zene–petroleum ether eluate there was isolated 1.1 g. of solid melting at 84–87° (VIIIb). The analytical sample, crystallized twice from cyclohexane, melted at 87–88°.

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.07; H, 5.54; N, 5.00.

The other eluates yielded only benzoic acid, small amounts of VIIIa and oils. The ultraviolet spectra of the two isomers were very similar: that of VIIIa (4.03×10^{-5} *M* in 95% ethanol) showed a maximum at 249 mμ, ε 12,900; that of VIIIb (4.17×10^{-5} *M* in 95% ethanol) showed a maximum at 248 mμ, ε 13,000.

1,4-Diphenyl-2-acetoxy-3-nitro-1-butanone (IXa).—Only the higher melting form VIIIa was converted into the acetate, for insufficient VIIIb was obtained for investigation. A solution of VIIIa (10 g., 0.035 mole) in dry benzene (150 cc.) containing acetic anhydride (4.0 g., 0.035 mole) and sulfuric acid (one drop) was warmed on the steam-bath for 30 minutes. The cooled solution was poured into water (150 cc.), the organic layer was removed, washed with water (three 100-cc. portions), dried (magnesium sulfate) and the solvent was removed under reduced pressure. The residual oil, when crystallized from methanol, yielded white plates of IXa (11 g., 96%) melting at 103–104°. The analytical sample, crystallized twice from methanol, melted at 103.5–104°. The ultraviolet absorption spectrum of IXa (4.63×10^{-5} *M* in 95% ethanol) showed a broad maximum at 247–250 mμ, ε 11,400.

Anal. Calcd. for $C_{18}H_{17}NO_5$: C, 66.05; H, 5.24; N, 4.28. Found: C, 66.28; H, 5.61; N, 4.38.

1,4-Diphenyl-3-nitro-2-butene-1-one (II).—The acetoxy compound IXa (1 g.) and lithium chloride (3 equiv.) were suspended in ether (225 cc.) containing triethylamine (1 equiv.), and the mixture was allowed to stand at room temperature for six hours with occasional shaking. The mixture was washed twice with hydrochloric acid (5%), then with water, and dried (magnesium sulfate). The solvent was removed under reduced pressure; the residual oil, fractionally crystallized from cyclohexane, yielded IIa (0.06 g.), IIb (0.1 g.), a mixture of IIa and IXa (0.5 g.) and a yellow oil (0.3 g.). The experiment described here was one of a series of nineteen such experiments in which the amount and nature of the base, time, temperature, solvent, and order of mixing the reagents were all varied. Only when trimethylamine was used was any IIa or IIb produced; always there was recovered some IXa, which was extremely difficult to separate from II. Once seed of IIa and IIb were available, isolation of these from the reaction product was facilitated, although it was never easy or clean-cut; however, when the reactions were continued until all of the IXa was consumed, the products were oils from which no solids could be isolated.

The analytical sample of IIa, crystallized from cyclohexane, melted at 104–104.5°. The analytical sample of IIb, crystallized (Dry Ice bath) first from ether and then from petroleum ether (b.p. 60–68°), melted at 53.5–54°.

Anal. Calcd. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: IIa, C, 71.77; H, 5.18; N, 5.11. Found: IIb, C, 71.26; H, 5.14; N, 5.42.

Both IIa and IIb decolorized an acetone solution of potassium permanganate; both compounds oxidized ferrous hydroxide. The ultraviolet spectra of the two compounds were different. That of IIa (5.85×10^{-5} *M* in 95% ethanol) showed a maximum at 243 mμ, ε 22,500; that of IIb (5.02×10^{-5} *M* in 95% ethanol) showed a maximum at 245–250 mμ, ε 13,000.

In one experiment the β,γ-isomer (E) of II was produced from IXa. A solution of IXa (1 g.) in cyclohexane (100 cc.) was refluxed while a solution of triethylamine (1 equiv.) in cyclohexane (50 cc.) was slowly (2.5 hours) added. The reaction mixture, processed as above, yielded 0.3 g. of E, m.p. and mixed m.p. 98°.[4] A mixture of E and IIa melted at 90–98°.

Ethyl 4-Benzyl-6-phenyl-2-pyrone-3-carboxylate (B).—A solution of sodioethyl malonate (from sodium, 0.024 g., and ethyl malonate, 0.189 g.) in dry ethanol (4 cc.) was refluxed through a small Soxhlet apparatus, the cup of which contained IIa (0.08 g.). After all the IIa had dissolved, the dark orange solution was refluxed for one hour, then cooled, acidified with acetic acid (0.062 g.), and allowed to stand for four hours at 5°. The white solid (0.05 g., inorganic) was removed; the filtrate was diluted with water (4 drops), seeded with a tiny crystal of B, and allowed to stand for 12 hours at 5°. As no crystallization occurred, the solvent was removed under reduced pressure, the residual oil (0.02 g.) was taken up in a little ether, and this solution was poured onto a column (1 × 20 cm.) of activated alumina which had been thoroughly washed with ethyl acetate and then with petroleum ether (b.p. 60–68°). The column was developed and eluted successively with mixtures of ether–petroleum ether (b.p. 60–68°) as follows: 1:9 mixture, 50 cc., 25 cc., 25 cc.; 1:4 mixture, 25 cc., 25 cc., 50 cc.; 3:7 mixture, 25 cc., 25 cc., 50 cc. These nine fractions were followed by two of ether alone (50 cc. each). No definite bands were observed on the column; each of the fractions (except the last), upon removal of the solvent, left a small amount of viscous oil. Each of these ten oils was dissolved in a drop or two of methanol; the solution of the second fraction, when cooled, deposited a yellow solid (2 mg.) which melted at 123–126°. A mixture of this substance with authentic B (m.p. 128–129°), melted at 123–128°. None of the other solutions yielded any solid material. The solution of the third fraction was saturated with dry ammonia, but no solid (pyridone) could be isolated; the only product was a dark red gum.

