

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

Experiments in the 4-Arylcycloalk-2-en-1-one Series. III.^{1a} 4-Phenylcyclohex-3-en-1-one and 4-Phenylcyclohept-3-en-1-oneBY ERNST D. BERGMANN AND SAMUEL YAROSLAVSKY^{1b}

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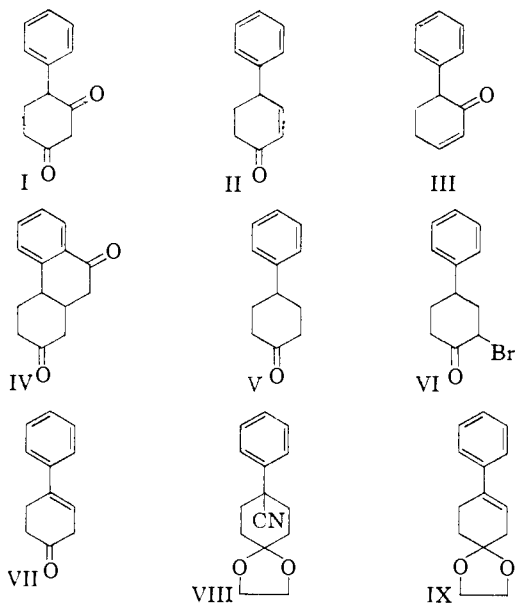
Dehydrobromination of 2-bromo-4-phenylcyclohexanone with collidine gives the β,γ -unsaturated ketone VII, its treatment with 2,4-dinitrophenylhydrazine the dinitrophenylhydrazone of the α,β -unsaturated ketone II. Hydrolysis of this latter dinitrophenylhydrazone leads to isomerization to VII. The 2,4-dinitrophenylhydrazone of 2-bromo-4-phenylcyclohexanone exists in a yellow *anti* and a red *syn* form. Exactly analogous observations have been made in the series of 4-phenylcycloheptanone, which is prepared in good yield by the reaction of diazomethane with 4-phenylcyclohexanone.

Bergmann and Szmuszkovicz² obtained from 4-phenylcyclohexane-1,3-dione (I) an inseparable mixture of two α,β -unsaturated ketones, 4-phenylcyclohex-2-en-1-one (II) and 6-phenylcyclohex-2-en-1-one (III). The observation that Michael reaction of II with diethyl malonate led eventually to the interesting 5,5a,6,7,8,9,9a,10-octahydrophenanthrene-7,10-dione (IV) invited a study of other methods for the preparation of II and similar 4-arylcycloalk-2-en-1-ones, of which to the best of our knowledge, no representative has yet been prepared.

The obvious route was the bromination and dehydrobromination of 4-phenylcyclohexanone (V) for which a good preparative method has been reported by Horning and co-workers.³ Treatment of V with N-bromosuccinimide in carbon tetrachloride gave the desired bromoketone VI in quantitative yield. Dehydrobromination with

infrared carbonyl peak at 1700 cm.^{-1} (Fig. 1b) and also an ultraviolet absorption band at $240\text{ m}\mu$ ($\log \epsilon\ 3.72$) (Fig. 2) which points to structure VII rather than to structure II. For comparison, the spectrum of 1-phenylcyclohex-2-ene was measured⁴ which showed a band at $248\text{ m}\mu$ (4.02). In accordance with formula VII, the 2,4-dinitrophenylhydrazone (m.p. 170°) of the solid ketone is yellow and absorbs at $355\text{ m}\mu$ (4.36), therefore, at a wave length similar to that of the DNP of V, $365\text{ m}\mu$ (4.38), whilst the DNP of an α,β -unsaturated ketone should absorb at $380\text{ m}\mu$.^{5,6} Hydrogenation of the ketone VII gives V. When the method of Mattox and Kendall^{5,7-9} for the preparation of unsaturated ketones (treatment of the α -bromo derivatives of corresponding saturated ketones with 2,4-dinitrophenylhydrazine in glacial acetic acid) was applied to 2-bromo-4-phenylcyclohexanone (VI), a red halogen-free 2,4-dinitrophenylhydrazone was obtained which absorbed at $375\text{ m}\mu$ ($\log \epsilon\ 4.32$) and was, therefore, obviously the expected derivative of the ketone II. Decomposition of this dinitrophenylhydrazone with levulinic acid¹⁰ gave the β,γ -unsaturated ketone VII; already the crude product of this reaction showed the infrared absorption band at 1700 cm.^{-1} and gave the yellow dinitrophenylhydrazone of VII, m.p. 170° ; it is thus established that the hydrolysis of the dinitrophenylhydrazone of II does not give the free ketone II at all, the β,γ -unsaturated form VII being the stable one. A similar observation was made by Soffer and Jevnik⁵ who obtained by "exchange fission" of the 2,4-dinitrophenylhydrazone of 4-isopropylcyclohex-2-en-1-one, at least partly the β,γ -unsaturated isomer, 4-isopropylcyclohex-3-en-1-one. On the other hand, we succeeded, by the application of alkali, to transform the DNP of VII to that of II, though only in moderate yield—considerable amounts of an amorphous, high-melting by-product were formed.

