[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Some Cyclopentenones and Supposed Cyclopentenones

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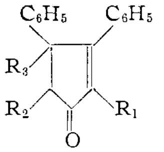
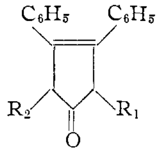
The products formed by hydriodic acid reduction of 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one (I) and its 2,5-dimethyl analog IV, formerly considered to be 3-cyclopenten-1-one derivatives, are shown to be the 2-cyclopenten-1-one derivatives III and VI, respectively. The product of base treatment of 3,5-dimethyl-2,6-diphenyltetrahydro-4-pyrone, previously assigned structure VI, is shown to be 2,4-dibenzal-3-pentanone (IX). The ultraviolet spectra of benzal derivatives of ketones are interpreted in terms of their conformations and the anomalous infrared spectrum of III is discussed.

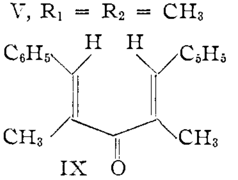
Reduction of 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one (I) with hydriodic acid gives a product, $C_{17}H_{14}O$, which has been assigned the structure 3,4-diphenyl-3-cyclopenten-1-one (II).[1] As noted earlier,[2] we have been led to the opinion that this structure is incorrect: this view was based on a consideration of the spectra of the compound and the conclusion that earlier evidence[1,3] placing the double bond in the 3-position was ambiguous. Allen and VanAllan[4] recently have reached the same conclusion on similar grounds and have proposed that the product is 3,4-diphenyl-2-cyclopenten-1-one (III). The evidence for structure III is good,[4,5] but we hesitated to make this assignment immediately because of the anomalous presence of *two bands in the carbonyl region* of its infrared spectrum; it also seemed necessary to clarify the relationship of this product with another compound, $C_{17}H_{14}O$, which also was claimed to have structure II.[6] A cognate case concerns the dimethyl analogs V and VI. Structure V has been assigned to the hydriodic acid reduction product of IV, while VI has been assigned to the product from the action of base on 3,5-dimethyl-2,6-diphenyltetrahydro-4-pyrone.[7] We discuss this case first since both compounds are well-characterized, *one has been converted to the other*,[7] and their infrared spectra show no anomalies.



I, $R_1 = R_2 = H$, $R_3 = OH$
III, $R_1 = R_2 = R_3 = H$
IV, $R_1 = R_2 = CH_3$, $R_3 = OH$
VI, $R_1 = R_2 = CH_3$, $R_3 = H$
VII, $R_1 = H$, $R_2 = CH_3$, $R_3 = OH$
VIII, $R_1 = CH_3$, $R_2 = H$, $R_3 = OH$



II, $R_1 = R_2 = H$
V, $R_1 = R_2 = CH_3$



IX

Reduction of IV gave the product $C_{19}H_{18}O$, m.p. 122°, previously reported.[7] This showed an infrared band at 5.89 μ ($CHCl_3$), which eliminates the structure V, since a 3-cyclopenten-1-one system would be expected to absorb *ca.* 5.70 μ.[2,8] The band position is in good accord with VI, however[2,8]; *cf.* IV, 5.88 μ ($CHCl_3$). The ultraviolet maximum $\lambda_{\max}^{\mathrm{EtOH}}$ 276 mμ (log ε 4.26) differs from that predicted for V, *i.e.*, *ca.* 255 mμ,[2,4] but fits well with VI, *cf.* 3-phenyl-2-cyclopenten-1-one, 281 mμ (log ε 4.36).[9] Here, the bathochromic shift of *ca.* 10 mμ usually effected by alkyl substitution on an α,β-unsaturated ketone system[10,11] must be overridden by an hypsochromic (and hypochromic) effect due to the influence of the 2-methyl substituent on the ability of the 3-phenyl and cyclopentenone rings to achieve coplanarity.[12] This effect is also exemplified by the maxima of VII and VIII, 286.5 mμ (log ε 4.30) and 276 mμ (log ε 4.20), respectively.[11] The latter compound, together with IV, $\lambda_{\max}^{\mathrm{EtOH}}$ 276 mμ (log ε 4.16), serve as close spectral analogs for VI. Since the spectral evidence favored structure VI for the reduction product, the compound which had earlier been assigned this structure[7] was re-examined.[13]

