16. *Acetylene Reactions. Part VI. Trimerisation of Ethynyl Compounds.*

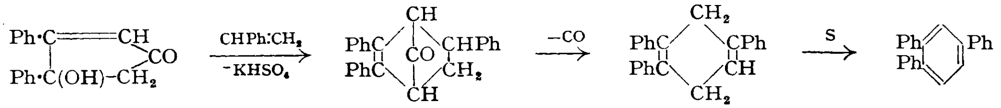
By J. D. Rose and F. S. Statham.

Dicarbonyldi(triphenylphosphino)nickel catalyses the polymerisation of phenylacetylene to the hitherto unknown 1 : 2 : 4-*triphenylbenzene*, the structure of which is demonstrated by unambiguous synthesis. Phenylethynylcarbinol is trimerised to 1 : 3 : 5-*tri*-(α-*hydroxybenzyl*)-*benzene*, which is oxidised to the known 1 : 3 : 5-tribenzoylbenzene.

Information from Germany after the end of the war (cf. F.I.A.T. Final Report No. 933, H.M.S.O., London, 1946) contains references to a catalyst, dicarbonyldi(triphenylphosphino)nickel, of the composition $(Ph_3P)_2Ni(CO)_2$, alleged to be active in the synthesis of acrylic acid derivatives from acetylenes and nickel carbonyl. A sample of this catalyst had been prepared in these laboratories, and on the appearance of the paper by Reppe and Schweckendiek (*Annalen*, 1948, **560**, 104) which contains, *inter alia*, an account of the trimerisation of propargyl alcohol by this catalyst to a mixture of 1 : 2 : 4- and 1 : 3 : 5-tri(hydroxymethyl)benzene, the trimerisation of a series of acetylenic compounds was investigated.

The catalyst is prepared by interaction of triphenylphosphine (2 moles) and nickel carbonyl (1 mole) in ether and separates as a pale cream-coloured crystalline powder which cannot be recrystallised without decomposition. From its solution in cold benzene nickel hydroxide is precipitated within a day or two and, although reasonably good analytical figures are obtained on a freshly prepared sample, after six months' storage the carbon content increases and the nickel content falls considerably; the catalytic activity also falls off markedly on storage.

Of a range of compounds investigated, only three acetylenic compounds were successfully trimerised; propargyl alcohol (see Reppe and Schweckendiek, *loc. cit.*), phenylethynylcarbinol (1-phenylpropargyl alcohol), and phenylacetylene. Phenylethynylcarbinol in boiling methyl alcohol was slowly trimerised to 1 : 3 : 5-*tri*-(α-*hydroxybenzyl*)*benzene*, the structure of which was demonstrated by its oxidation to the known *s*-tribenzoylbenzene. The polymerisation of phenylacetylene by the catalyst was violent and, unless the compound was diluted with a large volume of alcohol, was almost explosive. In 10% alcoholic solution, polymerisation is vigorous and exothermic, but can be controlled. The crude product, an orange-brown gum, was purified by distillation and repeated crystallisation, giving a white crystalline solid, m. p. 109°, with the molecular weight and the composition of a triphenylbenzene. Of the three theoretically possible triphenylbenzenes, only the 1 : 2 : 3-, m. p. 157° (Smith, *Ber.*, 1893, **26**, 65), and the 1 : 3 : 5-isomer, m. p. 170° (Vorländer, Fischer, and Wille, *Ber.*, 1929, **62**, 2836), are known. The hydrocarbon, m. p. 109°, was clearly different from either of these; the m. p. of *s*-triphenylbenzene was depressed to 80°—90° on admixture, and the formation of 1 : 2 : 3-triphenylbenzene would be very improbable, involving as it would the migration of a phenyl radical under relatively mild conditions. By elimination, therefore, it appeared probable that the substance in hand was the hitherto unknown 1 : 2 : 4-*triphenylbenzene*. This was established by synthesis, as follows



(I.) (II.) (III.) (IV.)

4-Hydroxy-3 : 4-diphenyl*cyclo*pent-2-en-1-one (I) (Japp and Miller, *J.*, 1885, 27) ("anhydromonoacetone benzil"), when heated with styrene in the presence of potassium hydrogen sulphate as dehydrant, affords the adduct 3 : 6-endo*keto*-1 : 2 : 4-*triphenyl*cyclo*hex*-1-*ene* (II), which on being heated above its melting point loses carbon monoxide and gives (presumably) a triphenyldihydrobenzene (*e.g.*, III), which could not be obtained crystalline but which, when dehydrogenated with sulphur, gave 1 : 2 : 4-triphenylbenzene (IV) identical with that obtained by polymerisation of phenylacetylene. Attempts to simplify the synthesis by interaction of (I) and phenylacetylene, which should have given (IV) more directly, *via* the (unstable) doubly unsaturated analogue of (II), were unsuccessful.

The formation of 1 : 2 : 4-triphenylbenzene unaccompanied by the 1 : 3 : 5-isomer is peculiar; Krasouskii and Kipryanov (*J. Phys. Chem. Russia*, 1925, **56**, 1; from *Chem. Abs.* 1925, **19**, 2817) showed that phenylacetylene, when heated with methylamine or ethylamine at 250—260° for 5—6 hours (sealed tube), affords *s*-triphenylbenzene. It is virtually certain that the *s*-isomer is not formed in the polymerisation described here; its solubility is much lower than that of the 1 : 2 : 4-isomeride, and it is clear that if both were formed together, the *s*-isomeride would be the more easily isolated. Attempted trimerisation of a variety of other ethynyl compounds, including 3-methylbut-1-yn-3-ol, 3-diethylaminobut-1-yne, benzoylacetylene, and phenylpropiolic acid, all failed or gave non-crystalline products which could not be identified.