MINNEAPOLIS 14, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rupe Rearrangement of 2,6-Dimethyl-2-carbethoxy-1-(phenylethynyl)-cyclohexanol (II) and 2,6-Dimethyl-2-carbethoxy-1-(3-isopropylphenylethynyl)-cyclohexanol (III)

BY WILLIAM E. PARHAM, EDWARD L. WHEELER,[1,2] R. M. DODSON AND STUART W. FENTON

RECEIVED APRIL 26, 1954

The Rupe rearrangement of the acetylenic carbinols II and III has been studied, and chemical and spectral evidence for the course of the reaction has been obtained. The principal products from these reactions are cyclic lactones to which the configurations shown in formulas VIIa and VIIb, and XIIa and XIIb, have been tentatively assigned. The synthesis of *m*-isopropylphenylacetylene is described.

Our interest in developing a synthetic method, subject to steric control, for 1-carboxy-12-alkyloctahydrophenanthrenes, has prompted us to investigate the Rupe rearrangement of the acetylenic carbinols II and III. The results of this investigation constitute the subject of this report.

The acetylenic alcohols II and III were prepared in 50 and 56% yields, respectively, by the reaction of the Grignard reagent, prepared from the corresponding phenylacetylene, with 2,6-dimethyl-2-carbethoxycyclohexanone (I).

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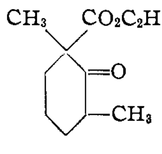
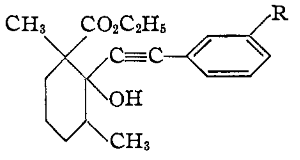
[1] From the Ph.D. Thesis of Edward L. Wheeler, University of Minnesota (1953).

[2] Parke, Davis Fellow (1952–1953). Part of this work was sponsored by the Greater University Fund of the University of Minnesota.

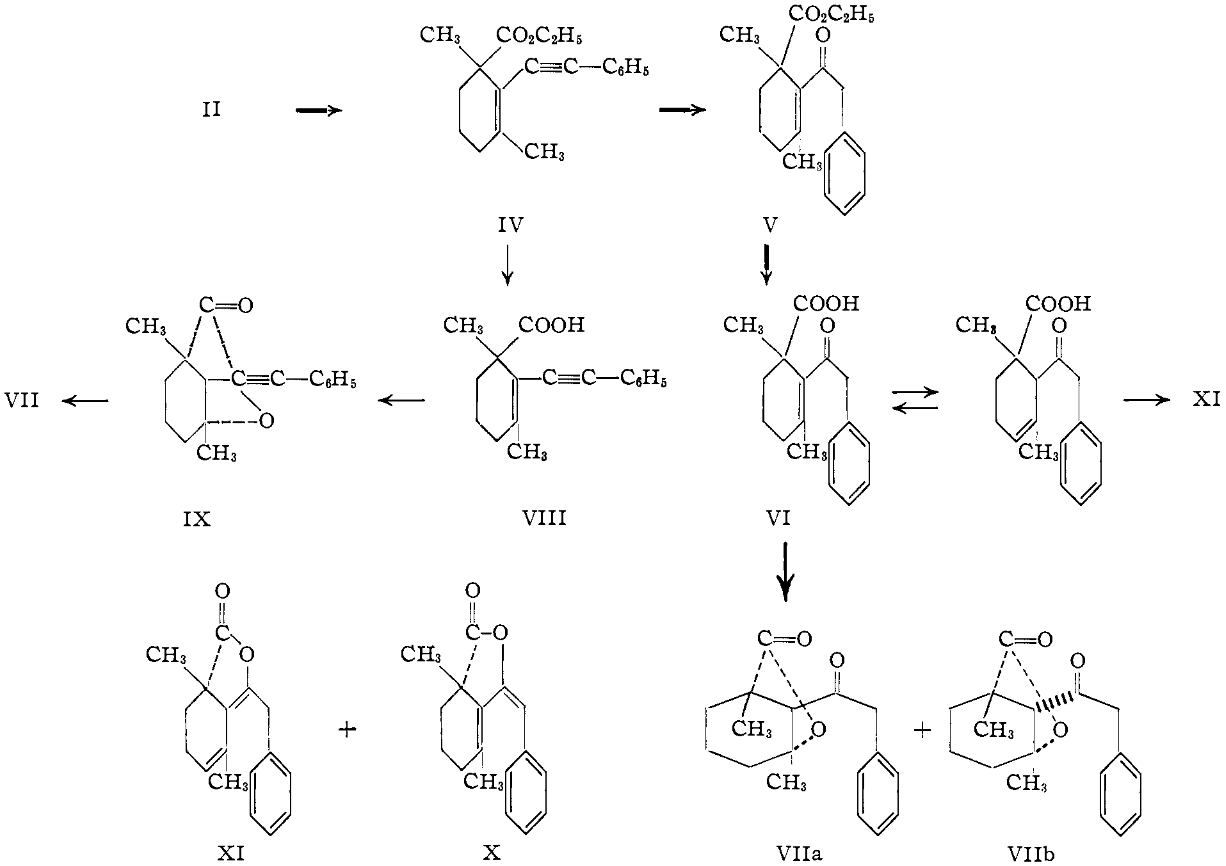


I



II, R = H
III, R = -CH(CH₃)₂

In order to obtain information concerning the course of the reaction of II with hot 80% formic acid, aliquots were removed from the reaction mixture at various time intervals, and the ultraviolet spectra of the acid and neutral fractions of each aliquot were determined. The spectra[3] of the neutral fractions, together with the chemical evidence discussed subsequently, indicated that the reaction followed principally the expected course[4] as described by the heavy lines in the accompanying series of equations.



