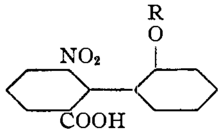
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Stereochemistry of Diphenyls. XL.[1] The Effect of Temperature and Solvent on the Rate of Racemization of 2-Nitro-6-carboxy-2′-alkoxydiphenyls

BY C. C. LI[2] AND ROGER ADAMS

Various investigators have shown that (1) the nature of the nuclei[3] attached to the 2,2′,6,6′ atoms combined with the ring in a diphenyl, (2) the temperature[4,5,6,7] and (3) the solvent[6,7,8] have an influence on the rate of racemization of optically active diphenyls. In this investigation a further study of these factors has been made on the members of a series of 2-nitro-6-carboxy-2′-alkoxydiphenyls (I)



R = CH_3, C_2H_5, (n)C_3H_7

I

The rate of racemization of the active compounds where the alkoxyl group was methoxyl, ethoxyl or propoxyl was made in different solvents at room temperature and in absolute ethyl alcohol at different temperatures. The data for the racemization of the diphenyls in different solvents are given in Table I, the effect of temperature on the rate of racemization of the three diphenyls, in Table II, and the mutarotation of the brucine salts and rates of racemization of the sodium salts in aqueous and alcoholic solution, in Table III.

From these data the following general conclusions may be drawn: (1) the size of the alkyl in the alkoxyl group influences the rate of racemization of the molecule. The ratio of the rates of racemization of the methoxy, ethoxy and propoxy derivatives is approximately 1:5:7 regardless of the nature of the solvent; (2) the higher the temperature, the greater the rate of racemization; (3) the nature of the solvent influences the rate of racemization.

The effect on the rate of racemization of nuclei attached to the atoms combined with the ring has been clearly demonstrated. The much greater increment in the effect on the rate of racemization from methoxyl to ethoxyl than from ethoxyl to propoxyl is striking.

As might be anticipated, the rates of racemization vary in the different solvents and no generalization in this regard can be made. The relative rates of racemization of the three compounds, however, remain essentially constant.

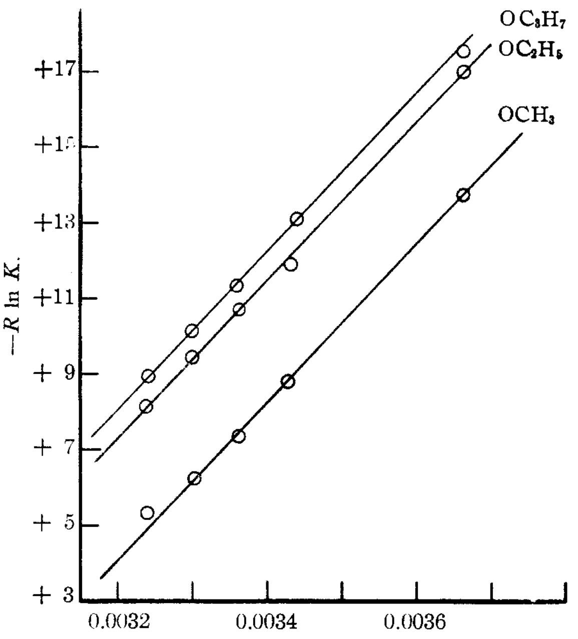


Fig. 1.

From a study of the rates of racemization of the three active diphenyls in absolute ethyl alcohol at five different temperatures, between 0 and 36°, velocity constants at the different temperatures were obtained. With these data it may be shown that the van't Hoff–Arrhenius equation representing temperature coefficients for chemical reactions applies to the rate of racemization of optically active diphenyls. Three parallel straight lines (Chart I) are obtained for each of the diphenyls when $-R \ln K$ is plotted against $1/T$, thus showing that the heat of activation for the

---

[1] For the last article in this series see (a) Patterson and Adams, THIS JOURNAL, **57**, 762 (1935). See also (b) Yuan and Adams, *Chem. Rev.*, **12**, 261 (1933).

[2] Part of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry, University of Illinois.

