hydrogen chloride-catalyzed rearrangement of mono- and dichlorobiphenyls and assumed the transition state of the phenyl migration to consist of a bridged phenonium ion as postulated by Cram.[6]

To obtain information on the migration of phenyl groups under Friedel-Crafts' conditions, the isomerization of *o*-, *m*-, and *p*-terphenyl with water-promoted aluminum chloride was investigated. In order to be independent of traces of moisture present in substrate and catalyst, as well as to promote the reaction (which in the absence of added water as co-catalyst is much slower and under strictly anhydrous conditions might not take place) a known, constant amount of water was added as cocatalyst in each experiment. The results are summarized in Table I.

TABLE I

ISOMERIZATION OF TERPHENYLS WITH WATER-PROMOTED ALUMINUM CHLORIDE

Terphenyl	Reaction time, hr.	Temp., °C.	% terphenyl isomer distribution *ortho*	normalized *meta*	*para*
ortho	2	140	70	30	0
	4	140	59	32	9
	19	140	7	70	23
	2.5	210	0	75	25
	4.5	210	0	62	38
	4.5	210	0	63	37
meta	2	140	0	84	16
	4	140	0	71	29
	19	140	0	63	37
	1.5	210	0	64	36
	4.5	210	0	63	37
para	5 min.	180	0	25	75
	10 min.	180	0	36	64
	15 min.	180	0	52	48
	20 min.	180	0	65	35
	1.25	200	0	63	37
	2.5	200	0	64	36
	1.25	210	0	63	37
	2.5	210	0	62	38

The equilibrium mixture obtained starting with any one of the isomers consists of about 63% *m*- and 37% *p*-terphenyl with no *ortho* isomer present. There is little variation in the composition of the final mixtures with temperature and time, and they are believed to be corresponding to thermodynamic equilibrium. From the figures for the rearrangement of *o*-terphenyl it appears that the migration of the phenyl group takes place by intramolecular 1,2-shift, the *para* isomer appearing only after the formation of a substantial amount of *meta*. A 1,2-shift is also assumed in the isomerization of *m*- and *p*-terphenyl. In all experiments the terphenyls accounted for 70 to 85% of the material balance, the rest being high molecular weight tarry materials which were not further investigated.

The absence of *o*-terphenyl in the equilibrium mixture is not surprising for steric reasons. X-ray diffraction studies showed the arrangement of the rings to be nonplanar, the two outer phenyl groups being rotated through approximately 45° in the same direction which brings them into a position roughly orthogonal to the central ring.[7] Assuming the compound to have a similar configuration under our experimental conditions, it appears that the steric requirements for the formation of *o*-terphenyl from the *meta* isomer are unfavorable. Models show that the spatial arrangement of the phenyl groups in *m*-terphenyl must be nearly co-planar and not too different from that of *p*-terphenyl which is known to be co-planar in the solid state.[8]

Experimental

Isomerizations were carried out in sealed Pyrex glass tubes at temperatures and periods of time given in Table I. The amounts of substrate and catalyst in each experiment were 3.0 g. of appropriate terphenyl isomer and 0.3 g. of Al_2Cl_6 (~8 mole %). To this mixture 0.015 ml. of water was added from a syringe. Products were recovered by extraction of the reaction mixtures with boiling carbon disulfide, in the presence of water. After drying with calcium chloride, the extract was submitted to infrared analysis using the following bands: 11.90 μ for *o*-terphenyl, 12.55 and 11.25 μ for *m*-terphenyl, and 11.95 μ for *p*-terphenyl. The accuracy of measurement is believed to be within ±3 relative per cent (as checked on mixtures of known composition). The terphenyls were Eastman grade laboratory chemicals. No impurity bands could be detected and purity of 99+% was assumed.

Acknowledgment.—We are indebted to D. T. Peterson for the infrared analyses.

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[8] L. W. Pickett, *Proc. Roy. Soc.* (London), **A142**, 333 (1933).

Cyclization of 2,4-Dinitrophenylacetic Acid

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During the course of investigation on reactive methylene compounds,[2–4] it was noticed that 2,4-dinitrophenylacetic acid, when heated in sulfuric acid for two hours at 120–130°, cyclized to a bicyclic compound (I), $C_7H_4N_2O_3$. I formed a salt with hydrazine hydrate and could be regenerated by hot water. It reduced Tollen's reagent and decolorized potassium permanganate solution. This compound on heating with sodium dichromate and sulfuric acid was oxidized to 5,5′-dinitroazoxybenzene-2,2′-dicarboxylic acid (II) and was hydrolyzed with sodium carbonate solution to 2-amino-4-nitrobenzoic acid. The properties and transformations indicate that the compound (I) is probably 6-

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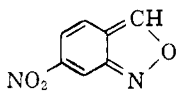
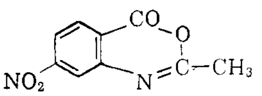
[2] H. G. Garg and S. S. Joshi, *J. Org. Chem.*, **26**, 946 (1961).

[3] H. G. Garg, *ibid.*, **26**, 948 (1961).

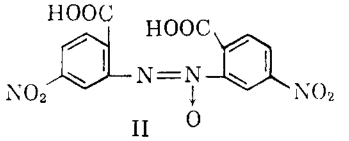
[4] H. G. Garg, *ibid.*, **27**, 1045 (1962).



