[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYL COMPOUNDS. THE PREPARATION AND RESOLUTION OF 2-METHYL-6-NITRO-2'-CARBOXYDIPHENYL. XI[1]

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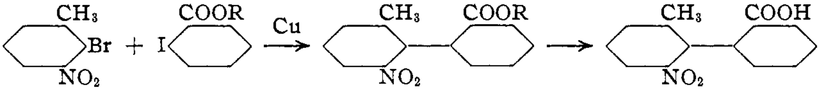
In a recent article[3] the desirability of studying 2,2',6'-trisubstituted diphenyls in connection with the stereochemistry of the diphenyl series was pointed out. In this first communication of several covering such compounds is given the description of the preparation and properties of 2-methyl-6-nitro-2'-carboxydiphenyl (I). This is the first diphenyl prepared which has had merely three groups substituted in the two rings, and in addition it is the first in which each of the 2,2',6'-positions has been filled by different groups.[4]



(I)

The compound was resolved and the two optical antipodes isolated. They racemized only very slowly and the properties were essentially in accord with what had been predicted from the x-ray data.

By boiling in butyl alcohol or in acetic acid, racemization took place partially over a period of thirty to forty hours. On the other hand, on boiling a sodium hydroxide solution of the compound, partial racemization occurred in four hours. Kuhn and Albrecht[5] have found when working with diphenyl derivatives that the decrease in optical activity obeys the law of a first order reaction and have expressed the speed of racemization in terms of the half-life periods. This furnishes at least a semi-quantitative measure of the stability of such compounds under different conditions. Using the same method, the half-life period at 117° in butyl alcohol is forty-two hours; at 118° in acetic acid is thirty-four hours; and at 100° in 0.1 N sodium hydroxide solution, four and one-half hours. This compound was stable to racemization at room temperatures in any of the solvents mentioned above.

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[1] For the last article in this series see Steele and Adams, THIS JOURNAL, **52**, 4528 (1930).

[2] This communication is in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Stearns and Adams, THIS JOURNAL, **52**, 2070 (1930).

[4] During the preparation of this manuscript an article has appeared by Lesslie, and Turner [*J. Chem. Soc.*, 1758 (1930)] describing another compound of this latter type 2,4-dinitro-6-carboxy-2'-methyldiphenyl.

[5] Kuhn and Albrecht, *Ann.*, **455**, 272 (1927); **458**, 221 (1927).

From x-ray data[6] the distances between the groups can be estimated. Using the values and calculations similar to those given in a previous paper, the interference between the methyl and the carboxyl groups will be +0.39 Å., between the nitro and the carboxyl groups +0.58 Å.; hence stability to racemization might be expected. The hydrogen and the nitro group or the hydrogen and the carboxyl group will not collide (−0.06 Å. and −0.42 Å., respectively).

In previous papers[2,3] the possibility of the rings bending toward each other when approaching the same plane so as to allow free rotation was discussed and this may account for the gradual racemization observed at high temperatures over a period of time. In sodium hydroxide solution at 100° the rate of racemization was almost ten times as fast as in butyl alcohol at 117°. Since it is known that an ionized carboxyl group is smaller than one which is un-ionized, such a difference in racemization rate is to be expected.

Kuhn has studied the ease of racemization of 2,4′-dinitro-6,6′-dicarboxydiphenyl and 2,4,4′-trinitro-6,6′-di-carboxydiphenyl and found them more easily racemized than the compound just described. This might be expected in the light of the same reasoning previously outlined.

The 2-methyl-6-nitro-2′-carboxydiphenyl was prepared by condensing under carefully specified conditions 3-nitro-2-bromotoluene with methyl *o*-iodobenzoate by means of copper. The resulting mixture was saponified, which allowed the removal of the alkali-insoluble 2,2′-dinitro-6,6′-dimethyldiphenyl. There was apparently little or no 2,2′-dicarboxydiphenyl found, so that on acidification essentially pure 2-methyl-6-nitro-2′-carboxydiphenyl was obtained. The compound was resolved through the brucine salt. The conversion of this nitro compound to the corresponding amine and thence to the corresponding halogen compounds is now under way so that a direct comparison of several groups on rate of racemization may be obtained.

