methanol. On standing overnight in the ice-box, there was obtained 54.5 g. of crystalline material. The mother liquors gave an additional 1.5 g. on dilution with methanol. Recrystallization from benzene–methanol gave 35 g. (30%) of long needles, m.p. 140–155°. An analytical sample had m.p. 155° (bubbly melt) with sintering at 150°, $[\alpha]_D$ +92° (dioxane). The analytical sample was dried under vacuum at 118° for 5 hours.

Anal. Calcd. for $C_{30}H_{46}O_5S_3$: C, 61.82; H, 7.96. Found: C, 61.64; H, 7.95.

Methyl Dehydrocholate Trihemithioethylene Ketal (III).—The above acid (33.5 g.) in 400 ml. of ether was treated with an excess of ethereal diazomethane. The crude product after drying and distillation of the ether weighed 34 g. (99%), m.p. 173–178°. Crystallization from methanol gave small feathery needles, m.p. 183° with sintering at 177°, $[\alpha]_D$ +90° (dioxane). The analytical sample was dried under vacuum at 100° for one hour.

Anal. Calcd. for $C_{31}H_{48}O_5S_3$: C, 62.38; H, 8.11. Found: C, 62.30; H, 7.86.

24-Hydroxycholane-3,7,12-trione Trihemithioethylene Ketal (IV).—The above ester (31 g.) in one liter of dry ether was added dropwise with stirring to a suspension of 3.8 g. of lithium aluminum hydride in 400 ml. of dry ether. The mixture was heated at the reflux temperature for two hours and allowed to stand overnight. The reaction mixture was worked up with dilute sulfuric acid in the usual manner. The crude product (29 g., 98%) had m.p. 222–228° and two recrystallizations from benzene–methanol gave needles with m.p. 233–235°, $[\alpha]_D$ +95° (dioxane). The analytical sample was dried under vacuum at 118° for 5 hours.

Anal. Calcd. for $C_{30}H_{48}O_4S_3$: C, 63.34; H, 8.51. Found: C, 62.95; H, 8.57.

Hydrolysis of 24-Hydroxycholane-3,7,12-trione Trihemithioethylene Ketal. A.—The above alcohol (2.0 g.) was dissolved in 150 ml. of dry methanol containing 3 ml. of acetyl chloride and the solution heated under reflux for five hours. The methanol was distilled, the residue taken up in ether, washed with sodium bicarbonate, the ether distilled and the residue chromatographed on silica. Elution with 15% ethyl acetate–benzene gave 0.74 g. (41%) of 24-hydroxycholane-3,7,12-trione 7,12-dihemithioethylene ketal (V). The product, thick needles after two crystallizations from benzene–cyclohexane, had m.p. 212.6–214.2°, $[\alpha]_D$ +43° (dioxane). The analytical sample was dried under vacuum at 118° for 5 hours.

Anal. Calcd. for $C_{28}H_{44}O_4S_2$: C, 66.10; H, 8.72. Found: C, 66.15; H, 8.77.

B.—Compound IV (7.0 g.) was dissolved in 315 ml. of dioxane containing 35 ml. of water and 8 ml. of concentrated sulfuric acid. The solution was heated under reflux for 22 hours, neutralized with solid sodium bicarbonate, and filtered. The filtrate was concentrated under reduced pressure and the residue taken up in methanol. On standing, 0.5 g. of material crystallized, m.p. 192–206°. The mother liquor was distilled to dryness, taken up in 15 ml. of benzene and diluted with 75 ml. of ether to give 1.7 g., m.p. 202–207°. The mother liquor was diluted with ether and gave 0.4 g., m.p. *ca.* 178° with previous sintering. Evaporation of the mother liquor to dryness and trituration with ether gave 1.5 g., m.p. *ca.* 170°.

Crops 3 and 4 (1.9 g.) were combined and crystallized twice from methanol, yielding 0.55 g. of 24-hydroxycholane-3,7,12-trione 12-hemithioethylene ketal (VI), m.p. 182–183°, $[\alpha]_D$ +57.5° (dioxane).

Anal. Calcd. for $C_{26}H_{40}O_4S$: C, 69.31; H, 8.99; S, 7.15. Found: C, 69.33; H, 8.93; S, 7.13.