The Rupe rearrangement of II was run for 40 hours, and the neutral[5] fraction was separated and purified by chromatography on silica gel. Three pure compounds were isolated. The principal product, obtained in 46% over-all yield, was a liquid lactone which was assigned structure VIIa,[6] on the basis of its composition, saponification equivalent, and infrared and ultraviolet absorption spectra. The ultraviolet spectrum of the lactone showed no absorption in the ultraviolet region other than that due to the benzene ring—this result is consistent only for the expected lactone VII. The infrared spectrum was also consistent with the structure assigned, and showed two carbonyl bands: the keto-group absorbed at 1730 cm.$^{-1}$ (unconjugated carbonyl), and the five-membered lactone at 1790 cm.$^{-1}$.[7] A weak band also appeared at 1660 cm.$^{-1}$. The keto group of this lactone is hindered, and typical carbonyl derivatives (oxime and semicarbazone) were not obtained. Benzal and piperonal derivatives also failed to form; however, action of bromine gave a solid monobromo derivative. The bromine is believed to be alpha to the carbonyl group but the position of substitution was not established.

The second product, a solid formed in small amount, was assigned structure VIIb,[6] *i.e.*, the stereoisomer of the first lactone, on the basis of its composition, saponification equivalent, and ultraviolet and infrared spectra. This lactone showed no absorption in the ultraviolet region other than that due to the aromatic system; the infrared spectrum showed three strong bands in the carbonyl region at 1810, 1730 and 1680 cm.$^{-1}$ (decreasing intensity, respectively).

The third compound, also isolated in very small amount, was assigned structure V, the α,β-unsatu-

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[3] Discussion of the spectra of these fractions, and evidence for the structure of the acidic intermediates, is found in the experimental section of this report.

[4] (a) G. F. Hennion, R. B. Davis and D. E. Maloney, THIS JOURNAL, **71**, 2813 (1949); see also (b) J. C. Hamlet, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 2652 (1951).

[5] The amount of acidic products decreased with time and after 40 hours amounted to only 5% of the total reaction mixture.

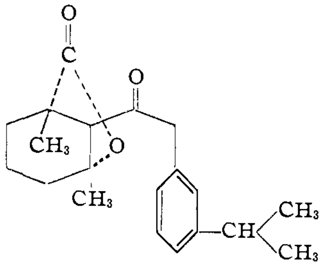
[6] The configuration of the lactone is discussed later in this report.

[7] H. Gilman, "Organic Chemistry—An Advance Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 139–154.

rated keto ester. This ester had the molecular formula $C_{19}H_{24}O_3$, and had a maximum in the ultraviolet region at 244 mμ (ε 16,200).

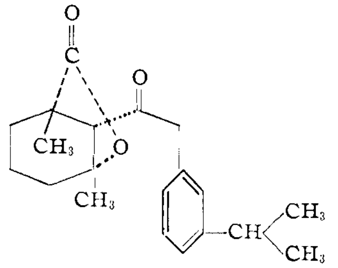
When the Rupe rearrangement of II was carried out over a period of 100 hours, only a few differences were noted. Slightly more of the isomeric ketolactones was obtained; there was much less of the compound containing the phenylacetylene group (forerun of chromatogram, see experimental) and, as before, very little of the α,β-unsaturated ketone.

The Rupe rearrangement of III was run for a period of 63 hours.



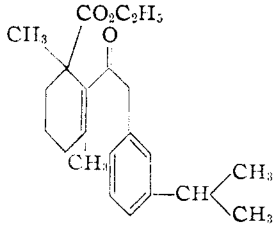
XIIa

+



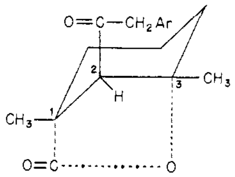
XIIb

+



XIII

The neutral fraction of the reaction product was chromatographed on silica gel, and was separated into three main fractions. The first two fractions consisted essentially of a pure liquid ketolactone which was assigned structure XIIa[6] on the basis of its composition, saponification equivalent and absorption spectra. This product showed no absorption in the ultraviolet region except that due to alkyl benzene. The infrared spectrum was consistent with the proposed structure and showed a lactone band at 1790 $cm.^{-1}$ [7] and a ketone band at 1720 $cm.^{-1}$. There was also a very weak absorption at 1660 $cm.^{-1}$, and a band of medium intensity at 1605 $cm.^{-1}$. The third fraction consisted largely of more of the liquid ketolactone, and also contained a solid, which proved to be a stereoisomer (XIIb)[6] of XIIa. As was the case with its stereoisomer, this lactone showed no absorption in the ultraviolet region except that due to alkylbenzene. The infrared spectrum showed a lactone band at 1805 $cm.^{-1}$, a ketone band at 1725 $cm.^{-1}$ and a weak absorption at 1660 $cm.^{-1}$. The liquid keto lactone was the principal product of the reaction and was obtained in 50% yield; the solid ketolactone was obtained in only small amounts. In addition, a small quantity of the α,β-unsaturated ketoester XIII was apparently present in one of the fractions obtained from the chromatogram, as evidenced by a maximum at 247 mμ, but no attempt was made to isolate this material.



