Alkylbenzenes. XI.[1] Rearrangements of Pentylbenzenes Induced by Aluminum Chloride

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The aluminum chloride-induced rearrangement reactions of the eight pentylbenzene isomers at 80° in benzene solution and at 100° without solvent have been studied with the aid of infrared spectrometry and vapor-phase chromatography. t-Pentylbenzene is rapidly isomerized to (1,2-dimethylpropyl)-benzene and the latter is more slowly isomerized to neopentylbenzene. Neopentylbenzene is very resistant toward rearrangement. (1-Methylbutyl)- and (1-ethylpropyl)-benzene are rapidly interconverted, and both are more slowly isomerized to (2-methylbutyl)-benzene. Isopentylbenzene is not isomerized by 24-hr. treatment at 80°. n-Pentylbenzene undergoes only 9% rearrangement under similar conditions. Possible mechanisms for the rearrangements are discussed and they are compared with those of propyl- and butylbenzenes.

Introduction

This paper presents data amplifying our earlier communication on rearrangements of three pentylbenzene isomers[3] and describes similar studies on the other pentylbenzene isomers.

The aluminum chloride-induced rearrangement of t-pentylbenzene to (1,2-dimethylpropyl)-benzene (2-methyl-3-phenylbutane) was first suggested by Schmerling and West[4] to explain the fact that the secondary alkylbenzene is the major product of alkylation with either t-pentyl or isopentyl halides. Nenitzescu and co-workers[5] later reported qualitative evidence of rearrangement of the tertiary to the secondary pentylbenzene resulting from treatment with aluminum chloride in benzene solution at 80° for a short time. They also reported rearrangement of the latter compound to neopentylbenzene as a result of more extended treatment with the same catalyst.

We now wish to report the results of a detailed study of the reactions of the eight pentylbenzene isomers with aluminum chloride, in which quantitative instrumental analysis of the products was made.

Results

The pentylbenzenes were treated with water-activated[6] aluminum chloride at 100° or in refluxing benzene solution at about 80–82°. After decomposing the catalyst with water, the pentylbenzene fraction was separated by fractional distillation from lower and higher-boiling materials and analyzed by vapor phase chromatography and infrared spectrometry. The recovery of the pentylbenzenes ranged from 7 to 51%, depending on the structure of the original pentylbenzene and the length and severity of the catalyst treatments (Tables I and II). Losses are attributable to disproportionation, dealkylation, and fragmentation reactions which accompany the rearrangements discussed in this paper. Disproportionation reactions of alkylbenzenes have already received considerable attention.[7] Dealkylation and fragmentation reactions are the subject of a subsequent paper.[8]

The results of experiments with t-pentyl-, (1,2-dimethylpropyl)-[9] and neopentylbenzene are summarized

TABLE I

REARRANGEMENTS OF t-PENTYLBENZENE, (1,2-DIMETHYLPROPYL)-BENZENE AND NEOPENTYLBENZENE INDUCED BY ALUMINUM CHLORIDE[a]

Expt.	Starting materials[b]	Time, hr.	Recov.[c]	TPB[d,g]	DMPB[e,g]	NPB[f,g]
				Pentylbenzene products, %		
1	TPB[d]	1.0[h]	12	5	31	65
2		0.25	..	15	60	25
3		0.5	33	13	60	27
4		1.0	27	12	56	31
5		12.0	19	11	44	46
6		24.0	13	8	29	62
7		48.0	9	4	15	81
8	Mixture[i]	12.0	24	0	5	95
9	DMPB[e]	8.5[h]	7	0	1	99
10		24.0	9	5	31	64
11	NPB[f]	1.0	51	0	0	100
12		24.0	33	0	2	98

[a] Temperature 80–82° unless otherwise noted. [b] All experiments unless otherwise noted were carried out with the following proportions of materials: pentylbenzene, 1.0 mole; benzene, 5.0 moles; AlCl₃, 0.4 mole; H₂O, 0.2 mole. [c] Based on starting material. [d] t-Pentylbenzene. [e] (1,2-Dimethylpropyl)-benzene. [f] Neopentylbenzene. [g] Of total pentylbenzene fraction recovered. [h] No benzene used in this expt.; temperature 100 ± 1°. [i] Pentylbenzene fraction recovered from expt. 5.