I



III



II

nitroanthranil. A mixed melting point determination with an authentic sample[5] showed no depression.

4-Nitroacetanthranil[6] (III) was obtained by heating I with acetic anhydride, which further confirmed its structure.

Experimental[7]

2,4-Dinitrophenylacetic acid was obtained by the nitration of phenylacetic acid with fuming nitric acid.[8]

6-Nitroanthranil (I).—A solution of 4.0 g. of 2,4-dinitrophenylacetic acid in 30 ml. of concentrated sulfuric acid was heated for 2 hr. at 120–130° in an oil bath. The mixture was poured over crushed ice. A dirty white precipitate so obtained was washed with sodium bicarbonate solution. The residue was purified with activated charcoal and recrystallized from alcohol to give 1.0 g. of colorless solid, m.p. 133°. A mixed melting point with 6-nitroanthranil[5] showed no depression.

Anal. Calcd. for $C_7H_4N_2O_3$: C, 51.2; H, 2.4; N, 17.1. Found: C, 50.8; H, 2.5; N, 16.6.

Hydrazine Salt of 6-Nitroanthranil.—A solution of 0.25 g. of I in 10 ml. of alcohol and 1.5 ml. of hydrazine hydrate was allowed to reflux for 0.5 hr. On cooling, 0.20 g. of yellow needles separated, m.p. 175° (lit.,[5] m.p. 175°).

Anal. Calcd. for $C_7H_8N_4O_3$: N, 28.6. Found: N, 28.3.

5,5′-Dinitroazoxybenzene-2,2′-dicarboxylic Acid (II).—A solution of 3 g. of sodium dichromate in 8 ml. of water was added gradually to a boiling solution of 0.5 g. of I in 10 ml. of acetic acid, 6 ml. of water, and 2.5 ml. of concentrated sulfuric acid and the mixture was refluxed for 1 hr. The acid crystallized from the cold solution in lemon yellow cubes, m.p. 295° (lit.,[5] m.p. 285°).

Anal. Calcd. for $C_{14}H_8N_4O_9$: neut. equiv., 188. Found: neut. equiv., 190.5.

2-Amino-4-nitrobenzoic Acid.—A solution of 1.5 g. of sodium carbonate in 10 ml. of water was added to 0.5 g. of I and refluxed for 0.5 hr. The filtrate on acidification gave orange plates, m.p. 264°. Mixed melting point with an authentic sample[5] of 2-amino-4-nitrobenzoic acid was undepressed.

4-Nitroacetanthranil (III).—A solution of 0.5 g. of 6-nitroanthranil, 6 ml. of acetic anhydride, and 0.5 g. of zinc acetate in 2 ml. of glacial acetic acid was refluxed for 4 hr. On cooling, the crystals were separated and on recrystallization from acetic acid yielded pale yellow crystals, m.p. 138°.

Anal. Calcd. for $C_9H_6N_2O_4$: C, 52.4; H, 2.9. Found: C, 52.3; H, 2.6.

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Synthesis of Polysubstituted Triptych-boroxazolidines[1,2]

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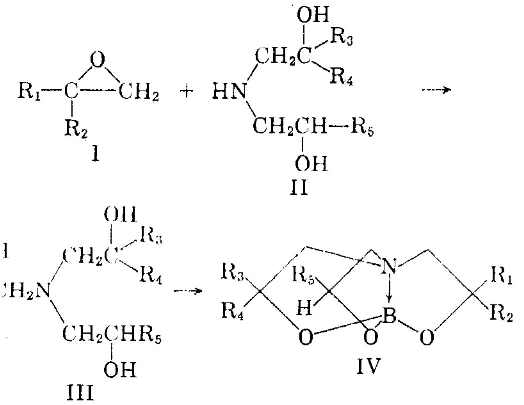
The synthesis of a series of monosubstituted triptych-boroxazolidines has been reported in a previous paper from this laboratory[3] in which the background for the undertaking is discussed. It was pointed out in that paper that Steinberg and Hunter[4] had detected a difference in rate of hydrolysis of *ca.* 10^5 between triptych-boroxazolidine itself and the much more slowly hydrolyzed *sym*-trimethyltriptych-boroxazolidine. Thus, in the hope of obtaining a water stable triptych-boroxazolidine unit to which an amino acid moiety could be attached, the series of polysubstituted triptych-boroxazolidines reported in this paper was prepared.

The synthetic methods employed were similar to those discussed previously.[3] The appropriately substituted triethanolamine (III) was prepared



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[6] I. R. Gambhir, Ph.D. thesis, University of Agra, 1956.

[7] Melting points are uncorrected.

[8] A. I. Vogal, "A Textbook of Practical Organic Chemistry," Longman Green and Co. Ltd., London, 1956, p. 758.

[1] This work was supported, in part, by Grant No. CY-3275 from the National Institutes of Health.

[2] The "triptych-boroxazolidine" nomenclature was proposed by H. K. Zimmerman [*Ann.*, **619**, 28 (1958); *ibid.*, **620**, 4 (1959)] based on an earlier suggestion of H. C. Brown [*J. Am. Chem. Soc.*, **73**, 2808 (1951)]. The Advisory Committee on Nomenclature of Organic Boron Compounds favors the designation of 2,8,9-trioxa-5-aza-1-borabicyclo[3.3.3]undecane (N-B) for the parent unsubstituted compound.

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