tion, steam distillation, crystallization and use of solid derivatives, as was appropriate to the compounds. The properties and analyses of four pyrroles apparently not reported earlier are given in Table II. Other products were identified through refractive indices, boiling points, melting points and solid derivatives.

Summary

Representative compounds, containing a pyrrolidine or piperidine nucleus, have been dehydrogenated in the liquid phase in benzene over a nickel catalyst, to compounds containing a pyrrole or pyridine nucleus.

MADISON, WISCONSIN RECEIVED DECEMBER 10, 1948

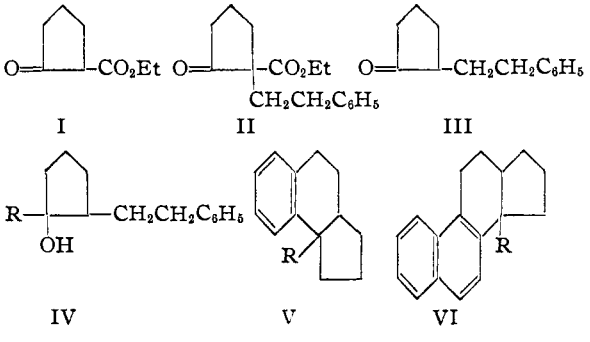
[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Synthesis of Cyclopentanohydronaphthalenes and Hydrophenanthrenes with Substituents in an Angular Position

BY HOMER ADKINS AND GLENN F. HAGER[1]

In connection with another investigation,[2] a series of compounds has been made, which have a substituent in an angular position of partially or completely hydrogenated derivatives of 1,2-cyclopentenonaphthalene or 1,2-cyclopentenophenanthrene. The methods used were developments of those described earlier.[3,4,5,6,7,8,9]

The naphthalene derivatives were made through a series of reactions in which 2-carbethoxycyclopentanone (I) was alkylated with β-phenethyl bromide to give the substituted keto ester II. For one group of compounds the keto ester was decarboxylated to the ketone III, and converted to a tertiary alcohol IV, through the use of a Grignard reagent.

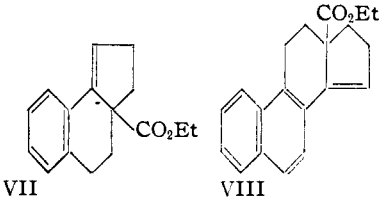


I II III IV V VI

The latter was cyclized to a 1-alkyl-1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene (V) where the alkyl group was methyl or *n*-butyl. The parent compound 1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene, where R equals H in formula V, was prepared by reducing the ketone III to an alcohol over copper–chromium oxide, and closing the ring as in converting IV to V.

A group of angular substituted hydrophenanthrenes was prepared, by modifying the synthesis outlined above, through the use of α-$C_{10}H_7CH_2CH_2Br$ instead of $C_6H_5CH_2CH_2Br$ in alkylating the keto ester I. Thus, three 1-alkyl-1,2-cyclopentano - 1,2,3,4 - tetrahydrophenanthrenes (VI) were obtained, where the alkyl group was methyl, ethyl or *n*-butyl.

A modification of the synthesis was made in that the keto ester II was cyclized with liquid hydrogen fluoride to give a 2-carbethoxy-1,2-cyclopenteno - 3,4 - dihydronaphthalene (VII). The corresponding 2-carbethoxy-1,2-cyclopenteno-3,4-dihydrophenanthrene (VIII) was similarly prepared. In this latter case the cyclization went so rapidly that it was complete within five minutes at 0°. This method of closure gave excellent yields of compounds with a carbethoxy group in an angular position, and seems preferable to that used by Ruzicka and his associates and more recently by Ehmann and Miescher.[10]



VII VIII

The carbethoxy groups in compounds VII and VIII were hydrogenated to methylol groups and ultimately to the 2-methyl-1,2-cyclopentanodecalin and 2-methyl-1,2-cyclopentanoperhydrophenanthrene. Three catalysts were used in sequence, *i. e.*, copper–chromium oxide, Raney nickel and finally nickel-on-alumina. Several of the dihydro- and tetrahydronaphthalene and phenanthrene derivatives were converted to the corresponding substituted decalins or perhydrophenanthrenes over Raney nickel. The hydrogenated compounds are listed in Table I and the details of hydrogenation are given under the experimental section. Chrysene and 4a-methyl-1,2,3,4,4a,11,12,12a-octahydrochrysene, prepared

