

### 520. An Unusual Product from Diphenylketen and Ethoxyacetylene.

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The product from reaction of diphenylketen and ethoxyacetylene in nitromethane has been shown to have an unusual perhydroazulene skeleton. In the reaction one of the phenyl residues of the diphenylketen is incorporated into a seven-membered ring whilst the ethoxyacetylene becomes part of a cyclopentenone ring. The complete structure of the adduct has been defined.

EXTENSIVE and important investigations of the chemistry of ethoxyacetylene have been carried out by Arens and his collaborators.<sup>1</sup> During this work Nieuwenhuis and Arens<sup>2</sup> studied the reaction between ethoxyacetylene and diphenylketen in nitromethane solution. An adduct was formed which, mainly by analogy, was at first assigned the constitution of a cyclobutenone (I). We were interested in cyclobutenones because there was reason to believe that they would be subject to photochemical cleavage. Thus it can be argued<sup>3</sup> that rings of  $(2n + 2)$  members and containing  $n$  conjugated double bonds should afford on photolysis either bridged derivatives or photochemical-cleavage products. The cleavage of cyclohexa-2,4-dienone rings on irradiation illustrates the cleavage principle nicely.<sup>4</sup> Irradiation of a typical cyclobutenone (II)<sup>3</sup> in the presence of water indeed gave the expected acid (IV), no doubt<sup>4</sup> *via* the keten (III). The reaction is, however, slower than with the six-membered analogues. In order to examine the reason for this relatively sluggish cleavage we turned to other cyclobutenones of which the compound described by Nieuwenhuis and Arens<sup>2</sup> seemed easily available. From the infrared spectrum of this adduct it was clear that the compound could not be a cyclobutenone. Later, Arens himself also realised this.<sup>1</sup> The carbonyl frequency of the adduct was indicative of a cyclopentenone formula. The formulation of the adduct as a  $\beta$ -ethoxy- $\alpha\beta$ -unsaturated ketone<sup>2</sup> cannot, on the other hand, be challenged.

Our work has shown that the adduct has the constitution (VII) and is formed by a reaction sequence which can be represented schematically as in (V)  $\longrightarrow$  (VI)  $\longrightarrow$  (VII). A preliminary report has already appeared.<sup>5</sup> The postulated intermediate (VI) in this sequence might well be expected to undergo the norcaradiene  $\longrightarrow$  cycloheptatriene rearrangement to give the true structure (VII). Initially (in 1958—1959), however, we considered both (VI and (VII) as possible representations for the adduct.

The quantitative nuclear magnetic resonance spectrum of the adduct showed 4 vinyl hydrogens (at positions 6, 7, 8, and 9) at  $\tau = 3.68$ , 1 vinyl hydrogen (at position 5) at  $\tau = 3.21$ , 5 aromatic hydrogen atoms (1 phenyl residue) at  $\tau = 2.83$ , 1 vinyl hydrogen (at position 2,  $\alpha$ - to the ketone) at  $\tau = 4.80$ , and bands for an ethoxy-group. Selective hydrogenation of the adduct over palladised catalyst or, in initial experiments, over

<sup>1</sup> See Arens in "Advances in Organic Chemistry. Methods and Results," Vol. II (ed. Raphael, Taylor, and Wynberg, Interscience Publishers Inc., New York, 1960, pp. 117—212.

<sup>2</sup> Nieuwenhuis and Arens, *Rec. Trav. chim.*, 1958, **77**, 1153.

