15. *Researches on Acetylenic Compounds. Part III. Diene Additions to Ethynyl Ketones.*

By Kenneth Bowden and E. R. H. Jones.

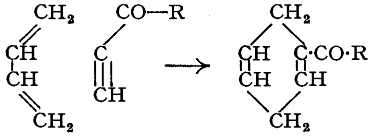
Diels–Alder addition reactions between conjugated dienes and ethynyl ketones take place readily at temperatures over the range 20—120°, excellent yields of the expected $\alpha\beta$-ethylenic ketones (*e.g.*, II, III, and IV) being obtained. Some of the adducts have been dehydrogenated with chloranil in boiling xylene to the corresponding aromatic ketones. With an ethylenic ethynyl ketone selective addition occurs, first at the acetylenic linkage.

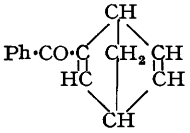
The employment of acetylenic compounds as dienophiles in the Diels–Alder reaction has been restricted mainly to the use of esters of acetylenedicarboxylic acid (*inter alia*, Diels, Alder, and Nienburg, *Annalen*, 1931, **490**, 236; Lohaus, *ibid.*, 1935, **516**, 295; Alder and Backendorf, *ibid.*, 1938, **535**, 101; Diels and Olsen, *J. prakt. Chem.*, 1940, **156**, 285) and of the acid itself (Brigl and Herrmann, *Ber.*, 1938, **71**, 2280; Diels, Alder, and Nienburg, *loc. cit.*; Alder and Backendorf, *Ber.*, 1938, **71**, 2199). The products obtained with a variety of dienes have been shown to be the expected dihydrophthalic acid derivatives but, in some cases, the primary adducts themselves also function as dienophiles and react with another diene molecule. Propiolic and tetrolic acids have been reacted with *cyclo*pentadiene (Diels and Olsen, *loc. cit.*; Alder *et al.*, *Annalen*, 1936, **525**, 183), but of the acetylenic carbonyl compounds only propiolic and tetrolic aldehydes and dibenzoylacetylene appear to have been used in Diels–Alder reactions. The aldehydes have been condensed with butadienes (F.P. 672,025) giving aldehydo-dihydrobenzenes, while Dupont and Paquot (*Compt. rend.*, 1937, **205**, 805) reacted isoprene and 2 : 3-dimethylbutadiene with dibenzoylacetylene obtaining dibenzoyl-dihydrobenzene derivatives. Comparatively vigorous conditions had to be employed to effect these addition reactions with the acetylenic carbonyl compounds.

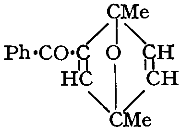
During the course of a systematic investigation of the reactions of ethynyl ketones, which are now readily available (see Part I), the Diels–Alder reactions of four of these compounds with various dienes have been examined. Addition takes place fairly readily at temperatures between 20° and 120°, depending mainly upon the particular diene, and the resulting unsaturated cyclic ketones are obtained usually in excellent yields. The ketones are not particularly sensitive to aerial oxidation but, on dehydrogenation with chloranil in boiling xylene (Arnold and Collins, *J. Amer. Chem. Soc.*, 1939, **61**, 1407), the expected benzenoid compounds are produced.

With butadiene at 120°, methyl ethynyl ketone (I; R = Me) gave a 75% yield of 2 : 5-*dihydroacetophenone* (II; R = Me) (2 : 4-*dinitrophenylhydrazone*), and on chloranil dehydrogenation acetophenone was obtained. Under similar conditions, propyl ethynyl ketone (I; R = Pr) gave an almost quantitative yield of 2 : 5-*dihydrobutyrophenone* (II; R = Pr) (2 : 4-*dinitrophenylhydrazone*) which was smoothly dehydrogenated to butyrophenone. In view of the results obtained with the primary adducts from derivatives of acetylenedicarboxylic acid, it was surprising that the dihydroacetophenone was recovered unchanged after heating with an excess of butadiene, even at 170—180° for six hours.

