Eigenberger,[5] followed by repeated fractional freezing. The final products had the following characteristic constants

	B. p. (750 mm.), °C.	F. p., °C.	n^{25}_D	d^{25} (g./cc.)
Benzene	79.7	5.5	1.4980	0.8732
Dioxane	101.0	11.8	1.4202	1.0280

All solutions were made by weight using weight burets; the exact compositions approximated 20, 35, 50, 65 and 80%. Moisture was excluded.

The refractive indices and densities at 25° are represented by the relations

$$n^{25}_D = 1.4980 - 0.0743x - 0.035x^2$$

and

$$d^{25}(\text{g./cc.}) = 0.8732 + 0.1514x + 0.0034x^2$$

where x is the mole fraction of the dioxane in the mixture.

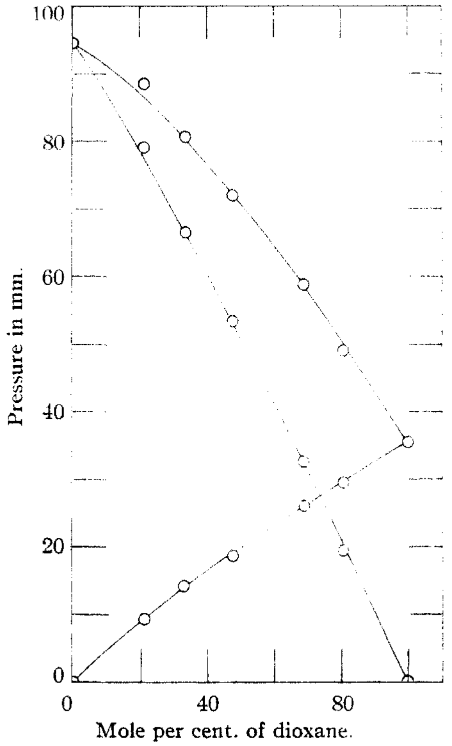

Fig. 1.

The partial pressure data are presented in the following table and in the figure.

Mole fraction of dioxane in solution	Total press., mm.	Mole fraction of dioxane in condensate	Partial pressures, mm. Dioxane	Partial pressures, mm. Benzene
0.000	94.4	0.000	. .	94.4
.212	88.5	.106	9.4	79.1
.334	80.7	.176	14.2	66.5
.478	72.0	.259	18.6	53.4
.689	58.7	.445	26.1	32.6
.806	49.0	.602	29.5	19.5
1.000	35.5	1.000	35.5	. .

The deviation from ideality is slight as was anticipated; this is shown in the figure.

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(5) Eigenberger, *J. prakt. Chem.*, **75**, 130 (1931).

The Addition of Triphenylmethyl to 2-Methyl-buten-1-yne-3

BY A. F. THOMPSON, JR., AND DOUGLAS M. SURGENOR

Some years ago, Conant[1] and two co-workers showed that triphenylmethyl, and other free radicals, entered into addition reactions with unsaturated substances, including conjugated dienes, pyrrole, and maleic anhydride. It seemed of interest to study the application of this reaction to enynes, and the interaction of triphenylmethyl with 2-methyl-buten-1-yne-3 was accordingly investigated.

2-Methyl-buten-1-yne-3 was prepared according to Thompson and Shaw.[2]

Triphenylmethyl chloride was recrystallized from benzene and acetyl chloride to give a product melting at 112–113°.[3] Addition of the free radical to the enyne was carried out by shaking together 14 g. (0.05 mole) of triphenylmethyl chloride, 50 g. of pure mercury, 12 g. (0.18 mole) of 2-methyl-buten-1-yne-3 (b. p. 34–35°) and 18 g. of dry, thiophene-free benzene at room temperature for five days in an atmosphere of dry nitrogen. The reaction mixture was then evaporated to dryness under reduced pressure, and the residue extracted with ether. From the ether solution, 6.5 g. of crystalline addition product was obtained, m. p. 182–184°, yield 47%. On recrystallization from benzene-petroleum ether, a melting point of 184–185.5° was obtained.

Anal.[4] Calcd. for $C_{43}H_{36}$: C, 93.47; H, 6.53. Found: C, 93.5, 93.0; H, 6.88, 6.78.

The addition product, in ethyl acetate solution, was hydrogenated with platinum oxide catalyst. The absorption by 0.340 g. (0.61 millimole) of the compound was 26.9 cc., corresponding to 1.97 double bonds, and indicating that the reaction stopped after addition of two triphenylmethyl radicals to the conjugated enyne system.

Ozonolysis of 3.8 g. (6.9 millimoles) of addition product was carried out by passing ozone through a solution in 70 cc. of dry ethyl acetate at 0°, during twelve hours. The ozonide solution was then hydrogenated according to F. G. Fischer,[5] using 0.75 g. of 5% Pd–$CaCO_3$ catalyst. On oxidation with silver oxide, and separation of the neutral and acid fractions with sodium carbonate, two substances were obtained.