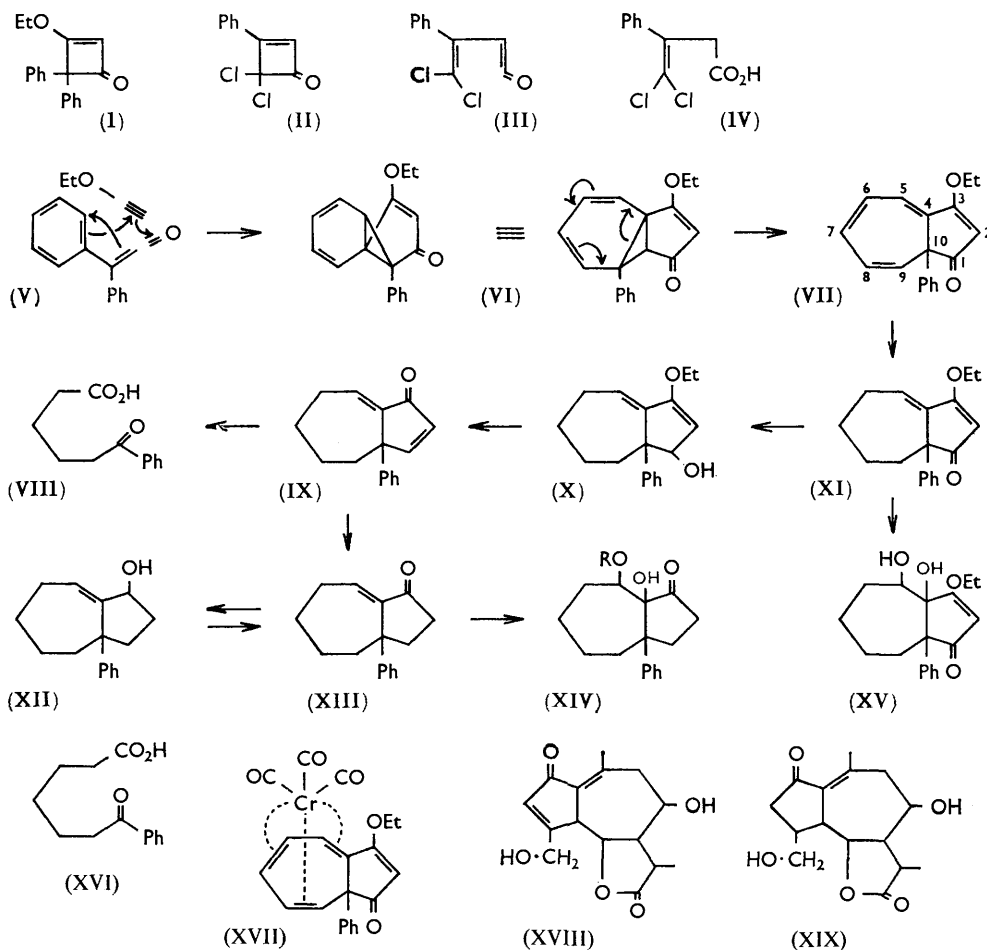
<sup>3</sup> Barton, *Helv. Chim. Acta*, 1959, **42**, 2604.

<sup>4</sup> Barton and Quinkert, *J.*, 1960, **1**.

<sup>5</sup> Barton, Gardner, Petterson, and Stamm, *Proc. Chem. Soc.*, 1962, **21**.

Raney nickel, benzene being used as solvent, gave a quantitative yield of a tetrahydro-adduct (XI). This showed 1 vinyl hydrogen (at position 5) at  $\tau = 3.40, 3.32, 3.26,$  and  $3.16\delta$  as well as signals for the phenyl residue, for the vinyl hydrogen at position 2, and for the ethoxyl group, just as in the spectrum of the original adduct. The tetrahydro-derivative was smoothly converted into the  $\alpha$ -glycol (XV) with osmium tetroxide. The latter showed  $\lambda_{\max.} 248 \text{ m}\mu$  ( $\epsilon = 13,500$ ), whilst the tetrahydro-adduct had  $\lambda_{\max.} 279 \text{ m}\mu$  ( $\epsilon = 16,600$ ). Both compounds showed an infrared carbonyl band near  $1700 \text{ cm.}^{-1}$  indicative of cyclopentenone. The change in ultraviolet absorption on treatment with osmium tetroxide shows that the tetrahydro-compound (XI) contains an extended conjugated dienone system.

Reduction of the compound (XI) with lithium aluminium hydride gave an allylic alcohol (X), which on mild acid treatment<sup>6</sup> afforded the cross-conjugated dienone (IX).