TABLE II

REARRANGEMENTS OF (1-METHYLBUTYL)-BENZENE, (1-ETHYLPROPYL)-BENZENE AND (2-METHYLBUTYL)-BENZENE INDUCED BY ALUMINUM CHLORIDE[a]

Expt.	Starting materials[b]	Time, hr.	Recov., %[c]	1-MBB,[d] %[g]	EPB,[e] %[g]	2-MBB,[f] %[g]
1	1-MBB[d]	0.5	..	64	20	16
2		1.0	51	63	19	17
3		12.0	38	56	14	30
4		24.0	25	51	14	35
5	Mixture[h]	12.0	44	50	12	38
6	EPB[e]	0.5	..	62	23	15
7		1.0	43	61	21	18
8		12.0	38	52	16	32
9		24.0	23	49	15	36
10	Mixture[i]	12.0	34	45	15	39
11	2-MBB[f]	1.0	51	0	0	100
12		12.0	35	7	1	92
13		24.0	31	10	2	88
14	Mixture[j]	12.0	30	8	1	91

[a] Temperature 80–82°. [b] All experiments were carried out with the following proportions of materials: pentylbenzene, 1.0 mole; benzene, 5.0 moles; AlCl₃, 0.4 mole; H₂O, 0.2 mole. [c] Based on starting material. [d] (1-Methylbutyl)-benzene. [e] (1-Ethylpropyl)-benzene. [f] (2-Methylbutyl)-benzene. [g] Of total pentylbenzene fraction recovered. [h] Pentylbenzene fraction recovered from expt. 3. [i] Pentylbenzene fraction recovered from expt. 8. [j] Pentylbenzene fraction recovered from expt. 12.

(1) Preceding paper: J. E. Douglass and R. M. Roberts, J. Org. Chem., in press.

(2) Taken from the Ph.D. Thesis of Y. W. Han, the University of Texas, 1960; General Electric Co. Fellow, 1959–1960.

(3) A preliminary description of part of this work was given in Tetrahedron Letters, 6, 5 (1959); most of the results were reported before the 139th National Meeting of the American Chemical Society at the Symposium on Carbonium Ions, St. Louis, Mo., March, 1961, p. 11-O of Abstracts.

(4) L. Schmerling and J. P. West, J. Am. Chem. Soc., 76, 1917 (1954).

(5) C. D. Nenitzescu, I. Necsoiu, A. Glatz and M. Zalman, Chem. Ber., 92, 10 (1959).

(6) R. M. Roberts, Y. W. Han, C. H. Schmid and D. A. Davis, J. Am. Chem. Soc., 81, 640 (1959); C. D. Nenitzescu, M. Avram and E. Sliam, Bull. soc. chim. France, 1266 (1955).

(7) Cf. (a) D. A. McCaulay and A. P. Lien, J. Am. Chem. Soc., 75, 2411 (1953); (b) H. C. Brown and C. R. Smoot, ibid., 78, 2176 (1956); (c) A. Streitwieser, Jr., and L. Reif, ibid., 82, 5003 (1960).

(8) R. M. Roberts, E. K. Baylis and G. J. Fonken, ibid., in press.

(9) For the sake of consistency in these papers on alkylbenzenes we prefer to use the names (1,2-dimethylpropyl)-benzene, (1-methylbutyl)-benzene, (1-ethylpropyl) benzene and (2-methylbutyl)-benzene rather than the more commonly used synonyms 2-methyl-3-phenylbutane, 2-phenylbutane, 3-phenylbutane and 2-methyl-1-phenylbutane.