(1) Monsanto Chemical Co. Fellow 1942–1943.
(2) Adkins and Hager, THIS JOURNAL, **71**, 2962 (1949).
(3) Bardhan and Sengupta, *J. Chem. Soc.*, 2520, 2798 (1932).
(4) Kon, *ibid.*, 1081 (1933).
(5) Bougault, *Compt. rend.*, **159**, 745 (1915).
(6) Von Auwers and Möller, *J. prakt. Chem.*, **109**, 124 (1925).
(7) Cook, Haslewood and Robinson, *J. Chem. Soc.*, 667 (1935).
(8) Ruzicka, Ehman, Goldberg and Hosli, *Helv. Chim. Acta*, **16**, 833 (1933).
(9) Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 295 (1936).
(10) Ehmann and Miescher, *Helv. Chim. Acta*, **30**, 413 (1947).

TABLE I

ANALYSES AND PROPERTIES OF COMPOUNDS

Abbreviations: naph. for naphthalene; cyp. for cyclopentano; phen. for phenanthrene.

Name	Mol. form.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	$n^{25}D$	d^{25}_4	M_R Calcd.	M_R Found	B. p. °C.	Mm.
1,2-Cyclopentanodecalin	$C_{15}H_{22}$	87.55	87.52	12.45	12.40	1.5020	0 9446	55.64	55.79	128–130	17
1-Methyl-1,2-cyclopentanodecalin	$C_{16}H_{24}$	87.42	87.55	12.58	12.52	1.5020	0.9379	60.64	61.00	115–117	7
1-(*n*-Butyl)-1,2-cyp.-1,2,3,4-tetrahydronaph.	$C_{17}H_{24}$	89.41	89.39	10.59	10.42	1.5372	0.9678	73.11	73.45	127–129	3
1-Methyl-2-decalol	$C_{11}H_{20}O$	78.51	78.43	11.98	11.86	1.4995				112–119	10
1-Methyl-1,2,3,4-tetrahydro-2-naphthol	$C_{11}H_{14}O$	81.44	81.40	8.70	8.81		M. p. 113°			125–130	3
1-Methyl-2-decalone	$C_{11}H_{18}O$	79.46	79.20	10.92	10.79	1.4894				105–107	7
1-Methyl-2-allyl-2-decalol	$C_{14}H_{24}O$	80.69	80.34	11.63	11.89	1.5030				133–138	7
1-Methyl-2-(*n*-propyl)-naphthalene	$C_{14}H_{18}$	91.25	91.39	8.75	8.58	1.5928	0.9904	60.37	62.98	145–146	10
1-Methyl-2-(*n*-propyl)-naphthalene picrate	$C_{20}H_{21}N_3O_7$	58.11	58.04	4.63	4.49		M. p. 82.5°				
1-Methyl-2-(*n*-propyl)-naph. trinitrobenzene	$C_{20}H_{21}N_3O_6$	60.45	60.56	4.82	4.99		M. p. 89.5°				
1-Methyl-1,2-cyp.-perhydrophenanthrene	$C_{15}H_{26}$	87.73	87.85	12.27	12.17	1.5172	0.9751	76.50	76.48	134–136	1
1-Ethyl-1,2-cyp.-1,2,3,4-tetrahydrophen.	$C_{16}H_{22}$	91.14	91.22	8.86	8.70	1.6145	1.0625	78.74	83.4	150–152	0.2
1-(*n*-Butyl)-1,2-cyp.-1,2,3,4-tetrahydrophen.	$C_{21}H_{34}$	90.59	90.92	9.41	9.05	1.5895	1.0201	88.03	91.70	140–143	0.1
2-(β-Phenethyl)-2-carbethoxy-1-cyclopentanol	$C_{16}H_{22}O_3$	73.25	72.97	8.45	8.24	1.5128				170–185	2
1-(β-Phenethyl)-1-carbethoxycyclopentane	$C_{16}H_{22}O_2$	78.65	78.53	8.25	8.06	1.5165				123–126	0.2
2-Carbethoxy-1,2-cyp.-3,4-dihydronaph.	$C_{16}H_{18}O_2$	79.30	79.28	7.49	7.46		M. p. 63–64°			125–128	0.2
2-Carbethoxy-1,2-cyp.-1,2,3,4-tetrahydronaph.	$C_{16}H_{20}O_2$	78.65	78.08	8.25	8.16	1.5314	1.096	68.14	70.55	125–128	0.4
2-Carbethoxy-1,2-cyclopentanodecalin	$C_{16}H_{26}O_2$	76.75	76.90	10.46	10.28	1.4970	1.029	71.31	71.33	116–118	0.5
2-Methylol-1,2-cyclopentanodecalin	$C_{16}H_{26}O$	80.69	80.65	11.63	11.46	1.5203					
2-Methyl-1,2-cyclopentanodecalin	$C_{16}H_{24}$	87.43	87.32	12.57	12.56	1.4950	0.9263	60.24	60.40	107–110	10
1-(*n*-Propyl)-2-methyldecalin	$C_{14}H_{26}$	86.51	86.69	13.49	13.14	1.4790	0.883	62.34	62.35	103–109	10
2-Carbethoxy-1,2-cyp.-3,4-dihydrophen.	$C_{20}H_{26}O_2$	82.16	82.13	6.89	6.87		M. p. 98–99°				
2-Carbethoxy-1,2-cyp.-perhydrophen.	$C_{20}H_{32}O_2$	78.89	79.85	10.59	10.90	1.5110				169–173	0.7
2-Methyl-1,2-cyp.-perhydrophenanthrene	$C_{15}H_{28}$	87.73	87.71	12.27	12.14	1.5130	0.965	76.55	76.65	117	0.2
1,2-Cyp.-3,4-dihydrophen.-2-carboxylic acid	$C_{15}H_{16}O_2$	81.79	81.83	6.10	6.05		M. p. 246°				
1,2-Cyclopentanoperhydrophenanthrene	$C_{17}H_{28}$	87.86	87.82	12.14	12.15	1.5160	0.973	71.95	72.10	167–170	9
4a-Methylperhydrochrysene	$C_{19}H_{32}$	87.61	87.46	12.39	12.55	1.5233	0.987	81.14	80.70	151–153	0.7
Perhydrochrysene	$C_{18}H_{30}$	87.73	87.66	12.27	12.19	1.5215				150–152	0.4