The ultraviolet absorption of this compound ( $\lambda_{\max.} 256 \text{ m}\mu$ ) is like that of dihydrolactucin<sup>7</sup> (XVIII) ( $\lambda_{\max.} 257 \text{ m}\mu$ ), and the infrared spectra in the carbonyl region are also comparable. In particular the dienone (IX) showed the same exalted intensity of the C=C stretching

<sup>6</sup> Procedure of Woodward, Sondheimer, Taub, Heusler, and McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223.

<sup>7</sup> Barton and Narayanan, *J.*, 1958, 963.

frequency as does dihydrolactucin, a feature which is due<sup>7, 8</sup> to the *cisoid* nature of the chromophore. Selective hydrogenation of the dienone (IX) gave largely the conjugated ketone (XIII). This, although contaminated with the fully hydrogenated saturated ketone, showed ultraviolet and infrared spectra consonant with the presence of a *cisoid*  $\alpha\beta$ -unsaturated ketone, as in tetrahydrolactucin (XIX).<sup>7</sup> Reduction of the ketone (XIII) with sodium borohydride gave an allylic alcohol (XII) showing only isolated benzene absorption. Oxidation with manganese dioxide re-formed the starting ketone (XIII).

On treatment with osmium tetroxide the ketone (XIII) gave the expected  $\alpha$ -glycol (XIV; R = H) from which a 3,5-dinitrobenzoate [XIV; R = 3,5-(NO<sub>2</sub>)<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CO] was readily prepared. This 3,5-dinitrobenzoate was stable to chromium trioxide and therefore contained only a tertiary hydroxyl group. In contrast, the parent glycol (XIV; R = H) was easily oxidised by this reagent.

Oxidation of the dienone (IX) with permanganate-periodate (Lemieux reagent) gave  $\delta$ -benzoylvaleric acid (VIII). For comparison we also prepared 6-benzoylhexanoic acid (XVI) by ozonolysis of 1-phenylcycloheptene. The isolation of the keto-acid (VIII) proves the relationship between the phenyl residue of the adduct (VII) and the butadiene system. From comparison of the ultraviolet absorption of the adduct ( $\lambda_{\text{max}}$ , 342 m $\mu$ ) with that of the dienone (XI) ( $\lambda_{\text{max}}$ , 279 m $\mu$ ) the butadiene system must clearly be conjugated with the dienone system. The totality of the evidence is decisively in favour of the constitution (VII). We have, of course, also considered how far a simple rearrangement on hydrogenation might also allow further consideration of structure (VI). The latter is excluded not by chemical evidence but by the nuclear magnetic resonance spectrum. Thus the vinyl proton at position 5 ( $\tau = 3.21$ ) could not possibly represent<sup>9</sup> the hydrogen at position 9 in formula (VI). However, we may add that the nuclear magnetic resonance spectra of the dienone (IX) and the enone (XIII) were at first misleading because the vinyl hydrogen at position 5 had been shifted in both cases so that it appeared under that of the phenyl residue. This was only revealed by quantitative measurements.

It is well known that cycloheptatrienes form chromium carbonyl complexes.<sup>10</sup> We therefore expected that the adduct (VII) would form such a complex. In the Experimental section we describe such a derivative which should have the constitution (XVII). This complex gave back the adduct (VII) on treatment with pyridine and showed the normal cyclopentenone carbonyl band in its infrared spectrum as expected if the five-membered ring of (VII) is not involved in the complexing. As also expected, the tetrahydro-adduct (VII) did not give a chromium carbonyl complex. The complex (XVII) is currently under X-ray investigation by Professor J. M. Robertson, F.R.S., Dr. G. A. Sim, and their collaborators at the University of Glasgow.

The work described in the present paper was incorporated into a N.A.T.O. report (J. N. G.; September, 1961). The same structure (VII) for the adduct has been suggested by Jenny, Schenker, and Woodward<sup>11</sup> on the basis of independent, but complementary, evidence.

