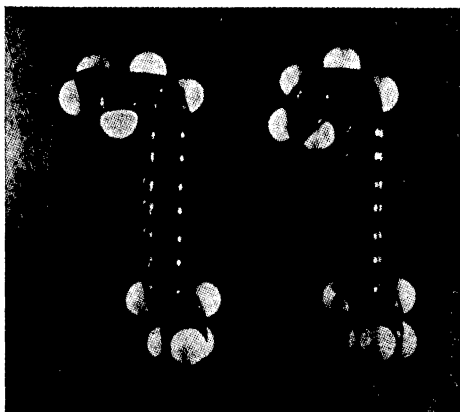


Fig. 4. The two planar conformations of 3-*cis* 1:3:11-triene-5:7:9-triynene (V, R = H).

the synthesis of the *cis* and *trans* isomers of this hydrocarbon by oxidative coupling of phenyl-acetylene with *cis* and *trans* pent-3-en-1-yne, respectively. The synthesis is described in the experimental part. Comparison with the synthetic isomer proved that the phenyl compound from *Coreopsis* leaves was 1-phenyl-1:3-diyn-5-*trans*-ene (I, R = H).

This correctional work revealed some interesting facts. First that the 5 acetylenic compounds so far isolated from annual *Coreopsis* species are all C₁₃-compounds.

The two new polyacetylenes described in this paper I, R = H, and V, R = H are isomeric C₁₃H₁₀-compounds differing only in the curling up of the dien-yne-tail of V, R = H, to the phenylresidue of I, R = H.

The same type of isomerism was demonstrated in our XIXth communication to exist between the *Carlina* acetate, V, R = OCOCH₃, and the 1-phenylhepta-1:3-diyn-5-en-7-ol acetate, I, R = OCOCH₃, from *Coreopsis*. Thus it seems possible that some *Compositae* are able to synthesise the phenyl residue in this direct way, not passing oxygenated 6-ring precursors.

EXPERIMENTAL

1. *Separation of the "3650"-hydrocarbon into components.* The starting material was a sample of 5 g of the essential oil of the flowering part of *Coreopsis cardaminifolia* harvested late in the autumn (Sept. 23rd). The main separational procedure was chromatography on the slightly deactivated alumina of Mancera *et al.*¹⁴ Washings with petroleum ether eluted only saturated paraffins and nonchromophoric hydrocarbons. Then followed elution with increasing concentrations of benzene, *viz.* 1.5 %, 2 %, 4 %, 10 % *etc.*

The first polyacetylenic substance to be eluted was the diene-tetraene (III, R = CH₃) mixed with the "3650"-hydrocarbon. When reaching 10 % benzene in petroleum ether there appeared mixtures exhibiting the "3650"-chromophore spectrum with the indistinct spectrum of the tetraene-diyne (II). II crystallised readily from these fractions in a pure state. All the fractions eluted between the polyenyne II and III showed ultraviolet spectra very similar to that originally given for the "3650"-hydrocarbon. When these fractions were inspected in infrared (mostly 12–20 fractions were taken between 2 % and 10 % benzene in petroleum ether) it turned out that the intensity of the peaks be-

longing to a monosubstituted phenyl-residue (1 493, 752 and 686 cm^{-1}) increased relative to the other infrared bands with increasing concentration of benzene. Chromatography alone only lead to a slight displacement of the concentrations. By fractional distillation at 10^{-3} – 10^{-4} mm Hg the phenyl-containing component was slightly more volatile than the aliphatic component. Redistillation, therefore, on the one hand was suitable to get rid of solvents and decomposition products, on the other hand some enrichment of the phenyl-compound took place in the most volatile part.

All fractions solidified at -40 to -70° ; also from petroleum ether crystals will mostly be deposited at -70° . The crystallisates were more or less greasy and mostly the solutions had the same composition as the whole fraction. However, when chromatography, distillation and rechromatography had brought the separation above a certain concentration, crystallisation at -70° sometimes gave the components nearly spectroscopically pure.

2. *n*-Trideca-1:3:11-triene-5:7:9-triyne, (*V*, *R* = *H*). The purest fraction obtained showed a rather unsharp m.p. at 51 – 56° , vacuum; the U.V.-spectrum is given in Fig. 2, the infrared spectrum in Fig. 3.

Catalytical hydrogenation: 30.8 mg *V*, *R* = *H*, were hydrogenated in absolute alcohol with 20 mg palladium on barium sulphate as catalyst. At 764 mm, $t = 20^\circ\text{C}$, 37.3 ml of hydrogen (8.25 $\bar{\text{F}}$) were taken up, calculated for 9 $\bar{\text{F}}$ 40.8 ml. The solution was worked up in the usual way. After distillation at 8 mm the distilled product melted at -7.5 to -6.8° . *n*-Tridecane¹ melted at -6.5 to -5.5° , mixed m. p. -7.3 to -6.3°C . The infrared spectrum agreed in every detail with that given for *n*-tridecane¹.