When 2,4-dinitrophenylhydrazine was added to 2-bromo-4-phenylcyclohexanone in glacial acetic acid, a yellow dinitrophenylhydrazone precipi-



collidine, however, had an unexpected result. The ketone of m.p. $47-48^\circ$ and of correct analytical composition, which was isolated and which liquefied upon standing for several days, showed the

(1) (a) Part II. E. D. Bergmann and S. Yaroslavsky, *THIS JOURNAL*, **81**, 2775 (1959); (b) part of the M.Sc. thesis, submitted to the Hebrew University, Jerusalem.

(2) E. D. Bergmann and J. Szmuszkovicz, *THIS JOURNAL*, **75**, 3226 (1953).

(3) E. C. Horning, M. G. Horning, M. S. Fish and M. W. Rutenberg, *ibid.*, **74**, 773 (1952).

(4) M. Pestemer and L. Wittig, *Monatsh.*, **66**, 119 (1935); B. Y. Mixer and W. G. Young, *THIS JOURNAL*, **78**, 3379 (1956); E. L. Eliel, J. W. McCoy and Ch. C. Price, *J. Org. Chem.*, **22**, 1533 (1957).

(5) M. D. Soffer and M. A. Jevnik, *THIS JOURNAL*, **77**, 1003 (1955).

(6) A. L. Wilds and N. A. Nelson, *ibid.*, **75**, 5360 (1953).

(7) V. R. Mattox and E. C. Kendall, *ibid.*, **70**, 882 (1948); **72**, 2290 (1950).

(8) C. Djerassi, *ibid.*, **71**, 1003 (1949).

(9) F. Ramirez and A. F. Kirby, *ibid.*, **74**, 4331 (1952); **75**, 6026 (1953).

(10) M. Keeney, *Anal. Chem.*, **29**, 1489 (1957).

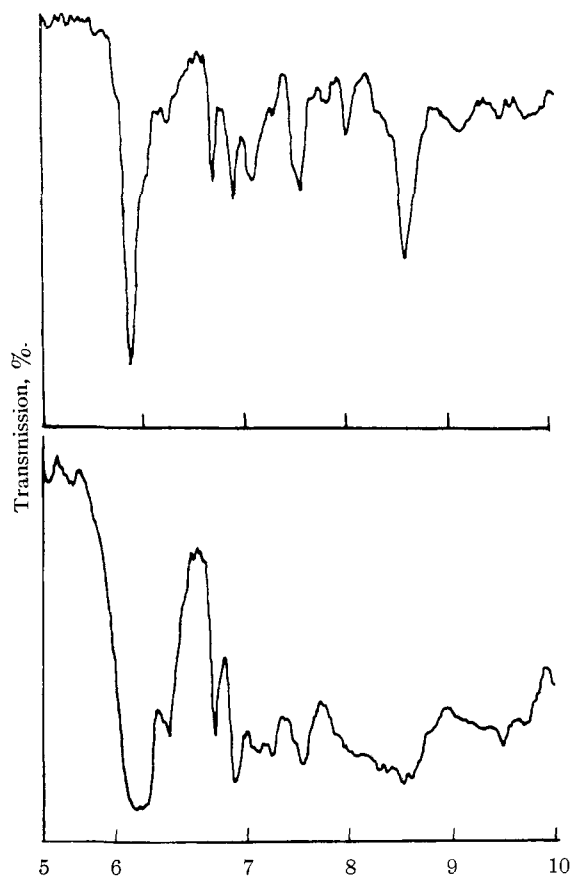


Fig. 1.—Infrared spectrum of (top) 4-phenylcyclohexanone (V) and (bottom) 4-phenylcyclohex-3-en-1-one (VII), both in potassium bromide pellets.

