

362. *Properties of Conjugated Compounds. Part XX.*
Diphenylketen as an Addendum.

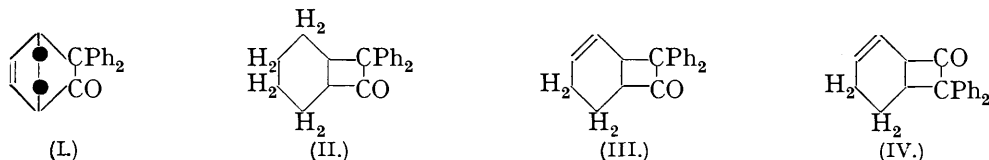
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The addition products obtained by Staudinger and his collaborators by the addition of diphenylketen to *cyclohexene* and to *cyclopentadiene* were formulated as containing additively-formed *cyclobutanone* rings, but their constitutions were not determined. It is here shown experimentally that *cyclohexene*, *cyclopentene*, *cyclohexadiene*, and *cyclopentadiene* are alike in yielding *cyclobutanone* derivatives, and also that the direction of addition of the ketenic reagent in the case of the cyclic dienes is that which would be anticipated having regard to the behaviour of the ketens with simple reagents. The polarised form of the ketens is discussed.

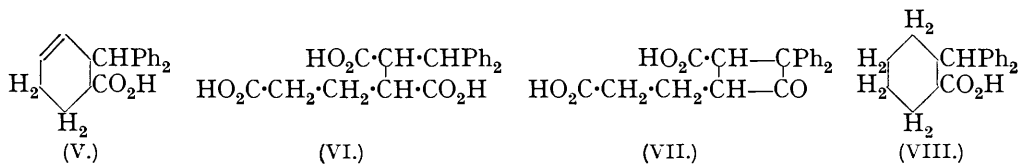
STAUDINGER in his well-known researches into the additivity of diphenylketen was successful in obtaining addition products with several unsaturated hydrocarbons. The constitutions of these adducts were not satisfactorily determined, although the result of addition in each case was represented to be a four-carbon ring structure. It is of some importance in connexion with general additive theory to determine with certainty the direction in which addition occurs in these examples, and also to discover whether ketonic additions to conjugated dienes are all of the same type, inevitably yielding four-carbon rings, just as Diels–Alder additions appear always to yield six-carbon rings.

Addition to cycloHexene and to cycloHexadiene.—Staudinger and Suter (*Ber.*, 1920, **53**, 1095) found that *cyclopentadiene* reacts readily with diphenylketen to give a crystalline mono-addition product, but they were unable at the time to examine whether *cyclopentene* also combines with the reagent. They showed, however, that both *cyclohexene* and styrene give crystalline adducts with diphenylketen, but did not examine the additivity of *cyclohexadiene*. The following observations show for the first time the mutual relationships and constitutions of the *cyclohexene* and *cyclohexadiene* adducts.

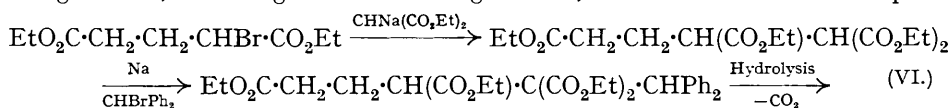
*cyclo*Hexadiene, like *cyclopentadiene*, combines readily at room temperature with diphenylketen, whereas *cyclohexene* combines with this reagent only on prolonged heating. The adduct from *cyclohexadiene* consists always of a single mono-olefinic substance, and this passes on hydrogenation into a dihydride identical with the adduct formed directly from the reagent and *cyclohexene*. This observation excludes at once the possibility that the *cyclohexadiene* adduct is the substance (I), formed by terminal addition of the reagent to the cyclic diene in the manner of the Diels–Alder reaction, and it also increases the probability that the *cyclohexene* unites with the reagent to form the *cyclobutanone* structure (II); but it does not distinguish between the rival formulæ (III) and (IV), corresponding to the alternative possible directions of 1 : 2-addition to the diene system.