Experimental

2-Bromo-3-nitrotoluene.—A solution of 38 g. of 3-nitro-*o*-toluidine (prepared by the method of Hadfield and Kenner),[7] in 650 cc. of glacial acetic acid, 60 cc. of water and 39 g. of concd. sulfuric acid, was cooled in an ice–salt bath and to it a solution of 45 g. of sodium nitrite in 75 cc. of water was added slowly with constant stirring. At the same time a cuprous bromide solution was prepared by refluxing a mixture composed of 46 g. of crystallized copper sulfate, 125 g. of sodium bromide, 75 g. of copper turnings, 80 g. of concd. sulfuric acid and 325 cc. of water, until its color was light yellow. After standing for two hours in the cold, the diazotized solution was added to the cuprous bromide solution and steam distilled. The distillate was extracted with ether. The product amounted to 37 g. (68%), boiling at 161–164° at 30 mm. and melting at 39–40.5°.[8]

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[6] Stanley and Adams, This Journal, **52**, 1200 (1930).

[7] Hadfield and Kenner, *Proc. Chem. Soc.*, **30**, 253 (1914).

[8] Gibson and Johnson, *J. Chem. Soc.*, 1244 (1929), give the boiling point as 135° at 6 mm., 157° at 22 mm., and the melting point as 41–42°.

Methyl *o*-Iodobenzoate.—*o*-Iodobenzoic acid was prepared by the method of Wachter[9] and esterified in the following manner. A solution of 62 g. of *o*-iodobenzoic acid in 500 cc. of absolute alcohol was saturated with dry hydrogen chloride and refluxed for five hours. This solution was then poured into water, neutralized with potassium carbonate and extracted with ether. It was finally distilled under diminished pressure. A yield of 50 g. (78%) boiling between 165–168° at 25 mm. was obtained.

2-Methyl-6-nitro-2′-carboxydiphenyl.—In a 200-cc. 3-necked flask fitted with a mechanical stirrer and reflux condenser, was placed 37 g. of bromonitrotoluene and 38 g. of methyl-*o*-iodobenzoate. This was heated in a metal-bath and as soon as the contents just began to boil, 50 g. of copper bronze was slowly added. During the addition, which required about three-quarters of an hour, the temperature of the bath was kept between 270 and 280°. When all of the copper had been added, the bath temperature was raised to 300° for fifteen minutes. During the course of the reaction the mixture turned dark brown and considerable heat was evolved. After cooling, it was thoroughly extracted with ether and filtered. The ether was removed by evaporation and the oily residue saponified by refluxing for four hours with 10% sodium hydroxide. A little black tar insoluble in the alkali remained, which proved to be 2,2′-dimethyl-6,6′-dinitrodiphenyl. This was removed by filtration and the filtrate acidified slowly with dilute hydrochloric acid. A brownish-black tar separated which quickly solidified. This crude product was dissolved in 400 cc. of benzene, boiled with norite for ten minutes and filtered. The color of the solution changed at this time from a dark brown to an orange red. After concentrating to 50–60 cc., the benzene solution was extracted twice with 10% sodium hydroxide, and upon acidification with dilute hydrochloric acid, 16 g. of crude yellow product was obtained. No diphenic acid, the third theoretical product of this reaction was isolated. The crude product was recrystallized three times from dilute alcohol. A yield of 12 g. (27%) of pure product was obtained. Pure methyl nitrocarboxydiphenyl is a pale yellow solid melting at 171–172°, soluble in the common organic solvents but insoluble in cold water.

Anal. Calcd. for $C_{14}H_{11}NO_4$: C, 65.35; H, 4.31. Found: C, 65.56; H, 4.44.

