heated to boiling and then allowed to stand for 15 minutes. It was poured into cold dilute hydrochloric acid. The precipitate weighed 18 g. (72%). After several recrystallizations from glacial acetic acid it melted at 188–189° (cor.).

Anal. Calcd. for $C_{19}H_{18}N_2O_4S_2$: C, 56.71; H, 4.48. Found: C, 56.75; H, 4.68.

3-Methyl-*o*-quinonedibenzenesulfonimide.—A mixture of 1 g. of 3-methyl-*o*-phenylenedibenzenesulfonamide and 1.1 g. of lead tetraacetate in 10 ml. of glacial acetic acid was stirred for 30 minutes at 85–90°. The red solution was cooled and the red diimide was filtered off. The yield was 0.3 g. (30%). It was recrystallized from a mixture of equal parts of anhydrous ether and petroleum ether (b.p. 30–60°) by cooling in a Dry Ice-acetone-bath; m.p. 133–135° (cor.) (dec.). It gives a light red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{19}H_{16}N_2O_4S_2$: C, 57.00; H, 4.00. Found: C, 57.29; H, 4.25.

4-Nitro-*o*-phenylenedibenzenesulfonamide.—To a solution of 10 g. of 4-nitro-*o*-phenylenediamine in 75 ml. of pyridine was added 24 g. of benzenesulfonyl chloride. The mixture was allowed to stand for 24 hours at room temperature. It was then poured into 200 ml. of concentrated hydrochloric acid and diluted with an equal volume of water. The brown precipitate was filtered off and stirred into 200 ml. of boiling ethanol and filtered. The residue was extracted with another 100 ml. of hot ethanol leaving 8.2 g. (23%) of product. It was purified by recrystallization from glacial acetic acid; white crystals, m.p. 199° (cor.).

Anal. Calcd. for $C_{18}H_{15}N_3O_6S_2$: C, 49.89; H, 3.46. Found: C, 49.98; H, 3.54.

The filtrates from the ethanol extractions were cooled and the precipitate collected. The yield was 14.5 g. of brown product which is probably the monobenzenesulfonyl derivative.

Attempts to oxidize the 4-nitro-*o*-phenylenedibenzenesulfonamide in acetic acid with lead tetraacetate were unsuccessful. Only starting material was recovered.

URBANA, ILLINOIS RECEIVED JUNE 2, 1951

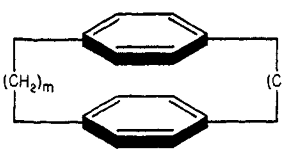
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Macro Rings. I. Preparation and Spectra of the Paracyclophanes

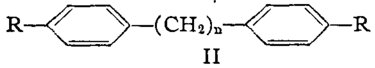
BY DONALD J. CRAM AND H. STEINBERG[1]

A macrocyclic system has been prepared by the use of high dilution techniques in which two benzene rings are joined in the para positions by two and two, two and three, two and four, and three and six carbon bridges. The name, "paracyclophane," is suggested for this class of compound. The ultraviolet and infrared absorption spectra of the cycles are compared to the open chain analogs, and the abnormalities of the cycles are attributed to interstitial resonance effects and to the effects of distortion of the benzene rings from planarity.

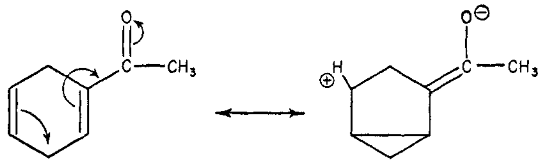
Of particular interest in the field of molecular structure is the system (I) in which two benzene rings are rigidly held in a face to face position by methylene bridges in the para positions. The name, "paracyclophane," is suggested for this class of compound. Such a system offers the unusual opportunity to study the effect of electronic interactions of unsaturated centers in a molecule whose geometry is known and capable of only small variations. When *m* and *n* are small, the proximity of the faces of the benzene rings may result in π-orbital overlap which would be expected to produce a marked change in the ultraviolet absorption spectrum of I as compared to the open chain analogs (II). Such a direct spatial electronic interaction is a probable explanation of the observed shift to longer wave lengths and decrease in intensity of the ultraviolet absorption maximum of 2,5-dihydroacetophenone (III) as compared to 1-acetylcyclohexene.[2,3] Bartlett, *et al.*,[4] have applied an analogous explanation to account for the abnormalities in the ultraviolet absorption spectrum of triptycene.