Phenyl ethynyl ketone (I; R = Ph) failed to react with butadiene at 50° (4 hours), but at 120°, 2 : 5-*dihydrobenzophenone* (II; R = Ph) was produced in 75% yield. 3 : 4-*Dimethyl*-2 : 5-*dihydrobenzophenone* was obtained in a similar manner from the ketone and 2 : 3-dimethylbutadiene, and both compounds were dehydrogenated to the expected aromatic ketones with chloranil. With *cyclo*pentadiene an extremely facile addition occurred, 2 : 5-endo*methylene*-2 : 5-*dihydrobenzophenone* (III) being formed at room temperature in practically theoretical yield. A corresponding endo-*oxido-compound* (IV), m. p. 89°, was obtained from 2 : 5-dimethylfuran, but more vigorous conditions were necessary in this case. All attempts to react (III) and (IV) with the usual carbonyl group reagents were unsuccessful.


(I.) (II.)

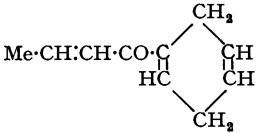

(III.)

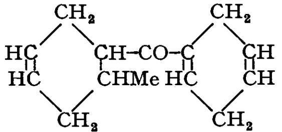

(IV.)

Addition of butadiene to propenyl ethynyl ketone (V) proceeds in two stages, addition apparently occurring first on the acetylenic bond and then subsequently on the ethylenic bond of the propenyl group. When the ketone is treated with an equi-molecular quantity of butadiene at 100°, 1-*crotonyl*-2 : 5-*dihydrobenzene* (VI) (2 : 4-*dinitrophenylhydrazone*) can be isolated in about 20% yield. It does not give a silver compound with ammoniacal silver nitrate and its light absorption properties (see later) also are in accord with the formulation (VI), rather than with the alternative structure arising from addition to the ethylenic linkage in (V). The dual addition reaction takes place with an excess of butadiene at 120—130° leading to 2-*methyl*-1 : 2 : 3 : 6 : 2′ : 5′-*hexahydrobenzophenone* (VII) which on dehydrogenation gives *o*-methylbenzophenone.

$Me{\cdot}CH{:}CH{\cdot}CO{\cdot}C{\vdots}CH$

(V.)


(VI.)


(VII.)

The light absorption properties (in alcohol solutions) of the αβ-unsaturated ketones mentioned above are indicated in the table. According to the known effects of alkyl substituents (cf. Woodward, *J. Amer. Chcm. Soc.*, 1942, **64**, 76; Evans and Gillam, *J.*, 1941, 815) the maximal absorption of ketones of type (II) should be located in the region of about 2350 A., as is the case with the closely related acetyl*cyclo*hexene. The marked differences in both location and intensity from the expected values suggest that either the ketones are not αβ-unsaturated (or are impure) or that a hitherto unobserved effect, due to the presence of the second cyclic ethylenic linkage, is operative. The first possibility was carefully examined by converting the ketone (II; R = Pr) into its *semicarbazone*, formed in practically quantitative yield, which showed light absorption (Max. 2600 A., ε = 21,000) typical of the derivative of an αβ-unsaturated ketone (Evans and Gillam, *J.*, 1943, 565). Regeneration from the semicarbazone gave a theoretical yield of the ketone having physical properties identical with those of the starting material. As a consequence, the last explanation is to be preferred and this is rendered the more probable by the known effects of cyclic location on the light absorption properties of conjugated dienes, *i.e.*, maxima at longer wavelengths and markedly reduced intensities.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
II; R = Me	2450	5,000
II; R = Pr	2450 2500	3,500 3,500
VII	2420	3,500
Acetyl*cyclo*hexene	2340	12,000
II; R = Ph	2470	12,500
3 : 4-Dimethyl-2 : 5-dihydrobenzophenone	2290 2340 *	12,000 11,500
III	2250 2500 2800 2880 *	6,000 9,000 5,500 4,500
IV	*ca.* 2280 *ca.* 2430 *ca.* 2560	*ca.* 8,000 *ca.* 8,000 *ca.* 9,000
VI	*ca.* 2350 *ca.* 2380 *ca.* 2430 *ca.* 2490	11,000
$Me{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH_2$	2280 2360	9,500 9,500

* Inflexion.

EXPERIMENTAL.

The preparation of the ketones is described in Part I of this series.