VIIa and XIIa

Barton[8] has concluded that the chair conformation of C-1 axial 1,2,2,6,6-pentachlorocyclohexanes is more stable than the corresponding C-1 equatorial conformation. If his arguments apply to the present case, then the following assignments for the configurations of VIIa and XIIa seem probable. The infrared spectra of the lactones are not inconsistent with this formulation.

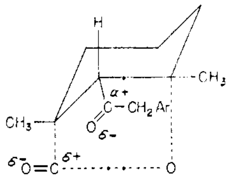
The decrease in wave length (increase in frequency) of the lactone carbonyl band in VIIb and XIIb, can be accounted for on the basis of dipole-dipole interaction. Such interaction, as depicted below for VIIb and XIIb, should result in a decrease in wave length. Since the equatorial acyl group (VIIb, XIIb) is closer to the lactone carbonyl than the axial acyl group (VIIa, XIIa), the effect should be greater in the b series. In view of the combined evidence, the configurations tentatively assigned to the γ-ketolactones appear reasonable.[9]

TABLE I

INFRARED ABSORPTION BANDS IN THE 6 μ REGION OF THE γ-KETOLACTONES

vs, very strong; s, strong; sm, strong to medium; m, medium; w, weak. Frequencies are in $cm.^{-1}$.

Compound	Lactone C=O	Keto C=O	—C=C--OH
VIIa	1790 vs	1730 vs	1660 w
VIIb	1810 vs	1730 sm	1680 sm
XIIa	1790 vs	1720 vs	1660 vw
XIIb	1805 vs	1725 m	1660 w



VIIb and XIIb

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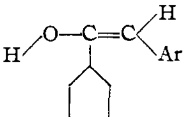
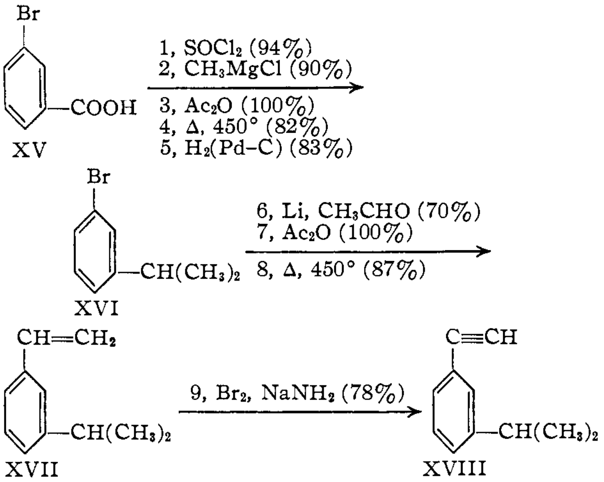
(8) D. H. R. Barton, *Chemistry and Industry*, 664 (1953).

(9) The strong absorption at 1680 $cm.^{-1}$ in VIIb is at an unusually high frequency for a carbon–carbon double bond as depicted for the enol isomers XIV for these ketolactones; however, there is previous evidence that such an assignment is possible. *Cf.* H. Rosenkrantz and M. Grut, *Helv. Chim. Acta*, **36**, 1000 (1953). It is of interest to note that models indicate the possibility for chelation between the enolic hydroxyl group and the lactone carbonyl group in VIIb and XIIb but not in VIIa and XIIa. The decrease in intensity of the ketone carbonyl group at 1725 $cm.^{-1}$, particularly evident for XIIb, may be due to such chelation; however, it must be noted that we have not detected a chelated carbonyl bond for these lactones, and the ultraviolet spectra do not show appreciable concentrations of XIV. The latter argument is tenuous, however, in that distortion of the double bond could inhibit styrene like absorption.



XIV

meta-Isopropylphenylacetylene, a required intermediate for this work, was not known. Its preparation is summarized in the equations



XV XVI XVII XVIII

Most of the intermediates in these reactions are new; these products were isolated and characterized, and details are described in experimental section of the report.

Experimental

2,6-Dimethyl-2-carbethoxy-1-phenylethynylcyclohexanol (II).—Phenylacetylene (41 g., 0.40 mole) in anhydrous ether (50 ml.) was added slowly (45 minutes) to the Grignard reagent prepared from ethyl bromide (44 g., 0.4 mole), magnesium (9.7 g., 0.40 mole) in anhydrous ether (100 ml.), and the resulting solution was heated at the reflux temperature for one hour. 2,6-Dimethyl-2-carbethoxycyclohexanone[10] (I, 69 g., 0.35 mole, b.p. 75° (1.3 mm.), n^{20}D 1.4491) was slowly added (40 minutes) to the reaction mixture, and the resulting solution was heated at the reflux temperature for one-half hour. The complex was then hydrolyzed with 60 ml. of saturated aqueous ammonium chloride. The ether layer was fractionally distilled to give 53 g. (50% yield) of II (b.p. 145–148° (0.8 mm.), n^{20}D 1.5405). This alcohol solidified and was recrystallized from ethanol–water to give a product melting at 77–78°.

Anal. Calcd. for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.95; H, 8.23.