tated initially which was gradually transformed into the expected red derivative of II, m.p. 122°. As this yellow compound appeared to be the dinitrophenylhydrazone derivative of the bromoketone, this observation was studied somewhat more closely. To this effect, the bromoketone was treated with the usual DNP reagent (dinitrophenylhydrazine in concentrated sulfuric acid and aqueous alcohol). At 0°, a yellow and at boiling point (*via* the yellow compound) a red 2,4-dinitrophenylhydrazone was obtained, m.p. 152 and 183°, respectively. These two compounds had *both* the expected composition of 2-bromo-4-phenylcyclohexanone 2,4-dinitrophenylhydrazone; the yellow compound absorbed at 260 and 360 m μ , the red at 265 and 385 m μ . We believe that the two compounds are stereoisomers of the type observed by Ramirez and Kirby^{9,11} and base this belief on the experience of these authors: The spectrum of the yellow compound shows a hypsochromic (5 m μ), that of the red one a bathochromic (20 m μ) shift as compared with the spectrum of the symmetrical parent compound 4-phenylcyclohexanone 2,4-dinitrophenylhydrazone (260, 365 m μ). The red DNP contains, therefore, most probably the bromine atom and the dinitrophenyl group in the *syn*, the yellow one in the *anti* position. Also

(11) F. Ramirez and A. F. Kirby, *THIS JOURNAL*, **76**, 1037 (1954); *cf.* also L. Hayashi, *Nature*, **178**, 40 (1956); R. Huisgen and V. Vossius, *Munsh.*, **88**, 517 (1957).

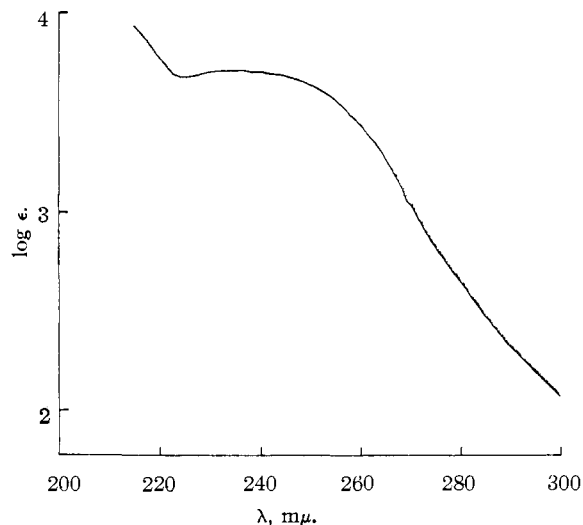
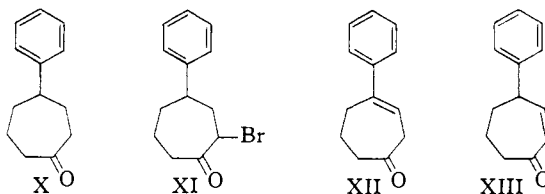


Fig. 2.—Ultraviolet spectrum of 4-phenylcyclohex-3-en-1-one (VII), in alcohol.

the higher intensity of the NH absorption of the red isomer, in comparison with that of the yellow isomer and the unsaturated compound, speaks for the *syn* structure of the red compound.

Analogous observations have been made in the study of the conversion of 4-phenylcycloheptanone (X) into the corresponding unsaturated ketone. Although X failed to give the desired product with N-bromosuccinimide, with bromine in carbon tetrachloride it yielded the monobromoketone, as a fairly unstable liquid. This bromoketone was dehydrobrominated with collidine to a liquid 4-phenylcycloheptenone, characterized as a β,γ -unsaturated ketone (XII) by its yellow 2,4-dinitrophenylhydrazone, ultraviolet absorption spectrum (253 m μ , 3.70) and broad carbonyl band at 1700 cm.⁻¹. That the double bond was conjugated with the phenyl ring, followed from the comparison of its spectrum with that of 1-phenylcyclohept-1-ene (260 m μ , 3.90).¹² Incidentally, these data prove that the bromoketone is the 2-compound XI and not the theoretically also possible 7-bromo-derivative.¹³



When, on the other hand, XI was dehydrobrominated by the method of Mattox and Kendall, the 2,4-dinitrophenylhydrazone of 4-phenylcyclohept-2-en-1-one (XIII), m.p. 107°, was obtained. It was red and absorbed at 375 m μ (4.20).