[3] Stanley, McMahon and Adams, THIS JOURNAL, **55**, 706 (1933); Kleiderer and Adams, *ibid.*, **55**, 4219 (1933). See also Ref. 1b.

[4] Kuhn and Albrecht, *Ann.*, **455**, 286 (1927); **458**, 221 (1927).

[5] Mills and Elliott, *J. Chem. Soc.*, 1296, 1300 (1932).

[6] Mills and Breckenridge, *ibid.*, 2209 (1928).

[7] Adams, *et al.*, THIS JOURNAL, **54**, 2966, 4426 (1932); **55**, 1649 (1933).

[8] Meisenheimer and Beisswenger, *Ber.*, **65B**, 32 (1932).

TABLE I

RATE OF RACEMIZATION OF FREE ACIDS IN VARIOUS SOLVENTS

Compound, group at 2'	Weight,[a] g.	Temp., °C.	Rotations in degrees[b,c]							Av. K	Av. dev. K	Half-life, min.	Period ratio
			Max. [α]D calcd.	Initial Time, min.	Initial αD	Initial [α]D	Final Time, hours	Final αD	Final [α]D				
					Pyridine								
OCH_3	0.0686	25 -25.3	+ 51.0	5	+0.51	+ 37.2	3	0	0	0.02368	0.00099	12.6	1
OC_2H_5	.0353	24.5-25	−179.2	7	−1.17	−165.7	11	0	0	.00484	.00008	62.2	4.9
OC_3H_7	.0350	24.3-25.3	−119.0	5	−0.80	−114.3	12	0	0	.00351	.00009	85.8	6.8
					Acetone								
OCH_3	0.0696	24 -24.3	+ 40.6	5	+0.43	+ 30.9	2.5	0	0	0.02407	0.00056	12.5	1
OC_2H_5	.0378	24.2-24.8	−137.3	5	− .95	−125.7	10	0	0	.00461	.00004	65.3	5.2
OC_3H_7	.0358	24.4-25.3	− 85.8	5	− .59	− 82.4	10	0	0	.00350	.00011	86.0	6.9
					Absolute Ethyl Alcohol								
OCH_3	0.0662	24 -24.5	+ 53.1	6	+0.50	+ 37.8	3	0	0	0.02473	0.00085	12.2	1
OC_2H_5	.0522	24 -24.5	−143.7	5	−1.42	−136.0	12	0	0	.00458	.00018	65.8	5.4
OC_3H_7	.0546	24 -25	−106.7	5	−1.12	−102.6	20	0	0	.00337	.00009	89.3	7.3
					Glacial Acetic Acid								
OCH_3	0.0691	25 -25.4	+ 14.8	5	+0.155	+ 11.2	1.7	0	0	0.02202	0.00121	13.7	1
OC_2H_5[d]	.0381	25.2-25.5	− 72.8	5	− .53	− 68.2	Reference [e]			.00404	.00009	74.5	4.9
OC_3H_7[d]	.0374	24.9-25.2	− 33.2	5	− .24	− 32.1	Reference [e]			.00279	.00007	107.8	7.9
					Absolute Methyl Alcohol								
OCH_3	0.0662	24.5-25.1	+ 31.4	5	+0.325	+ 24.6	$2^2/_3$	0	0	0.02151	0.00056	14.0	1
OC_2H_5	.0354	24.5-25	−117.9	7	− .78	−110.2	$10^1/_3$	0	0	.00407	.00012	74.0	5.3
OC_3H_7	.0345	25 -25.3	− 79.3	5	− .53	− 76.8	15	0	0	.00270	.00010	111.5	8.0
					Ethyl Acetate								
OCH_3	0.0611	24.5-25	+ 40.9	5	+0.41	+ 33.6	$2^1/_6$	0	0	0.01795	0.00031	16.8	1
OC_2H_5	.0413	24.5-25	−147.7	5	−1.17	−141.6	19.5	0	0	.00391	.00007	77.0	4.6
OC_3H_7	.0381	24.3-25.1	− 93.3	5	− .69	− 90.6	20	0	0	.00262	.00008	114.9	6.8
					Dioxane								
OCH_3	0.0713	25 -25.3	+ 52.6	5	+0.63	+ 44.2	3.5	0	0	0.01524	0.00051	19.8	1
OC_2H_5	.0354	24.5-25	−199.9	5	−1.365	−194.2	20	0	0	.00325	.00011	92.6	4.7
OC_3H_7	.0351	24.6-25.1	−122.7	5	− .84	−119.9	22	0	0	.00214	.00010	140.7	7.1