Reaction of 3,5-dimethyl-2,6-diphenyltetrahydro-4-pyrone with ethanolic potassium hydroxide gave the product $C_{19}H_{18}O$, m.p. 128°, previously reported.[7] That this could be neither VI nor V was evident from its infrared spectrum which showed a composite carbonyl band at 6.15 μ ($CHCl_3$), indicating a more highly conjugated system. Mild hydrogenation gave a tetrahydro compound, $C_{19}H_{22}O$, which had a simple carbonyl band at 5.85 μ ($CHCl_3$). This was shown to be 2,4-dimethyl-1,5-diphenyl-3-pentanone by its independent synthesis by self condensation of methyl 2-methyl-3-phenylpropionate, followed by acid hydrolysis and decarboxylation. These data lead to the conclusion that the compound m.p. 128° must be 2,4-dibenzal-3-pentanone (IX), an assignment which is lent support by the fact that it is converted to VI by hydrochloric acid in close analogy to similar cyclizations studied by Braude.[14]

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[1] F. R. Japp and C. I. Burton, *J. Chem. Soc.*, **51**, 420 (1887); F. R. Japp and G. D. Lander, *ibid.*, **71**, 123 (1897).

[2] P. Yates and G. H. Stout, THIS JOURNAL, **76**, 5110 (1954).

[3] S. Ruhemann and W. J. S. Naunton, *J. Chem. Soc.*, **101**, 42 (1912); S. Ruhemann and S. I. Levy, *ibid.*, **103**, 551 (1913).

[4] C. F. H. Allen and J. A. VanAllan, THIS JOURNAL, **77**, 2315 (1955).

[5] H. Burton and C. W. Shoppee, *J. Chem. Soc.*, 567 (1939).

[6] E. Lippmann and R. Fritsch, *Ber.*, **38**, 1626 (1905).

[7] F. R. Japp and W. Maitland, *J. Chem. Soc.*, **85**, 1473 (1904).

[8] J. F. Grove and H. A. Willis, *ibid.*, 877 (1951); R. N. Jones and F. Herling, *J. Org. Chem.*, **19**, 1252 (1954).

[9] A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, T. L. Johnson and C. H. Shunk, THIS JOURNAL, **69**, 1985 (1947).

[10] R. B. Woodward, *ibid.*, **63**, 1123 (1941); **64**, 76 (1942).

[11] H. S. French, *ibid.*, **74**, 514 (1952).

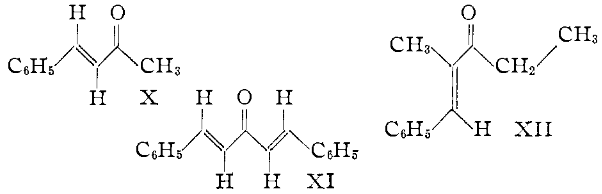
[12] *Cf.* E. A. Braude and E. S. Waight in "Progress in Stereochemistry," W. Klyne, ed., Vol. 1, Butterworths Scientific Publications, London, 1954, Ch. 4; E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754, 3773 (1955); E. A. Braude and C. J. Timmons, *ibid.*, 3766 (1955).

[13] It appeared unlikely that these compounds were diastereomers since each was formed under equilibration conditions.

[14] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1430 (1952); E. A. Braude, W. F. Forbes and E. A. Evans, *ibid.*, 2202 (1953); E. A. Braude and W. F. Forbes, *ibid.*, 2208 (1953).

The obstacle to the assignment of structure VI to the compound m.p. 122° is thus removed.

The ultraviolet spectrum of IX, λ_{max}^{EtOH} 287 mμ (log ε 4.44), calls for comment. The maximum is only 10 mμ higher than that of benzal-3-pentanone, 277 mμ (log e 4.27), although its intensity is considerably greater. It is in striking contrast to that of dibenzalacetone, 330 mμ (log ε 4.54),[15] which differs considerably from that of benzalacetone, 286 mμ (log ε 4.37).[9] Two effects may be engendered by alkyl substitution on the ethylenic bonds of benzalketones: (i) change in gross conformation and (ii) hindrance to coplanarity (*vide supra*). Examination of scale molecular molecules and dipole moment data[16] lead to the assignment of preferred conformations X and XI to mono- and dibenzalacetone, respectively,[17] while it appears most likely that those of mono- and dibenzal-3-pentanone are XII and IX. Woodward[18] has already drawn attention to the fact that, while the maximum of phorone, 259 mμ (log ε 4.37),[19] occurs at a considerably longer wave length than those of simple α,β-unsaturated ketones, the maxima of 1,4-cyclohexadien-3-one derivatives differ little from those of related compounds with a single conjugated double bond. It is proposed that the hypsochromic shift of 43 mμ produced by the introduction of the methyl groups into XI is due, in large part, to the change from a system with an *s-cis–cis* conformation analogous to phorone[16] to one, X, with the *s-trans–trans* arrangement of the cyclohexadienones.[20]