#### EXPERIMENTAL

M. p.s were taken on the Kofler block. Unless otherwise specified ultraviolet absorption spectra were taken in ethanol and infrared absorption spectra are for Nujol mulls. The light petroleum was the fraction of b. p. 60—80°. Nuclear magnetic resonance spectra were taken in deuteriochloroform at 56.4 megacycles.

*Irradiation of 2,2-Dichloro-3-phenylcyclobutenone* (II).—The cyclobutenone (II)<sup>12</sup> (kindly provided by Professor J. D. Roberts, California Institute of Technology) (10.3 mg.) in ether

<sup>8</sup> Erskine and Waight, *J.*, 1960, 3425.

<sup>9</sup> Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

<sup>10</sup> Abel, Bennett, Burton, and Wilkinson, *J.*, 1958, 4559.

<sup>11</sup> Jenny, Schenker, and Woodward, *Angew. Chem.*, 1961, 73, 756.

<sup>12</sup> Silversmith, Kitahara, Caserio, and Roberts, *J. Amer. Chem. Soc.*, 1958, 80, 5840, and references there cited.

(50 ml.) saturated with water was irradiated over a bare mercury arc lamp (125 w) for 8 hr. (ultraviolet control). Removal of the ether and separation into neutral (negligible) and acidic fractions gave (in the latter) 4,4-dichloro-3-phenylbut-3-enoic acid (IV). After crystallisation from light petroleum this (7 mg.) was identified<sup>12</sup> by m. p., mixed m. p., and ultraviolet and infrared spectra. The appropriate blank reaction in the absence of light gave back starting material (100%). Irradiation of 6-acetoxy-6-methylcyclohexa-2,4-dienone<sup>4</sup> was complete (ultraviolet control) under the same conditions in 2 hr. Irradiation of the cyclobutenone (II) under the same conditions in the presence of cyclohexylamine<sup>4</sup> caused no significant change (ultraviolet control) in the rate of the photochemical reaction (the amide produced was not characterised).

*Formation of the Adduct (VII).*—The adduct was prepared according to the directions of Nieuwenkuis and Arens,<sup>2</sup> except that the reaction was shown to be complete at  $-25$  to  $-35^\circ$  in 3 hr. (instead of 7 days). It formed yellow prisms, m. p.  $161$ — $162^\circ$  (from ethanol),  $\lambda_{\max}$ . 248 and 360  $m\mu$  ( $\epsilon$ , 16,800 and 4400),  $\epsilon$  (206  $m\mu$ ) = 28,000,  $\lambda_{\text{infl.}}$  211  $m\mu$  ( $\epsilon$ , 18,000),  $\lambda_{\text{min.}}$  234 and 285  $m\mu$  ( $\epsilon$ , 12,000 and 3000) respectively,  $\nu_{\max}$ . 1689 (cyclopentenone),  $\nu_{\max}$ . ( $\text{CHCl}_3$ ) 1689  $\text{cm}^{-1}$  [Found: C, 81.5; H, 6.25; OEt, 16.0%;  $M$  (Rast), 253. Calc. for  $\text{C}_{18}\text{H}_{16}\text{O}_2$ : C, 81.8; H, 6.1; OEt, 17.0%;  $M$ , 264].

*The Tetrahydro-derivative (XI) of the Adduct (VII).*—The adduct (500 mg.) in "AnalaR" benzene (50 ml.) was hydrogenated over palladised calcium carbonate or strontium carbonate (5%; 170 mg.) (2.0 mol. uptake). The tetrahydro-derivative (XI) (395 mg.) formed long prisms, m. p.  $165$ — $166^\circ$  (from ethanol),  $\lambda_{\max}$ . 213 and 279  $m\mu$  ( $\epsilon$ , 17,000 and 16,000),  $\lambda_{\text{min.}}$  244  $m\mu$  ( $\epsilon$ , 5000),  $\nu_{\max}$ . 1681 (cyclopentenone),  $\nu_{\max}$ . ( $\text{CCl}_4$ ) 1686  $\text{cm}^{-1}$  [Found: C, 80.3; H, 7.5; OEt, 17.2%;  $M$  (Rast), 236.  $\text{C}_{18}\text{H}_{20}\text{O}_2$  requires C, 80.55; H, 7.5; OEt, 16.8%;  $M$ , 268].