in Table I. As shown by the table, treatment of either *t*-pentyl- or (1,2-dimethylpropyl)-benzene with aluminum chloride gave a mixture of all three of these isomers (expt. 1–10) and none of the other five isomers. Neopentylbenzene was much more stable, but gave a trace of rearrangement to (1,2-dimethylpropyl)-benzene after extended catalyst treatment (expt. 11, 12). *t*-Pentylbenzene is rapidly isomerized to (1,2-dimethylpropyl)-benzene and the latter is more slowly isomerized to neopentylbenzene. Thus, depending on the temperature and/or length of treatment with catalyst, either (1,2-dimethylpropyl)- or neopentylbenzene may be found as the major rearrangement product of *t*-pentylbenzene (*e.g.*, expt. 1, 2, 6). Almost the same mixture of isomers was produced by 24-hr. treatment of *t*-pentyl- and (1,2-dimethylpropyl)-benzene (*e.g.*, expt. 6, 10). Heating with aluminum chloride at 100° without solvent for one hour was equivalent to heating in benzene solution at 80° for 24 hr. (expt. 1, 6). De-activation of the catalyst toward rearrangement of the type observed with propylbenzene[10] was demonstrated by the greater effect produced by expt. 5 and 8 than by expt. 6 (or 7).

In Table II are summarized results of experiments with (1-methylbutyl)-, (1-ethylpropyl)- and (2-methylbutyl)-benzene.[9] These three isomers comprise a second trio of alkylbenzenes which are interconverted by aluminum chloride without observable production of any of the other five isomers. (1-Methylbutyl)- and (1-ethylpropyl)-benzene are rapidly interconverted (expt. 1, 6); (2-methylbutyl)-benzene is formed more slowly from both of these isomers. Approximately the same mixture of isomers was produced by treatment of either (1-methylbutyl)- or (1-ethylpropyl)-benzene with aluminum chloride in benzene solution at 80° for one-half hour or longer. (2-Methylbutyl)-benzene was more stable toward rearrangement than the other two isomers, but less stable than neopentylbenzene. Treating a partially isomerized mixture with fresh catalyst had a much smaller effect in this system than in the case of the first three isomers.

Isopentylbenzene was reported by Nenitzescu[5] to undergo no rearrangement when heated with aluminum chloride in benzene solution for 24 hr., on the basis of the identity of the bis-acetylamino derivative prepared from recovered alkylbenzene. We found no evidence of other pentylbenzene isomers produced when isopentylbenzene was heated with aluminum chloride at 100° for three hours and the recovered hydrocarbon was analyzed by vapor phase chromatography.[11] When *n*-pentylbenzene was treated similarly, the recovered pentylbenzene was found to be 91% *n*-pentyl- and 9% isopentylbenzene.[11]

Discussion

The interconversions of the first trio of pentylbenzene isomers can be explained plausibly in terms of the mechanism of Fig. 1. The route from *t*-pentylbenzene (I) to (1,2-dimethylpropyl)-benzene (V) is very similar to that proposed by Schmerling and co-workers[4,12] and the over-all scheme consolidates some of the steps outlined by Nenitzescu.[5] The dashed arrows indicate that there may be a direct conversion of phenonium ion II to carbonium ions IV and VI, analogous to steps proposed for the propylbenzene rearrangement.[13]

(10) R. M. Roberts and J. E. Douglass, *Chem. Ind.* (London), 1557 (1958); *J. Org. Chem.*, in press.

(11) These experiments were carried out by Dr. E. K. Baylis.[8]

(12) L. Schmerling, R. W. Welch and J. P. Luvisi, *J. Am. Chem. Soc.*, **79**, 2636 (1957).

(13) J. E. Douglass and R. M. Roberts, *Chem. Ind.* (London), 926 (1959); *J. Org. Chem.*, in press.
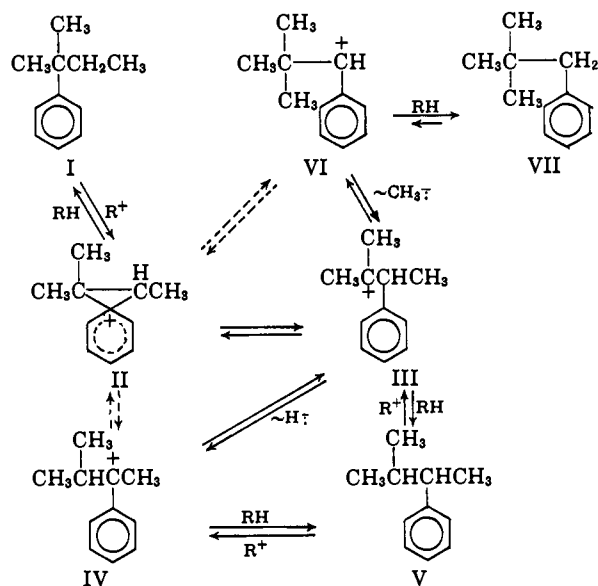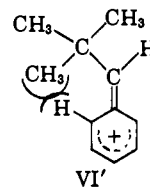
Figure 1.