X XI XII

In the case of the unmethylated compounds II and III, it was necessary to re-examine the product, $C_{17}H_{14}O$, from acetone and benzaldehyde, described as brown-yellow flakes, m.p. 167° dec.[6] Several repetitions of the original procedure gave a product which, although melting near the recorded m.p., was amorphous, did not give consistent analytical figures, and was shown to be polymeric. The infrared spectrum of the total product failed to show the presence of III and indicated the absence of II, since it showed no band in the carbonyl region below 5.85 μ. The only crystalline product isolated was dibenzalacetone. Thus this anomaly in the assignment of structure III to the reduction product of I may be discounted.

The anomalous infrared spectrum[21] of this product prompted us to subject it to intensive purification, but no change in the spectrum was effected. Examination of the spectra in a variety of media and at varying concentrations in chloroform solution (Tables I and II) showed that the relative intensities of the two bands vary considerably with variation of the medium but are independent of the concentration of the chloroform solutions. The orderly variation of the relative intensities with change of medium confirms the fact that the duality is not due to the presence of adventitious impurity. Nor can it be attributed to an equilibrium mixture of II and III, since the former would be expected to absorb at an appreciably lower wave length than that of the lower of the two bands.[2,8] Molecular weight determinations in solutions of different concentrations also confirmed that the phenomenon was not due to equilibration of III with a dimer. It must therefore be concluded that the spectrum of III is *sui generis*[22] and that the weight of other evidence compels the acceptance of this structure for the reduction product of I.[23]

Experimental[24]

4-Hydroxy-2,5-dimethyl-3,4-diphenyl-2-cyclopenten-1-one (IV).[25]—Benzil (60 g.) and 3-pentanone (25 g.) were stirred with a solution of potassium hydroxide (3.0 g.) in ethanol (10 ml.). Initially, considerable evolution of heat occurred and the reaction mixture was maintained at room temperature by cooling with ice. After *ca.* 5 hr. the mixture solidified to a grayish-white mass. This was washed well with water and ether to give the product (71 g., 88%) as a white solid, m.p. 149–150°. Recrystallization from methanol gave colorless prisms, m.p. 152–153° (lit. m.p. 150°), $\lambda_{max}^{CHCl_3}$ 2.8–3.0 and 5.88 μ, λ_{max}^{EtOH} 276 mμ (log ε 4.16).

Reduction of IV: 2,5-Dimethyl-3,4-diphenyl-2-cyclopenten-1-one (VI).—4-Hydroxy-2,5-dimethyl-3,4-diphenyl-2-cyclopenten-1-one (40 g.) was reduced with hydriodic acid (sp. gr. 1.96; 5 ml.) and red phosphorus (9.0 g.) in acetic acid (160 g.) by a procedure modeled on that of Geissman and Koelsch[26] for the reduction of 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one. The product (20 g., 50%) was obtained as a crystalline solid, m.p. 117–118°, after two recrystallizations from 95% ethanol with treatment with Norit. Chromatography on alumina using benzene–petroleum ether as eluent followed by three recrystallizations from 95% ethanol afforded colorless plates, m.p. 121.5–122° (lit.[7] m.p. 122°), $\lambda_{max}^{CHCl_3}$ 5.89 μ, λ_{max}^{EtOH} 276 mμ (log ε 4.26).

Anal. Calcd. for $C_{19}H_{18}O$: C, 86.98; H, 6.91; mol. wt., 262. Found: C, 86.87; H, 6.78; mol. wt. (Rast), 275.