[a] Made up to 10 cc. [b] $l = 2$. [c] Results have been readily duplicated unless otherwise stated. [d] Results have not been duplicated. [e] Not carried to completion.

three diphenyls is the same, a rather unexpected result. The value for E was approximately 20,000 calories.

Two or three interesting experimental facts were observed in this investigation. Only one alkaloidal salt of each acid could be isolated. The brucine salt of the methoxy derivative proved to be a derivative of the *d* form of the acid, whereas the brucine salts of the ethoxy andpro poxy derivatives were derived from the *l* modifications. The melting points of the active methoxy and ethoxy derivatives were the same as for the inactive acids, indicating racemization before melting. In the case of the propoxy, however, a double melting point was observed, first at 95-97°; then resolidification took place and the compound remelted at 132°. This, presumably, represents the melting point of the active form first, racemization to the inactive form which then melts at a higher temperature. It demonstrates clearly the greater stability of the propoxy molecule over the other two.

Experimental

The series of diphenyls studied in the present investigation was prepared according to the following series of equations

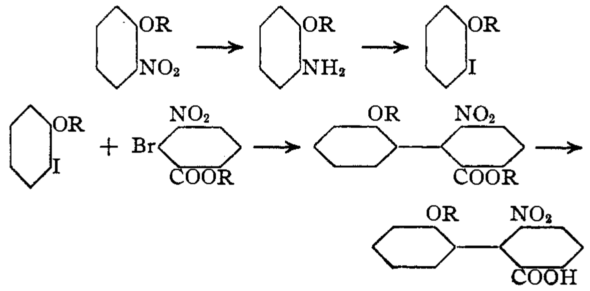


TABLE II

RATE OF RACEMIZATION OF FREE ACIDS IN ABSOLUTE ETHYL ALCOHOL AT DIFFERENT TEMPERATURES

Compound Group at 2'	Weight,[a] g.	Temp., °C.	Rotations in degrees							Av. K	Av. dev. K	Half-life, min.	Period ratio
			Max. $[\alpha]_D$ calcd.	Initial			Final						
				Time, min.	α_D	$[\alpha]_D$	Time, hours	α_D	$[\alpha]_D$				
0°[b,c]													
OCH_3	0.0771	0	+ 25.3	21	+0.18	+ 23.3	24	0	0	0.000993	0.000081	303.2	1
OC_2H_5	.0640	0	−152.3	11	− .97	−151.5	19	0	0	.000190	.000010	1584.4	5.2
OC_3H_7	.0670	0	−118.4	10	− .79	−117.9	31	0	0	.000144	.000003	2084.7	6.9
17.6°–18.8°[b,c]													
OCH_3	0.1004	18.5–18.8	+ 26.9	15	+0.18	+ 17.9	15	0	0	0.01200	0.00063	25.1	1
OC_2H_5	.0608	18.3–18.5	−145.6	11	− .83	−136.5	27.5	0	0	.002522	.000144	119.4	4.8
OC_3H_7	.0663	17.6–17.8	−110.6	5	− .72	−108.6	22	0	0	.001369	.000033	219.9	8.8
24°–25°[d,e]													
OCH_3	0.0662	24 –24.5	+ 53.1	6	+0.50	+ 37.8	3	0	0	0.02473	0.00085	12.2	1
OC_2H_5	.0522	24 –24.5	−143.7	5	−1.42	−136.0	12	0	0	.00458	.00018	65.8	5.4
OC_3H_7	.0546	24 –25	−106.7	5	−1.12	−102.6	20	0	0	.00337	.00009	89.3	7.3
29.6°–30.3°[b]													
OCH_3	0.1004	29.6–29.8	+ 23.9	5	+0.15	+ 14.9	0.55	0	0	0.04306	0.00150	7.0	1
OC_2H_5	.0622	29.7–30.3	−136.7	5	− .77	−123.3	17.5[c]	0	0	.00864	.00017	34.8	5
OC_3H_7	.0606	29.8–30.3	−111.2	5	− .63	−104.4	15[c]	0	0	.00601	.00023	50.1	7.2
35°–35.8°[b]													
OCH_3	0.1069	35.2–35.7	+ 29.0	6	+0.12	+ 11.2	0.55	0	0	0.06939	0.00846	4.3	1
OC_2H_5	.0608	35.5–35.8	−146.4	6	− .71	−116.8	34.5[c]	0	0	.01660	.00057	18.1	4.2
OC_3H_7	.0611	35.0–35.8	−107.9	5	− .58	− 94.9	12[c]	0	0	.01107	.00061	27.2	6.3