Under the usual conditions for the preparation of 2,4-dinitrophenylhydrazones, XI gave two iso-

(12) E. D. Bergmann and R. Ikan, unpublished results.

(13) Provided that dehydrobromination is not accompanied by rearrangement of the type observed in the steroid series or for 3-bromo-1-methyl-*trans*-2-decalone which can either give the $\Delta^{1,2}$ - or $\Delta^{3,4}$ -unsaturated ketone; M. Yanagita and K. Yamakawa, *J. Org. Chem.*, **21**, 500 (1956).

meric dinitrophenylhydrazones, the yellow *anti* compound of m.p. 76° (260, 363 m μ), and the red *syn* compound of m.p. 115° (262 m μ , 395 m μ). Again, comparison with the spectrum of the 2,4-dinitrophenylhydrazone of X, of which only one of the possible isomers has been observed, shows a hypsochromic and bathochromic shift, respectively. Also the infrared spectra of the two isomers show the same significant differences which have been observed in the case of the two isomeric 2,4-dinitrophenylhydrazones of VI.

For the preparation of X, the reaction between diazomethane and 4-phenylcyclohexanone (V) has been used¹⁴; under the conditions specified in the Experimental part, a yield of 80% can be obtained. The ketone is different from the known 2- and 3-phenylcycloheptanones.¹⁵

In the preparation of 4-phenylcyclohexanone, an interesting observation has been made which deserves reporting. In accordance with the observations of Hauser and Brasen¹⁶ we expected to be able to remove the cyano group from the intermediate VIII by means of sodamide and thus to obtain the ketal of 4-phenylcyclohex-3-en-1-one (IX). This was not the case. When, however, VIII was added to the *blue* solution of sodium in liquid ammonia, it was converted smoothly into the ketal of 4-phenylcyclohexanone. This observation appears to represent an improvement over the original method.³

Experimental

The synthesis of 4-phenylcyclohexanone was carried out according to the literature³; it was recrystallized from petroleum ether and had m.p. 78–79°; $\lambda_{\text{max}}^{\text{EtOH}}$ 247 (2.23), 253 (2.34), 259 (2.38), 260 (2.32), 264 (2.27), 266 (2.19), 269 m μ (2.06). (See Fig. 3).

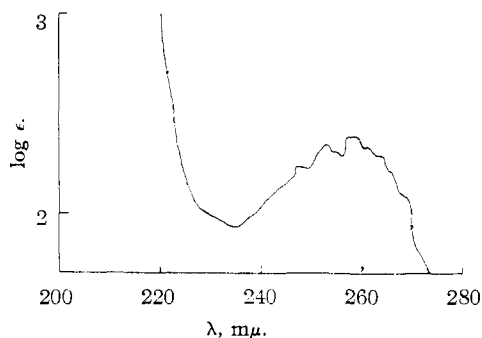


Fig. 3.—Ultraviolet spectrum of 4-phenylcyclohexanone (V), in alcohol.

The 2,4-dinitrophenylhydrazone formed yellow crystals of m.p. 188°, after recrystallization from butanol; $\lambda_{\text{max}}^{\text{EtOH}}$ 260 (4.03), 365 m μ (4.38).

Decyanation of the ketal (VIII) of 4-phenyl-4-cyanocyclohexanone.—To the blue solution of 0.47 g. of sodium metal in 100 ml. of liquid ammonia, 5 g. of 4-phenyl-4-cyanocyclohexanone ethyleneketal in 20 ml. of ether was added. After one hour (stirring) the color had disappeared. Work-up gave 3.5 g. (80%) of 4-phenylcyclohexanone ethyleneketal, m.p. 54–55°, after recrystallization from aqueous ethanol.³ It was identified by the mixed m.p. and by conversion into the 2,4-dinitrophenylhydrazone of 4-phenylcyclohexanone, m.p. 188°.

(14) Cf. the reaction of 2-phenylcyclohexanone; C. D. Gutsche, H. F. Strohmayer and J. M. Chang, *J. Org. Chem.*, **23**, 1 (1958).

(15) C. D. Gutsche, *THIS JOURNAL*, **71**, 3513 (1949).

(16) C. R. Hauser and W. R. Brasen, *ibid.*, **78**, 82 (1956).