Condensation of 3-Pentanone with Benzaldehyde: 3,5-Dimethyl-2,6-diphenyltetrahydro-4-pyrone (VII) and 2,4-Diphenyl-1,5-diphenyl-1,4-pentadien-3-one (IX).—Benzaldehyde (120 g.) and 3-pentanone (40 g.) were condensed in basic medium using the procedure of Japp and Maitland,[7] with the substitution of mechanical stirring for shaking. The crude product (82 g.) was dissolved in the minimum amount of boiling methanol and the solution was cooled slowly to *ca.* 40°. The crystalline product which separated was filtered rapidly and recrystallized three times from carbon tetrachloride to yield colorless needles (1.2 g.), m.p. 267–268° dec., $\lambda_{max}^{CHCl_3}$ 5.84 μ, λ_{max}^{EtOH} 258 mμ (log ε 2.00).

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(15) E. A. Braude, *Ann. Rep. Chem. Soc.*, **42**, 105 (1945); *cf.* P. Grammaticakis, *Bull. soc. chim. France*, 865 (1953).

(16) J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949).

(17) It is assumed with earlier authors[9,16] that the compounds under discussion are in the more stable configuration, *i.e.*, the phenyl group is *trans* to carbonyl.

(18) R. B. Woodward, THIS JOURNAL, **62**, 1208 (1940).

(19) G. Scheibe, *Ber.*, **58**, 586 (1925).

(20) The origin of this type of shift may lie in the different distances, and therefore different interactions, between like charges in the ionic contributors to the ground and excited states of the two kinds of dienone system.

(21) The ultraviolet spectrum λ_{max}^{EtOH} 285 mμ (log ε 4.30) is in excellent accord with the structure III[4]; *cf.* the ultraviolet spectra of VIII (*vide supra*) and I, λ_{max}^{EtOH} 287 mμ (log ε 4.31).

(22) The hydrogenation product of III, *cis*-3,4-diphenylcyclopentanone, shows a normal, single band at 5.74 μ.

(23) The infrared spectrum of I also shows a split carbonyl band in certain solvents; however, the relative intensities of the bands are dependent on solution concentration and here the phenomenon can be interpreted in terms of intermolecular hydrogen-bonding.

(24) All melting points are corrected.

(25) F. R. Japp and A. N. Meldrum, *J. Chem. Soc.*, **79**, 1024 (1901).

(26) T. A. Geissman and C. F. Koelsch, *J. Org. Chem.*, **3**, 489 (1939).

Anal. Calcd. for $C_{38}H_{40}O_4$: C, 81.39; H, 7.19; mol. wt., 561. Found: C, 81.50; H, 7.01; mol. wt. (Rast), 560.

The methanolic mother liquor was cooled to *ca.* 15° when further crystalline material was deposited (1.7 g.). Purification by chromatography on alumina using benzene–petroleum ether as eluent and four recrystallizations from methanol gave IX as colorless plates, m.p. 127.5–128°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.15 μ, $\lambda_{\max}^{\mathrm{EtOH}}$ 287 mμ (log ϵ 4.44).

Anal. Calcd. for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.52; H, 6.85.

The mother liquor from which the crude IX had separated was cooled at 0° overnight when the major product separated as colorless needles (46 g.). Purification by chromatography on alumina using benzene–petroleum ether as eluent and three recrystallizations from methanol gave VII as colorless needles, m.p. 113.5–114°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.84 μ, $\lambda_{\max}^{\mathrm{EtOH}}$ 290 mμ (log ϵ 2.08).

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19; mol. wt., 280. Found: C, 81.71; H, 7.01; mol. wt. (Rast), 270.

Action of Base on 3,5-Dimethyl-2,6-diphenyltetrahydro-4-pyrone (VII): 2,4-Dimethyl-1,5-diphenyl-1,4-pentadien-3-one (IX).—3,5-Dimethyl-2,6-diphenyltetrahydro-4-pyrone (24 g.) was treated with potassium hydroxide (75 g.) in ethanol (300 g.) using the procedure of Japp and Maitland,[7] with the substitution of mechanical stirring for shaking. The crude product (10.5 g.) was separated by fractional crystallization from methanol into two components: the major constituent (8.9 g.) was obtained as colorless plates, m.p. 127.5–128°, shown to be identical with the product of the same m.p. obtained from the reaction of benzaldehyde with 2-pentanone by mixed m.p. and infrared spectral comparison. The other component (0.7 g.) was obtained as needles, m.p. 267–268° dec., and shown by similar means to be identical with the high melting product from that reaction.