[a] Made up to 10 cc. [b] $l = 1$. [c] After several K had been obtained, the solution was allowed to stand at room temperature over 10–33 hours. The final reading was then taken. [d] $l = 2$. [e] Results have been readily duplicated.

TABLE III

RATE OF RACEMIZATION OF BRUCINE AND SODIUM SALTS

Compound Group at 2'	Weight, g.	Temp., °C.	Rotations in degrees[a]							Av. K	Av. dev. K	Half-life, min.	Period ratio
			Max. $[\alpha]_D$ calcd.	Initial			Final						
				Time, min.	α_D	$[\alpha]_D$	Time hours	α_D	$[\alpha]_D$				
Brucine Salts in Chloroform[b,c]													
OCH_3	0.0665	24 –24.8	+ 97.9	6	+0.37	+ 69.6	6.5	−0.065	−12.2	0.02161	0.00096	13.9	1
OC_2H_5	.0592	24.5–25	− 220.2	5	−0.98	−206.9	24.5	− .055	−11.6	.00466	.00009	64.6	4.5
OC_3H_7	.0615	24 –24.7	− 182.9	4	− .87	−176.5	32	− .04	− 8.13	.00356	.00012	84.5	6.0
Sodium Salts in Water[d,e]													
OCH_3	0.0618	25.3–25.7	+ 115.3	10	+0.42	+ 85.0	4	0	0	0.01341	.00077	22.4	1
OC_2H_5	.0500	25 –25.5	− 370.0	12	−1.37	−342.5	21.5	0	0	.00279	.00012	107.9	4.8
OC_3H_7	.0501	25 –25.5	− 371.0	10	−1.41	−345.6	21	0	0	.00230	.00007	130.9	5.8
Sodium Salts in Absolute Ethyl Alcohol[d,f]													
OCH_3	0.0401	25.5–25.7	+2232.0	5	+0.72	+ 89.8	0.85	0	0	0.07899	.00144	3.8	1
OC_2H_5	.0301	25 –25.7	− 596.5	8	−2.60	−431.9	4.0	0	0	.01742	.00026	17.3	4.6
OC_3H_7	.0303	24.9–25.4	− 490.1	5	−2.56	−422.4	5.5	0	0	.01290	.00025	23.3	6.1

[a] $l = 2$. [b] Made up to 25 cc., 10 cc. was used for racemization experiment. The remaining solution was transferred into a 15-cc. volumetric flask and allowed to stand at room temperature for time stated. It was then used for the determination of final rotation. [c] Results have been readily duplicated. [d] Made up to 25 cc. [e] 0.0257 N NaOH solution was used. [f] A solution of 0.1 g. of sodium in 100 cc. of absolute ethyl alcohol was used.

***o*-Nitro-alkoxybenzenes.**—Haworth and Lapworth's[9] method of methylation was used for the preparation of *o*-nitroalkoxybenzenes with yields of 75–85%. The ethoxy, propoxy, butoxy and pentoxy derivatives were synthesized using as alkylating agents diethyl sulfate, *n*-propyl iodide, *n*-butyl and *n*-pentyl bromide. *o*-Nitro-ethoxybenzene was purified first by steam distillation, the distillate extracted with ether and finally vacuum distilled. The other derivatives were purified directly by vacuum distillation.