The rapid rate of formation of V from I and the much slower rate of formation of VII from either I or V may be explained in terms of the potential energy of the intermediates IV and VI. Not only is VI a secondary carbonium ion whereas IV is tertiary and may be stabilized more by the hyperconjugative effect, but also VI is probably destabilized by a steric effect, since the *t*-butyl group causes severe steric inhibition of resonance in structure VI′.[14]

VI′

Since neopentylbenzene (VII) is much more stable toward any rearrangement than either *t*-pentylbenzene (V) or (1,2-dimethylpropyl)-benzene, another factor must be involved. We suggest that this is steric hindrance to abstraction of a hydride ion from neopentylbenzene. There are no β-hydrogens, the γ-hydrogens are all primary, and the two α-hydrogens are shielded by a *t*-butyl group. This will be discussed further below.

The interconversion of the second trio of pentylbenzene isomers probably occurs *via* the intermediate phenonium ion IX (Fig. 2).

An interesting difference in the behavior of the two trios of isomers becomes apparent upon study of Tables I and II. After extended heating with aluminum chloride, *t*-pentyl- and (1,2-dimethylpropyl)-benzene disappear and neopentylbenzene remains (expt. 9, Table I); the members of the second trio seem to be more evenly matched in stability. This is largely owing to the presence of both the least stable (*t*-pentyl) and most stable (neopentyl) isomers among the first trio.

Relationship between Structure and Susceptibility to Internal Rearrangement of Alkylbenzenes.—We have now studied the behavior of all of the alkylbenzenes having from two to five carbon atoms in the side chain in reaction with aluminum chloride, and we should like to draw some generalizations, in spite of the fact that

(14) G. Baddeley, J. Chadwick and H. T. Taylor, *J. Chem. Soc.*, 2405 (1954); T. C. Van Hoek, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **77**, 559 (1958).
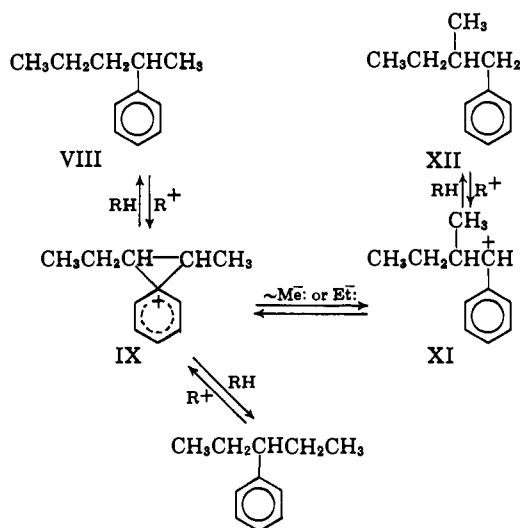

$CH_3CH_2CH_2CHCH_3$ (VIII) with phenyl

$CH_3CH_2CHCH_2$ with CH_3 (XII)

VIII

RH ‖ R⁺

$CH_3CH_2CH—CHCH_3$ (IX, with phenyl, +)

~Me⁻ or Et⁻

CH_3CH_2CHCH with CH_3 (XI)

IX   XI

RH / R⁺

$CH_3CH_2CHCH_2CH_3$

Figure 2.

data are still limited. All of these alkylbenzenes fall into two rather distinct groups with respect to suscepti-bility toward internal rearrangement of side chains; (1) those which undergo rearrangement readily: *n*-propyl-, isobutyl-, *sec*-butyl-, *t*-pentyl-, (1,2-dimethyl-propyl)-, (1-methylbutyl)- and (1-ethylpropyl)-ben-zene; (2) those which do not undergo rearrangement readily: ethyl-, isopropyl-, *n*-butyl-, *t*-butyl-, *n*-pentyl-, isopentyl-, neopentyl- and (2-methylbutyl)-benzene.