3. *trans*-1-phenylhepta-1:3-diyn-5-ene from *Coreopsis*. The purest fraction obtained melted at 22 – 24° . The U.V.-spectrum is given in Fig. 2, the infrared spectrum in Fig. 3.

Synthesis of cis and trans hepta-1:3-diyn-5-ene. The synthesis was achieved by oxidative coupling of phenylacetylene with *cis* and *trans*-pentyne. The pentyne isomers were prepared according to Eglinton and Whiting¹⁵, the fractionation being controlled by infrared measurements. Both oxidative couplings were carried out under the same experimental conditions, as exemplified for the *cis* compound:

2 ml of *cis*-pentyne and 4 ml of phenylacetylene were dissolved in 200 ml of a 1:1 mixture of methanol and acetone at -20°C ; to this mixture was slowly added a solution of 15 g of cuprous chloride, 40 g of ammonium chloride, 2 g of iron(III) chloride and 1 ml of conc. hydrochloric acid in 125 ml of water with a vivid stream of oxygen bubbling through the solution. The flask containing the mixture was kept in a bath of acetone-carbon dioxide maintained at -20° for 18 h. The reaction mixture was extracted with ether; the ether solution on evaporation left a crystalline mass. Some of the diphenyl-diacetylene remained undissolved by washing with ether. This ether solution again was evaporated and the residue dissolved in petroleum ether and chromatographed on alumina with 2 % benzene in petroleum ether.

The first fractions were oily at room temperature, these fractions were distilled at 0.0001 mm. At room temperature deca-diene-2:8-diyne-4:6 went off, at 50° (bath temperature) 0.15 g of a colourless liquid distilled off. This fraction remained as a liquid at -20°C .

Ultraviolet absorption of *cis*-1-phenylhepta-1:3-diyn-5-ene in hexane:

ϵ_{max}	20 400	24 000	17 800	10 800	32 400	33 900	
λ_{max}	3 190	2 990	2 800	2 650	2 520	2 410	Å

The maxima differ neither in position nor in intensity from the naturally occurring and the synthetic *trans* isomer within the limits of experimental errors (*cf.* below). The synthetic *trans* isomer melted at 23 – 24°C .

Ultraviolet absorption of *trans*-1-phenylhepta-1:3-diyn-5-ene in hexane:

ϵ_{max}	19 300	22 650	18 200	11 750	26 900	29 200	
λ_{max}	3 180	2 975	2 795	2 645	2 525	2 410	Å

As will be seen from Fig. 3 the *cis* and *trans* isomers differ appreciably in the infrared and just in the positions expected. The infrared spectra confirm the conclusion from the melting point that the *Coreopsis* Compound is the *trans* isomer. At the same time small

additional peaks in the infrared spectrum of the phenylheptadiynene from *Coreopsis* species just agree with the strongest peaks in the *n*-decatrienetriyne, and clearly indicate that the separation was not completely successful, although the contamination is so small that it does not disturb the identification.

Acknowledgements. Grants from *Norges Almenvitenskapelige Forskningsråd*, which have enabled these investigations to be carried out, are gratefully acknowledged.

REFERENCES

1. Sørensen, J. Stene and Sørensen, N. A. *Acta Chem. Scand.* **8** (1954) 1743.
2. Bruun, T., Skattebøl, L. and Sørensen, N. A. *Acta Chem. Scand.* **8** (1954) 1757.
3. Bohlmann, F. and Mannhardt, H.-J. *Chem. Ber.* **88** (1955) 1330.
4. Jones, E. R. H., Thompson, J. M. and Whiting, M. C. *Acta Chem. Scand.* **8** (1954) 1944.
5. Skattebøl, L. *Studies in the field of highly unsaturated systems, Thesis*, Manchester 1956.
6. Bohlmann, F. *Chem. Ber.* **88** (1955) 1755.
7. Bruun, T., Haug, C. M. and Sørensen, N. A. *Acta Chem. Scand.* **4** (1950) 850; Sørensen, J. Stene, Bruun, T., Holme, D. and Sørensen, N. A. *Acta Chem. Scand.* **8** (1954) 26.
8. Bohlmann, F., Mannhardt, H.-J. and Viehe, H. G. *Chem. Ber.* **88** (1955) 361.
9. Stavholt, K. and Sørensen, N. A. *Acta Chem. Scand.* **4** (1950) 1567.
10. Bohlmann, F. and Viehe, H. G. *Chem. Ber.* **87** (1954) 712.
11. Sørensen, J. Stene, and Sørensen, N. A. *Acta Chem. Scand.* **12** (1958) 765.
12. Sørensen, J. Stene, and Sørensen, N. A. *Acta Chem. Scand.* **8** (1954) 1763.
13. Bohlmann, F. and Inhoffen, E. *Chem. Ber.* **89** (1956) 21.
14. Mancera, O., Barton, D. R. H., Rosenkranz, G. and Djerassi, C. *J. Chem. Soc.* **1925** 1025.
15. Eglinton, G. and Whiting, M. C. *J. Chem. Soc.* **1950** 3653.

Received February 14, 1958.