2-Bromo-4-phenylcyclohexanone (VI).—A mixture of 30 g. of 4-phenylcyclohexanone, 27.3 g. of *N*-bromosuccinimide, 0.05 g. of benzoyl peroxide and 150 ml. of carbon tetrachloride was cautiously heated on the water-bath. When the exothermic reaction had subsided, the mixture was refluxed for 20 minutes, cooled, filtered and concentrated *in vacuo*. The remaining solution deposited on cooling with ice 48 g. (quantitative yield) of VI, which was recrystallized from cyclohexane and melted at 104–105°. The compound is apt to decompose; therefore, the concentration of its solution *in vacuo* must not be pushed too far; $\nu_{\text{max}}^{\text{KBr}}$ 1724 cm.⁻¹ (carbonyl).¹⁷

Anal. Calcd. for C₁₂H₁₃BrO: C, 56.9; H, 5.2. Found: C, 57.3; H, 5.8.

***anti*-2,4-Dinitrophenylhydrazone.**—To a solution of 0.5 g. of VI in 20 ml. of ethanol, a solution of 0.5 g. of 2,4-dinitrophenylhydrazine in 10 ml. of ethanol, 2 ml. of concd. sulfuric acid and 3 ml. of water was added at 0°. The yellow precipitate, which separated at once, was recrystallized from cyclohexane or butanol and melted at 152°; $\lambda_{\text{max}}^{\text{EtOH}}$ 260 (4.14), 360 m μ (4.50).

Anal. Calcd. for C₁₈H₁₇BrN₄O₄: C, 50.0; H, 3.8. Found: C, 50.9; H, 4.3.

***syn*-2,4-Dinitrophenylhydrazone.**—The reaction was carried out as in the foregoing experiment, but at reflux temperature (2 hours). The initial yellow precipitate turned dark red. From nitromethane, it crystallized in red crystals of m.p. 183°. The same product was obtained when the *anti* compound was refluxed for 2 hours in alcoholic solution, containing a small amount of concentrated sulfuric acid; $\lambda_{\text{max}}^{\text{EtOH}}$ 265 (4.14), 385 m μ (4.42).

Anal. Calcd. for C₁₈H₁₇BrN₄O₄: C, 50.0; H, 3.8. Found: C, 49.5; H, 4.2.

4-Phenylcyclohex-3-en-1-one (VII).—A solution of 10 g. of VI in 30 ml. of collidine was refluxed for 15 minutes in an atmosphere of nitrogen. After cooling, the precipitate was filtered and washed with ether and the ethereal solution treated with 5% hydrochloric acid, sodium bicarbonate solution and water. The product had b.p. 118–120° (1 mm.); its yield was 3.5 g. (50%). The distillate crystallized spontaneously; by recrystallization from petroleum ether, it gave colorless crystals of m.p. 47–48°, which liquefy on standing; $\lambda_{\text{max}}^{\text{EtOH}}$ 240 m μ (3.72); $\nu_{\text{max}}^{\text{KBr}}$ 1700 cm.⁻¹ (broad, carbonyl).

Anal. Calcd. for C₁₂H₁₂O: C, 83.7; H, 7.0. Found: C, 83.5; H, 7.3.

The 2,4-dinitrophenylhydrazone was obtained by recrystallization from butanol in brownish-yellow crystals of m.p. 168–170°; $\lambda_{\text{max}}^{\text{EtOH}}$ 255 (4.19), 355 m μ (4.36).

Anal. Calcd. for C₁₈H₁₆N₄O₄: C, 61.4; H, 4.5. Found: C, 61.4; H, 4.9.

The structure of the ketone was proved by catalytic hydrogenation (alcoholic solution, platinum oxide) to 4-phenylcyclohexanone, m.p. 77–79°; 2,4-dinitrophenylhydrazone, m.p. 188°.

4-Phenylcyclohex-2-en-1-one (II) 2,4-Dinitrophenylhydrazone. (a).—To a hot solution of 1 g. of VI in 30 ml. of glacial acetic acid, 0.82 g. of 2,4-dinitrophenylhydrazine was added and the mixture refluxed for 2 minutes; the yellow dinitrophenylhydrazone of VI, which precipitated initially, dissolved. No crystals appeared upon cooling. The mass was, therefore, diluted with chloroform and the solution washed with 5% sodium carbonate solution and water, dried with sodium sulfate and concentrated. The dark solid which remained was recrystallized from butanol. In addition to some amorphous, insoluble material, brown-red crystals of m.p. 122° were obtained; yield 1 g. (88%).