The ultraviolet spectrum of II showed two maxima: 242 mμ (ε 18,800) and 252 mμ (ε 15,900). The infrared spectrum showed an ester carbonyl band at 1740 cm.$^{-1}$, and a weak hydroxyl band at 3650 cm.$^{-1}$.

2-(3-Bromophenyl)-2-propanol.—3-Bromobenzoyl chloride (310 g., 1.41 moles, b.p. 84.5–86.5° (3 mm.), n^{21}D 1.5955, 90% yield from XV)[11] in 1 l. of anhydrous ether was added slowly (four hours) to a solution of methylmagnesium chloride (prepared from 75.3 g. (3.0 g. atoms) of magnesium filings) in 1 l. of anhydrous ether. The mixture was stirred for 90 minutes and then 3 l. of 25% aqueous ammonium chloride and 2 kg. of ice was added. The organic layer was separated with ether and dried over magnesium sulfate. The ether was removed, and the residue was distilled through a 16 cm. packed column (Cannon protruded metal packing)[12] to give 272 g. (90%) of 2-(3-bromophenyl)-2-propanol boiling at 85–86° (1 mm.), n^{25}D 1.5584.

Anal. Calcd. for $C_9H_{11}OBr$: C, 50.25; H, 5.16. Found: C, 50.20; H, 4.92.

1-Methyl-1-(3-bromophenyl)-ethylene.—A solution of 272 g. (1.26 moles) of 2-(3-bromophenyl)-2-propanol in 254 g. (2.49 moles) of acetic anhydride was heated at reflux temperature for one hour. The mixture was poured into 500 ml. of water and heated on the steam-bath for 30 minutes. After the acetic acid had been neutralized with 200 g. of sodium carbonate, the 1-methyl-1-(3-bromophenyl)-ethyl acetate was extracted with ether. The ether was removed by distillation, and the crude ester was pyrolyzed at 425–450°. The pyrolysis apparatus consisted of a Pyrex tube (1.5 × 36 cm.) surrounded by an electrically heated jacket. The tube was inclined at an angle of 30° from the vertical. An addition funnel with a gas inlet tube was attached to the top, and a short tube (1.5 × 13 cm.) was attached below. A three-necked flask fitted with a vertical reflux condenser was attached to the short, exit tube. Above the water-cooled condenser was a Dry Ice condenser. A small, loose plug of glass wool was put in the water-cooled condenser to facilitate the condensation of the vapors. Nitrogen was passed through the system at a rate which prevented backup of the vapor, but did not allow much of the vapor to escape.

The pyrolysis required ten hours for completion. The pyrolysate was neutralized with 10% aqueous sodium carbonate, and the olefin was extracted with ether. When the solution had been dried over magnesium sulfate, the ether was removed by distillation at reduced pressure. The residue was distilled through a 16 cm. packed column (Cannon protruded metal packing) with a partial take-off head. 1-Methyl-1-(3-bromophenyl)-ethylene (203 g., 82%) was collected at 85–86° (3 mm.); n^{23}D 1.5787 (reported b.p. 68–72° (2 mm.), n^{20}D 1.5779[13]). Unchanged ester (25 g.) was recovered.

3-Bromoisopropylbenzene (XVI).—A solution of 1-methyl-1-(3-bromophenyl)-ethylene (56.0 g., 0.283 mole) in 150 ml. of U.S.P. ethyl acetate was hydrogenated over 1.5 g. of 10% palladium-on-charcoal at an initial pressure of three atmospheres. One mole of hydrogen was absorbed in one hour. If the reduction period was prolonged, considerable hydrogenolysis of the carbon–bromine bond occurred. The product was distilled through a 16-cm. packed column previously described. 3-Bromoisopropylbenzene (47 g., 83%) was collected at 89.5–91.0° (15 mm.); n^{25}D 1.5351 (reported b.p. 94–96 (20 mm.)[12]).

Anal. Calcd. for $C_9H_{11}Br$: C, 54.29; H, 5.57. Found: C, 54.47; H, 5.87.

1-(3-Isopropylphenyl)-ethanol.—In a 1-l. three-necked flask, equipped with a stirrer, reflux condenser and dropping funnel, was placed 200 ml. of anhydrous ether. Small pieces of lithium metal (10.08 g., 1.45 g. atoms) were added to the ether and the mixture was stirred for five minutes to ensure the removal of traces of water. 3-Bromoisopropylbenzene (137.5 g., 0.69 mole) in 200 ml. of anhydrous ether was added over a period of two hours and the solution was stirred and heated at reflux temperature for an additional two hours. Freshly prepared acetaldehyde (31.3 g., 0.71 mole) in 100 ml. of anhydrous ether was added to the cooled reaction mixture (25°) over a period of 70 minutes. The solution was stirred and heated at reflux temperature for one hour after the addition.

The complex was hydrolyzed by pouring it into a mixture of 2 l. of 25% aqueous ammonium chloride and 1 kg. of ice. The organic material was extracted with ether and dried over magnesium sulfate. The ether was distilled, and the residue fractionally distilled through the 16-cm. packed column previously described. 1-(3-Isopropylphenyl)-ethanol (88 g., 78%) was collected at 104.5–105.0° (3 mm.); n^{25}D 1.5110.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.27; H, 9.58.

3-Isopropylphenylethylene (XVII).—The procedure used was the same as that described for 1-methyl-1-(3-bromophenyl)-ethylene. From 209 g. (1.27 moles) of 1-(3-isopropylphenyl)-ethanol there was obtained 162 g. (87% yield) of XIX (b.p. 79° (13 mm.), n^{25}D 1.5253).

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.05; H, 9.47.

