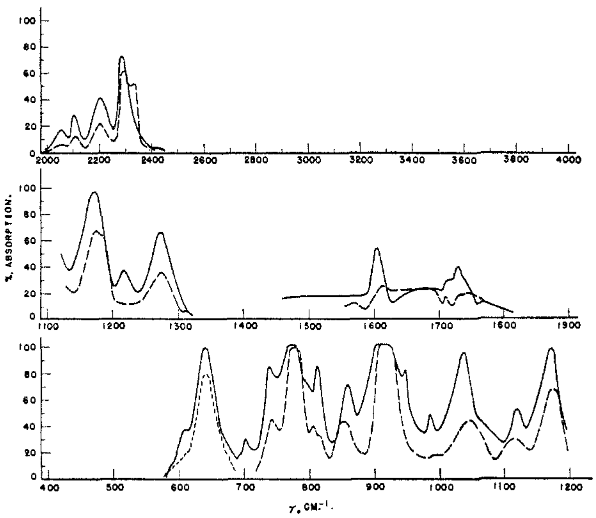

Fig. 3.—Infrared spectrum of $CD_3CCl{=}CDCl$ low boiling, *trans* isomer: ——, liquid, 0.025 mm.; - - -, gas, 60 mm.; — — —, gas 36 mm.

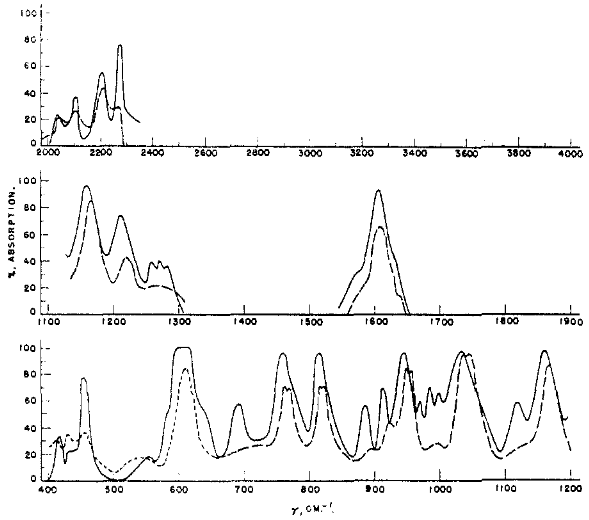

Fig. 4.—Infrared spectrum of $CD_3CCl{=}CDCl$, high boiling *cis* isomer: ——, liquid, 0.025 mm.; - - -, gas, 50 mm.; — — —, gas, 36 mm.

Perkin–Elmer infrared spectrometer (Model 12C) used in conjunction with a Brown recorder. Sodium chloride and potassium bromide optics were used where required. The results are recorded in the figures.

Without attempting an assignment of the various bands to particular vibrational modes it is possible to obtain good supporting evidence that the low boiling isomer has the *trans* configuration from the following considerations, The selection rules forbid the presence in the infrared spectrum of the band corresponding to the mode of vibration associated with the stretching and contraction of the C=C bond in a pure *trans* compound with a center of symmetry such as *trans*-dichloroethylene, whereas the corresponding band in the *cis* compound is quite strong.[5] Substitution of a CH_3 group for H in *trans*-dichloroethylene hardly alters the over-all electrical symmetry (since the electric moment of CH_3 is about the same as the electric moment of CH) of the molecule and allows the CC vibration to be observed in the infrared almost entirely because of the mass asymmetry. One might expect therefore that the C=C band in *trans*-dichloropropene would be considerably weaker than the C=C band in the *cis* compound. The same argument would also predict that the number of strong bands in the infrared spectrum of the *cis* compound would be far greater than in the *trans* compound. Both criteria should be useful therefore in distinguishing between the *trans* and *cis* spectra. In fact one observes that the C=C band in heavy *trans*-dichloropropene is 1605 cm.$^{-1}$, and 1615 cm.$^{-1}$ for the light compound and that the bands in both *trans* forms are very much weaker than the corresponding bands in the *cis* forms, *viz.* 1606 cm.$^{-1}$ and 1614 cm.$^{-1}$ for the heavy and light *cis* compound, respectively. Also as can be seen from the figures there are about 20 strong bands in the *cis* spectrum and only about one-half as many in the spectrum of the *trans* compound. The spectroscopic evidence then can be interpreted unambiguously in terms of *cis* and *trans* structures.

Thanks are due to Miss K. West for reduction of the spectra.

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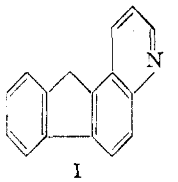
[5] H. J. Bernstein and D. A. Ramsay, *J. Chem. Phys.*, **17**, 556 (1949).