Crops 1 and 2 (2.2 g.) were crystallized from methanol and gave 1.3 g. of 24-hydroxycholane-3,7,12-trione (VII), m.p. 212–213°, $[\alpha]_D$ +28° (dioxane).

Anal. Calcd. for $C_{24}H_{36}O_4 \cdot {}^1/_2CH_3OH$: C, 72.74; H, 9.47. Found: C, 72.47; H, 9.12; S, 0.0.

The triketone alcohol (0.5 g.) was acetylated with pyridine and acetic anhydride. The product was recrystallized from benzene–petroleum ether (b.p. 60–70°) and gave 24-acetoxycholane-3,7,12-trione (VIII), m.p. 203–204°, $[\alpha]_D$ +26° (dioxane). The analytical sample was dried under vacuum at 56°.

Anal. Calcd. for $C_{26}H_{38}O_5$: C, 72.52; H, 8.90. Found: C, 72.37; H, 8.95.

C.—Trihemithioethylene ketal alcohol (2.0 g.) was dissolved in 50 ml. of glacial acetic acid. One ml. of concentrated hydrochloric acid was added and the solution heated under reflux for 22 hours. The acid was distilled under reduced pressure and the residue triturated with ether which gave 0.9 g. (59%) of 24-acetoxycholane-3,7,12-trione, m.p. 191–200°. Crystallization from benzene–petroleum ether (b.p. 60–70°) yielded 0.7 g. of needles, m.p. 202°, which did not depress the melting point of authentic cholanetrione acetate (m.p. 202–203°).

The acetate (0.207 g.) was dissolved in 8 ml. of 4% potassium hydroxide in methanol, the solution concentrated to 5 ml. and allowed to stand, giving in two crops 0.139 g. (74%) of long colorless needles. The analytical sample was crystallized from 80% methanol, had m.p. 212.2–212.8°, and was dried under vacuum at 118° for 5 hours. The infrared spectrum was identical with that of the triketone alcohol (m.p. 212–213°) obtained previously.

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Heterocyclic Derivatives of Arsenic: Some Corrected Statements

BY F. G. MANN

RECEIVED NOVEMBER 28, 1955

It has been stated by Weston[1] that Chatt and Mann[2] have resolved 5,10-di-*p*-tolyl-5,10-dihydroarsanthrene into optically active forms. A statement to the same effect is made by Costain and Sutherland.[3] Actually Chatt and Mann separated this compound into two geometric isomers. Each isomer possesses a plane of symmetry and therefore no question of optical resolution arises.

Garascia and Mattei[4] have stated that Cookson and Mann[5] have "prepared several 9-substituted arsafluorenes." Our compounds were, however, 10-substituted 9,10-dihydroarsanthridines, the central ring system being six-membered and not five-membered. Garascia and Mattei's further statement that we record 9-arsafluorinic acid, m.p. 299°, is therefore also incorrect, for no arsafluorene compounds are described in our paper.

(1) R. E. Weston, THIS JOURNAL, **76**, 2645 (1954).
(2) J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1184 (1940).
(3) C. C. Costain and G. B. B. M. Sutherland, *J. Phys. Chem.*, **56**, 321 (1952).
(4) R. J. Garascia and I. V. Mattei, THIS JOURNAL, **75**, 4589 (1953).
(5) G. H. Cookson and F. G. Mann, *J. Chem. Soc.*, 2888 (1949).

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Condensation of Chloral Hydrate with 8-Quinolinol

BY KONOMU MATSUMURA AND MOTOKO ITO

RECEIVED JULY 26 1955

Chloral hydrate reacts with 8-quinolinol to form predominantly 5-(α-hydroxy-β-trichloroethyl)-8-quinolinol (I). On alkaline hydrolysis with methanolic potassium hydroxide I yielded 5-carboxy- and 5-formyl-8-quinolinol (IV) and a compound which is soluble in sodium bisulfite. Hydrolysis with sodium methoxide in methanol gave IV and a compound V which is insoluble in sodium bisulfite and which gives some indication of possessing the carboxy and methoxy groups. Thus, I on alkaline hydrolysis appears to undergo only partial hydrolysis to V; the remainder of V undergoes