From the acid fraction 24 mg. (0.083 millimole) of tri-

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(1) (a) Conant and Scherp, THIS JOURNAL, **53**, 1959 (1931); (b) Conant and Chow, *ibid.*, **55**, 3475 (1933).

(2) Thompson and Shaw, *ibid.*, **64**, 365 (1942).

(3) All melting points in this paper are corrected.

(4) The authors wish to acknowledge the courtesy of Malcolm Brown, who carried out the semi-micro combustion analyses.

(5) F. G. Fischer, Düll and Ertel, *Ber.*, **65**, 1467 (1932).

phenylacetic acid was isolated, m. p. 262–264°. On esterification with diazomethane, 12 mg. of methyl triphenylacetate was obtained, m. p. 185–187°.

The neutral fraction, recrystallized from benzene-petroleum ether, yielded 25 mg. (0.083 millimole) of 1,1,1-triphenylbutanone-3, m. p. 141–142°, no depression with an authentic sample prepared according to Conant and Scherp.[1]

No other products were obtained from the addition product, which therefore appears to be 4-methyl-1,1,1,6,-6,6-hexaphenyl-hexadiene-2,3.

Study of the reaction is being extended to various substituted enynes and dienynes, and to conjugated dienes with substituents at the terminal carbon atoms of the conjugated system. As is well known[6] the presence of terminal substituents limits the use of maleic anhydride for characterizing butadienes. It is hoped that triphenylmethyl, which seems not to be subject to this limitation,[1] will be useful for this purpose and for the characterization of enynes and dienynes, since the reaction in this case proceeded smoothly, and the product was readily isolated.

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(6) (a) Bacon and Farmer, *J. Chem. Soc.*, 1065 (1937); (b) Bachman and Goebel, THIS JOURNAL, **64**, 787 (1942).

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS
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NEW COMPOUNDS

Diethyl Acetal of 3-Methylbuten-3-al-1

The method used was the orthoformate synthesis, independently discovered by Tschitschibabin and Bodroux.[1] To an ethereal solution of the Grignard reagent prepared from 18.1 g. of methallyl chloride and 14.4 g. of magnesium, after thirty minutes, 25 g. of ethyl orthoformate was added with stirring and the solution allowed to boil under gentle reflux for six and one-half hours after addition was complete. The bulk of the ether was then distilled and the cooled residue hydrolyzed with ice-water. The acetal was isolated by distillation of the organic layer formed upon hydrolysis. The product was a colorless liquid which possessed a sharp odor, b. p. 154–155°; $n^{20}D$ 1.4098, d^{20} 0.8316; yield, 5.9 g. (24%).

The *p*-nitrophenylhydrazone, 2,4-dinitrophenylhydrazone and semicarbazone of the aldehyde were prepared according to the directions of Shriner and Fuson.[2] The *p*-nitrophenylhydrazone crystallized as golden plates from 95% ethanol, m. p. 157°.

Anal. Calcd. for $C_{11}H_{13}N_3O_2$: N, 19.18. Found: N, 19.08. The 2,4-dinitrophenylhydrazone crystallized as shining red needles from 95% ethanol, m. p. 181°. *Anal.* Calcd. for $C_{11}H_{12}N_4O_4$: N, 21.21. Found: N, 21.14. The semicarbazone crystallized from 95% ethanol as shining white needles, m. p. 204–205°. *Anal.* Calcd. for $C_6H_{11}N_3O$: N, 29.79. Found: N, 30.08.

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(1) Tschitschibabin, *Ber.*, **37**, 186 (1904); Bodroux, *Compt. rend.*, **138**, 93 (1904).

(2) Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., pp. 145, 148.

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Esters of Methylneopentylacetic Acid

The ethyl, *n*-propyl, *n*-butyl, *n*-hexyl esters of methylneopentylacetic acid[1] were prepared by treating 60-g. (0.34 mole) portions of the acid chloride with an excess (100 g.) of the corresponding alcohols. The acid chloride was prepared from thionyl chloride and the acid. The ester was washed with water and 5% sodium carbonate solution, and dried over freshly dehydrated sodium sulfate. Upon fractionating the ester through a column of 20 theoretical plates, packed with $^3/_{32}$-in. stainless steel helices, constant boiling, constant index material was obtained in each case.

Ester	Yield, %	$n^{20}D$ Valentine	d^{20}	Cottrell b. p. at 734 mm.	Mol. refraction Obs.	Calcd.
Ethyl	89	1.4131	0.8586	176.8	49.99	50.05
n-Propyl	75	1.4174	.8569	196.6	54.65	54.67
n-Butyl	77	1.4207	.8556	213.8	59.32	59.29
n-Hexyl	87	1.4271	.8545	247.2	68.59	68.53

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RECEIVED SEPTEMBER 3, 1942

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(1) Whitmore and co-workers, THIS JOURNAL, **63**, 2028 (1941).