The tetrahydro-adduct (839 mg.) in dry ether (130 ml.) and pyridine (10 ml.) was treated with osmium tetroxide (830 mg.) in dry ether (21 ml.) at room temperature in the dark for 24 hr. The complex so formed was filtered off and the mother liquors concentrated to give further material (total 2.01 g.). This complex (1.83 g.) in aqueous ethanol (1 : 1, 300 ml.) was treated with saturated aqueous pyrosulphite (50 ml.) under reflux in a nitrogen atmosphere for 1 hr. After filtration, the filtrate was concentrated; it furnished the  $\alpha$ -glycol (XV) (664 mg.). After purification by sublimation at  $130^\circ/2 \times 10^{-5}$  mm. this formed needles, m. p.  $216$ — $219^\circ$ ,  $\lambda_{\max}$ . 248 and 294  $m\mu$  ( $\epsilon$ , 13,500 and 730),  $\nu_{\max}$ . ( $\text{CHCl}_3$ ) 3450 (OH) and 1700 (cyclopentenone)  $\text{cm}^{-1}$  (Found: C, 71.3; H, 7.1; OEt, 15.25.  $\text{C}_{18}\text{H}_{22}\text{O}_4$  requires C, 71.5; H, 7.2; 1OEt, 14.9%).

*Reduction of the Tetrahydro-adduct (XI) with Lithium Aluminium Hydride.*—The tetrahydro-adduct (XI) (2.0 g.) in dry ether (300 ml.) was refluxed with lithium aluminium hydride (1.37 g.) in the same solvent (50 ml.) for 1 hr. The excess of reductant was destroyed with ethyl acetate. Working up in the usual way with saturated aqueous sodium sulphate gave the alcohol (X) (1.97 g.) which slowly crystallised. Owing to the ease of the conversion described below, it was not possible to obtain this alcohol pure.

The crude alcohol (1.97 g.) in dioxan (125 ml.) and 6N-sulphuric acid (5 ml.) was kept at room temperature for 20 hr. The pH was adjusted to 8—9 and the dioxan was removed *in vacuo*. The residue was extracted with ether, and the product chromatographed over alumina (Grade III). Elution with benzene—light petroleum (2 : 1) and crystallisation from aqueous propan-2-ol gave the dienone (IX) (1.05 g.) as prisms, m. p.  $122$ — $123^\circ$  (softens at  $115^\circ$ ),  $\lambda_{\max}$ . 256  $m\mu$  ( $\epsilon$ , 10,000; broad band),  $\epsilon$  (209  $m\mu$ ) = 13,500,  $\lambda_{\text{infl.}}$  213  $m\mu$  ( $\epsilon$ , 12,300),  $\lambda_{\text{min.}}$  225  $m\mu$  ( $\epsilon$ , 7400),  $\nu_{\max}$ . ( $\text{CCl}_4$ ) 1708 (cyclopentenone) and 1659 (strong *cisoid* C=C)  $\text{cm}^{-1}$  (Found: C, 85.35; H, 7.15.  $\text{C}_{16}\text{H}_{16}\text{O}$  requires C, 85.65; H, 7.2%).

*Selective Hydrogenation of the Dienone (IX).*—The dienone (IX) (133 mg.) in ethanol (5 ml.) was hydrogenated over palladised strontium carbonate (5%; 8.6 mg.) until 0.98 mol. of hydrogen was taken up. The product [ $\lambda_{\max}$ . 242  $m\mu$  ( $\epsilon$ , 6000)] was chromatographed over alumina (Grade III), eluting with benzene—light petroleum (2 : 3). Although pure  $\alpha\beta$ -unsaturated ketone (XIII) could not be obtained in this way (infrared spectra of fractions), it was easily isolated as its 2,4-dinitrophenylhydrazone. Prepared and purified in the usual way, it formed red plates, m. p.  $196$ — $197^\circ$  (from ethanol),  $\lambda_{\max}$ . 385  $m\mu$  ( $\epsilon$ , 23,900 in  $\text{CHCl}_3$ ) (Found: C, 64.9; H, 5.4; N, 13.8.  $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_4$  requires C, 65.0; H, 5.5; N, 13.8%).