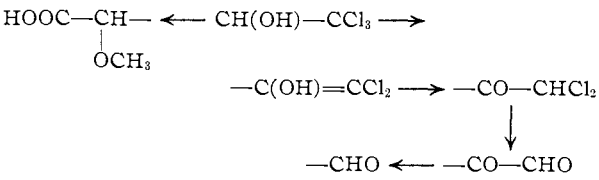
TABLE I

DERIVATIVES OF 5-(α-HYDROXY-β-TRICHLOROETHYL)-8-QUINOLINOL

Compound	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	M.p., °C.	Description	Solvents
Hydrochloride[a]	$C_{11}H_8Cl_3NO_2 \cdot HCl$[c]	40.12	41.05	2.74	2.91	>310	Colorless prisms	Dil. HCl
Picrate	$C_{11}H_8Cl_3NO_2 \cdot C_6H_3N_3O_7$[d]					204 dec.	Yellow prisms	Ethanol
Diacetyl[b]	$C_{11}H_{12}Cl_3NO_4 \cdot 0.5H_2O$[e]	46.71	46.35	3.14	3.13	158–159	Colorless plates	50% acetic acid

[a] Partially hydrolyzes in water. [b] An aqueous solution is colorless with ferric chloride but develops a green color on standing or heating. [c] Calcd. Cl, 43.16; found 42.05. [d] Calcd. N, 10.73; found 10.86. [e] Vacuum-dried over potassium hydroxide at room temperature.

elimination of hydrogen chloride and subsequent hydrolyses and degradations



5-Formyl-8-quinolinol (IV) behaves as a phenol-aldehyde. It is readily soluble in dilute sodium carbonate and concentrated sodium bisulfite and resists oxidation by dilute nitric acid, alkaline silver, halogen or chromic oxide solution. With one mole of bromine, IV gave the bromoaldehyde; with two moles 5,7-dibromo-8-quinolinol was obtained, indicating that the second mole was consumed in substituting the aldehyde with bromine, instead of oxidizing it to carboxyl. In a similar way, the iodoaldehyde on bromination gave a compound identified as 5-bromo-7-iodo-8-quinolinol by comparison with a sample obtained by appropriate halogenations of 8-quinolinol. Thus, the point of attachment of chloral hydrate to 8-quinolinol in compound I should be the 5-position. An additional confirmation for the structure was obtained by the fact that alkaline fusion of IV gave 5-carboxy-8-quinolinol, identified by comparison with an authentic specimen. The oxime of IV, on treatment with acetic anhydride at room temperature gave the diacetyloxime; at 140° 5-cyano-8-acetoxyquinoline was obtained. Assuming that this conventional method of *anti–syn* discrimination is safely applicable to this aldoxime, it should be the *syn*-form, in accordance with present concepts of spatial configuration.

The Results of Biological Study.[1]—Several of the compounds reported here have been tested for tuberculostatic action *in vitro*. For human tubercle-bacilli H 37 R V., IV is found to be more active, 5-cyano-8-quinolinol as active, IV-thiosemicarbazone and I one tenth as active as sodium *p*-aminosalicylate in 10% serum–Youmans media. Animal assays are now under way.

Experimental

Condensation of Chloral Hydrate with 8-Quinolinol.—Powdered 8-quinolinol (14.5 g., 0.1 mole) was dissolved portionwise in 95% sulfuric acid (45 g.) with stirring at below 10° and chloral hydrate (18.2 g., 0.11 mole) was added at a time. The reaction mixture was shaken for 3 hours in a tightly stoppered flask at room temperature and then for 7 hours at 70°. The resulting viscous fluid was poured into ice-water (400 ml.) to give a light yellow oily mass which crystallized in the cold and a mother liquor (A). The crystals were filtered and heated for 2 hours with a solution of sodium acetate (30 g.) in water (400 ml.) to give an orange yellow solid and a mother liquor (B). The solid was filtered, heated for 2 hours with 5% hydrochloric acid (70 ml.) with frequent stirring and cooled to give a solid hydrochloride and a mother liquor (C).

