The infrared spectrum has a strong, slightly unsymmetrical band at 1683 cm.$^{-1}$, which may be attributed to the presence of a conjugated carbonyl group. The 6 $\mu$ aromatic bands are split and relatively strong, as is usually the case when there is conjugation outside the ring.

**Reduction of 1,3-Dibenzoyl-2-phenylcyclopentane (IV).**—To a mixture of 1.92 g. of magnesium, 40 ml. of dry *n*-butyl ether and 80 ml. of dry toluene was added, with stirring, 9.8 g. of iodine. The mixture was heated under reflux and, when the iodine color had disappeared, 1.5 g. of 1,3-dibenzoyl-2-phenylcyclopentane was added in 40 ml. of hot dry toluene. After being heated under reflux, with stirring, for 19 hours, the reaction mixture was poured into iced hydrochloric acid. The product, crystallized from methanol, melts at 82–83°; slightly above this temperature it resolidifies and melts again at 167°.

*Anal.* Calcd. for $C_{25}H_{24}O_2$: $CH_3OH$: C, 80.83; H, 7.27. Found: C, 79.50; H, 7.17.

Since the composition of the low-melting crystals (m.p. 82–83°) corresponds approximately to that of the glycol solvated with a molecule of methanol, the compound was heated at the boiling point of acetone for four days under reduced pressure. It was then found to melt at 167–168° without previous melting.

*Anal.* Calcd. for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79. Found: C, 84.28; H, 7.03.

The infrared spectrum still has strong absorption between 1000 and 1100 cm.$^{-1}$.

**Oxidation of the Glycol V.**—A solution of 250 mg. of potassium permanganate in 50 ml. of reagent acetone was added, with stirring, over a period of 30 minutes to a solution of 50 mg. of the glycol in 50 ml. of reagent acetone. The excess permanganate was carefully reduced to manganese dioxide with aqueous sodium bisulfite and the mixture filtered. The organic product separated from benzene as colorless crystals, m.p. 162.5–163.5°, and was shown by a mixed melting point determination to be 1,3-dibenzoyl-2-phenylcyclopentane.

**Reduction of 1,4-Dibenzal-1,4-dimesitoylbutane.**[3]—A mixture of 1.92 g. of magnesium, 40 ml. of dry *n*-butyl ether, 80 ml. of dry toluene and 9.8 g. of iodine was heated under reflux until the iodine color had disappeared. A hot solution of 10.5 g. of the diketone in 40 ml. of toluene was added, and the mixture was heated for 20 hours under reflux, with stirring. After being allowed to cool, the mixture was treated with iced hydrochloric acid; the product, isolated by conventional procedures, was a viscous yellow oil which crystallized from ethanol. The crystallization occurred over a period of several days, yielding starting material as well as the cyclohexane derivative VII which, after repeated recrystallization, melted at 312°. It was observed to change its crystalline form before melting.

*Anal.* Calcd. for $C_{38}H_{40}O_2$: C, 86.32; H, 7.62. Found: C, 86.06; H, 7.95.

The infrared spectrum has absorption bands assignable to a hindered, unconjugated carbonyl group (at 1683 cm.$^{-1}$), a mesityl group (at 1611 and 852 cm.$^{-1}$) and monosubstituted phenyl (at 698 cm.$^{-1}$).

**Degradation of the Cyclohexane Derivative VII.**—Five hundred milligrams of the reduction product was heated at 300° *in vacuo* for one hour with a palladium-on-charcoal catalyst. During the heating a gas was evolved, a liquid was produced which could be condensed in a solid carbon dioxide trap, and a solid sublimed. The liquid separated into two layers, one of which proved to be water; it was identified by boiling point and melting point and by the fact that it converted acetyl chloride to acetic acid. The other layer had the boiling point of mesitylene.

The material which sublimed from the reaction mixture was warmed with a 10% solution of sodium bicarbonate, and the aqueous layer was extracted with benzene and then with ether. Careful acidification of the water layer yielded a solid which was shown, by the method of mixed melting points and by a comparison of infrared spectra, to be mesitoic acid. The organic layer was distilled and the residue was sublimed under diminished pressure, *in vacuo* at 50°. The solid so obtained, after further purification by resublimation, melted at 66–67°. This compound has the composition of an aromatic hydrocarbon but was not studied further.

*Anal.* Found: C, 92.69; H, 7.96.

The residue, which remained after the easily sublimed hydrocarbon had been removed, was sublimed at 100° *in vacuo* and recrystallized from benzene; m.p. 59°. Although the infrared spectrum of this compound is superimposable upon that of *o*-terphenyl, a mixed melting point determination with an authentic specimen of *o*-terphenyl was depressed. Analytical values show also that, if the solid is *o*-terphenyl, it is not pure. Lack of material prevents further examination of this compound.