***o*-Amino-alkoxybenzenes.**—These compounds were prepared by reducing in the usual manner with iron powder and water, the corresponding nitro compound; yields were 54–83%. The benzoyl derivative of the propoxy compound was synthesized. The butoxy and pentoxy homologs turned dark upon standing. Their *p*-toluenesulfonyl derivatives were prepared and were found to be insoluble in alkali.

***o*-Iodo-alkoxybenzenes.**—The above *o*-amino-alkoxybenzenes were diazotized at 0 to −5° in the usual manner

---

(9) Haworth and Lapworth, *J. Chem. Soc.*, **123**, 2986 (1923).

TABLE IV

o-NITRO-ALKOXYBENZENES

Compound	B. p.		d^{20}_4	n^{20}_{20}	Formula	% Nitrogen (micro Dumas)	
	°C.	mm.				Calcd.	Found
OC_2H_5[a]	146–148	15	....	....	....	..	..
OC_3H_7	155–156.5	15	1.1508	1.5386	$C_9H_{11}O_3N$	7.74	7.91
OC_4H_9	171–172	19	1.1168	1.5274	$C_{10}H_{13}O_3N$	7.17	7.21
OC_5H_{11}	177–178	15.5	1.0905	1.5222	$C_{11}H_{15}O_3N$	6.70	6.91

[a] This compound has been previously prepared by Van Erp,[10] who reported a b. p. of 149.3° at 16 mm.

TABLE V

o-AMINO-ALKOXYBENZENES

Compound	B. p., °C.	d^{20}_4	n^{20}_{20}	Formula	% Nitrogen (micro Dumas)	
					Calcd.	Found
OC_2H_5[a]	224–229	....	....	....	..	..
OC_3H_7	120–130 (14–15 mm.)	[b]	[b]	....	..	..
Benzoyl deriv.	M. p. 49–51°	....	....	$C_{16}H_{17}O_2N$	5.49	5.56
OC_4H_9	138–139 (15.5 mm.)	1.0062	1.5340	$C_{10}H_{15}ON$	8.49	8.69
p-Toluenesulfonyl deriv.	M. p. 85–88°	....	....	$C_{17}H_{21}O_3NS$	4.40	4.70
OC_5H_{11}	152.5–153.5 (16.5 mm.)	0.9757	1.5278	$C_{17}H_{17}ON$	7.83	7.89
p-Toluenesulfonyl deriv.	M. p. 88–90°	....	....	$C_{18}H_{23}O_3NS$	4.21	4.45

[a] This compound has been previously prepared by Groll and Förster,[11] who reported boiling points of 228 and 229°, respectively, at 756 mm. [b] This compound was not purified but was used directly for conversion to the corresponding iodo compound.

TABLE VI

o-IODO-ALKOXYBENZENES

Compound	B. p.,		d^{20}_4	n^{20}_{20}	Formula	% Iodine (micro)	
	°C.	mm.				Calcd.	Found
OC_2H_5[a]	121–131	17–18	....	....	......	...	...
OC_3H_7	138–139	15	1.5722	1.5810	$C_9H_{11}OI$	48.44	48.33
OC_4H_9	152–154	18	1.5094	1.5699	$C_{10}H_{13}OI$	45.98	45.88
OC_5H_{11}	126–129	1–1.5	1.4482	1.5601	$C_{11}H_{15}OI$	43.76	43.53

[a] This compound has been previously prepared by Reverdin[12] who reported a boiling point of 245° at 735.5 mm.

in about 10% sulfuric acid solution containing 2.5 moles of sulfuric acid for each mole of amine. The diazotized solution, after standing with constant stirring in an ice-salt bath for one-half hour, was added to a solution of twice the amount of potassium iodide required in dilute sulfuric acid solution. The methoxy and ethoxy derivatives were purified first by steam distillation and then by vacuum distillation. The propoxy, butoxy and pentoxy were taken up in chloroform and then purified by vacuum distillation. Yields were 58–68%. The *o*-iodopentoxybenzene decomposed when distilled at 15 mm. pressure.