3-Isopropylphenylacetylene (XVIII).—A solution of 73 g. (0.50 mole) of 3-isopropylphenylethylene in 150 ml. of anhydrous ether was stirred and maintained at 0–5°. Bromine (92 g., 0.575 mole) was added dropwise over a period of 30 minutes, and the solution was stirred for 30 minutes after the addition. The ether was then evaporated at reduced pressure, maintaining a temperature of 0–5°. The crude dibromide was then added over a period of 70 minutes to a solution of sodium amide in liquid ammonia which was pre-

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[10] R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, 1299 (1939).

[11] J. F. Norris and V. W. Ware, THIS JOURNAL, **61**, 1418 (1939).

[12] M. R. Cannon, *Ind. Eng. Chem.*, **41**, 1953 (1949).

[13] S. Seymour and H. B. Wolfstein, THIS JOURNAL, **70**, 1178 (1948).

pared from sodium (27.5 g., 1.2 g. atoms), liquid ammonia (500 ml.), ferric nitrate (0.6 g.) and aniline (1.5 g.). The resulting mixture was stirred for 3.5 hours, then *carefully* hydrolyzed with 80 ml. of concentrated ammonium hydroxide, and finally with 250 ml. of water. The mixture was allowed to stand overnight, then extracted with ether. The ether solution was washed twice with 5% hydrochloric acid and once with water. The washings were repeated, then the ether extracts were dried over magnesium sulfate. The ether was distilled, and the residue was fractionally distilled through the 16-cm. column previously described to give 56 g. (78%) of 3-isopropylphenylacetylene (b.p. 67.5–69.0° (12 mm.), n^{25}D 1.5300).

Anal. Calcd. for $C_{11}H_{12}$: C, 91.66; H, 8.33. Found: C, 91.48; H, 8.31.

Hydrogenation (atmospheric pressure) of a solution of 1.04 g. of 3-isopropylphenylacetylene in 60 ml. of ethyl acetate in the presence of 100 mg. of 10% palladium-on-charcoal was complete in ten minutes, and 100.5% of two molar equivalents of hydrogen was absorbed.

The ultraviolet spectrum of XVIII showed two maxima, 237 mμ (ε 15900) and 246 mμ (ε 14200). The infrared spectrum showed a strong band at 3300 cm.$^{-1}$ and a medium band at 2120 cm.$^{-1}$.

2,6-Dimethyl-2-carbethoxyl-(3-isopropylphenylethynyl)-cyclohexanol (III).—The procedure was essentially the same as that described for II. From 72 g. (0.5 mole) of XVIII there was obtained 96 g. (56%) of III (b.p. 157–162° (0.5 mm.), n^{25}D 1.5298–1.5302. The sample used for analysis boiled at 138–144° (0.2 mm.); n^{25}D 1.5308.

Anal. Calcd. for $C_{22}H_{30}O_3$: C, 77.15; H, 8.83. Found: C, 76.82; H, 8.83.

The ultraviolet spectrum of III showed two maxima: 243 mμ (ε 17600) and 253 mμ (ε 16900). The infrared spectrum showed a band in the carbonyl region at 1735 cm.$^{-1}$, a strong band at 3550 cm.$^{-1}$ in the hydroxyl region, and a weak band at 2250 cm.$^{-1}$.

The Action of Formic Acid on 2,6-Dimethyl-2-carbethoxy-1-phenylethynylcyclohexanol (II). A. The Use of Ultraviolet Spectra to Follow the Course of the Reaction.—A mixture of 1.0 g. of II and 20 ml. of 80% formic acid was heated at the reflux temperature. At the various time intervals the reaction mixture was cooled, and 1 ml. of the solution was removed. The aliquot was made basic with 10% aqueous sodium hydroxide and extracted with ether. The ether was evaporated and the residue dissolved in 95% U.S.P. ethanol. The basic extract was acidified with 10% hydrochloric acid and extracted with ether. The ether was removed and the residue was dissolved in 95% ethanol.

Neutral Products.—The spectra of the neutral fractions indicated that the vinylacetylene (IV) was formed in high concentration within the first half-hour, as evidenced by the appearance of the absorption band with a maximum at 287 mμ. This band decreased in intensity and practically disappeared after two hours. The acetylenic group in IV underwent hydration, so that during the first hour the α,β-unsaturated ketone was present at its highest concentration as indicated by a maximum at 245 mμ (pure V was subsequently found to have an absorption maximum at 244 mμ (ε 16,200)). After one hour this maximum decreased and resolved into two maxima at 240 and 250 mμ, respectively. These maxima are characteristic of the phenylacetylene group II or IX, and in view of the rapid initial decrease in concentration of II, these bands are most probably due to the formation of lactone IX. The maxima at 240 and 250 mμ gradually decreased, and after 24 hours only absorption due principally to the benzene ring was present indicating the formation of lactones VII.

Acidic Products.—The total amount of acidic products decreased with time (20% of total products after four hours, 5% after 41 hours). The absorption of 287 mμ (2.5–4 hour curves) was evidence for the formation of VIII, which was ultimately converted to VII. The formation of the transient peak at 245 mμ was attributed to the intermediate VI.

B.—A mixture of II (25 g., 0.083 mole) and 80% formic acid was heated at the reflux temperature for 41 hours. The mixture was separated into acidic and neutral products as described in Part A.

The neutral material (21 g.) was chromatographed using 180 g. of silica gel (previously activated by heating for 24 hours at 200°). The eluants used in developing the column are shown below.