The direction of addition to *cyclohexadiene* is shown definitely by the nature of the degradation products obtainable from the adduct. By hydrolytic fission with alkali the adduct yields two (and two only) isomeric monocarboxylic acids, m. p.'s 148–149° and 112°, which might be regarded (a) as derived from (III) and (IV) respectively, (b) as representing isomeric Δ^α - and Δ^β -acids, both derived from (IV), (c) as formed from (III) or from (IV) by fission at different points in the *cyclobutanone* ring, *i.e.*, on either side of the carbonyl group, or (d) as a stereoisomeric (*cis-trans*) pair derived either from (III) or from (IV). Actually the two fission acids have proved to be a stereoisomeric pair possessing the formula (V), since both of them give a tribasic acid, 5 : 5-diphenylpentane-1 : 3 : 4-



tricarboxylic acid (VI), m. p. 210°, on oxidation with permanganate, and one of them in addition a hygroscopic and difficultly purifiable acid, which may possibly represent a stereoisomeric form of (VI). The solid tribasic acid (VI) has been synthesised from ethyl α -bromoglutarate, according to the following scheme, and it is found that the principal



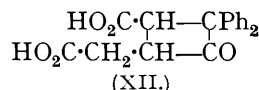
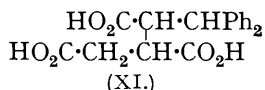
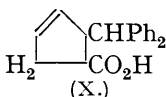
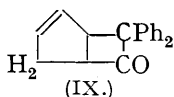
product, the acid, m. p. 210°, is accompanied by a hygroscopic, difficultly purifiable acid similar to the foregoing one.

Exactly the same tribasic acid can be obtained from the *cyclohexadiene* adduct if the above-mentioned two stages of degradation are reversed, so that oxidation precedes hydrolytic fission. By this route the acid (VII) is first obtained (one pure form isolated), which on heating with alkali yields (VI).

The structure of the *cyclohexene* adduct follows from the fact that this substance undergoes fission with alkali, yielding thereby a monobasic acid which cannot be other than (VIII), since it proves to be identical with the dihydride formed by hydrogenation of the fission product (V) from the *cyclohexadiene* adduct. Clearly, therefore, the adducts formed from *cyclohexadiene* and *cyclohexene* are (III) and (II) respectively.

Addition to cycloPentene and to cycloPentadiene.—Similar degradations have been carried out with Staudinger's adduct from *cyclopentadiene* and diphenylketen, whereby this substance has been converted by one route successively into the hydrolytic fission product (X) and its oxidation product (XI), or by the reverse route into a gummy oxidation

product, presumably (XII), and its hydrolytic fission product (XI). Two forms (m. p.'s 148—149° and 120—121°) of a monobasic acid corresponding in composition to (X) were obtained, and these yielded respectively on oxidation different isomeric forms (m. p.'s

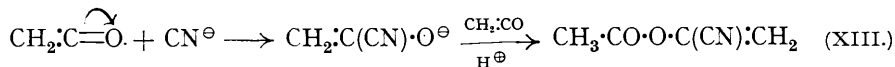


186—187° and 208—209°) of a tribasic acid agreeing in composition with (XI); and by the reverse route the gummy oxidation product proved to be unresolvable into crystalline acids, but its major or sole hydrolysis product was one of the above-mentioned forms of the tribasic acid, *viz.*, that of m. p. 208—209°. The nature of the two forms of the tribasic acid thus obtained—whether structural isomerides formed by hydrolytic fission of the *cyclobutanone* ring in (IX) at different points, or mere stereoisomeric varieties—required to be determined. The synthesis of the tricarboxylic acid (XI) by a method similar to that described above for the *cyclohexadiene* derivative (VI) was in progress when Lewis, Ramage, Simonsen, and Wainwright (J., 1937, 1838) published an account of the degradation of the *cyclopentadiene*–diphenylketen adduct by a route different from the two indicated above. The end-product of these authors was a stereoisomeric pair of tribasic acids the constitutions of which were established by synthesis and these corresponded so closely in melting point and general character with our pair of acids that it seemed unnecessary to proceed further with our synthesis. It is abundantly established, therefore, that the direction of diphenylketen addition to *cyclopentadiene* is that indicated in (IX).