Action of Acid on IX: Conversion to VI.—2,4-Dimethyl-1,5-diphenyl-1,4-pentadien-3-one was treated with ethanolic hydrogen chloride using the procedure of Japp and Maitland.[7] The isomerization product was recrystallized from 95% ethanol and from ethyl acetate–petroleum ether to give colorless leaflets, m.p. 121–122°, shown to be identical with the product, m.p. 121.5–122°, obtained by reduction of 4-hydroxy-2,5-dimethyl-3,4-diphenyl-2-cyclopenten-1-one by mixed m.p. and infrared spectral comparison.

Hydrogenation of IX: 2,4-Dimethyl-1,5-diphenyl-3-pentanone.—A suspension of IX (2.5 g.) in ethanol (20 ml.) was hydrogenated at atmospheric pressure and room temperature over 10% palladium-on-charcoal (0.50 g.); absorption of hydrogen ceased after the uptake of approximately two molar equivalents. After removal of the catalyst and solvent the crude hydrogenation product was obtained as a pale yellow oil, which was fractionally distilled. The bulk of the product distilled at 151–154° (9 mm.); the distillate (1.9 g.) solidified to a crystalline mass, m.p. 47–50°. This was recrystallized three times from petroleum ether to give colorless prisms, m.p. 55–56°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.85 μ.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.33. Found: C, 85.56; H, 8.19.

The 2,4-dinitrophenylhydrazone was purified by two recrystallizations from 95% ethanol–ethyl acetate and obtained as golden yellow needles, m.p. 127–128°.

Anal. Calcd. for $C_{25}H_{26}N_4O_4$: C, 67.25; H, 5.87; N, 12.55. Found: C, 67.50; H, 5.81; N, 12.51.

2,4-Dimethyl-1,5-diphenyl-3-pentanone.[27]—Methyl α-benzylpropionate was prepared by esterification of α-benzylpropionic acid[28] with ethereal diazomethane and obtained as a colorless liquid, b.p. 239–240° (lit.[29] b.p. 239°), n^{23}D 1.4940, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.80 μ. The ester (13.0 g., 0.073 mole) was added to a solution of triphenylmethylsodium[30] (*ca.* 0.075 mole) in ether (420 ml.). The mixture was shaken well and left to stand for 70 hr., protected from the atmosphere. Acetic acid (7 ml.) was added and the mixture was extracted with water (30 ml.). The ethereal extract was washed with 10% aqueous sodium carbonate, dried and concentrated. A few drops of ethanol were added and the mixture was cooled overnight at 0°; the triphenylmethane which separated was filtered and the filtrate was freed of solvent. The residual oil was fractionated to give the condensation product as an oil, b.p. 198–200° (2 mm.), n^{23}D 1.5448, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.75 and 5.85 μ, yield 3.0 g. (23%). This product (1.5 g.) was heated on the steam-bath with 5% aqueous sodium hydroxide (6 ml.) and dioxane (10 ml.) for 30 hr. Water (10 ml.) was added and the mixture boiled under reflux for 10 min. The solution was cooled, brought to *p*H 3–4 with dilute hydrochloric acid and extracted with ether. The ethereal extract was dried and freed of solvent to yield the product as an oil. This was purified by chromatography on alumina; the column was eluted with petroleum ether and benzene–petroleum ether (1:1). The solvent mixture gave an eluate which yielded colorless crystals (0.70 g., 47%), $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.85 μ, on removal of solvent. Four recrystallizations from petroleum ether gave colorless prisms, m.p. 55.5–56°. This product was shown to be identical with that obtained by hydrogenation of IX by infrared spectral comparison and mixed m.p., and also by preparation of its 2,4-dinitrophenylhydrazone which was obtained as golden yellow needles, m.p. 127–128°, undepressed by admixture with the corresponding derivative of the hydrogenation product.

2-Methyl-1-phenyl-1-penten-3-one (XII) was prepared by the method of Vorländer[31]; m.p. 30–31° (lit. 31°), $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.00 and 6.15 μ, $\lambda_{\max}^{\mathrm{EtOH}}$ 277 mμ (log ϵ 4.27).