as by Perlman, Davidson and Bogert,[9] were hydrogenated to perhydrochrysenes.

1-Methyl-2-(*n*-propyl)-naphthalene was made through a series of reactions from 2-naphthol. The latter was converted to 2-hydroxy-1-naphthaldehyde by the Reimer–Tiemann reaction. The aldehyde was hydrogenated over Raney nickel to 1-methyl-2-decalol and the latter oxidized to 1-methyl-2-decalone. The decalone was converted to a tertiary alcohol with allylmagnesium bromide. Attempts to cyclodehydrate the resulting alcohol to 1-methyl-1,2-cyclopentanodecalin gave a mixture of dienes. Dehydrogenation of either the alcohol or the diene mixture in benzene gave 1-methyl-2-(*n*-propyl)-naphthalene.

Procedures

2-Carbethoxycyclopentanone.—Diethyl adipate (606 g., b. p. 135–137° (17 mm.), $n^{25}D$ 1.4256) was slowly added to a mixture of powdered sodium (100 g.), dry benzene (2.5 l.) and dry alcohol (5 ml.) held at 0–5°. After the addition of the ester the mixture was refluxed for twelve hours. The solid sodium salt was filtered off and decomposed with ice and dilute hydrochloric acid. The oil was separated and the water solution extracted twice with benzene. The oil and ether extractions were combined, washed with water and dried over anhydrous sodium sulfate. The ester (384 g. or 81%, $n^{25}D$ 1.4526) was distilled at 113–115° (20 mm.). The procedure is that suggested but not described in detail by Linstead and Meade.[11]

2-(β-Phenethyl)-2-carbethoxycyclopentanone (II).—2-Carbethoxycyclopentanone (78 g. in 50 ml. of toluene) was added to 19.5 g. of powdered potassium suspended in 750 ml. of dry toluene. The potassium was powdered in two portions in a liter flask and transferred in an atmosphere of nitrogen to the 2-liter reaction flask. No more than 15 g. of the ester was added to the flask until reaction was definitely underway. After the potassium salt of the keto ester had formed, 94.4 g. of β-phenethyl bromide was added rapidly and the mixture refluxed for twenty-eight hours. The mixture was cooled and the solid potassium bromide was separated, dissolved in water and extracted twice with benzene. The benzene and toluene solutions were combined, washed with water and dried over anhydrous sodium sulfate. The product II (96 g., 74%, $n^{25}D$ 1.5120) was distilled at 157–163° (2 mm.).