I



II



III

Should there exist interstitial resonance effects of some sort between the two benzene rings in I,[5] the aromatic properties of this type of compound should be considerably modified. Thus the rates of aromatic substitution of the paracyclophanes as compared to their open chain analogs should be different. With the introduction of groups into one ring the question of the directive and activating (or deactivating) effect on the introduction of groups into the other ring becomes pertinent. A further point of interest in this class of compound lies in the types of molecular asymmetry (due to restricted rotation) that become possible with the successive introduction of functional groups into the benzene rings. Finally, it is hoped that the construction of intramolecular "molecular complexes" (*e.g.*, intramolecular picrate-like salts) will be possible in this system. Thus substitution of electron releasing groups in one ring and electron withdrawing groups in the other should set up strong attractive forces between the aromatic

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(1) Atomic Energy Commission Predoctoral Fellow, 1949–1951.

(2) K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 52 (1946).

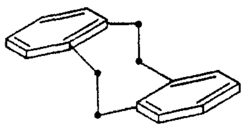
(3) E. A. Braude, E. R. H. Jones, F. Sondheimer and J. B. Toogood, *ibid.*, 607 (1949); see also J. C. Lunt and F. Sondheimer, *ibid.*, 3361 (1950).

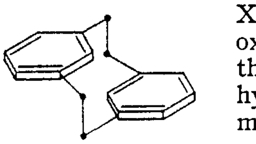
(4) P. D. Bartlett and E. S. Lewis, THIS JOURNAL, **72**, 1005 (1950).

(5) M. J. S. Dewar, *Nature*, **156**, 784 (1945), and *J. Chem. Soc.*, 406 (1946), has discussed the possible existence of π-complexes as intermediate species in intramolecular rearrangements involving aromatic nuclei (such as the benzidene rearrangement). In each case, however, the complex was composed of a cationic and an anionic part rather than two electronically equivalent components. See G. S. Hammond and H. J. Shine, THIS JOURNAL, **72**, 220 (1950).

nuclei, and since the geometry of the paracyclophanes is known, a comparison of the properties of such a system and an analogously constructed intermolecular complex should be instructive. Investigations of the above phenomena are in progress.

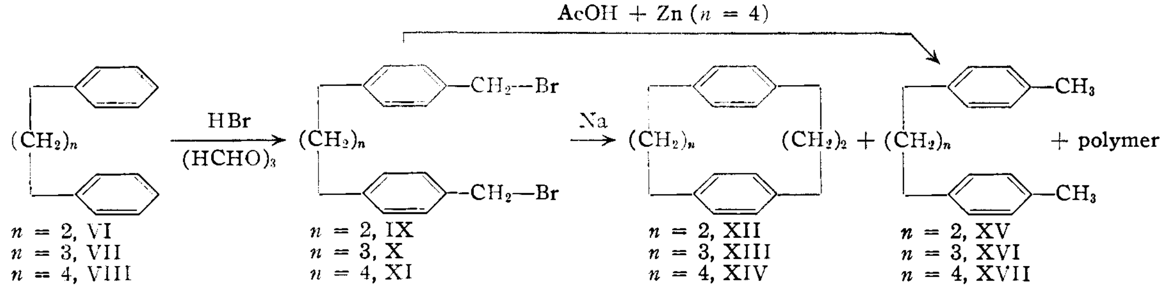
Although an attempt to prepare a paracyclophane has been made in the past,[6] the first compound of this class was reported while this investigation was in progress.[7] A number of compounds which incorporate two benzene rings as part of a large ring structure are known; however, most of them contain ether or thioether linkages as part of their ring system.[8] A number of rings have also been prepared which can be regarded as ortho and meta isomers of I with $m = n = 2$ (IV and V).[9,10]