It may be noted that three of the latter group have only primary β-hydrogens (ethyl-, isopropyl- and *t*-butylbenzene) and a fourth has no β-hydrogens (neo-pentylbenzene). Examination of the mechanisms sug-gested for rearrangements of pentylbenzenes in this paper and for propyl- and butylbenzenes[13] reveals that lability of β-hydrogens in the form of hydride ions is essential to some of the rearrangement steps. The ex-pected order of ease of removal of hydride ions from hydrocarbons is primary < secondary < tertiary, which, considering the β-hydrogens, is in accord with the experimentally observed order of ease of rearrange-ment of ethylbenzene < *n*-propylbenzene < isobutyl-benzene.

The remaining members of the second (rearrange-ment-stable) group are all *primary* alkylbenzenes. Any rearrangement of one of these which may occur by a mechanism analogous to those of Fig. 1 and 2 would entail a primary carbonium ion intermediate, rather than a secondary or tertiary ion which would result from one of the compounds in the first group (with the exception of *n*-propyl- and isobutylbenzene, which are discussed below). For example, isotopic rearrange-ment of *n*-butylbenzene might be formulated as in Fig. 3. Although we may envision that the shift of the ethyl group may be concerted with that of the phenyl (an analogy to the implications of the dashed arrows in Fig. 1), the transition state would still partake to some extent of primary carbonium ion character, and would be expected to be of higher energy than a transition state related to a secondary or tertiary car-bonium ion.

Thus, a fairly consistent explanation for the dif-ference in stability of the two groups of alkylbenzenes toward rearrangement by aluminum chloride can be given in terms of two factors: (a) lability of β-hydro-gens and (b) potential energy of the intermediate or transition state, *except for the behavior of n-propyl-and isobutylbenzene*, which do rearrange—the latter quite readily. We wish to speculate briefly at this
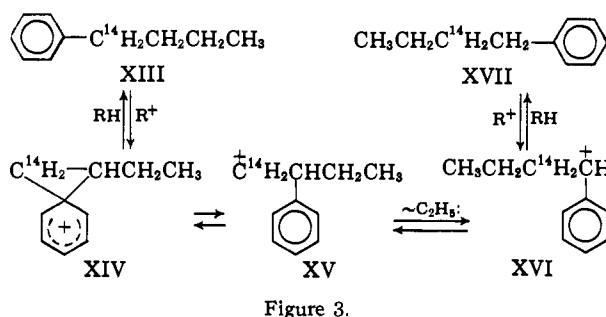
$C^{14}H_2CH_2CH_2CH_3$ (XIII, with phenyl) $CH_3CH_2C^{14}H_2CH_2—$ (XVII, with phenyl)

XIII   XVII

RH ‖ R⁺   R⁺ ‖ RH

$C^{14}H_2—CHCH_2CH_3$ (XIV, +) $\overset{+}{C}^{14}H_2CHCH_2CH_3$ (XV) $CH_3CH_2C^{14}H_2\overset{+}{C}H$ (XVI)

⇌   ~C₂H₅⁻ / ⇌

XIV   XV   XVI

Figure 3.

time about additional effects which may be involved here.

Other things being equal,[15] there may be a steric factor for β-hydride abstraction. A similar steric factor for α-hydride abstraction may be responsible for the unusual stability of neopentylbenzene toward *dispro-portionation*[7a]; according to Streitwieser and Reif,[7c] α-hydrogen abstraction is involved in the rate-deter-mining step of disproportionation of primary alkyl-benzenes. *n*-Butylbenzene and the other higher pri-mary alkylbenzenes of the second group have ethyl or larger alkyl groups attached to the β-carbon atom, while *n*-propyl- and isobutylbenzene have only methyl groups attached to the β-carbon atom. Although we must admit that the difference in stability of *n*-propyl- and *n*-butylbenzene is more than might be expected as a result of the steric effect of methyl compared to ethyl, some support for the theory may be found in a compari-son of the stability of isobutylbenzene and (2-methyl-butyl)-benzene, which have the same structural dif-ference as *n*-propyl- and *n*-butylbenzene, and which show about the same relative stabilities toward rear-rangement.[15]

Another possible factor, which is difficult to assess, is the relative "migrational aptitudes" of alkyl groups. For example, the difference in the ease of rearrange-ment of *n*-propyl- and *n*-butylbenzene might be ascribed to the relative ease of methyl and ethyl anion shifts. Experiments are in progress which it is hoped will shed further light on these uncertainties.