The chromatographically concentrated ketone (XIII) (57 mg.) in ethanol (6 ml.) was left for 2.5 hr. with excess of sodium borohydride. The solution was cautiously neutralised with sulphuric acid and the product was extracted with ether. Removal of the ether, dissolution in benzene—ether (9 : 1), and filtration through alumina (Grade III; 3 g.) gave the unsaturated

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alcohol (XII) (52 mg.), b. p.  $90^{\circ}/5 \times 10$  mm.,  $\lambda_{\max}$ , 241, 248, 253, 255, 258, 262, 265, and 269  $\mu$  ( $\epsilon$ , 190, 200, 250, 250, 260, 250, 200, and 170),  $\nu_{\max}$ . ( $\text{CHCl}_3$ ) 3550 (OH). This alcohol (XII) (9 mg.) in methylene chloride (6 ml.) was shaken with manganese dioxide (75 mg.) for 20 hr. The product gave the 2,4-dinitrophenylhydrazone of the unsaturated ketone (XIII) (m. p., mixed m. p., and ultraviolet spectrum).

*Further Reactions of the Unsaturated Ketone (XIII).*—The crude ketone (XIII) (85 mg.) in dry ether (7 ml.) was treated with osmium tetroxide (120 mg.) in the same solvent (3 ml.) for 24 hr. at room temperature in the dark. The precipitated complex and sodium pyrosulphite (219 mg.) were heated under reflux in aqueous ethanol (50%; 20 ml.) for 2 hr. in a nitrogen atmosphere. Filtration and concentration of the solution gave the *diol* (XIV; R = H) (59 mg.) as needles. After purification by chromatography over alumina (Grade V; 4 g.) in methylene chloride, the diol (XIV; R = H) had m. p.  $93$ – $96^{\circ}$  (from pentane),  $\lambda_{\max}$ , 248, 253, 259, 265, and 269  $\mu$  ( $\epsilon$ , 180, 200, 235, 180, and 130),  $\nu_{\max}$ . ( $\text{CHCl}_3$ ) 3550 (OH), 1725  $\text{cm}^{-1}$  (hydrogen-bonded cyclopentanone) (Found: C, 74.0; H, 7.8.  $\text{C}_{16}\text{H}_{20}\text{O}_3$  requires C, 73.8; H, 7.7%). The diol gave a *mono-3,5-dinitrobenzoate* [XIV; R = 3,5-( $\text{NO}_2$ ) $_2$ · $\text{C}_6\text{H}_3$ ·CO] as needles, m. p.  $217$ – $220^{\circ}$  (from aqueous ethanol),  $\nu_{\max}$ . ( $\text{CHCl}_3$ )  $\nu$  3620 and 3440 (OH) and 1730  $\text{cm}^{-1}$  (ester and cyclopentanone) (Found: C, 61.05; H, 5.2; N, 6.15.  $\text{C}_{23}\text{H}_{23}\text{N}_2\text{O}_8$  requires C, 60.8; H, 4.9; N, 6.2%). This 3,5-dinitrobenzoate was recovered after 2.5 hr. at  $0^{\circ}$  with a five-fold excess of chromic acid in acetone. Under the same conditions the starting diol (XIV; R = H) was immediately oxidised to unidentified products.