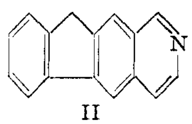
The Synthesis of 1-Hydroxy-11-indeno(2,1-f)-quinoline

BY KEITH BREMER AND CLIFF S. HAMILTON

While studying the behavior of fluorene compounds, Diels and Staehlin[1] applied the Skraup reaction to 2-aminofluorene and showed that an indenoquinoline was formed, but they were unable to decide between the angular structure I and the linear structure II for the substance. Apparently only one quinoline derivative was produced, indicating definite predisposition toward ring closure in a particular way.



I



II

Hughes, Lions and Wright[2] condensed ethyl acetoacetate with 2-aminofluorene at 100° in the presence of a very small amount of hydrochloric acid to form ethyl β-(2-fluorenylamino)-crotonate. Upon cyclization of this compound, a solid was obtained to which they gave the formula corresponding to 1-hydroxy-3-methyl-11-indeno-(2,1-f)quinoline, thus assuming ring closure in the 1-position.

Neish[3] condensed 2-aminofluorene with pyruvic

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[1] Diels and Staehlin, *Ber.*, **35**, 3275 (1902).

[2] Hughes, Lions and Wright, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 449 (1938).

[3] Neish, *Rec. trav. chim.*, **67**, 349, 357 (1948).

acid and dihydroxymalonic ester. The compounds obtained on ring closure were given the structures corresponding to 6-methyl-2′,1′,2,3-fluorenopyridine-4-carboxylic acid and ethyl fluorenodioxindolecarboxylate, respectively, thus assuming ring closure in the 1-position also.

In this work it has been demonstrated conclusively that the cyclization of diethyl 2-fluorenylaminomethylenemalonate yields a derivative of 11-indeno(2,1-f)quinoline (I).

The study involved first the condensation of diethyl ethoxymethylenemalonate with 2-amino-3-nitrofluorene to produce diethyl 2-(3-nitrofluorenyl)-aminomethylenemalonate (III). Cyclization of III in hot diphenyl ether gave 1-hydroxy-2-carbethoxy-5-nitro-11-indeno(2,1-f)quinoline (IV). Hydrolysis of IV yielded 1-hydroxy-2-carboxy-5-nitro-11-indeno(2,1-f)quinoline (V). This acid was decarboxylated by heating in boiling diphenyl ether, producing 1-hydroxy-5-nitro-11-indeno(2,1-f) quinoline (VI). Reduction of the nitro group of VI to yield 1-hydroxy-5-amino-11-indeno(2,1-f)-quinoline (VII) was followed by deamination to form 1-hydroxy-11-indeno(2,1-f)quinoline (VIII).

Diethyl 2-fluorenylaminomethylenemalonate (IX) was obtained by condensing diethyl ethoxymethylenemalonate with 2-aminofluorene. Cyclization of IX, followed by hydrolysis and decarboxylation, also yielded 1-hydroxy-11-indeno-(2,1-f)quinoline.

Experimental

Diethyl 2-(3-Nitrofluorenyl)-aminomethylenemalonate (III).—2-Amino-3-nitrofluorene[4a,b] (28 g.) was placed in a 500-ml. suction flask with 28 g. of diethyl ethoxymethylenemalonate[5] and 20 ml. of 1,4-dioxane. The flask was heated in an oil-bath at 120–125°, and kept under reduced pressure (20–30 mm.) for 15 hours. The crude product was washed with hot ethyl alcohol, and then recrystallized using charcoal from cellosolve; yield 42 g. (88.3%) of bright yellow needles, m.p. 211–213°.

Anal. Calcd. for $C_{21}H_{20}N_2O_6$: C, 63.62; H, 5.08. Found: C, 63.54. 63.66; H, 5.21, 5.28.

1-Hydroxy-2-carbethoxy-5-nitro-11-indeno(2,1-f)quinoline (IV).—Diethyl 2-(3-nitrofluorenyl)-aminomethylenemalonate (III) (36 g.) was added portionwise to 180 ml. of diphenyl ether previously heated to 240°. After the addition the solution was kept at 245° for 20 minutes. After cooling, an equal volume of petroleum ether was added and the mixture cooled in the refrigerator for two hours. The product was filtered, washed with petroleum ether and recrystallized from cellosolve; yield 31 g. (95%) of brown crystals which did not melt below 355°.

Anal. Calcd. for $C_{19}H_{14}N_2O_6$: C, 65.14; H, 4.00. Found: C, 64.98, 65.07; H, 4.24, 4.19.

1-Hydroxy-5-nitro-11-indeno(2,1-f)quinoline (VI).—1-Hydroxy-2-carbethoxy-5-nitro-11-indeno(2,1-f)quinoline (IV) (19 g.) was added to 1 l. of a 5% alcoholic potassium hydroxide solution and heated under a reflux condenser for four hours. The solution was filtered with suction and the filtrate added to hot water. The hot solution was acidified with dilute hydrochloric acid and a brown precipitate separated out. The resulting suspension was allowed to cool and filtered. The yield of 1-hydroxy-2-carboxy-5-nitro-11-indeno(2,1-f)quinoline (V) was 16 g. (97%). No satisfactory solvent was found for recrystallization, so the acid was not isolated in pure form for analysis.