2 : 5-*Dihydroacetophenone* (II; R = Me).—A mixture of methyl ethynyl ketone (6·8 g.) and butadiene (8·1 g.) on being heated in a small autoclave at 120—130° for 3 hours gave, after distillation, 2 : 5-*dihydroacetophenone* (9·15 g.), b. p. 80—81°/14 mm., $n_D^{16°}$ 1·5135 (Found : C, 78·25; H, 8·2. $C_8H_{10}O$ requires C, 78·65; H, 8·25%). The 2 : 4-*dinitrophenylhydrazone* crystallised from benzene in scarlet needles, m. p. 212° (Found : N, 18·4. $C_{14}H_{14}O_4N_4$ requires N, 18·5%). The ketone (2·4 g.) was heated with chloranil (5·4 g.) in boiling xylene (17 c.c.) for 4 hours; the reaction mixture was filtered and, after removal of the solvent under diminished pressure, distillation of the residue gave acetophenone

(1·3 g.), b. p. 77—78°/9 mm., $n_D^{15^\circ}$ 1·5363 (Bruhl, *J. prakt. Chem.*, 1894, **50**, 131, gives b. p. 94·5°/20 mm., $n_D^{19\cdot6^\circ}$ 1·5342). The dinitrophenylhydrazone had m. p. 237°, undepressed on admixture with an authentic specimen.

2 : 5-*Dihydrobutyrophenone* (II; R = Pr).—This was prepared from propyl ethynyl ketone (14·4 g.) and butadiene (8·9 g.), heated together at 120—130° for 3 hours. Distillation gave 2 : 5-*dihydrobutyrophenone* (21·1 g.), b. p. 101—102°/10 mm., $n_D^{18^\circ}$ 1·5010 (Found : C, 79·95; H, 9·4. $C_{10}H_{14}O$ requires C, 79·55; H, 9·3%). The 2 : 4-*dinitrophenylhydrazone* crystallised from dioxan–methanol in scarlet needles, m. p. 176° (Found: N, 16·9. $C_{16}H_{18}O_4N_4$ requires N, 16·95%). The *semicarbazone*, formed in 95% yield by the usual method, crystallised from alcohol in needles, m. p. 173° (Found : N, 20·1. $C_{11}H_{17}ON_3$ requires N, 20·25%). On regeneration, a 95% yield of ketone was obtained having b. p. 119°/20 mm., $n_D^{20^\circ}$ 1·5001 and light absorption properties identical with those of the original material. Dehydrogenation of the ketone (2·0 g.) with chloranil (3·6 g.) as above gave butyrophenone (1·5 g.), b. p. 223° (*lit.* b. p. 220—222°, 218—221·5°). The semicarbazone had m. p. 188—189° (Sorge, *Ber.*, 1902, **35**, 1074, gives m. p. 188°).

2 : 5-*Dihydrobenzophenone* (II; R = Ph).—On heating a mixture of phenyl ethynyl ketone (10 g.) and butadiene (5·2 g.) in an autoclave at 120—130° for 3 hours a semi-solid mass was obtained which was purified by chromatography on a 15 × 1 cm. column of alumina from pentane solution. Evaporation of the eluate and sublimation of the residue at 70° (bath temp.)/10^{-4} mm., gave 2 : 5-*dihydrobenzophenone* (10·5 g.) as a crystalline mass, m. p. 52° (Found : C, 85·05; H, 6·5. $C_{13}H_{12}O_2$ requires C, 84·75; H, 6·55%). The 2 : 4-*dinitrophenylhydrazone*, which formed slowly, crystallised from alcohol–ethyl acetate, in red needles, m. p. 208° (Found : N, 15·0. $C_{19}H_{16}O_4N_4$ requires N, 15·35%). Treated with chloranil (2·7 g.), as above, the ketone (1·8 g.) gave an oil (1 g.) distilling at 70° (bath temp.)/10^{-4} mm., which gave benzophenone 2 : 4-dinitrophenylhydrazone, m. p. 229°, undepressed on admixture with an authentic specimen.