The hydrochloride was treated with hot sodium acetate solution to give crude 5-(α-hydroxy-β-trichloroethyl)-8-quinolinol (I) (15.4 g.). Recrystallization from 25% acetic acid gave orange yellow prisms, which become light yellow at 170–180°, darken around 280°, and become a black solid until 320°. Solutions of I give a green color with ferric chloride; it is almost insoluble in ether and benzene, somewhat soluble in hot water and fairly soluble in hot ethanol.

Anal. Calcd. for $C_{11}H_8Cl_3NO_2 \cdot 1.5H_2O$[2]: C, 41.25; H, 3.44; Cl, 33.28; N, 4.38. Found: C, 41.47; H, 3.27; Cl, 34.50; N, 4.37. Calcd. for $C_{11}H_8Cl_3NO_2 \cdot H_2O$[3]: C, 42.51; H, 3.22. Found: C, 42.44; H, 2.90.

Concentration of the solution B, addition of hydrochloric acid and cooling gave 5-sulfo-8-quinolinol (3 g.). Recrystallization from water gave crystals having water of crystallization and melting at 316–317° alone or on admixture with an authentic sample.[4]

The mother liquor C gave, on concentration, I hydrochloride, and on further concentration II hydrochloride and a mother liquor (D). The free base II, on recrystallization from 25% acetic acid yielded 0.7 g. of garnet colored cubes, which became semi-fluid with foaming at 135°, solidified around 190° and became a black solid at 320°.

This compound II appears to be I or a position isomer of I.

Anal. Calcd. for $C_{11}H_8Cl_3NO_2 \cdot 0.5H_2O$[5]: C, 43.78; H, 2.99. Found: C, 43.61; H, 3.58.

Neutralizing the filtrate D with sodium acetate yielded a dark green solid III (2.1 g.). Recrystallizations from 60% acetic acid and subsequently from ethanol gave a minute amount of colorless plates, m.p. 246° dec. This compound might be α,α,α-trichloro-β,β-di-8-quinolinolylethane.

Anal. Calcd. for $C_{20}H_{13}Cl_3N_2O_2$: C, 57.21; H, 3.10. Found: C, 57.35; H, 3.14

On neutralizing the solution A, first with sodium hydroxide (22 g.), then with sodium acetate a yellow solid (5.1 g.) was obtained which on further separation gave I (1.6 g.), II (1.3 g.) and III (0.5 g.), respectively.

Reaction of two moles of 8-quinolinol with one mole of chloral hydrate gave nearly identical results.

5-Formyl-8-quinolinol. a.—A solution of I (4 g.) and potassium hydroxide (5 g.) in methanol (245 ml.) was refluxed for 3 hours, and the solvent removed at reduced pressure. The residue was dissolved in water (30 ml.), filtered and acidified with acetic acid to give a yellow solid (1.9 g., m.p. 160–165°). A solution of this solid in warm 5% hydrochloric acid, after standing overnight, deposited a crystalline hydrochloride which was filtered from a mother liquor (E). The free base, liberated from the hydrochloride by the use of sodium acetate, was dissolved in hot benzene (100 ml.), some insoluble matter (F) was removed and the solvent was evaporated to give colorless needles of 5-formyl-8-

(1) We are indebted to Dr. Katsuhiko Tago of our Institute who has kindly performed the biological testing and reported the results.

(2) Vacuum-dried over potassium hydroxide at room temperature.

(3) Vacuum-dried over phosphorus pentoxide at 110°.

(4) 7-Sulfo-8-quinolinol (m.p. 313 sintering at 300°) was synthesized also by the reported method (T. Ohta and O. Okuda, *J. Pharm. Soc. Japan*, **71**, 784 (1951)); mixed m.p. with 5-sulfo isomer, 315–316° sintering at 280° and showing no appreciable depression. And besides, from the fact also that when crystallized from water, 7-sulfo possesses no water of crystallization while 5-sulfo- always has 1.5 moles of water, our material may be identified with 5-sulfonic acid.

(5) Vacuum-dried over potassium hydroxide at room temperature.