Although Staudinger and his collaborators did not prepare an adduct directly from *cyclopentene* and diphenylketen, and so enable the identity (or otherwise) of the latter with the dihydride of his *cyclopentadiene*–diphenylketen adduct to be determined, it appears from the literature that this comparison of adduct and dihydro-adduct was actually made at a later date (although no details have been published) by Alder and Stein ("Handbuch der Biologischen Arbeitsmethoden," Abderhalden, Abteil. I, p. 3107). It follows, therefore, that the *cyclopentene* adduct has the same relationship to the *cyclopentadiene* derivative as the *cyclohexene* adduct has to the *cyclohexadiene* derivative.

Direction of Ketenic Addition to Olefinic Systems.—Staudinger early showed that substances of the type HX (hydrogen halide, hydrogen sulphide, amines, organic acids, etc.) form addition products with members of the keten group uniformly according to the equation $\text{CRR}'\text{:CO} + \text{HX} \longrightarrow \text{CHRR}'\text{CXO}$ and it appears, indeed, that in all the numerous observed examples in which a dividing addendum adds to the ethylenic centre of

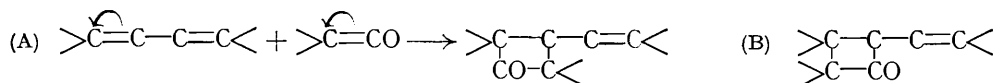
a keten, polarisation of the latter occurs exclusively in the direction $\text{CRR}'\text{=}\overleftarrow{\text{C}}\text{=O}$. The capacity of the carbonyl group of a keten to react additively in its normal kationoid manner seems to have been observed in a single example cited by Wilsmore and Deakin (J., 1910, 97, 1969), in which unsubstituted keten (2 mols.) reacts with hydrogen cyanide (1 mol.) to give an unstable compound (presumably XIII),* which is hydrolysable to acetic acid and hydrogen cyanide:



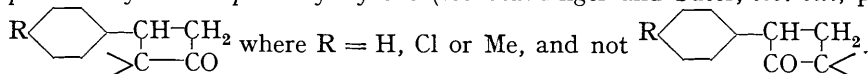
For the second group of reactions, however, in which members of the keten group function as addenda (necessarily, of course, undividing addenda) instead of compounds to which addition is made, there has hitherto been insufficient evidence to show whether or not the

* Staudinger has expressed the opinion that certain addenda of the type HX, *e.g.*, water and ammonia, are capable of adding themselves to the carbonyl double bond in the ketens (see *Helv. Chim. Acta*, 1922, 5, 87), and has suggested that Wilsmore and Deakin's reaction involves the formation of a hydrate of the keten, followed by migration of hydrogen, rather than the addition of hydrogen cyanide. The successful formation of derivatives with Grignard reagents (Gilman and Heckert, *Chem. Zentr.*, 1920, III, 310) may perhaps express kationoid reactivity of the carbonyl group of ketens, but seems to us more likely to result from C:C additivity.

above-mentioned dominant polarising tendency is the only one to be displayed. There is, *a priori*, every reason to expect that this will be the case, and that a conjugated diene will always combine with the keten in the manner (A) rather than give the isomeric form (B);



likewise it is to be expected that the adducts formed by treatment of a keten with styrene, *p*-chlorostyrene or *p*-methylstyrene (see Staudinger and Suter, *loc. cit.*, p. 1092) will be



The above-mentioned results obtained with cyclic olefins and diolefins unambiguously fulfil this expectation, as also do certain new results relating to the addition of diphenylketen to styrene which have been published during the course of the present work (Bergmann and Blum-Bergmann, this vol., p. 727). If, however, the polarisation

$\begin{array}{c} \curvearrowright \\ >C=C=O \\ \curvearrowleft \end{array}$ holds for all additions of ketens to unsaturated substances, it would seem to be necessary, in order to be able to account for the published results of Staudinger and his collaborators on the additivity of the systems $>C=N-$, $-N=O$, and $>C=S$ ("Die Ketene," p. 7688; Klever and Kober, *Annalen*, 1911, **374**, 11), to assume that polarisation of these systems can ordinarily take place in either of the possible directions.