3 : 4-*Dimethyl*-2 : 5-*dihydrobenzophenone*.—Phenyl ethynyl ketone (10 g.) was heated at 120—130° for 3 hours with 2 : 3-dimethylbutadiene (10 g.), giving 3 : 4-*dimethyl*-2 : 5-*dihydrobenzophenone* (11·5 g.) as needles, m. p. 70—71°, from ligroin (b. p. 40—60°) (Found : C, 85·1; H, 7·6. $C_{15}H_{16}O$ requires C, 84·85; H, 7·6%). The 2 : 4-*dinitrophenylhydrazone*, which formed slowly, crystallised from ethyl acetate in small red needles, m. p. 224—225° (Found : N, 14·3. $C_{21}H_{20}O_4N_4$ requires N, 14·3%). Dehydrogenation of the ketone (2·5 g.) with chloranil (2·12 g.) as above gave an oil (2 g.), which distilled at 70° (bath temp.)/10^{-4} mm., giving the 2 : 4-dinitrophenylhydrazone of 3 : 4-dimethylbenzophenone, m. p. 249° (Allen, *J. Amer. Chem. Soc.*, 1940, **62**, 660, gives m. p. 252°).

2 : 5-endo*Methylene*-2 : 5-*dihydrobenzophenone* (III).—Phenyl ethynyl ketone (6 g.) was mixed with freshly distilled *cyclo*pentadiene (4 g.) at 20°. After a short induction period, reaction ensued and the temperature of the mixture was kept at 20—30° by occasional cooling. On removing the excess of diene under diminished pressure, the residual oil solidified and crystallisation from alcohol or acetic acid gave the *adduct* (9 g.) as leaflets, m. p. 159° (Found : C, 85·45; H, 6·25. $C_{14}H_{12}O$ requires C, 85·7; H, 6·15%).

2 : 5-endo-*Oxido*-2 : 5-*dimethyl*-2 : 5-*dihydrobenzophenone* (IV).—After a mixture of phenyl ethynyl ketone (3·75 g.) and 2 : 5-dimethylfuran (2·9 g.) had been heated in a sealed glass tube at 100° for 3 hours, the product was sublimed at 60° (bath temp.)/10^{-4} mm. and then crystallised from ligroin (b. p. 40—60°) giving the *adduct* (3 g.) as large rectangular plates, m. p. 89° (Found : C, 79·2; H, 6·35. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·25%).

1-*Crotonyl*-2 : 5-*dihydrobenzene* (VI).—The product, obtained by heating a mixture of propenyl ethynyl ketone (9·4 g.) and butadiene (5·95 g.) at 90—100° for 3 hours, on fractional distillation gave 1-*crotonyl*-2 : 5-*dihydrobenzene* (3 g.), b. p. 112—114°/10 mm., $n_D^{13^\circ}$ 1·5405 (Found : C, 80·6; H, 8·2. $C_{10}H_{12}O$ requires C, 81·0; H, 8·15%). The 2 : 4-*dinitrophenylhydrazone* crystallised from dioxan–methanol in scarlet leaflets, m. p. 191—192° (Found: N, 17·1. $C_{16}H_{16}O_4N_4$ requires N, 17·05%).

2-*Methyl*-1 : 2 : 3 : 6 : 2′ : 5′-*hexahydrobenzophenone* (VII).—After heating propenyl ethynyl ketone (9·4 g.) with butadiene (11·9 g.) at 120—130° for 3 hours the diene polymer was removed by filtration and washed with ether. The filtrate was evaporated and distillation of the residue in the presence of a little hydroquinone gave 2-*methyl*-1 : 2 : 3 : 6 : 2′ : 5′-*hexahydrobenzophenone* (7·2 g.), b. p. 124—125°/1 mm., $n_D^{13^\circ}$ 1·5385 (Found: C, 83·2; H, 8·95. $C_{14}H_{18}O$ requires C, 83·1; H, 8·95%). Heating the ketone (2 g.) with chloranil (8 g.) in the usual way gave, on distillation at 70° (bath temp.)/10^{-4} mm., an oil (0·5 g.) which was converted into its oxime by heating with hydroxylamine hydrochloride (0·5 g.) in pyridine (5 c.c.) for 6 hours on the steam-bath. On crystallisation from aqueous methanol *o*-methylbenzophenone *anti*-oxime (0·45 g.) was obtained as leaflets, m. p. 105° (Smith, *Ber.*, 1891, **24**, 4046, gives m. p. 105°).

The authors thank the Rockefeller Foundation and I.C.I. Ltd., Dyestuffs Division, for financial assistance and Dr. E. A. Braude for the light absorption data.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7.

[*Received, September 24th,* 1945.]