TABLE II

DERIVATIVES OF 5-FORMYL-8-QUINOLINOL

Compound	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	M.p., °C.	Description	Solvent
7-Bromo-[a]	$C_{10}H_6BrNO_2$	47.65	47.55	2.40	2.64			232 dec.	Orange plates	Ethanol
7-Iodo-[b]	$C_{10}H_6INO_2$	40.16	39.89	2.02	2.41			240 dec.	Orange needles	Ethanol
7-Nitro-[c]	$C_{10}H_6N_2O_4$					12.84	12.81	301–311[d]	Yellow needles	Gla. acetic acid
Sodium salt[e]	$C_{10}H_6NO_2Na\cdot 0.5H_2O$[f,h]								Colorless needles	Ethanol
Hydrochloride[e]	$C_{10}H_7NO_2\cdot HCl\cdot 0.5H_2O$[g]	54.92	55.39	4.12	4.08			274 dec.	Colorless column	Dil. HCl
Picrate	$C_{10}H_7NO_2\cdot C_6H_3N_3O_7$					13.93	13.58	234.5 dec.	Yellow prisms	Ethanol
Dinitrophenylhydrazone	$C_{16}H_{11}N_5O_6\cdot 2H_2O$[f]					17.99	17.94	286 dec.[i]	Violet needles	Acetic acid
Thiosemicarbazone	$C_{11}H_{10}N_4OS\cdot 0.5H_2O$[f]					21.95	22.25	265 dec.	Yellow needles	20% acetic acid
Oxime	$C_{10}H_8NO_2\cdot 0.5H_2O$[f]					14.21	14.35	202	Colorless plates	Ethanol

[a] Made by dropwise addition of a solution of bromine (160 mg.) in glacial acetic acid (1 ml.) during 20 minutes to the aldehyde (173 mg.) in glacial acetic acid (20 ml.) in the cold. [b] Made by dropwise addition of a solution of iodine (254 mg.) and potassium iodide (0.4 g.) in water (16 ml.) during 50 minutes to a cold solution of the aldehyde (173 mg.) and sodium hydroxide (40 mg.) in a mixture of water (15 ml.) and ethanol (5 ml.). [c] Made by warming the mixture of the aldehyde (200 mg.) and 20% nitric acid (2 g.) for 2 minutes, or better by heating the mixture of the aldehyde (173 mg.) and 9% nitric acid (4 ml.) at about 90° for an hour. [d] Dec. without melting. [e] Slightly hydrolyzes in water. [f] Vacuum-dried over phosphorus pentoxide at 110°. [g] Vacuum-dried over potassium hydroxide at room temperature. [h] Calcd. Na, 11.27; found, 11.22. [i] Fades into a red brown color at 200°.

quinolinol, yield 0.8 g. (38%), m.p. 178° (lit. m.ps. 178°,[6] 250 °[7]).

Anal. Calcd. for $C_{10}H_7NO_2$: C, 69.35; H, 4.02; N, 8.09. Found: C, 69.31; H, 3.86; N, 7.89.

An aqueous solution of this compound gave a green color with ferric chloride. It was soluble in ether, benzene, ethanol, hot water, dilute sodium carbonate and its adduct with bisulfite was soluble in concentrated sodium bisulfite.

The free base (0.5 g.) regenerated from E was treated with concentrated sodium bisulfite, filtered and the filtrate acidified with hydrochloric acid. Addition of sodium acetate yielded a yellow solid which on recrystallization first from benzene, then twice from ethanol, gave light yellow needles, m.p. 232–235° with preliminary sintering (*Anal.* Found: N, 7.56).

Solid F was converted to the hydrochloride and the regenerated free base repeatedly recrystallized from ethanol to give yellow needles, m.p. 280° dec. The analytical figures agree with those of 5-carboxy-8-quinolinol.

Anal. Calcd. for $C_{10}H_7NO_3$: C, 63.49; H, 3.70. Found: C, 63.52; H, 3.85.