2 - Nitro - 6 - carboxy - 2′ - alkoxydiphenyls.—2-Nitro-6-carboxy-2′-methoxydiphenyl was prepared according to the method of Stoughton and Adams.[13] The remaining four diphenyls were made by condensing *o*-iodo-alkoxybenzene and methyl 2-bromo-3-nitrobenzoate by Ullmann's reaction.

In a 200-cc., 3-necked flask fitted with a mechanical stirrer, a reflux condenser and a stopper, was placed a mixture of 20–26 g. of *o*-iodo-alkoxybenzene and 10–13 g. of methyl-2-bromo-3-nitrobenzoate (ratio 2:1). This was gradually heated in a Wood's metal bath and 35–40 g. of purified copper[14] was added in small portions over a period of one-half to three-quarters of an hour. During the addition of the copper, the bath was kept at the temperature stated in Table VII and then raised 10–15° for a quarter of an hour to an hour. After cooling, the reaction mixture was transferred into a Soxhlet extractor and extracted with 250 cc. of 95% alcohol for more than twelve hours. The alcohol extract was concentrated to about one-half of its original volume and to it was added 200 cc. of 10% sodium carbonate solution. The alkaline solution was refluxed for five hours. The aqueous solution was decanted from the unsaponified oil and the filtrate was acidified slowly with dilute hydrochloric acid. A brownish black tar separated which solidified upon standing.

The crude product was dissolved in 10% sodium carbonate solution, boiled with norite, filtered, and precipitated with dilute hydrochloric acid. It was extracted with 200 cc. of hot benzene in 40-cc. portions and filtered. The benzene was removed and crude 2-nitro-6-carboxy-2′-alkoxybenzene was dissolved in the minimum amount of ether and to it was added a large amount of petroleum ether until slight turbidity occurred. After the ether–petroleum ether solution was allowed to stand for several hours, tar separated. The solution was then decanted into a clean beaker and was allowed to stand again. This process was repeated until no more tar appeared.

---

(10) Van Erp, *Ber.*, **56**, 217 (1923).

(11) Groll, *J. prakt. Chem.*, [2] **12**, 208 (1875); Förster, *ibid.*, [2] **21**, 344 (1880).

(12) Reverdin, *Ber.*, **29**, 2596 (1896).

(13) Stoughton and Adams, THIS JOURNAL, **54**, 4426 (1932).

(14) Kleiderer and Adams, *ibid.*, **55**, 4219 (1933).

TABLE VII

2-NITRO-6-CARBOXY-2′-ALKOXYDIPHENYLS

Compound group at 2′	Temp. of coupling bath, °C.	Yield, %	Form and color	Solvent	M. p., °C.	Formula	% Nitrogen (micro Dumas) Calcd.	Found
OCH_3	240–250	18.4	Yellowish needles	85% ethanol	196–197[13]			
OC_2H_5	240–250	16.5	Yellowish needles	80% ethanol	153–155	$C_{15}H_{13}O_5N$	4.88	4.93
OC_3H_7	250–260	6.7	Yellowish microcrystals	50% ethanol	133–135	$C_{16}H_{15}O_5N$	4.65	4.66
OC_4H_9	210–220	10.6	Yellowish microcrystals	Ether and pet. ether	117–119	$C_{17}H_{17}O_5N$	4.44	4.54
OC_5H_{11}	220–230	11.0	Colorless plates	Ether and pet. ether	89– 92	$C_{18}H_{19}O_5N$	4.26	4.45

TABLE VIII

RESOLUTION AND PHYSICAL PROPERTIES OF BRUCINE SALTS

Compound group at 2′	Racemic acid, g.	Anhydrous brucine, g.	Absolute C_2H_5OH, cc.	Color and crystalline form	M. p., °C.	Formula	Microanalysis of salts % Calcd. C	H	% Found C	H
OCH_3[b]	1.46	2.11	150	Yellow	219–220[13]					
OC_2H_5	1.33	1.83	140	micro-	167–176[a]	$C_{38}H_{39}O_9N_3$	66.93	5.77	66.96	5.89
OC_3H_7	1.28	1.67	150	crystals	157–162[a]	$C_{39}H_{41}O_9N_3$	67.31	5.94	67.36	6.12

[a] Melting with evolution of gas. [b] Crystallizes with one molecule of water.