2-(β-1′-Naphthylethyl)-2-carbethoxycyclopentanone.—This compound was prepared as described above except that 221 g. of β-(1-naphthyl)-ethyl bromide[12,13] was used instead of β-phenethyl bromide. The quantities of other reagents were 37 g. of potassium, 147 g. of 2-carbethoxycyclopentanone in 1 liter of xylene. The yield was 205 g. (70%) boiling 210–215° (1 mm.).

2-(β-Phenethyl)-cyclopentanone.—The keto ester II (47 g.) in a mixture of 200 ml. of glacial acetic acid, 150 ml. of concentrated hydrochloric acid and 50 ml. of water was refluxed for six hours in an oil-bath maintained at 160–170° as by Bachmann and Struve.[13a] The cold mixture was diluted with 250 ml. of water and extracted with three 200-ml. portions of ether. The combined extracts were washed with water and dried. There was obtained by distilling at 163–166° (12 mm.) 28.4 g. of the desired product, $n^{25}D$ 1.5240.

2-(β-1′-Naphthylethyl)-cyclopentanone.—This compound, b. p. 160–165° (0.1 mm.) was obtained in 71% yield by the hydrolysis of the corresponding keto ester, by refluxing for ten hours under the conditions described just above.

1-Alkyl-1,2-cyclopentano-1,2,3,4-tetrahydro Derivatives of Naphthalene and Phenanthrene.—Several com-

(11) Linstead and Meade, *J. Chem. Soc.*, 935 (1934).

(12) Wilds, THIS JOURNAL, **64**, 1424 (1942).

(13) Hoch, *Bull. Soc. Chim.*, [5] **4**, 268 (1938).

(13a) Bachmann and Struve, THIS JOURNAL, **63**, 2589 (1941).

pounds of this type were prepared by essentially the same procedure,[4] the difference being in the particular ketone and alkyl halide used and in the reagent for ring closure. A representative procedure was to add 37 g. of 2-(β-phenethyl)-cyclopentanone (III) to a 100-ml. ether solution of methylmagnesium iodide, which had been prepared from 6 g. of magnesium and 35.5 g. of methyl iodide. The mixture was allowed to stand overnight, refluxed for one hour and decomposed in an ice-cold saturated solution of ammonium chloride. The alcohol was extracted with ether and the crude alcohol left after the evaporation of the ether used for the next step.

The crude tertiary alcohol was heated with 80 g. of phosphoric acid for twenty-five minutes under a pressure of 6 mm. in a flask suspended in an oil-bath held at 135–140°.[3] The temperature of the bath was then raised to 170° and the crude product (29.3 g.) distilled over. The 1-methyl-1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene (28.5 g., $n^{25}D$ 1.5449) was distilled from sodium at 128–129° (12 mm.). The yield for the *n*-butyl compound was 56%. The secondary alcohol 2-(β-phenethyl)-cyclopentanol (28 g.) was also dehydrated by the procedure just described to 1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene (20.8 g., $n^{25}D$ 1.5490, b. p. 131–133° (15 mm.)).

The tertiary alcohols (50 g.) resulting from the reaction of 2-(β-1′-naphthylethyl)-cyclopentanone and a Grignard reagent were cyclized with 85% sulfuric acid (25 g.) in 50 ml. of petroleum ether at 0° as described.[9] The yields for the methyl, ethyl and *n*-butyl tetrahydrophenanthrenes were 72, 44 and 35%, respectively. The methyl compound had been previously prepared[4]; it distilled at 157–160° (0.6 mm.) and had $n^{25}D$ 1.6205.