As regards the tendency for four-membered rather than six-membered rings to be formed by the action of ketens on conjugated dienes it appears fairly certain from preliminary experiments which we have carried out with open-chain butadienes that the latter are uniform in behaviour with their cyclic analogues, although both mono- and di-addition products seem in some cases at least to be obtainable.

EXPERIMENTAL.

Addition of cycloHexene to Diphenylketen.—This adduct, obtained in good yield under the conditions described by Staudinger and Suter (*loc. cit.*), melted at 130° (Staudinger and Suter, m. p. 129—130°) (Found: C, 87.05; H, 7.25. Calc. for C₂₀H₂₀O: C, 86.95; H, 7.25%).

Fission with alkali. The adduct was refluxed for 1 hour with a solution formed from sodium (0.23 g.), methyl alcohol (20 c.c.) and water (4 drops). The alcohol was evaporated from the product, and the residue then acidified and extracted with ether. A syrupy acid was obtained which, dissolved in light petroleum, slowly separated in small prisms, m. p. 131—135°. Repeated crystallisation of the substance from the same solvent gave 2-benzhydrylhexahydrobenzoic acid, m. p. 151—152° (Found: C, 81.4; H, 7.25; equiv., 290. C₂₀H₂₂O₂ requires C, 81.6; H, 7.5%; equiv., 294). The mother-liquors gave on evaporation a gummy residue, which, dissolved in light petroleum, gradually separated as a crystalline powder, m. p. 123°. This was without doubt a stereoisomeric form of 2-benzhydryl hexahydrobenzoic acid, but was extremely difficult to crystallise and hence to purify completely from traces of gummy matter (Found: C, 80.9; H, 7.4%; equiv., 285).

Adduct of Δ^{1:3}-cycloHexadiene with Diphenylketen (7-Keto-8:8-diphenyl-Δ²-bicyclo[4:2:0]-octene).—A mixture of the diene (1 mol.) with diphenylketen (1 mol.) was kept overnight. Combination took place rapidly with generation of heat, yielding a solid adduct. This after two recrystallisations from methyl alcohol and one from light petroleum formed colourless needles, m. p. 132—133°. No second adduct was formed (Found: C, 87.4; H, 6.55. C₂₀H₁₈O requires C, 87.6; H, 6.55%).

Fission of adduct with alkali. The adduct (2.74 g.) was refluxed on a sand-bath for 70 mins. with a solution of caustic potash (5.6 g.) in methyl alcohol (25 c.c.). The product was in turn freed from alcohol, taken up in water, filtered, and acidified. The precipitate thus obtained (m. p. 130—135°) was dried and crystallised several times from light petroleum. Crystals of (presumably *trans*) 2-benzhydryl-Δ³-tetrahydrobenzoic acid were deposited as colourless needles, m. p. 148—149° (Found: C, 82.35; H, 6.7; equiv., 286. C₂₀H₂₀O₂ requires C, 82.2; H, 6.85%; equiv., 292). The mother-liquors, on standing, yielded further crystals, which after several recrystallisations from light petroleum formed fine needles, m. p. 112°. This was an isomeric form (presumably *cis*) of the same acid (Found: C, 82.1; H, 6.85%; equiv., 288).

Oxidation of fission products. (a) Oxidation of the acid, m. p. 148—149°, with permanganate (4 atoms of oxygen) was conducted both in aqueous and in acetone solution. The product in each case formed a brown, sticky mass; this, after dissolution in ether, gradually separated in crystals which melted from 165° to 198°. Several crystallisations of this product gave 5 : 5-diphenylpentane-1 : 3 : 4-tricarboxylic acid (high-melting form), crystallising in colourless prisms, m. p. 210° (rapid heating, 228°) (Found : C, 67·2; H, 5·6; equiv., 113. $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·6%; equiv., 118).

(b) Oxidations of the acid, m. p. 112°, carried out as described for the preceding acid gave always a gummy acidic product which, when dissolved in ether and treated cautiously with small amounts of benzene, deposited slowly first a quantity of 5 : 5-diphenylpentane-1 : 3 : 4-tricarboxylic acid, m. p. 210°, and subsequently a very hygroscopic, strongly acidic powder. The latter resembled the residual acid obtained during the synthesis of 5 : 5-diphenylpentane-1 : 3 : 4-tricarboxylic acid, but it could not be satisfactorily purified.