(b).—A solution of I (4.8 g., 0.015 mole) with sodium (1.4 g., 0.06 mole) in methanol (120 ml.), was refluxed for 8 hours, the methanol removed and the residue dissolved in water, filtered and acidified with acetic acid to give a yellow solid (2.3 g.). This was treated with sodium bisulfite (5 g.) in water (10 ml.) and allowed to stand; a yellow solid V (0.32 g.) was separated. The filtrate, on acidification with hydrochloric acid, removal[8] of sulfur dioxide and addition of sodium acetate, deposited colorless needles (1.3 g., 50% yield, m.p. 173–177°) which crystallized from benzene as colorless needles, m.p. 178°, undepressed on mixture with 5-formyl-8-quinolinol obtained by method (a).

Solid V, on recrystallization from ether and then from ethanol gave colorless prismatic needles, m.p. 103–104°. This compound was readily soluble in cold dilute sodium carbonate (*Anal.* Found: C, 62.47; H, 4.85; OCH_3, 19.54). The picrate formed as yellow needles from ethanol, m.p. 192° (*Anal.* Found: N, 12.07).

5,7-Dibromo-8-quinolinol.—To a water cooled solution of 5-formyl-8-quinolinol (87 mg., 0.0005 mole) in glacial acetic acid (10 ml.) was added dropwise with stirring a solution of bromine (160 mg., 0.001 mole) in glacial acetic acid (1 ml.). After standing a few hours, water and sodium acetate were added to the reaction mixture to give a solid (120 mg.) which was crystallized from glacial acetic acid as colorless needles, m.p. 196°, undepressed on mixture with an authentic sample of 5,7-dibromo-8-quinolinol (m.p. 196°).[9]

5-Bromo-7-iodo-8-quinolinol. a.—To a solution of 5-formyl-7-iodo-8-quinolinol (145 mg., 0.0005 mole) in glacial acetic acid (15 ml.) was added with stirring a solution of bromine (96 mg., 0.0006 mole) in glacial acetic acid (0.6 ml.). On addition of water and sodium acetate to the reaction mixture, a solid (170 mg., m.p. 186–187°) deposited which, after three recrystallizations from ethanol, gave colorless needles, m.p. 193°, undepressed on admixture with a sample obtained by the method b.

(b).—A solution of iodine (127 mg., 0.0005 mole) and potassium iodide (0.2 g.) in water (5 ml.) was added to a water-cooled solution of 5-bromo-8-quinolinol (112 mg., 0.0005 mole) in ethanol (20 ml.) during 15 minutes. To the resulting bordeau red clear solution was added a solution of sodium acetate (0.5 g.) in water (15 ml.) with stirring during 10 minutes to give slightly yellowish white needles (170 mg., m.p. 186°) which crystallized from ethanol (60 ml.) as glistening prismatic needles, m.p. 193°. The reaction with less dilute solutions of the reactants led to the formation of undesirable by-products.

Anal. Calcd. for C_9H_5BrINO: N, 4.00. Found: N, 4.20.

5-Carboxy-8-quinolinol.—5-Formyl-8-quinolinol (100 mg.) was fused with potassium hydroxide (1 g.) on a silver plate for about 7 minutes with stirring. The resulting homogeneous yellow paste was cooled, dissolved in water (20 ml.) and acidified with acetic acid to give well-defined yellow needles (100 mg., m.p. 248–255° dec.), which gave a green color reaction with ferric chloride.[10] The product was converted to the hydrochloride (m.p. 239° dec., lit. m.p.'s 239° dec.,[11] 260° dec.[12]) and the regenerated free base (50 mg.) was crystallized from ethanol to give yellow needles, m.p. 263° dec. in a sealed capillary. The mixed m.p. with a sample (m.p. 278° dec.)[13] of 5-carboxy-8-quinolinol, prepared by the reaction of carbon tetrachloride with 8-quinolinol, was 263° dec.

Anal. Calcd. for $C_{10}H_7NO_3$: C, 63.49; H, 3.70. Found: C, 63.27; H, 3.73.

With less alkali and shorter fusing period, the reaction led to a product extremely difficult to purify.

Diacetyl Derivative of the Oxime.—A mixture of 5-aldoxime-8-quinolinol (200 mg.) and acetic anhydride (1 ml.), dissolved at room temperature in an hour, was allowed to stand for 16 hours, and was poured into water to give a white solid (200 mg.). Crystallized from ether (150 ml.), it formed as short columns, m.p. 140–143°.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44. Found: C, 61.20; H, 4.31.