Resolution of 2-Nitro-6-carboxy-2′-alkoxydiphenyls.—The methoxy, ethoxy and propoxy diphenyls were all resolved by means of brucine in absolute ethyl alcohol. Table VIII contains the quantities of diphenyl, brucine and solvent and the physical properties and analyses of the salts formed.

Only one form of each salt could be isolated. In the case of the ethoxy and propoxy derivatives the brucine salt of the *l*-modification was isolated, whereas the salt of the *d*-modification separated in the case of the methoxy.

With the butoxy and pentoxy derivatives no crystalline salts could be isolated from a variety of alkaloids and solvents.

Active (*d* or *l*)-2-Nitro-6-carboxy-2′-alkoxydiphenyls.—About 2 g. of solid brucine salt was treated with 100 cc. of ice-cold hydrochloric acid (1:1) in a 125-cc. Erlenmeyer flask. The flask was cooled in an ice–salt bath for one hour with vigorous shaking from time to time. The active acid was then filtered on a sintered glass funnel and treated with a fresh portion (100 cc.) of ice-cold hydrochloric acid of the same strength. It was allowed to stand in an ice–salt bath which was placed in an ice-box for not less than twelve hours. It was then filtered and washed, first with dilute hydrochloric acid until the washings gave no test for brucine, and then with water until free from chloride ion. The temperature was kept at 0° until the acid was obtained in the solid state. Table IX contains the quantities of salt decomposed and yields and physical properties of active acids.

TABLE IX

PERCENTAGE YIELD AND PHYSICAL PROPERTIES OF ACTIVE ACIDS

Compound group at 2′	Weight of salt decomposed, g.	Weight of active acid obtained, g.	Yield, %	M. p., °C.
OCH_3	2	0.63	74	195–197
OC_2H_5	1.96	.74	90	153–155
OC_3H_7	1.83	.62	80	95– 97 and 132.5–133.5

The melting point of *d*-2-nitro-6-carboxy-2′-methoxydiphenyl and *l*-2-nitro-6-carboxy-2′-ethoxydiphenyl is the same as that of the racemic form. However, the *l*-2-nitro-6-carboxy-2′-propoxydiphenyl melted first at 95–97° which is, probably, the melting point of active acid resolidified and then melted again at 132.5–133.5° which is the melting point of the racemic form.

Racemization Experiments of Active 2-Nitro-6-carboxy-2′-alkoxydiphenyls.—The results of racemization in different solvents are given in Table I.

For temperatures between 0° and room temperature, running water of constant pressure was passed through the jacket used for the determination of rotation at 0° carrying an automatic siphon and a thermometer. By regulating the rate of flow it was possible to keep a constant quantity of moving water in the jacket and to maintain the temperature within a range of one-half of a degree for several hours. For temperatures above room temperature running water of constant pressure was passed first into a tube heated with a current which could be varied by change of resistance and then when constant in temperature passed through the jacket of the rotation tube as described above. By regulating the rate of water flowing into the tube and of the current through it, it was possible to keep any temperature above room temperature and below 60° in a range of one-half of a degree for several hours.

The absolute alcohol was warmed to the constant temperatures to be used before making up the solution.

Summary

Three 2-nitro-6-carboxy-2′-alkoxydiphenyls have been prepared in which the alkoxy group is methoxyl, ethoxyl and propoxyl. A study of these products indicates (1) an increase in the rate of racemization from methoxyl to propoxyl, (2) more rapid racemization with increase in temperature, (3) the change in rate of racemization with temperature, (4) identical heats of activation within experimental error for the three compounds.

URBANA, ILLINOIS RECEIVED JUNE 13, 1935