Fraction	Vol., ml.	Eluant	Material, g.
1–2	2400	Pet. ether–benzene (3/1)	0.4
3	2200	Pet. ether–benzene (1/2)	3.6
4–6	3600	Benzene	11.3
	1500	Benzene–chloroform (1/1)	
7	2000	Chloroform	3.5
8	2000	Chloroform	2.4
9–11		Chloroform–ethanol, ethanol	0.2

Fraction 3 showed a double maximum in the ultraviolet, 240 and 250 mμ, and contained II and/or IX.

Isolation VIIa.—Fractions 4–6 (11.3 g., 46% yield, n^{20}D 1.5318) was practically pure VIIa. A sample distilled in a sublimation apparatus boiled at *ca.* 120–130° (0.2 mm.); n^{20}D 1.5318.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40; sapon. equiv., 272. Found: C, 75.04; H, 7.69; sapon. equiv., 279.

This lactone had no maximum in the ultraviolet spectrum in the region 220–300 mμ. The infrared spectrum showed two bands in the carbonyl region: 1730 and 1790 cm.$^{-1}$.

VIIa reacted with bromine in carbon tetrachloride with the evolution of hydrogen bromide to give a solid which melted at 89–90° (from petroleum ether (60–90°)).

Anal. Calcd. for $C_{17}H_{19}O_3Br$: C, 58.13; H, 5.53. Found: C, 58.09; H, 5.51.

Isolation of VIIb.—Fraction 8 solidified after standing for several days. This material melted at 133.5–134.5° after recrystallization from benzene–petroleum ether.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40; sapon. equiv., 272. Found: C, 75.23; H, 7.32; sapon. equiv., 273.

This product showed no maximum in the ultraviolet spectrum in the region 220–300 mμ. The infrared spectrum showed three bands in the carbonyl region: 1680, 1730 and 1810 cm.$^{-1}$.

Isolation of V.—Another solid was obtained from the residue of fraction 8, in very small yield, which was purified by recrystallization from petroleum ether–benzene mixture to a constant melting point of 151–152°.

Anal. Calcd. for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.22; H, 8.02.

The ultraviolet spectrum showed a maximum at 244 mμ (ε 16200). The composition and ultraviolet spectrum of this product suggest the structure V; however, sufficient material was not available for further characterization.

C.—A mixture of 10 g. of II in 100 ml. of 80% formic acid was heated at the reflux temperature for four hours. The neutral and acidic components were separated as in Part A.

Lactonization of the Acidic Components.—A mixture containing the acid material (1.9 g.), ethanol (8 ml.), water (12 ml.) and sulfuric acid (5 drops) was heated at the reflux temperature for 14 hours. The mixture was diluted with water and extracted with ether. The ether layer was extracted with 10% aqueous bicarbonate, then with 1% hydrochloric acid.

The bicarbonate extract was acidified and extracted with ether. The ether was removed and the residue was distilled in a sublimation tube. The distillate, n^{24}D 1.5832, solidified and melted at 108–109° after recrystallization from alcohol. The solid was insoluble in 5% sodium hydroxide.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.24; H, 7.24.

This product was assigned structure X on the basis of its composition and spectra. The ultraviolet spectrum showed a maximum at 289 mμ (ε 28500). The infrared spectrum showed one band in the carbonyl region at 1820 cm.$^{-1}$ and a strong band at 1660 cm.$^{-1}$.

The ether solution, from which the acid material of the lactonization reaction had been removed, was distilled in a sublimation tube. The product, n^{20}D 1.5598, had the composition calculated for a mixture of XI and VII. The ultraviolet spectrum showed a maximum at 260 (ε 7300) which can be attributed XI.

Anal. Calcd. for $C_{17}H_{18}O_2$ (XI): C, 80.28; H, 7.13. Calcd. $C_{17}H_{12}O_3$ (VII): C, 74.97; H, 7.40. Found: C, 78.29; H, 7.54.

The Action of Formic Acid on the Acetylenic Alcohol III.—The reaction of III (60 g.) and 80% formic acid was carried out for 63 hours, and processed as described for II (part B). The neutral fraction weighed 55 g.; the acidic fraction weighed 2 g. and was discarded.

The neutral fraction was chromatographed using 750 g. of activated silica gel in a column of dimensions 2 × 20 inches. Four major fractions were obtained: A, 1.6 g., 16 l. of petroleum ether–benzene (max. ratio 1:2); B, 16.6 g., 5 l. of benzene and 5 l. of 1:1 benzene–chloroform; C, 19.9 g., 26 l. of benzene–chloroform (max. ratio-pure chloroform); and D 17.6 g., chloroform.

Isolation XIIa.—Distillation of fraction B, using a short path distillation apparatus (0.5 mm.), gave 11.5 g. of a yellow oil (n^{25}D 1.5247).

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34; sapon. equiv., 314. Found: C, 76.47; H, 8.21; sapon. equiv., 311.

This product showed no maximum in the ultraviolet spectrum in the region 220–300 mμ. The infrared spectrum showed two bands in the carbonyl region: 1720 and 1790 cm.$^{-1}$.

Distillation of fraction C gave an additional 16.6 g. (28.1 g. combined, 47% yield distilled) of XIIa (n^{25}D 1.5218). The ultraviolet and infrared spectra of this material were identical to those obtained from fraction B.

Isolation of XIIb.—Fraction D partially solidified and 1.5 g. of XIIb was obtained which melted at 119–120° after recrystallization from petroleum ether (60–68°)–benzene.