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## An Improved Synthesis of Fluorene-1-carboxylic Acid[1]

BY HELMUT R. GUTMANN AND PAUL ALBRECHT

RECEIVED JULY 8, 1954

The preparation of fluorene-1-carboxylic acid from fluorenone-1-carboxylic acid by a modified Wolff–Kishner reduction has been reported recently by Bergmann and Orchin.[2] However, the yields in this reduction were unsatisfactory in our hands and never exceeded 30%. Nearly quantitative yields and products of satisfactory purity were obtained consistently by a modification of the Clemmensen–Martin reduction.[3] The success of the method depends on the presence of sufficient glacial acetic acid (98 ml./g. of ketone) to keep the ketone in solution and on the addition of enough concentrated hydrochloric acid (2 ml./g. of zinc amalgam) over a period of 40 hours. A similar modification using glacial acetic acid to solubilize the ketone has been employed previously for the reduction of fluorenone to fluorene.[4]

The general applicability of this method to fluorenone and its derivatives is of some importance since many compounds of the fluorene series can only be prepared from the corresponding fluorenone.

### Experimental

Zinc amalgam (200 g.) was prepared according to the directions of Martin[3] and placed into a 3-liter three-necked flask fitted with a reflux condenser and a Hershberg stirrer.[5] To the zinc amalgam were added 60 ml. of glacial acetic acid and 60 ml. of concentrated hydrochloric acid and the mixture was heated to boiling. Fluorenone-1-carboxylic acid (10.0 g.), m.p. 191–194°,[6] was dissolved in 600 ml. of hot glacial acetic acid and introduced over a period of 15 minutes into the reaction mixture which was stirred and refluxed vigorously throughout the entire run. A total of 395 ml. of concentrated hydrochloric acid and 235 ml. of glacial acetic acid was delivered into the solution in 20–25 ml. portions during the following 18 hours. Freshly prepared zinc amalgam (60 g.) then was added, followed by a total of 330 ml. of concentrated hydrochloric acid and 100 ml. of glacial acetic acid during the next 6 hours. The addition of fresh zinc amalgam (60 g.) was repeated followed by 300 ml. of concentrated hydrochloric acid and 150 ml. of glacial acetic acid over a period of 7 hours. At the end of this time all of the zinc amalgam had been used up in the reduction. To isolate the product, the dark-green solution was then reduced to one-third of its volume by distillation under reduced pressure. The concentrated mixture was next boiled for 5 minutes and then cooled in an ice-bath. The dark-brown precipitate was collected on a Büchner funnel and washed free of acid with distilled water. It was then

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(1) Supported by a grant from the Graduate School, University of Minnesota.

(2) E. Bergmann and M. Orchin, THIS JOURNAL, **71**, 1111 (1949).

(3) E. L. Martin, *ibid.*, **58**, 1438 (1946).

(4) J. H. Peters, unpublished experiments.

(5) E. B. Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

(6) All melting points are corrected.

extracted with hot 1.5 *M* sodium hydroxide and the extract filtered. The clear filtrate was heated almost to boiling and the hot solution acidified with concentrated hydrochloric acid. After cooling, the white product was collected on a Büchner funnel, washed with distilled water and dried *in vacuo* over calcium chloride; weight 9.0 g. (96% yield), m.p. 239–243°. This material can be used without purification for further synthesis. One recrystallization from benzene afforded pure fluorene-1-carboxylic acid, m.p. 245–247°.

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## Preparation and Properties of 3-Chloro-1-iodo-1-propyne and 3-Bromo-1-iodo-1-propyne[1]

BY LEWIS F. HATCH AND DONALD J. MANGOLD

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The use of hypohalite ion for the replacement of acetylenic hydrogen atoms in the preparation of 1-haloacetylenes has been reported for the preparation of 1-chloro-1-propyne[2] and 1-bromo-1-propyne.[3] 1,3-Dibromo- and 1-bromo-3-chloro-1-propyne also have been prepared by this method.[3a] The reaction now has been extended to include 3-chloro-1-iodo-1-propyne and 3-bromo-1-iodo-1-propyne.

The only previously reported preparation of 1-iodoacetylenes by the use of hypoiodite ion is that of Blitz and Kupper[4] who prepared diiodo-acetylene by this method. Jacobs and Whitcher[5] used this method in an attempt to prepare iodophenoxyacetylene but obtained triiodophenoxyethylene instead. The formation of the triiodo compound was accounted for by the initial formation of iodophenoxyacetylene followed by the addition of iodine to the triple bond. The yields of 3-chloro- and 3-bromo-1-iodo-1-propyne from the corresponding 3-halo-1-propyne and hypoiodite ion in the present work were relatively low because the distillation of the product was not taken to completion. Previous experience with compounds of this type indicated that they might vigorously decompose during the latter part of a distillation.