(b).—A solution of 1 g. of the *anti*-2,4-dinitrophenylhydrazone of VI in 30 ml. of glacial acetic acid was refluxed for 2 minutes in an atmosphere of nitrogen. Water was added and the precipitate formed recrystallized from butanol. The product which was obtained in a yield of 0.6 g. (83%) melted at 122°; $\lambda_{\text{max}}^{\text{EtOH}}$ 258 (4.30), 329 (4.20), 375 m μ (4.32).

Anal. Calcd. for C₁₈H₁₆N₄O₄: C, 61.4; H, 4.5. Found: C, 61.5; H, 4.5.

A mixture of 5 g. of the dinitrophenylhydrazone of II, 90 ml. of levulinic acid and 10 ml. of *N*-hydrochloric acid

(17) The shift of 24 cm.⁻¹, as compared with the absorption of 4-phenylcyclohexanone, shows that the bromine is equatorial. This point will be discussed in a later publication.

was heated at 100° for 5 minutes. After three hours at room temperature, water was added and the product extracted with petroleum ether. The extract was washed with sodium carbonate solution and water, dried and concentrated. The residue (0.3 g., 12%) showed both before and after distillation (b.p. about 120° (0.1 mm.)) an infrared absorption of 1700 cm^{-1} and gave the yellow 2,4-dinitrophenylhydrazone of VII, m.p. 168–170°, after recrystallization from butanol.

When the dinitrophenylhydrazone of VII was kept with a methanolic solution of sodium hydroxide at room temperature for 3 hours, it was transformed into the 2,4-dinitrophenylhydrazone of II, m.p. 122°, but a great part was converted into an insoluble, amorphous product of unknown structure.

4-Phenylcycloheptanone (X).—To a solution of 15 g. of 4-phenylcyclohexanone in 50 ml. of 95% alcohol, 1 ml. of water and 50 ml. of ether, 10 g. of nitrosomethylurea was added, and the stirrer adjusted so that it only agitated the surface of the liquid, without affecting the solid nitroso derivative on its bottom. At 0°, a solution of 12 g. of potassium hydroxide in 40 ml. of 50% alcohol was added during 2.5 hours. The reaction mixture was then kept for 12 hours and 20 ml. of 2 *N* hydrochloric acid and 200 ml. of water added successively. The ether layer was separated, neutralized, dried and concentrated. The product boiled at 132–134° (3 mm.), 115–118° (0.5 mm.) and crystallized upon cooling; it had m.p. 23–25° and n_D^{25} 1.5381; the yield was 12.5 g. (80%); $\lambda_{\text{max}}^{\text{EtOH}}$ 247 (2.22), 253 (2.34), 258 (2.40), 264 (2.30), 267 μ (2.28); $\nu_{\text{max}}^{\text{EtOH}}$ 1700 cm^{-1} (carbonyl) (2- and 3-phenylcycloheptanone: 1688 cm^{-1}).¹⁵

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 83.0; H, 8.5. Found: C, 82.6; H, 8.2.

The 2,4-dinitrophenylhydrazone crystallized from 1-butanol in yellow crystals of m.p. 158°, while for the 2- and the 3-isomers melting points of 171–172° and 145–146° have been recorded, respectively¹⁵; $\lambda_{\text{max}}^{\text{EtOH}}$ 260 (4.03), 378 μ (4.38).

2-Bromo-4-phenylcycloheptanone (XI).—To an ice-cold solution of 10 g. of X in 50 ml. of carbon tetrachloride, 10.2 g. of bromine in 75 ml. of the same solvent was added slowly. The reaction started after a brief inhibition period; the bromine was introduced so that a new portion was added after the previous one had been completely decolorized. After one hour, the solution was washed with water, sodium carbonate solution and water, dried and concentrated. The remaining oil was used for the further reactions. Distillation led to partial decomposition even under 1 mm. pressure (b.p. 180°) (the starting material boils at

115° (1 mm.)), and the distillate blackened quickly upon standing. Therefore, no satisfactory analysis could be secured, and the crude bromoketone was best characterized as the red 2,4-dinitrophenylhydrazone of m.p. 115° (see below).