Resolution of **2-Methyl-6-nitro-2′-carboxydiphenyl.**—To a boiling solution of 2 g. of 2-methyl-6-nitro-2′-carboxydiphenyl in 1500 cc. of water was added 3.07 g. of anhydrous brucine. As soon as solution was complete, it was filtered and at the end of one-half hour 2.1 g. of flaky white crystals had deposited. These were collected and after three recrystallizations from water yielded one gram of salt of constant rotation melting from 169–175°. This salt was found to contain water which corresponds to one molecule of water of crystallization. The analytical sample was dried over phosphorus pentoxide in a vacuum at 117° for twenty-four hours. The melting point of the anhydrous form is 173–175°.

Rotation. Hydrated *l*-salt: 0.1368 g. made up to 25 cc. with chloroform at 20° gave $\alpha_D = +0.33°$; $l = 2$; $[\alpha]_D^{20}$ +30.4°.

Anal. 0.3304 g. lost 0.0086 g. on drying. Calcd. for $C_{37}H_{37}N_3O_8 \cdot H_2O$: H_2O, 2.69. Found: H_2O, 2.60. Calcd. for $C_{37}H_{37}N_3O_8$: C, 68.17; H, 5.73. Found: C, 67.67; H, 5.75.

Upon concentrating the mother liquors to 100 cc., 1.8 g. of impure *d*-salt was obtained. This was recrystallized from water and on each crystallization the very first crystals that separated were discarded. Five recrystallizations in this manner yielded 0.5 g. of salt with a constant rotation melting from 145–155°. This salt appears to contain water equivalent to one and one-half molecules of water of crystallization. The anhydrous form which was used for analysis melts at 172° with softening beginning at 145°.

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[9] Wachter, *Ber.*, **26**, 1744 (1893).

Rotation. Hydrated *d*-salt. 0.0850 g. made up to 15 cc. with chloroform at 20° gave $\alpha_D = -0.65°$; $l = 2$; $[\alpha]^{20}_D$ −57.3°.

Anal. 0.1780 g. lost 0.0070 g. on drying. Calcd. for $C_{37}H_{37}N_3O_8\cdot 1.5\ H_2O$; H_2O, 3.98. Found: H_2O, 3.93. Calcd. for $C_{37}H_{37}N_3O_8$: C, 68.17; H, 5.73. Found: C, 67.86; H, 5.93.

l and *d*-**2-Methyl-6-nitro-2′-carboxydiphenyl.**—The active acids were liberated from their salts by treatment with hydrochloric acid in the cold. The organic acid was obtained as a fine cream-colored powder when 0.77 g. of the *l*-salt (less soluble) was shaken with 6 *N* hydrochloric acid for one hour. This was filtered, washed with dilute hydrochloric acid and finally with water. After two recrystallizations from dilute methyl alcohol, 0.21 g. remained melting at 174–175° with slight softening at 168°.

Rotation. *l*-acid. 0.2052 g. made up to 25 cc. with methyl alcohol at 20° gave $\alpha_D = -1.11°$; $l = 2$; $[\alpha]^{20}_D$ −67.7°.

The *d*-acid was obtained in exactly the same way; melting point 171–173° with slight softening at 167°.

Rotation. *d*-acid. 0.0309 g. made up to 15 cc. with methyl alcohol at 20° gave $\alpha_D = +0.26°$; $l = 2$; $[\alpha]^{20}_D$ +63.1°.

Racemization Experiments

1. A sample of the *l*-acid was dissolved in ordinary ethyl alcohol and refluxed in a flask with a ground-glass joint for twenty-four hours. No change in rotation was observed.

Rotation. 0.0950 g. made up to 25 cc. with ethyl alcohol at 20° gave $\alpha_D = -0.52°$; $l = 2$; $[\alpha]^{20}_D$ −68.4°.