2-Carbethoxy-1,2-cyclopenteno-3,4-dihydronaphthalene.—2-(β-Phenethyl)-2-carbethoxycyclopentanone (25 g.) was placed in a 500-ml. platinum vessel, which was cooled in an ice-salt-bath while approximately 150 ml. of liquid hydrogen fluoride was added. After standing one and one-half hours in an ice-salt-bath, the reaction mixture was poured over 400 g. of ice. The product was extracted with ether, the latter washed with a 5% sodium hydroxide solution until the washings were alkaline to litmus and the ether solution washed with water. After the solution was dried and the ether distilled there was obtained a crude product (15.5 g.) distilling at 160–170° (1 mm.). Upon fractionation through a modified Widmer column there was obtained at 125–128° (0.2 mm.) 14.5 g. of product which solidified. After crystallization from 95% alcohol the m. p. was 63–64°.

2-Carbethoxy-1,2-cyclopenteno-3,4-dihydrophenanthrene.—2-(β-1′-Naphthylethyl)-2-carbethoxycyclopentanone (50 g.) was cyclized in liquid hydrogen fluoride as described above. However, the cyclization was allowed to proceed for only five minutes instead of one and one-half hours. The product, after removal of the ether used in the extraction, was crystallized from 100 ml. of hot 95% alcohol giving 33 g., m. p. 96–98°. An additional 8 g. of product was obtained by distilling the mother liquors. After recrystallization the compound had a m. p. of 98–99°.

1-Methyl-2-decalol and 1-Methyl-5,6,7,8-tetrahydro-2-naphthol.—These compounds were obtained by the hydrogenation of 2-hydroxy-1-naphthaldehyde in ethanol over Raney nickel at 200° under 3600 p. s. i. of hydrogen during two and one-half hours. The aldehyde, m. p. 79–80°, was prepared in 40% yield as described.[14] The yield of the decalol in the hydrogenation was over 80%. Combination of the higher boiling fractions from several hydrogenations indicated the yield of the tetrahydronaphthol to be about 5%.

1-Methyl-2-decalone.—1-Methyl-2-decalol (99 g.) was slowly added to a solution of 120 g. of sodium dichromate in 100 g. of concentrated sulfuric acid and 500 ml. of water, the reaction mixture being kept below 45°. Stirring was continued for thirty minutes after all the alcohol had been added. The mixture was transferred to a separatory funnel and twice swirled, not shaken, with 200 ml. of ether. The ether was separated and the water layer again extracted by shaking with ether. The combined ether extracts were washed in a 5% sodium hydroxide solution until the ether was a light amber color. After drying and removal of the ether, the ketone (80 g.) was distilled at 105–107° (7 mm.).

1-Methyl-2-allyl-2-decalol.—The decalone (65 g. in 100 ml. of ether) was added at such a rate as to give gentle refluxing to allylmagnesium bromide in 400 ml. of ether, as obtained from allyl bromide (60.5 g.) and magnesium (72.9 g.). The addition product was decomposed by carefully mixing it with 500 ml. of a saturated solution of ammonium chloride. The desired alcohol (70 g.) was distilled 133–138° (7 mm.) and dehydrated to a mixture of dienes (30 g., $n^{25}D$ 1.4985–1.5250) distilling at 99–115° (7 mm.). The dehydration of 40 g. of the alcohol was made in a stream of nitrogen with a mixture of 40 g. of phosphoric anhydride and 200 ml. of phosphoric acid held in a bath at 180°. Dehydrogenation of the mixture of dienes in benzene over a nickel-on-alumina catalyst at 350° for twelve hours, gave 1-methyl-2-propylnaphthalene, b. p. 145–146° (10 mm.), $n^{25}D$ 1.5928. The same product was obtained in 53% yield by the dehydrogenation of the decalol.