anti-2,4-Dinitrophenylhydrazone.—At 0°, 0.5 g. of 2,4-dinitrophenylhydrazine in a mixture of 2 ml. of concd. sulfuric acid, 3 ml. of water and 10 ml. of alcohol was added to 0.5 g. of XI in 20 ml. of alcohol. The yellow product crystallized nicely from butanol; it melted at 76°. Upon standing and more quickly upon drying, it is transformed into the red *syn* compound; $\lambda_{\text{max}}^{\text{EtOH}}$ 260 and 363 μ ; quantitative data could not be obtained, as the product could not be dried without change.

syn-2,4-Dinitrophenylhydrazone.—The above reaction was repeated, but the mixture refluxed for 2 hours. The red product was recrystallized from nitromethane and melted at 115°; $\lambda_{\text{max}}^{\text{EtOH}}$ 262 (4.20), 395 μ (4.20).

Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{BrN}_4\text{O}_4$: C, 51.0; H, 4.4. Found: C, 51.9; H, 4.2.

4-Phenylcyclohept-3-en-1-one (XII).—A solution of 3 g. of XI in 30 ml. of collidine was refluxed for one hour. After cooling, the solid product was filtered off and washed with ether and the filtrate was diluted with water and ether. The ethereal extract was washed with dilute hydrochloric acid and water, dried and evaporated. The product boiled at 128–130° (3 mm.); its yield was 1.5 g. (75%); $\lambda_{\text{max}}^{\text{EtOH}}$ 253 μ (3.70); $\nu_{\text{max}}^{\text{EtOH}}$ 1700 cm^{-1} (carbonyl, broad band).

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}$: C, 83.8; H, 7.5. Found: C, 83.4; H, 7.7.

The 2,4-dinitrophenylhydrazone formed yellow crystals of m.p. 136° after recrystallization from butanol; $\lambda_{\text{max}}^{\text{EtOH}}$ 250 (4.11), 365 μ (4.34).

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4$: C, 62.3; H, 4.9. Found: C, 62.4; H, 4.9.

4-Phenylcyclohept-2-en-1-one (XIII) 2,4-Dinitrophenylhydrazone.—The mixture of 1 g. of XI, 0.8 g. of 2,4-dinitrophenylhydrazine and 20 ml. of glacial acetic acid was heated for 5 minutes in a current of nitrogen. The product was precipitated by addition of water and recrystallized from butanol; red crystals of m.p. 107°; $\lambda_{\text{max}}^{\text{EtOH}}$ 258 (4.20), 375 μ (4.20).

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4$: C, 62.3; H, 4.9. Found: C, 62.3; H, 4.8.

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[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

Experiments in the 4-Arylcycloalk-2-en-1-one Series. II.¹ The Stobbe and Darzens Reactions of Ethyl β -Benzoylpropionate

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Ethyl β -benzoylpropionate condenses with diethyl succinate (Stobbe reaction) to give 4-carbomethoxy-5-oxo-2-phenylcyclopent-1-enyl-acetic acid (VI) and with ethyl chloroacetate in the presence of sodium *t*-pentoxide (Darzens reaction) to yield diethyl 1,2-epoxy-2-phenyladipate (III). Some transformations of these two products are described, and some observations on the infrared spectra of glycidic esters reported.

A general method for the preparation of 4-aryl-cyclohexanones capable of extension to higher 4-arylated cycloalkanones appeared to consist in the application of the Stobbe and the Darzens reactions to ethyl β -aroylpropionates (I), according to schemes A and B.

To our best knowledge, the Darzens reaction has not been applied to any ketoester; as to the

Stobbe reaction, β -ketoesters fail to react³ and γ -ketoesters have not been studied. Only one δ -ketoester has been reported to react normally in the Stobbe reaction, *viz.*, ethyl γ -anisoylbutyrate.⁴

The condensation of ethyl β -benzoylpropionate (I) with 3 moles of diethyl succinate and 3 moles of sodium hydride gave a mixture of neutral and acidic products. The neutral products contained, apart

(1) Part I: E. D. Bergmann and J. Szmuszkovicz, *THIS JOURNAL*, **75**, 3226 (1953).

(2) Part of the M.Sc. Thesis, submitted to the Hebrew University, Jerusalem.

(3) W. S. Johnson, J. W. Petersen and C. D. Gutsche, *ibid.*, **69**, 2942 (1947).

(4) W. S. Johnson, A. R. Jones and W. P. Schneider, *ibid.*, **72**, 2395 (1950).