4-Hydroxy-3,4-diphenyl-2-cyclopenten-1-one (I) was prepared by the method of Japp and Lander.[1] Recrystallization from ethanol or benzene failed to remove a persistent yellow impurity.[1] Chromatography on alumina using ether and a 1% solution of methanol in ether as eluents yielded the pure product as colorless needles, m.p. 148–149° (lit. 149°); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.75, 2.90, 5.84 and 5.90 μ, $\lambda_{\max}^{\mathrm{KBr}}$ 3.00, 5.94 μ; $\lambda_{\max}^{\mathrm{EtOH}}$ 287 mμ (log ϵ 4.31). Rechromatography failed to change the m.p. or the infrared spectrum of the product.

Reduction of I: 3,4-Diphenyl-2-cyclopenten-1-one (III).—The procedure of Geissman and Koelsch[26] was used. The product was obtained as colorless needles, m.p. 108–109° (lit. 108–110°), $\lambda_{\max}^{\mathrm{EtOH}}$ 285 mμ (log ϵ 4.30); for infrared spectrum see Tables I and II. Chromatography on alumina and recrystallization failed to change the m.p. or the infrared spectrum of the product.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.03; H, 6.04.

TABLE I

INFRARED SPECTRUM OF III IN VARIOUS MEDIA

Medium	Infrared bands, μ	ϵ_1/ϵ_2[a]
Carbon disulfide	5.83, 5.91	2.1
Carbon tetrachloride	5.82, 5.90	1.7
Dioxane	5.84, 5.91	1.0
Chloroform	5.83, 5.92	0.68
Nujol	5.81, 5.94	.38
Potassium bromide	5.82, 5.96	.27

[a] Ratio of the apparent molar extinction coefficients of the lower and higher wave length bands.

TABLE II

INFRARED SPECTRUM OF III IN CHLOROFORM AT VARIOUS CONCENTRATIONS

Concentration, mg./ml.	ϵ_1/ϵ_2[a]
10.0	0.68
5.0	.67
2.5	.66
1.25	.71

[a] Ratio of the apparent molar extinction coefficients of the bands at 5.83 and 5.92 μ.

The molecular weight of III in ethylene bromide was determined cryoscopically at a series of fifteen different concentrations, varying from 0.0105 g./g. of solvent to 0.00232 g./g. of solvent; the values obtained, 221–268 (calcd. 234), showed no concentration dependency.

***cis*-3,4-Diphenylcyclopentanone.**[5]—A solution of III (0.50 g.) in acetic acid (5 ml.) and ethanol (10 ml.) was hydro-

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[27] *Cf.* B. E. Hudson and C. R. Hauser, THIS JOURNAL, **63**, 3156 (1941).

[28] M. Conrad and C. A. Bischoff, *Ann.*, **204**, 177 (1880).

[29] L. Edeleano, *J. Chem. Soc.*, **53**, 558 (1888).

[30] W. B. Renfrow and C. R. Hauser, "Organic Syntheses," Coll. Vol. **11**, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

[31] D. Vorländer, *Ann.*, **294**, 253 (1897).

genated over platinum; reduction was stopped after the uptake of 1.15 molar equivalents of hydrogen. Recrystallization of the crude product from ethanol gave colorless needles, m.p. 107–108° (lit. 105–106°,[5] 110°[32]), $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.74 μ.

Condensation of Acetone with Benzaldehyde.—Benzaldehyde (20 g.) and acetone (5.4 g.) were heated with pulverized, freshly fused zinc chloride (10 g.), following the procedure of Lippmann and Fritsch.[6] Extraction of the resulting dark brown gum with ether and precipitation with a large volume of methanol gave a yellow-brown solid. Three recrystallizations of this material from ethyl acetate gave **dibenzalacetone** (1.8 g.) as yellow leaflets, m.p. 111–112°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.05 and 6.16 μ, identified by infrared spectral comparison and mixed m.p. with authentic dibenzalacetone,[33] m.p. 111.5–112°. **2,4-Dinitrophenylhydrazone:** deep red rods, m.p. and mixed m.p. 176–177° (lit.[34] 179–180°). On removal of ether and methanol from the original filtrate, a dark brown, resinous mass remained (16.5 g.), from which no crystalline product could be obtained. Chromatography on alumina with benzene–petroleum ether as eluent yielded further dibenzalacetone (0.8 g., combined yield 14%); elution with ether gave a yellow resin (4.75 g.), m.p. 83–96°, from which no pure component could be separated; final elution with methanol gave a yellow-brown powder (0.2 g.), which softened *ca.* 165° with subsequent decomposition (*cf.* the m.p. of 167° dec. recorded by Lippmann and Fritsch[6] for "stilbeneacetone"). Several attempted crystallizations of this material from benzene–petroleum ether gave an amorphous, pale yellow solid, decomposing *ca.* 188°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.85(m) μ.