*Oxidation of the Dienone (IX) to  $\delta$ -Benzoylvaleric Acid.*—The dienone (IX) (88 mg.) and potassium carbonate (474 mg.) in aqueous *t*-butyl alcohol (13 : 8; 21 ml.) were treated with saturated aqueous sodium metaperiodate (5.5 ml.) and aqueous potassium permanganate (104 mg.; 5 ml.) (permanent pink colour). After 2 hr. at room temperature, with occasional addition of potassium permanganate solution to maintain the pink colour, the solution was treated with sulphur dioxide until the precipitated manganese dioxide dissolved. Acidification with concentrated hydrochloric acid, saturation with sodium chloride, and extraction with methylene chloride gave the acidic product. This was processed in the usual way to furnish an acid (56 mg.) which, on sublimation at  $120^{\circ}/10^{-5}$  mm. and crystallisation from ether–pentane, afforded  $\delta$ -benzoylvaleric acid (VIII), identified by m. p., mixed m. p., and ultraviolet and infrared spectra.

*6-Benzoylhexanoic Acid.*—1-Phenylcycloheptene (813 mg.) in methylene chloride (35 ml.) was ozonised at  $-8^{\circ}$  for 2 hr. (ultraviolet control). Water (10 ml.), sodium carbonate (excess), and 30% hydrogen peroxide (excess) were added and the mixture was heated at  $100^{\circ}$  for 10 min. (removal of the methylene chloride). Isolation of the acidic product in the usual way, and crystallisation from hexane, gave *6-benzoylhexanoic acid* (XVI) (566 mg.), m. p.  $83$ – $84^{\circ}$ ,  $\lambda_{\max}$ , 278 and 241  $\mu$  ( $\epsilon$ , 1200 and 13,300),  $\nu_{\max}$ . ( $\text{CHCl}_3$ ) 2500–3500 and 1710 (C=O) and 1680 (phenylketone)  $\text{cm}^{-1}$  (Found: C, 70.5; H, 7.45.  $\text{C}_{13}\text{H}_{16}\text{O}_3$  requires C, 70.9; H, 7.3%).

*Preparation of the Adduct–Chromium Carbonyl Complex.*—1,2-Dimethylthioethanechromium tetracarbonyl (kindly provided by Professor G. Wilkinson and Miss Christina Mannerskantz) (382 mg.) and the adduct (305 mg.) were refluxed in ethylene glycol dimethyl ether (100 ml.) under nitrogen for 50 min. The solvent was removed at  $100^{\circ}/1$  mm. and the residue taken up in methylene chloride and filtered through alumina (Grade III, 55 g.). Unreacted adduct (150 mg.) was eluted first and then the *adduct–chromium carbonyl complex* (XVII) (386 mg.). This crystallised from acetone–di-isopropyl ether as very dark red needles, m. p.  $207$ – $210^{\circ}$  (decomp.),  $\lambda_{\max}$ . ( $\text{CHCl}_3$ ) 340, 420, and 538  $\mu$  ( $\epsilon$ , 9400, 5400, and 890),  $\nu_{\max}$ . ( $\text{CS}_2$ ) 1915, 1930, and 1992 (chromium carbonyl), and 1698 (cyclopentenone)  $\text{cm}^{-1}$  (Found: C, 63.25, 62.9; H, 4.7, 4.2; CO, 21.5, 19.0, and 19.5.  $\text{C}_{21}\text{H}_{16}\text{CrO}_5$  requires C, 63.0; H, 4.0; 3CO, 21.0%). The carbon monoxide determinations were carried out by the following procedure. Iodine (300 mg.) in methanol (5 ml.) was placed in both flasks of a Towers microhydrogenator and equilibrium was established (30 min.). The chromium complex (10–15 mg.), weighed out into the boat, had been previously placed in the side arm of one of the flasks. The sample was introduced into the iodine solution in the usual way and equilibrium again established. This gave the volume of carbon monoxide evolved.

Treatment of the adduct–chromium carbonyl complex (3.5 mg.) with pyridine (1.0 ml.) under reflux, and removal of the pyridine *in vacuo*, afforded a gum. Sublimation at  $10^{-5}$  mm. gave back the original adduct (VII) (1 mg.), identified by m. p., mixed m. p., and ultraviolet spectrum.

The tetrahydro-adduct (XI) did not furnish a chromium carbonyl complex and was recovered unchanged.

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