(6) In a paper presented at the 8th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1955, C. Hamada, Y. Hirano and T. Iida have reported the Reimer–Tiemann synthesis of 8-quinolinol-aldehyde without any definite statement with respect to the position of the aldehyde group introduced.

(7) R. N. Sen and S. K. Ray, *J. Indian Chem. Soc.*, **9**, 173 (1932).

(8) Otherwise, the sulfur dioxide adduct was isolated as colorless crystals, m.p. 173° dec.

(9) A. Claus and H. Howitz, *J. prakt. Chem.*, [2] **44**, 444 (1891).

(10) 7-Carboxy-8-quinolinol is reported to give a violet red to deep brown color with ferric chloride (R. Schmitt and F. Engelmann, *Ber.*, **20**, 1217 (1887)).

(11) K. Matsumura and C. Sone, THIS JOURNAL, **53**, 1494 (1931).

(12) St. von Niementowski and Ed. Sucharda, *Ber.*, **49**, 12 (1916).

(13) Our observation indicates that samples of 5-carboxy-8-quinolinol which appear practically pure from different runs show, perhaps because of the presence of a trace of impurity, various m.p. within the range of 263–285°.

5-Cyano-8-acetoxyquinoline.—A solution of the oxime (100 mg.) in acetic anhydride (0.5 ml.) was heated at 140° for 2 hours and poured, after cooling, into ice-water to give grey-white needles (100 mg.). Crystallization from benzene, yielded almost colorless prismatic needles, m.p. 153°. The solution in dilute ethanol gave no color reaction with ferric chloride.

Anal. Calcd. for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80. Found: C, 67.91; H, 3.77.

5-Cyano-8-quinolinol.—A solution of 5-cyano-8-acetoxyquinoline (200 mg.) in 10% sodium carbonate (15 ml.) and ethanol (5 ml.) was refluxed for 2 hours. After removal of ethanol, the solution was acidified with acetic acid to give a colorless solid (quantitative yield) which crystallized from ethanol as prisms, m.p. 176.5–177°, mixed m.p. with the aldehyde (m.p. 178°) 158–165°. It gave a deep green color with ferric chloride and was readily soluble in dilute sodium carbonate.

Anal. Calcd. for $C_{10}H_6N_2O$: C, 70.60; H, 3.53. Found: C, 70.08; H, 3.73.

Picrate.—This formed as short prisms from ethanol; m.p. 251°.

Anal. Calcd. for $C_{10}H_6N_2O \cdot C_6H_3N_3O_7$: N, 17.54. Found: N, 17.56.

Hydrochloride.—This formed as yellowish white prismatic needles from dilute hydrochloric acid; m.p. 277° dec. It hydrolyzed in water.

Anal. Calcd. for $C_{10}H_6N_2O \cdot HCl$: N, 13.56. Found: N, 13.15.

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Chemistry of Hexachlorocyclopentadiene. VI. Diels–Alder Adducts with Alkynes[1]

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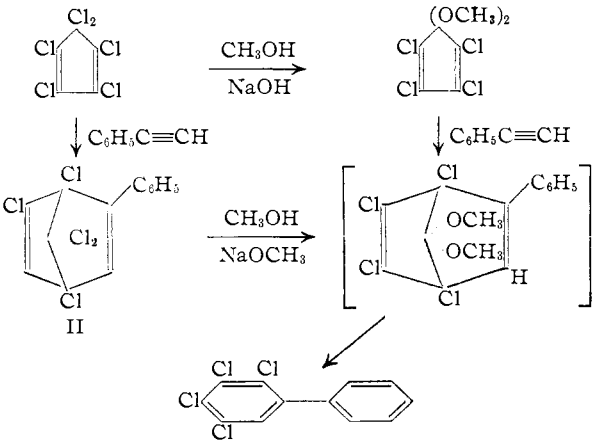
RECEIVED AUGUST 18, 1955

The Diels–Alder reaction with hexachlorocyclopentadiene (I) and various alkenes has been extensively studied.[3–7] The reactivity of I toward alkynes, which also may act as dienophiles,[8] however, has received very limited attention. Fields[4] has described an adduct prepared from I and 3-bromopropyne and the reaction of I with phenylacetylene has been investigated in this Laboratory and elsewhere.[7]

We have extended the reaction of I with alkynes to several other members of the series. 1-Hexyne, 1-heptyne and acetylenedicarboxylic acid gave monoadducts in yields varying from about 20–40% (see Table I).