Hydrogenation of fission product, m. p. 148—149°. The acid absorbed 1 mol. of hydrogen (Adams's catalyst), giving 2-benzhydrylhexahydrobenzoic acid (colourless prisms from methyl alcohol, m. p. 150—151°), and proved to be identical with the acid, m. p. 151—152° (mixed m. p. 151—152°), obtained by hydrolytic fission of the adduct from cyclohexene and diphenylketen (above).

Hydrogenation of adduct. The adduct absorbed 1 mol. of hydrogen (Adams's catalyst), giving a dihydride (colourless prisms), m. p. 130°. This strongly depressed the m. p. when mixed with the original adduct, but caused no depression of m. p. when mixed with the adduct (m. p. 130°) formed directly from cyclohexene and diphenylketen (see above) (Found : C, 86·9; H, 7·1. Calc. for $C_{20}H_{20}O$: C, 86·95; 7·25%).

Oxidation of adduct. The adduct (2·74 g.) was refluxed with acetone into which potassium permanganate (4·5 g.) was very gradually introduced. After $\frac{1}{2}$ hour the mixture was worked up and there was obtained a sticky, brown acid which, when it had been dissolved in light petroleum, slowly separated in crystalline form, leaving in solution a very small quantity of a gummy acid. The crystalline solid was 2 : 2-diphenylcyclobutanone-3-carboxylic-4-propionic acid, which, after recrystallisation from ether-benzene, formed colourless prisms, m. p. 205—206° (Found : C, 71·1; H, 5·25; equiv., 165. $C_{20}H_{16}O_5$ requires C, 71·0; H, 5·3%; equiv., 169).

Hydrolytic fission of oxidation product. The above acid, m. p. 205—206°, was refluxed for 1 hour with methyl-alcoholic sodium hydroxide. The reaction mixture gave on working up a gummy acid which solidified on treatment with ether-benzene. This acid, which crystallised from the same solvent in shining prisms, m. p. 209—210°, was the higher-melting form of 5 : 5-diphenylpentane-1 : 3 : 4-tricarboxylic acid, identical (mixed m. p. 209—210°) with that obtained above (Found : C, 67·05; H, 5·3%; equiv., 115).

Synthesis of 5 : 5-diphenylpentane-1 : 3 : 4-tricarboxylic acid. Ethyl α -bromoglutarate (1 mol.) was added to granular ethyl sodiomalonate (1 mol.) suspended in dry benzene, and the mixture heated on a steam-bath for 48 hours. The product was treated with water, and the benzene layer separated, dried and freed from solvent. The residual oil, ethyl butane-1 : 1 : 2 : 4-tetracarboxylate, boiled on distillation at 168—170°/0·5 mm. Yield, 62% (Found : C, 55·2; H, 7·2. $C_{16}H_{26}O_8$ requires C, 55·5; H, 7·5%).

This ester (9·5 g.) was added to pulverised sodium (0·64 g.) suspended in dry benzene (20 c.c.), and the whole refluxed for 24 hours. To the cooled product, bromodiphenylmethane (6·78 g.) in dry benzene (20 c.c.) was added, and the mixture refluxed for 72 hours. The cooled product, on being worked up as before, gave an oily ester which distilled at 252°/1 mm., together with a small quantity of a crystalline hydrocarbon. The latter proved to be tetraphenylethane, m. p. 224° (Found : C, 93·25; H, 6·25. Calc. for $C_{26}H_{22}$: C, 93·4; H, 6·6%). The ester was directly hydrolysed by refluxing for 4 hours with a slight excess of alcoholic potassium hydroxide. The reaction mixture gave, on being worked up, a crude crystalline powder, m. p. 90—150° : this slowly lost carbon dioxide and passed into solution when boiled for many hours with dilute sulphuric acid. The hot filtered liquor deposited, on cooling, crystals of 5 : 5-diphenylpentane-1 : 3 : 4-tricarboxylic acid. These melted after several crystallisations from ether-benzene in shining needles, m. p. 210° (228° rapid heating) and proved to be identical (mixed m. p. 209—210°) with the acid, m. p. 210° (rapid heating, 228°), obtained by degradation of the cyclohexadiene adduct in the two ways described above (Found : C, 67·0; H, 5·7%; equiv., 118). The ether-benzene mother-liquor contained a highly hygroscopic acid, which could be precipitated as a white powder but on account of its rapid absorption of moisture could not be satisfactorily purified or identified as a stereoisomeric form of 5 : 5-diphenylpentane-1 : 3 : 4-tricarboxylic acid.