Experimental

Materials.—The eight pentylbenzenes were synthesized by conventional methods. *n*-Pentyl-, isopentyl- and (2-methyl-butyl)-benzene were prepared by Friedel–Crafts acylation fol-lowed by Wolff–Kishner (Huang-Minlon) reduction. (1,2-Di-methylpropyl)-, (1-methylbutyl)- and (1-ethylpropyl)-benzene were prepared by addition of phenylmagnesium bromide to the appropriate ketone, dehydration of the carbinol and low-pressure hydrogenation of the alkene using palladium-on-charcoal catalyst. *t*-Pentylbenzene was prepared by alkylation of benzene with *t*-pentyl alcohol, using ferric chloride catalyst. Neopentylbenzene was prepared by the Grignard coupling reaction between phenyl-magnesium chloride and *t*-butyl alcohol. All of the pentyl-benzenes were checked for purity by infrared spectrophotometry and vapor phase chromatography before use.

Aluminum chloride was B. and A., anhydrous sublimed rea-gent, used as received.

Analytical Procedures.—Qualitative analysis of starting mate-rials and products was made by means of a Baird double beam recording infrared spectrophotometer, model 4–55, using sodium chloride cells. Qualitative and quantitative analysis of starting materials and products was made by means of a Perkin–Elmer vapor phase chromatograph, model 154-B. Two-meter columns A and B supplied by Perkin–Elmer were used in series. The

(15)) (1-Methylbutyl)-benzene, which rearranges readily and which has an ethyl group attached to the β-carbon atom, might be considered to constitute an anomaly to the foregoing theory. However, this is a secondary alkylbenzene, and we may assume that the intermediate ion energy factor is of more importance than the steric factor.

hydrocarbons were diluted with anhydrous ether before injection, and retention times were calculated from the ether peak. The columns were operated at 160°. Separation and identification of the various isomers were demonstrated with authentic samples.

Treatment of Pentylbenzenes with Aluminum Chloride.—In all experiments the pentylbenzene, water-activated aluminum chloride and benzene (in the proportions specified in Tables I and II) were stirred continuously by means of a Teflon-covered magnetic stirrer in a flask equipped with an efficient reflux condenser

protected by a calcium chloride tube. At the conclusion of the reaction, the flask was cooled and water was added cautiously through the condenser. The organic layer was separated, the water layer was washed with three portions of ether, and these were combined with the organic layer. The ether solution was washed with 10% sodium bicarbonate solution and water, dried over calcium chloride, and distilled through an 80-cm. Nichrome spiral column. The pentylbenzene fraction which was analyzed was usually about a 10° cut. Results of the analyses are given in Tables I and II.

The Molecular Structure and Electronic Spectrum of [8]Paracyclophane. A New Synthetic Method for the Preparation of Strained Large Rings[1,2]
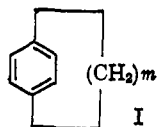
BY NORMAN L. ALLINGER, LESLIE A. FREIBERG, ROBERT B. HERMANN AND MARY ANN MILLER

The synthesis of the [8]paracyclophane ring system by a ring contraction via the photolysis of an α-diazoketone is described. The ultraviolet spectrum of the compound was calculated by the method of Pariser and Parr for various degrees of non-planarity of the aromatic ring. The observed spectrum shows shifts relative to a planar ring which are similar to those calculated, which allows an estimate of the degree of non-planarity of the ring to be made.