2. A second sample of the *l*-acid was refluxed in butyl alcohol in the same manner as in ethyl alcohol; 0.0583 g. was made up to 15 cc. at 20°, $l = 2$. $k = l/t \log_{10} \alpha_0/\alpha_t$; half-life period $= l/k \log_{10} 2$.

Time in minutes	α_D	$[\alpha]^{20}_D$	k	Av. k
0	−0.56°	−72.0°	....	
360	− .49°	−63.0°	0.00016	
1080	− .42°	−54.0°	.00012	0.00115
1740	− .35°	−45.0°	.00010	
2460	− .32°	−41.3°	.00010	

Half-life period = 2510 minutes = 42 hrs.

3. A sample was then dissolved in glacial acetic acid and treated in the same manner: 0.0840 g. was made up to 15 cc. at 20°, $l = 2$.

Time in minutes	α_D	$[\alpha]^{20}_D$	k	Av. k
0	−0.97°	−86.6°	....	
180	−0.90°	−80.4°	0.00018	
540	−0.82°	−73.2°	.00013	0.00015
1080	−0.69°	−61.6°	.00014	

Half-life period = 2007 minutes = 34 hrs.

4. The *l*-acid was dissolved in 5% sodium carbonate and allowed to stand for twenty-four hours at room temperature. The rotation did not change.

Rotation. 0.1148 g. made up to 15 cc. with 5% sodium carbonate solution at 20° gave $\alpha_D = +0.33°$; $l = 2$; $[\alpha]^{20}_D$ +21.6°.

5. A sample of *l*-acid dissolved in 0.1 *N* sodium hydroxide solution did not change in rotation upon standing for twenty-four hours at room temperature, nor upon heating for two hours at 80°. The solution was then refluxed but due to the small rotation in sodium hydroxide the rotations were taken on the free acid in methyl alcohol.

Rotation. 0.1140 g. made up to 15 cc. with 0.1 *N* NaOH at 20° gave $\alpha_D = +0.19°$, $l = 2$; $[\alpha]^{20}_D +12.6°$.

Time in minutes	$[\alpha]^{20}_D$ in CH_3OH	*k*	Av. *k*
0	−67.7°	....	
120	−50.6°	0.0011	0.00115
300	−29.0°	.0012	

Half-life period = 262 minutes = 4.5 hrs.

Summary

1. The compound 2-methyl-6-nitro-2′-carboxydiphenyl has been prepared and resolved.

2. The active forms racemize slowly in boiling alkali and still more slowly in neutral or acid solvents.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

HEXA-OMEGA-TERTIARY-BUTYLPROPINYLETHANE AND SOME NEW ACETYLENIC CARBINOLS

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In attempting to find some aliphatic unsaturated hydrocarbons which would resemble the hexa-arylethanes, several tetra- and hexa-acetylenic ethanes have been prepared in this Laboratory.[1] All of the compounds which have been described heretofore have had as the acetylenic group the radical *tert.*-butylethinyl, $(CH_3)_3C—C{\equiv}C—$. In order to learn more about compounds of this general type, the work has now been extended to cover hydrocarbons in which other than tertiary alkyl groups are attached to the ethinyl group. It has been shown[2] that a tertiary alkyl group directly attached to the central carbon of a hexasubstituted ethane has a greater effect in producing dissociation than does a secondary alkyl group, and this in turn has a greater effect than does a primary alkyl group. It has seemed of interest to determine whether this effect is transmitted through the acetylenic structure to the central ethane carbon. As the first step in this study, the preparation and properties of a hexa-

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[1] The publications describing these compounds are Salzberg and Marvel, THIS JOURNAL, **50**, 1737, 2840 (1928); Rossander and Marvel, *ibid.*, **51**, 932 (1929); Gillespie and Marvel, *ibid.*, **52**, 3368 (1930).

[2] Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926); Conant and Bigelow, *ibid.*, **50**, 2041 (1930).