The compounds were characterized by the usual physical properties, halogen analysis and infrared spectra. There was no indication of an acetylenic-allenic rearrangement which would have been evident by a sharp allene band at 5.1 μ.[6] The unexplained band near 5.85 μ found in the spectra of some propargylic halides was also absent in the spectra of 3-chloro- and 3-bromo-1-iodo-1-propyne. Both of the 1-iodo- compounds showed a strong, sharp band at 4.58 μ ($\mathrm{—C{\equiv}C—}$) but no band at 4.65 μ, the $\mathrm{—C{\equiv}C—}$ stretching band found in the 3-halo-1-propynes.[6] There were also strong bands at 7.05, 7.95, 9.68 and 14.3 μ for the 3-chloro-1-iodo-1-propyne and 7.08, 8.35 and 9.65 μ for the 3-bromo-1-iodo-1-propyne.

The spectra of 3-chloro-, 3-bromo- and 3-iodo-1-propyne also were obtained. The spectra of 3-chloro-1-propyne and 3-bromo-1-propyne failed to show an absorption at 5.10 μ which would have indicated the presence of halopropadiene from an acetylenic–allenic rearrangement. The spectrum of 3-iodo-1-propyne showed a sharp band at 5.10 μ and a weak band at 5.85 μ which confirms the observation of Jacobs and Brill[6] that the iodo compound is actually a mixture of 3-iodo-1-propyne and iodopropadiene. Pauling, Gordy and Saylor[7] have reported that in the 3-halo-1-propynes the carbon–halogen bond distance is longer than normal with the difference being greatest for the carbon–chlorine bond and least for the carbon–iodine bond. They explained this observation by the presence of resonance between the $\mathrm{H—C{\equiv}C—CH_2X}$ and an ionic structure $\mathrm{H—\overset{+}{C}{=}C{=}CH_2X^-}$ in addition to the usual ionic structure $\mathrm{H—C{\equiv}C—CH_2{}^+X^-}$. Since both Jacobs and Brill and this work failed to find evidence of the $\mathrm{CH_2{=}C{=}CHX}$ structure in the spectra of 3-chloro-1-propyne and 3-bromo-1-propyne it would seem to indicate that the unusually long carbon–chlorine and carbon–bromine bonds did not result from an allene type of structure. Because of the presence of iodopropadiene in the 3-iodo-1-propyne it should follow from Pauling, *et al.*, that the carbon–iodine bond should show the greatest deviation rather than the least, consequently we are unable to correlate our observations with their conclusions.

### Experimental

**3-Chloro-1-iodo-1-propyne.**—3-Chloro-1-iodo-1-propyne was prepared by the reaction between 3-chloro-1-propyne and hypoiodite ion. The 3-chloro-1-propyne was prepared from propargyl alcohol and phosphorus trichloride (in pyridine).[8] The product obtained had the following physical properties: b.p. 57–59° (751 mm.), $n^{20}\mathrm{D}$ 1.4320; lit.[8] b.p. 56–57°, $n^{20}\mathrm{D}$ 1.4329.

3-Chloro-1-propyne (35 g., 0.5 mole) and 127 g. (0.5 mole) of iodine in 250 ml. of saturated potassium iodide solution were added simultaneously with rapid stirring to a cold aqueous solution (*ca.* 5°) of 224 g. (4.0 moles) of potassium hydroxide over a period of one and a half hours, after which stirring was continued for four hours. The 3-chloro-1-iodo-1-propyne was extracted using diethyl ether and dried over magnesium sulfate.

The 3-chloro-1-iodo-1-propyne was distilled under a nitrogen atmosphere to give 49 g. (49% yield); however, the distillation flask was not taken to dryness because of the danger of violent decomposition. About one-third of the original solution was left in the distillation flask. The product had the following physical properties: b.p. 46.5–47.5° (4 mm.), $n^{20}\mathrm{D}$ 1.5890, $n^{25}\mathrm{D}$ 1.5863, $n^{30}\mathrm{D}$ 1.5836, $d^{20}_4$ 2.1426, $d^{25}_4$ 2.1333, $d^{30}_4$ 2.1249; *MR*(obsd.) 31.55, *MR*(sum) 31.72. The compound is unstable and turns dark brown on standing for a few minutes in the atmosphere.

*Anal.* Calcd. for $\mathrm{C_3H_2ClI}$: Cl, 17.7; I, 63.3. Found: Cl, 17.5; I, 63.6.

**3-Bromo-1-iodo-1-propyne.**—The 3-bromo-1-iodo-1-propyne was prepared by the reaction between 3-bromo-1-propyne and hypoiodite ion.

3-Bromo-1-propyne (119 g., 1.0 mole) (General Aniline and Film Corp.) and 254 g. (1.0 mole) of iodine in 250 ml. of saturated potassium iodide solution were added simultaneously with rapid stirring to a cold aqueous solution (*ca.* 5°) of 224 g. (4.0 moles) of potassium hydroxide. The addition took place over a period of one and a half hours

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[5] T. L. Jacobs and W. J. Whitcher, THIS JOURNAL, **64**, 2635 (1942).

[6] T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953).

[7] L. Pauling, W. Gordy and J. H. Saylor, *ibid.*, **64**, 1753 (1942).

[8] L. F. Hatch and V. Chiola, *ibid.*, **73**, 360 (1951).