Addition of cycloPentadiene to Diphenylketen.—This adduct, obtained as described by Staudinger and Suter (*loc. cit.*), melted at 89—90° (Found : C, 87·7; H, 5·95. Calc. for $C_{19}H_{16}O$: C, 87·7; H, 6·15%). Yield, 85%. Careful fractional crystallisation of the numerous batches of the crude adduct showed that no second addition product was formed.

Fission of adduct with alkali. The addition product was hydrolysed for 1 hour with a *very slight* excess of methyl-alcoholic potash. The product was freed from alcohol, dissolved in water, filtered, and acidified. The precipitated crystalline acid (m. p. 125—127°) was fractionally crystallised from light petroleum, and thereby yielded two isomeric forms of 2-benzhydrylcyclopentene-1-carboxylic acid. One of these, m. p. 148—149°, formed long shining needles, sparingly soluble in petroleum (Found : C, 82·1; H, 6·6; equiv., 282. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%; equiv., 278); the other formed crystalline aggregates, m. p. 121—122°, very soluble in petroleum (Found : C, 81·9; H, 6·45%; equiv., 280). The same two acids were obtained also when greatly increased proportions of caustic alkali were used, and also when the duration of hydrolysis was increased (up to 18 hours).

Oxidation of the fission product. (a) The acid of m. p. 148—149° (0·5 g.), dissolved in 10 c.c. of acetone, was heated while potassium permanganate (0·9 g.), dissolved in boiling acetone, was gradually introduced. The product when freed from manganese oxide and acidified gave a white acidic precipitate : this was filtered off, and the remainder of the acidic product extracted with ether. The 4 : 4-diphenylbutane-1 : 2 : 3-tricarboxylic acid thus obtained, after repeated crystallisations from benzene-ether, formed colourless plates, m. p. 186—187° (Found : C, 66·7; H, 5·4; equiv., 115. Calc. for $C_{19}H_{18}O_6$: C, 66·6; H, 5·3%; equiv., 114).

(b) Oxidation of the acid, m. p. 121—122°, conducted in a similar way, gave a solid acid which crystallised from ether-benzene in small colourless needles, m. p. 208—209°. This acid was a higher-melting form of 4 : 4-diphenylbutane-1 : 2 : 3-tricarboxylic acid (Found : C, 66·8; H, 5·5%; equiv., 116).

Lewis, Ramage, Simonsen, and Wainwright (*loc. cit.*) assign to the two isomeric forms of 4 : 4-diphenylbutane-1 : 2 : 3-tricarboxylic acid synthesised by them the m. p.'s 186—187° and 208—209°.

Oxidation of the adduct. The adduct (0·26 g.) in acetone (16 c.c.) was refluxed for $\frac{1}{2}$ hour with potassium permanganate (0·5 g.) dissolved in acetone (30 c.c.). The liquid was filtered, and the manganese mud dried and extracted with warm water. The aqueous extract yielded on acidification a gummy acid which could not be obtained in solid condition.

Hydrolytic fission of the oxidation product. The gummy acid (0·1 g.) was refluxed for 25 mins. with a slight excess of methyl-alcoholic sodium hydroxide. The product being worked up, a white crystalline acid was obtained which after twice recrystallising from ether-benzene melted at 208—209°. This acid was found by direct comparison to be identical with the higher-melting acid (m. p. 208—209°) obtained by the hydrolytic fission-oxidation procedure described above (Found : C, 66·5; H, 5·3%; equiv., 112).

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