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34; sapon. equiv., 314. Found: C, 76.36; H, 8.47; sapon. equiv., 314.

This product showed no maximum in the ultraviolet spectrum in the region between 220–300 mμ. The infrared spectrum showed two strong bands in the carbonyl region: 1805 and 1725 cm.$^{-1}$.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Reaction between Diazoacetic Ester and Allylic Halides

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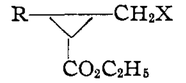
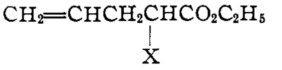
Diazoacetic ester reacts with allyl bromide to give ethyl 2-bromo-4-pentenoate (IIa) rather than the expected cyclopropane derivative. Similar results with allyl iodide, methylvinylcarbinyl and allylidene chloride indicate the generality of the reaction. The possibility of rationalizing the formation of these unsaturated esters on the basis of an S_N2' type mechanism is discussed.

An abnormal reaction recently has been reported to occur when allyl bromide is treated with diazoacetic ester,[1a] in that ethyl 2-bromo-4-pentenoate (IIa) is formed instead of the expected cyclopropane (I).[2] Similar findings in these laboratories are in substantial agreement with the Russian work and our extensions of the reaction to substituted allylic halides form the basis for the present communication.

Whereas the degradative reactions reported[1a] in most cases agreed with the assigned structure, IIa the ozonolysis results are sufficiently different from those obtained in our work to merit a brief discussion of our proof of structure. This was based on the following



I, X = Halogen
R = H or alkyl



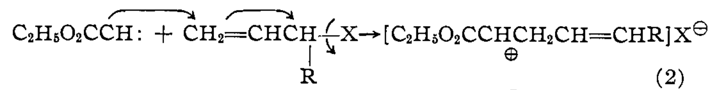
$$CH_2{=}CHCH_2\underset{\displaystyle X}{\underset{|}{C}}HCO_2C_2H_5$$

IIa, X = Br
b, X = I

facts: (1) The compound IIa showed a double bond peak in the infrared spectrum at 6.10 μ as well as absorption at 10.07 and 10.85 μ, characteristic of the grouping $CH_2{=}CHR$.[3] (2) Reduction with zinc and acetic acid gave ethyl allylacetate. (3) Reductive ozonolysis yielded formaldehyde and ethyl aldehydosuccinate. (4) Reaction with thiourea produced a thiazolidinone, thus confirming the presence of an α-haloester grouping.[4] (5) Lithium aluminum hydride reduced the compound to 4-pentene-1-ol.

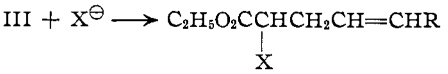
A possible mechanism to account for the formation of IIa and other α-haloesters (*cf.* Chart 1) is summarized in equations 1–3.[5]

$$N_2CHCO_2C_2H_5 \xrightarrow{Cu} N_2 + :CHCO_2C_2H_5 \quad (1)$$



$$C_2H_5O_2CCH: + CH_2{=}CH\underset{\displaystyle R}{\underset{|}{C}}H{-}X \rightarrow [C_2H_5O_2C\underset{\oplus}{C}HCH_2CH{=}CHR]X^{\ominus} \quad (2)$$

III



$$III + X^{\ominus} \longrightarrow C_2H_5O_2C\underset{\displaystyle X}{\underset{|}{C}}HCH_2CH{=}CHR \quad (3)$$

The formation of the highly reactive "carbethoxycarbene" fragment in equation 1 has been postulated previously.[6,7] Nucleophilic attack at the double bond could then proceed with subsequent ejection of halide ion in a manner closely resembling the S_N2' mechanism.[8,9] Uptake of the halide

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(1) (a) I. A. D'yakonov and N. B. Vinogradova, *J. Gen. Chem.*, **21**, 851 (1951); (b) *ibid.*, **23**, 66 (1953).

(2) The reaction between diazoacetic ester and suitably activated olefins has long been known as a preparative method for cyclopropanes, *e.g.*, E. Buchner, *Ber.*, **21B**, 2637 (1888); *ibid.*, **23B**, 701 (1890).

(3) N. Sheppard and D. M. Simpson, *Quart. Rev.*, **6**, 1 (1952); and many references contained therein.

(4) B. H. Nicolet and L. F. Bate, THIS JOURNAL, **49**, 2064 (1927).

(5) In view of the results of Gutsche and Hillmann (*ibid.*, **76**, 2236 (1954)) it has been suggested by a referee that an equally plausible mechanism for these reactions would be the initial attack of the "carbethoxycarbene"[6] ($:CHCO_2C_2H_5$) fragment at the *halogen* atom with synchronous rearrangement to give the observed products. This mechanism fits the benzal chloride case for which it was first suggested because the chlorine represents the only electron-rich center in the molecule. It does not necessarily hold for allylidene chloride (see later discussion) where for both steric and electronic reasons, the double bond represents an equally likely site of attack. However, neither mechanism is unequivocally established at this time and a decision between the two must await further study.

(6) W. von E. Doering and L. H. Knox, Abstracts of Papers, 119th Meeting of the Am. Chem. Soc., April, 1951, p. 2M.

(7) M. S. Kharasch, T. Rudy, W. Nudenberg and G. Buchi, *J. Org. Chem.*, **18**, 1030 (1953).

(8) G. Stork and W. N. White, THIS JOURNAL, **75**, 4119 (1953), give a brief history of the S_N2', reaction.

(9) The species $C_2H_5O_2CCH$: with its open sextet is unique in