Hydrogenations.—A number of compounds were hydrogenated in chrome–vanadium steel vessels having voids of 90 to 270 ml. at 1500 and 4500 p. s. i. of hydrogen with the standard copper–chromium oxide or W-2 Raney nickel catalyst. The hydrogenations listed immediately below were over W-2 Raney nickel. Both 1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene (16 g.) and 1,2-cyclopentenonaphthalene (6.3 g.) were hydrogenated with 5 g. of catalyst in methylcyclohexane at 250° within less than an hour to 1,2-cyclopentanodecalin. 1-Methyl-1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene (22 g.) at 200° for three hours gave 1-methyl-1,2-cyclopentanodecalin. 1-Methyl-1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene (20 g.) after a preliminary treatment at 250° in methylcyclohexane was again submitted to hydrogenation with fresh catalyst at 250° for three hours to give 1-methyl-1,2-cyclopentanoperhydrophenanthrene. 1,2-Cyclopentenophenanthrene (2 g.) in methylcyclohexane at 250° for five hours gave 1,2-cyclopentanoperhydrophenanthrene. 4a-Methyl-1,2,3,4,4a,11,12,12a-octahydrochrysene (11.5 g.) in 90 ml. of methylcyclohexane at 250° for two hours gave 4a-methylperhydrochrysene. Chrysene (3.5 g.) was similarly hydrogenated to perhydrochrysene. The yields in all of the hydrogenations described above were 80–95%, the discrepancy between the amount obtained and 100% being largely due to losses in handling small quantities with relatively large amounts (5 g.) of catalyst. 2-Carbethoxy-1,2-cyclopenteno-3,4-dihydronaphthalene and 2-carbethoxy-1,2-cyclopenteno-3,4-dihydrophenanthrene were hydrogenated to the tetrahydro compounds, at 50° over W-4 Raney nickel within an hour. Conversion of the dihydro or the tetrahydro to the perhydro compounds required in the case of decalin three hours at 175°, while two hydrogenations at 250° for several hours each were necessary in order to obtain perhydrophenanthrenes free of unsaturated compounds.

The keto groups in 2-(β-phenethyl)-cyclopentanone (27.5 g.) and 2-(β-phenethyl)-2-carbethoxycyclopentanone (100 g.) in ethanol were hydrogenated over 10% of their weight of copper–chromium oxide to the corresponding pentanols in yields of 90% at 160–175° in one to one and one-half hours.

The carbethoxy group in 2-carbethoxy-1,2-cyclopentanodecalin (10 g.) was converted in 80% yield to a methylol group after thirty-six hours at 250° over 2 g. of copper–chromium oxide. 2-Carbethoxy-1,2-cyclopenteno-3,4-dihydrophenanthrene in dioxane was hydrogenated as described just above to give a methylol derivative of a hydrophenanthrene containing two double bonds per molecule according to analysis. The hydrogenation to 2-methylol-1,2-cyclopentanoperhydrophenanthrene was completed with Raney nickel at 250° in six hours. 2-

(14) Russell and Lockhard, "Organic Syntheses," Vol. XXII, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 63.

Methylol-1,2-cyclopentano-decalin (9 g.) was hydrogenated over 4 g. of nickel-on-alumina for eight hours at 325° to give a 79% yield of 2-methyl-1,2-cyclopentanodecalin. 2-Methyl-1,2-cyclopentanoperhydrophenanthrene was prepared from the methylol compound under the conditions just stated.

Summary

A number of derivatives of 1,2-cyclopentanohydronaphthalenes and of 1,2-cyclopentanohydrophenanthrenes, with a substituent in an angular position, have been prepared by development of the methods of Bardhan, Sengupta, Kon, Bougault, Bogert and Cook. The use of liquid hydrogen fluoride at 0° has made possible the cyclization in excellent yields of certain substituted β-keto esters with the formation of 1,2-cyclopentenodihydronaphthalenes and phenanthrenes, with a carbethoxy group in an angular position. The carbethoxy group in these compounds has been reduced to methylol and methyl groups. Derivatives of chrysene have been prepared by a modified Bogert–Cook synthesis. A practical synthesis of 1-methyl-2-alkylnaphthalenes from 2-naphthol has been illustrated.