Introduction

A number of compounds are known which contain benzene rings that are seriously distorted from their regular hexagonal geometry by steric constraints.[3] Perhaps the simplest case in which an attempt has been made to study systematically a series of compounds in which the distortion of the ring is progressively increased is that of the paracyclophanes (I).[4,5] These compounds are known for $m = 12$,[4] 10,[4] 9[4,6] and 8.[5] When m is 10 or greater, the electronic properties of the aromatic ring are essentially indistinguishable from

$$(CH_2)_m$$

I

those of an open chain analog, but as m is decreased the ultraviolet spectra become abnormal, and models suggest that this abnormality may be associated with the sterically induced non-planarity of the aromatic ring. While [9]paracyclophane has been known for many years,[6] the procedure by which it was prepared did not lead successfully to the next smaller homolog. The objectives of this work were to prepare the [8]-paracyclophane by a general synthetic method developed for the purpose, and to study the properties of the compound, both experimentally and theoretically.

While this work was in progress Cram and Knox reported an elegant synthesis of [8]paracyclophane.[5] The synthetic method used in the present work, while more laborious and less imaginative, does appear to offer the advantage of greater generality.

(1) A preliminary communication of some of the results of this work has been published; *J. Org. Chem.*, **27**, 1490 (1962).

(2) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) For example the [2.2]paracyclophane (C. J. Brown, *J. Chem. Soc.*, 3265 (1953)); and the [2.2]metacyclophane (C. J. Brown, *ibid.*, 3278 (1953)).

(4) D. J. Cram, N. L. Allinger and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954), and earlier papers.
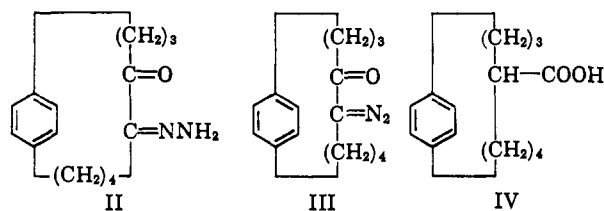
(5) D. J. Cram and G. R. Knox, *ibid.*, **83**, 2204 (1961).

(6) M. F. Bartlett, S. K. Figdor and K. Wiesner, *Can. J. Chem.*, **30**, 291 (1952).

(7) Subsequent to completion of this work, A. T. Blomquist and F. W. Schlaefer, *J. Am. Chem. Soc.*, **83**, 4547 (1961), independently reported the application of this method to the preparation of other medium rings, and mentioned that [8]paracyclophane-4-carboxylic acid had also been obtained by this method by L. Chow.

Results

In general a cyclic structure can be synthesized by ring closure, by ring contraction or by ring expansion. The first of these methods has previously failed to yield [8]paracyclophane, the last looked unpromising and the method of ring contraction was therefore considered. The photolysis of an α-diazoketone is a type of Wolff rearrangement which has recently been shown to yield ring contraction of small rings, even when the product being formed is highly strained.[8] Since 4,5-diketo-[9]paracyclophane (II) monohydrazone was a known compound,[9] the reaction sequence shown was considered worth investigating.

II　　　　　　　III　　　　　　　IV

Compound II (prepared by a straightforward but lengthy sequence[9] which began with γ-phenylbutyric acid and involved an acyloin ring closure as a key step) was oxidized[10] with manganese dioxide and gave III. The latter was not isolated, but was identified in solution by strong absorption bands in the infrared at 2030 and 1640 cm.$^{-1}$. Irradiation of III gave IV (25% yield from II). The structure of IV was established by analysis, by the fact that from the infrared spectrum the compound was a carboxylic acid, and by the analysis of the p-bromophenacyl ester, which showed the compound to be monomeric.

The proton magnetic resonance spectrum of the compound was also informative, and showed resonance at: $-1.70\ \tau$ (COOH), $+2.95\ \tau$ (Ar–H), and a poorly resolved group of peaks at 7.15, 7.62, 8.50 and 9.35 τ. According to the theory of aromatic ring currents,[11]

(8) (a) L. Horner and E. Spietschka, *Ber.*, **88**, 934 (1954); (b) M. P. Cava, R. L. Little and R. D. Napier, *J. Am. Chem. Soc.*, **80**, 2257 (1958); (c) J. Meinwald and P. Gassman, *ibid.*, **82**, 2857 (1960).

(9) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3103 (1958).

(10) H. Morrison, S. Danishefsky and P. Yates, *J. Org. Chem.*, **26**, 2617 (1961).

(11) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, p. 180.