EXPERIMENTAL.

Dicarbonyldi(triphenylphosphino)nickel, $[(CO)_2Ni(Ph_3P)_2]$.—Triphenylphosphine (13·1 g.) in ether (30 c.c.) was refluxed gently on the steam-bath, and nickel carbonyl (4·2 g.; 3·2 c.c.) was gradually added. Carbon monoxide was evolved briskly and, after addition of half of the nickel carbonyl, crystals were deposited from the solution. When addition of the nickel carbonyl was complete, the mixture was refluxed for a further 30 minutes, cooled, and filtered. Dicarbonyldi(triphenylphosphino)nickel (13·9 g.) was obtained as a pale cream-coloured crystalline solid, m. p. 210—215° (decomp.) when plunged into a bath preheated to 210° (Reppe and Schweckendiek, *loc. cit.*, gave m. p. 206—209°) (Found: C, 70·7; H, 5·0; Ni, 8·5. Calc. for $C_{38}H_{30}O_2P_2Ni$: C, 71·3; H, 4·7; Ni, 9·2%).

s-*Tri-(α-hydroxybenzyl)benzene*.—Phenylethynylcarbinol (1-phenylpropargyl alcohol) (10 g.) and the catalyst (0·5 g.) were refluxed in methyl alcohol (10 c.c.) overnight; there was no exothermic reaction. Evaporation of the solution, finally at 100°/16 mm., gave a brown gum which slowly crystallised; trituration with ether gave a cream-coloured solid (1·6 g.), m. p. 169—173°, which after repeated crystallisation from benzene afforded 1 : 3 : 5-*tri-(α-hydroxybenzyl)benzene*, m. p. 181° (Found: C, 81·3; H, 6·2. $C_{27}H_{24}O_3$ requires C, 81·8; H, 6·1%)

s-*Tribenzoylbenzene*.—The above trimer (0·35 g.) in acetone (5 c.c.) was oxidised by dropwise addition of chromium trioxide (0·2 g.) in water (0·6 c.c.) containing sulphuric acid (0·2 g.). The temperature rose spontaneously to 40°, and after 30 minutes' stirring water was added and the precipitated solid was collected (0·32 g.; m. p. 113—115°). One recrystallisation from alcohol afforded *s*-tribenzoylbenzene, m. p. 117°, undepressed by admixture with an authentic specimen, m. p. 116—118° (Found: C, 83·1; H, 4·2. Calc. for $C_{27}H_{18}O_3$: C, 83·1; H, 4·6%).

1 : 2 : 4-*Triphenylbenzene. Polymerisation of Phenylacetylene*.—Phenylacetylene (10 g.) in alcohol (100 c.c.) was heated under reflux on the steam-bath with the catalyst (0·5 g.). At 70° (internal temperature) a violent reaction occurred which was checked by cooling; when this had subsided the mixture was boiled under reflux for 1 hour, a dark oil separating. The mixture was poured into water and the oil extracted with ether, dried, and distilled. Fractions (*a*), b. p. about 160°/0·15 mm., and (*b*), b. p. about 190°/0·15 mm., were collected. Fraction (*a*) solidified and after 3 recrystallisations from alcohol afforded 1 : 2 : 4-*triphenylbenzene* as colourless prisms, m. p. 109° (Found: C, 94·25; H, 5·85; *M*, cryoscopic in benzene, 303. $C_{24}H_{18}$ requires C, 94·1; H, 5·9%; *M*, 306). Fraction (*b*), an orange viscous oil, deposited some crystalline material on cooling. It was dissolved in alcohol and cooled, and the mother-liquor decanted. Spontaneous evaporation of the liquor gave a yellow amorphous solid which on repeated recrystallisation from alcohol, and finally from light petroleum, gave white crystals, m. p. 109°, identical with those from fraction (*a*).

3 : 6-endo*Keto*-1 : 2 : 4-*triphenyl*cyclo*hex*-1-*ene*.—4-Hydroxy-3 : 4-diphenyl*cyclo*pent-2-en-1-one ("anhydromonoacetone benzil") (10 g.; Japp and Miller, *loc. cit.*), potassium hydrogen sulphate (10 g.), and styrene (20 g.) were refluxed for 2·5 hours. The hot supernatant styrene solution was decanted from the cake of potassium hydrogen sulphate, cooled, and diluted with ether. A pale yellow solid (5·25 g.), m. p. 183—184°, separated. Recrystallisation from alcohol–acetone gave white needles of 3 : 6-endo-*keto*-1 : 2 : 4-*triphenyl*cyclo*hex*-1-*ene*, m. p. 188° with effervescence (Found: C, 89·2; H, 5·95. $C_{25}H_{20}O$ requires C, 89·3; H, 5·95%).

When heated at 220—230°, 3 : 6-*endo*keto-1 : 2 : 4-triphenyl*cyclo*hex-1-ene (5 g.) evolved carbon monoxide briskly. The resulting yellow gum could not be induced to crystallise, and was mixed with powdered sulphur (1 g.) and heated at 250° for 4 hours. The product was distilled (b. p. about 170°/0·1 mm.) giving an orange viscous oil, which was dissolved in light petroleum (b. p. 60—80°) and set aside. After 3 days clusters of crystals separated; these were recrystallised twice from light petroleum, sublimed at 100°/0·1 mm., and finally recrystallised, giving white crystals of 1 : 2 : 4-triphenylbenzene, m. p. 109°, undepressed by admixture with material obtained from the polymerisation of penylacetylene.

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