It was observed that the dichloromethylene bridge in hexachlorocyclopentadiene–alkyne adducts exhibits a unique lability not found in the alkene adducts. Thus, when the phenylacetylene adduct (II) was treated in methanol with two equivalents of sodium methoxide 2,3,4,5-tetrachlorobiphenyl was obtained. The same biphenyl derivative has been isolated from the reaction product of 5,5-dimethoxytetrachlorocyclopentadiene and phenylacetylene, the adduct apparently constituting an intermediate in this reaction.[9] The same intermediate would theoretically result from treatment of the adduct II with two equivalents of methoxide. The fate of the bridge is uncertain since no fragments were isolated by us or previous workers.[9]

Experimental[10]

Preparation of Adducts.—Equimolar portions of hexachlorocyclopentadiene[11] and the alkyne were mixed and refluxed (or heated to 150°, whichever was the lower temperature) for periods ranging from 24 to 120 hr. The unreacted starting materials and product were separated and purified by distillation. In the case of acetylenedicarboxylic acid which was insoluble in hexachlorocyclopentadiene, benzene was employed as the reaction medium and the acid was purified by recrystallization from a benzene–acetone mixture.

TABLE I
DIELS–ALDER ADDUCTS OF HEXACHLOROCYCLOPENTADIENE

Alkyne	Adduct formula	B.p., °C. 2 mm.	$n^{20}D$	Analyses, %[a] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found	Yield, %
$C_6H_5C{\equiv}CH$	$C_{13}H_6Cl_6$	150–152	1.5498	41.60	41.91	1.60	1.90	56.90	56.51	21
n-$C_4H_9C{\equiv}CH$	$C_{11}H_{10}Cl_6$	124–128	1.5334	37.25	27.33	2.80	3.08	59.90	59.80	26
$HOOCC{\equiv}CCOOH$	$C_9H_2O_4Cl_6$	162–163[b]		27.85	27.84	0.51	0.76	55.02	54.97	45
n-$C_5H_{11}C{\equiv}CH$	$C_{12}H_{12}Cl_6$	160[c]	1.5305	38.00	37.67	3.40	3.33	...	...	18

[a] Analyses by Galbraith Micro-analytical Laboratories and Mrs. T. R. Yeh, Purdue University. [b] Melting point. [c] 5 mm. pressure

2,3,4,5-Tetrachlorobiphenyl.—Compound II, 1,4,5,6,7,7-hexachloro-2-phenylbicyclo[2.2.1]hepta-2,5-diene (9 g., 0.033 mole) was refluxed for 24 hr. in a solution of 3.6 g. (0.066 mole) of sodium methoxide in 75 ml. of methanol. The residue remaining after distillation of the solvent was dissolved in benzene and the solution decolorized with Norite. The filtrate was evaporated and the solid residue

(1) Paper V, E. T. McBee, H. Rakoff and R. K. Meyers, THIS JOURNAL, **77**, 4427 (1955).

(2) From a thesis submitted by James D. Idol, Jr., to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1955.

(3) E. A. Prill, THIS JOURNAL, **69**, 62 (1947).

(4) E. K. Fields, *ibid.*, **76**, 2709 (1954).

(5) A. A. Danish, M. Silverman and Y. A. Tajima, *ibid.*, **76**, 6144 (1954).

(6) H. Rakoff, Ph.D. Thesis, Purdue University.

(7) Velsicol Corp., British Patent 614,931.

(8) H. L. Holmes in "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 60 et. seq.

(9) E. T. McBee, W. R. Diveley and J. E. Burch, THIS JOURNAL, **77**, 385 (1955).

(10) Melting points are uncorrected.

(11) Generously supplied by Hooker Electrochemical Co.