MADISON, WISCONSIN RECEIVED DECEMBER 10, 1948

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE AND THE POLYTECHNIC INSTITUTE OF BROOKLYN]

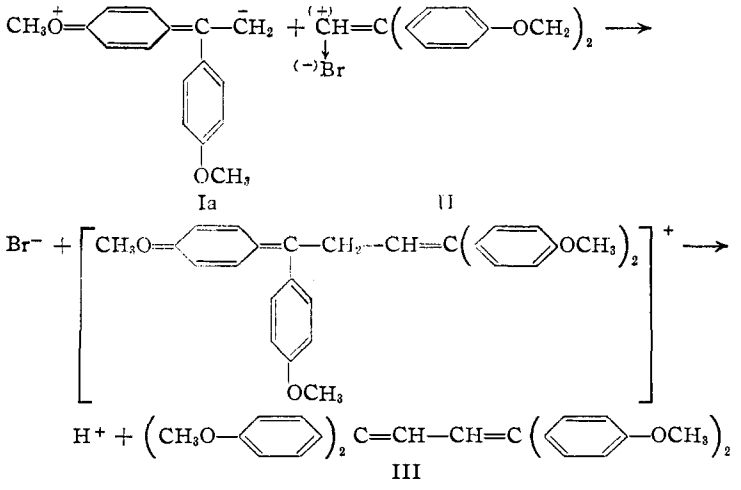
1,1,4,4-Tetraanisyl-1,3-butadiene

BY FELIX BERGMANN, JACOB SZMUSZKOWICZ AND ELCHANAN DIMANT[1]

Although 1,1-diphenylethylene can be dimerized by a variety of agents,[2] no success attended experiments to dimerize 1,1-di-(*p*-anisyl)-ethylene (I).[3] However, when we tried to convert (I) into the corresponding vinyl bromide (II) in acetic acid solution, we obtained a light-yellow substance of m. p. 207°, which we considered previously to be a "dimer,"[4] Addition of sodium acetate to the bromination mixture prevented the formation of the yellow compound and stopped the reaction at the intermediate stage (II).

We have now found that the substance of m. p. 207° is not a dimer, but represents 1,1,4,4-tetraanisylbutadiene (III).[5] Proof of this structure can be given in the following way: (a) All unsaturated dimers of diarylethylenes represent butenes[2] and consequently absorb one mole of hydrogen. Compound (III) however takes up two moles of hydrogen. (b) Reaction of (II) with Grignard magnesium gives (III), in analogy to the synthesis of 1,1,4,4-tetraphenylbutadiene.[6] (c) The absorption spectrum of (III) is similar to that of 1,1,4,4-tetraphenylbutadiene (see Fig. 1).[7] Moreover, as in the latter compound, V, the spectrum remains unchanged after three hours of irradiation indicating a structure in which there is no possibility of a *cis–trans* transformation.

The direct formation of (III) during the bromination of dianisylethylene is probably to be interpreted in the following way



If this explanation is correct, then (I) and (II) should react with each other to form (III). This reaction was found to proceed smoothly at 120° and to give a quantitative yield of (III). The above reaction scheme also explains why (I) cannot be dimerized by strong acids: The intermediate carbonium ion $R_2{}^+CCH_3$, because of resonance stabilization through the *p*-methoxy group, cannot attack the β-carbon of a second ethylene molecule. In the formation of the butadiene (III) the resonance form (Ia) acts as a nucleophilic agent, directly substituting the β-bromine atom. Experiments now under hand will show whether this reaction presents a general method for the synthesis of 1,1,4,4-tetraarylbutadienes.[8]

(1) Part of a thesis, submitted to the Hebrew University, Jerusalem, 1949.

(2) Staudinger and Kon, *Ann.*, **384**, 38 (1911); E. Bergmann and Weiss, *ibid.*, **480**, 49 (1930).

(3) Schmitz-Dumont, Thömke and Diebold, *Ber.*, **70**, 175 (1937).

(4) F. Bergmann and Szmuszkowicz, THIS JOURNAL, **69**, 1777 (1947).

(5) The analytical figures for a dimer of I ($C_{32}H_{32}O_4$—calcd., C, 80.0; H, 6.7) and for III ($C_{32}H_{30}O_4$—calcd., C, 80.3; H, 6.3) are too near to permit a distinction between these two structures.

(6) Lipp, *Ber.*, **56**, 571 (1923).

(7) Hirschberg, Bergmann and Bergmann, in preparation.

(8) *E. g.*, 1,1,4,4-tetraphenylbutadiene is obtained likewise by direct interaction of 1,1-diphenylethylene with 1,1-diphenylvinyl bromide. However, due to the absence of the activating *p*-methoxy groups the conditions of this reaction are much more drastic than in the synthesis of tetraanisylbutadiene. These and other experiments will be reported in a forthcoming paper.