Sixteen grams of V was added portionwise to 200 ml. of boiling diphenyl ether. The temperature was maintained for 15 minutes. An equal volume of petroleum ether was added and the mixture cooled in the refrigerator for two hours. The product was filtered and washed thoroughly with petroleum ether. The dark brown solid was heated under reflux for one hour in 200 ml. of 95% alcohol and filtered. The alcoholic solution was poured into 250 ml. of water and an orange suspension resulted. The mixture was partially evaporated and allowed to cool. A reddish-brown solid separated which was filtered and dried; yield 7.4 g. (52%). Recrystallization from ethyl alcohol gave light reddish-brown crystals which did not melt below 355°.

Anal. Calcd. for $C_{16}H_{10}N_2O_3$: C, 69.06; H, 3.60. Found: C, 68.84, 68.91; H, 3.74, 3.82.

1-Hydroxy-5-amino-11-indeno(2,1-f)quinoline (VII).—Seven grams of VI was suspended in 300 ml. of 80% ethyl alcohol. A solution of 3 g. of calcium chloride in 5 ml. of water, together with 70 g. of zinc dust was added to the suspension, and the whole was thoroughly mixed. The mixture was heated under reflux for two hours. The sludge of zinc dust and zinc oxide was filtered from the boiling solution and extracted with 20 ml. of boiling 80% alcohol. The combined filtrates were then poured into 600 ml. of water, whereupon a light tan precipitate was obtained. This was filtered with suction and dried. The product was recrystallized from ethyl alcohol; yield 3.3 g. (53%), m.p. 239° dec.

Anal. Calcd. for $C_{16}H_{12}N_2O$: C, 77.42; H, 4.84; N, 11.29. Found: C, 77.27, 77.33; H, 5.03, 5.11; N, 11.06.

1-Hydroxy-11-indeno(2,1-f)quinoline (VIII).—Three grams of VII was placed in a mixture of 3.5 ml. of concentrated hydrochloric acid and 6 ml. of water. The suspension was cooled to approximately 0° and a solution of 0.7 g. of sodium nitrite in 2 ml. of water was added with stirring over 30 minutes. Stirring was continued for five minutes after all of the sodium nitrite solution was added. Then 15 ml. of a cold (0°) 50% hypophosphorous acid solution was added during an interval of about five minutes. Stirring was continued for two hours at 0°, and the mixture set in the refrigerator for 20 hours. A light brown solid was filtered off with suction and recrystallized from ethyl alcohol; yield, 1.1 g. (47%), m.p. 284–286°.

Anal. Calcd. for $C_{16}H_{11}NO$: C, 82.40; H, 4.72; N, 6.00. Found: C, 82.29, 82.34; H, 4.77, 4.91; N, 6.21.

Diethyl 2-fluorenylaminomethylenemalonate (IX).—This compound, melting at 143–145°, was prepared in almost quantitative yields by the procedure outlined for III.

Anal. Calcd. for $C_{21}H_{21}NO_4$: C, 71.79; H, 5.98. Found: C, 71.94, 71.87; H, 6.17, 6.26.

1-Hydroxy-2-carbethoxy-11-indeno(2,1-f)quinoline (X).—X was prepared by ring closure of IX by the method used for IV; yield 53%, m.p. 283–285°.

Anal. Calcd. for $C_{19}H_{15}NO_3$: C, 74.75; H, 4.92. Found: C, 74.73, 74.65; H, 5.21, 5.15.

1-Hydroxy-2-carboxy-11-indeno(2,1-f)quinoline (XI).—Twenty-two grams of X was hydrolyzed as for V to yield 18.4 g. (94.8%) of XI, m.p. 309° dec.

Anal. Calcd. for $C_{17}H_{11}NO_3$: C, 73.65; H, 3.97. Found: C, 73.57, 73.51; H, 4.11, 4.16.

1-Hydroxy-11-indeno(2,1-f)quinoline was also prepared in 62% yields from XI by the procedure used for VI; m.p. 287–288°. A mixed melting point with compound VIII gave no depression.

Anal. Calcd. for $C_{16}H_{11}NO$: C, 82.40; H, 4.72. Found: C, 82.39, 82.26; H, 4.81, 4.87.

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[4] (a) Diels, Schill and Tolson, *Ber.*, **35**, 3284 (1902); (b) Porai-Koshits and Nikiforova, *J. Applied Chem.* (*U. S. S. R.*), **13**, 215 (1940); *C. A.*, **35**, 625 (1941).

[5] Fuson, Parham and Reed, *J. Org. Chem.*, **11**, 194 (1946).

The Exchange Reaction between Manganate and Permanganate Ions

BY NORMAN A. BONNER AND HERBERT A. POTRATZ

The exchange between manganate and permanganate ions was first investigated by Libby,[1] who found the rate of exchange to be immeasurably

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[1] Libby, THIS JOURNAL, **62**, 1930 (1940).