Anal. Found: C, 86.20, 87.70, 88.38; H, 6.30, 6.07, 6.24; mol. wt. (Rast), 1015, 1018, 1083.

Variation of the reaction conditions failed to yield a more tractable product. When the reaction was carried out at 120° for 6 hr., the yield of dibenzalacetone was increased to 51%, but again no other crystalline product could be isolated. A run at 210–220° for 11 hr. gave an increased yield of the amorphous type of product obtained in the first run, after chromatography of the crude product on silica, but again crystallization was unsuccessful.

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CAMBRIDGE, MASSACHUSETTS

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[32] H. Burton and C. W. Shoppee, *J. Chem. Soc.*, 1408 (1939).

[33] C. R. Conard and M. A. Dolliver, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 167.

[34] G. D. Johnson, THIS JOURNAL, **75**, 2720 (1953).

[CONTRIBUTION NO. 2229 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

On the Ultrasonic Cleavage of Some Aromatic and Heterocyclic Rings

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It was reported earlier that upon exposure to ultrasonic waves in the presence of silver nitrate, certain halogen derivatives yielded silver halide precipitates which contained silver acetylide, silver diacetylide and (when pyridine was treated) also silver cyanide. It has now been shown that similar cleavage reactions also can be realized in the absence of silver, with benzene, bromobenzene, phenol, tropolone, pyridine and pyrrole. Under these conditions free acetylene and/or hydrogen cyanide evolved. In some instances the ultrasonic cleavage was accelerated by the presence of argon.

When in the course of a recent study[2] some halogen derivatives such as bromobenzene, iodobenzene, α-iodothiophene, α-bromofuran, etc., were suspended in aqueous silver nitrate and exposed to ultrasonic waves, a silver halide precipitate that also contained silver acetylide and small amounts of the diacetylide appeared. However, the presence of halogen in the molecule was not necessary for the cleavage of the pyridine ring. Indeed, free pyridine yielded, in addition to the products mentioned, some silver cyanide.[3,4] Analytical methods for the separation and estimation of the three silver salts were developed,[3] and the same methods now have been applied to pyrazine and pyrrole.

While in all these experiments the acetylene formed was retained in the system, in a solid phase, we have now investigated whether or not ultrasonic ring cleavage can be realized and the evolution of acetylene gas detected in the absence of silver nitrate. For this purpose the starting material was suspended in pure water and, during the ultrasonic treatment, the volatile products were swept continuously by means of an inert gas into a trap containing ammoniacal cuprous solution. Reddish-purple cuprous acetylide appeared. This precipitate was collected and titrated for acetylene as described in our first communication.[2]

When the compound contained heterocyclic nitrogen, a parallel experiment was run in which a potassium hydroxide solution was substituted for the cuprous reagent. The alkaline solution, which trapped the hydrogen cyanide formed, was treated in the same manner as the ammoniacal extracts of silver-containing precipitates mentioned in our recent paper.[3] Finally, after conversion into prussian blue, the cyano group was estimated colorimetrically.

The results are summarized in Table I (benzene, bromobenzene, phenol, tropolone) and Table II (pyridine, pyrazine, pyrrole).

These tables show that the ultrasonic conversion does take place in the absence of silver, and hence that the formation of silver complexes is not a necessary prerequisite of the cleavage process.

When comparing the acetylene yields obtained in the presence and absence of silver, it should be noted that, with the sole exception of pyridine, the compounds treated yielded more acetylene when silver nitrate was present; this effect is very conspicuous in the case of phenol. A tempting ex-

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[2] L. Zechmeister and L. Wallcave, THIS JOURNAL, **77**, 2853 (1955).

[3] L. Zechmeister and E. F. Magoon, *ibid.*, **78**, 2149 (1956).

[4] L. Zechmeister and E. F. Magoon, "Festschrift Arthur Stoll," Birkhäuser, Basel, 1957, p. 59.