IV


V

The literature contains numerous examples of one benzene ring incorporated in a macro ring. Notable among those containing para bridges are the cyclic diesters of Spanagel and Carothers,[11] the cyclic ketone of Fourneau[12] and Ruzicka,[13] the cyclic ethers of Luttringhaus[14] and Ziegler,[15] and the cyclic ketol of Wiesner.[16]

This paper deals with the preparation of four of the paracyclophanes (formula I: $m = 2, n = 2$; $m = 2, n = 3$; $m = 2, n = 4$; $m = 3, n = 6$), and with a study of their ultraviolet and infrared spectra.



Results

The cycles containing one two-membered methylene bridge were prepared by intramolecular Wurtz reactions with the dibromides IX, X and XI, the reduction and linear polymerization of the bromides occurring as a side reaction. The dibromides were in turn prepared by the bromomethylation of the corresponding hydrocarbons[17] which were synthesized in each case by a separate method. Thus VI was prepared by the action of magnesium on benzyl chloride, VII by the reduction of dibenzylketone with hydrazine,[18] and VIII by the catalytic reduction of 1,4-diphenylbutadiene.[34c] Compound XI was also reduced to the hydrocarbon XVII with zinc and acetic acid after the method of Reichstein.[4] The bromides IX and X were also prepared by an alternate route (the over-all yield from dibenzyl ketone to X amounted to 46%) in which the hydrocarbons were acetylated to give XVIII and XIX, respectively, which in turn were oxidized; the acidic products were esterified and the esters were reduced with lithium aluminum hydride to give the alcohols XX and XXI. Treatment of these carbinols with phosphorus tribromide gave the bromides IX and X.

Attempts to chloromethylate[19] VII gave only low yields of 1,3-bis-[4-chloromethylphenyl]-propane, whose structure was demonstrated by its reduction with zinc and acetic acid to XVI, according to the method of Reichstein.[6] The ketones XVIII and XIX were reduced with hydrazine[18] to 4,4'-diethyldibenzyl (XXII) and 1,3-bis-(4-ethylphenyl)-propane (XXIII), compounds needed as models for spectral comparisons.

The paracyclophane (XXVII) was prepared by reduction of the corresponding cyclic acyloin (XXV) to the ketone (XXVI) after the method of Stoll,[20] followed by further reduction of XXVI with either hydrazine[18] or zinc and hydrochloric acid[21] to the hydrocarbon (XXVII). The cyclic acyloin was synthesized in good yield by the treatment of the appropriate ester (XXIV) with highly dispersed sodium according to the method of Prelog, *et al.*,[22] and Stoll, *et al.*,[23] and modified by the recent high dilution technique of Cope and Herrick.[24] The acyloin condensation has recently been used to prepare a cycle containing one benzene

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(6) T. Reichstein and R. Oppenauer, *Helv. Chim. Acta*, **16**, 1373 (1933).

(7) C. J. Brown and A. C. Farthing, *Nature*, **164**, 915 (1949).

(8) (a) R. Adams and N. Kornblum, THIS JOURNAL, **63**, 188 (1941); (b) A. Luttringhaus, *Ann.*, **528**, 211 (1937); W. Autenrieth and F. Beuttel, *Ber.*, **42**, 4346, 4357 (1909).

(9) W. Baker, R. Banks, D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 27 (1945); see also A. C. Cope and S. W. Fenton, THIS JOURNAL, **73**, 1668 (1951).

(10) W. Baker, J. F. W. McOmie and J. M. Norman, *Chemistry & Industry*, 77 (1950).

(11) E. W. Spanagel and W. A. Carothers, THIS JOURNAL, **57**, **935** (1935).

(12) E. Fourneau and P. M. Baranger, *Bull. soc. chim.*, **49**, 1161 (1931).

(13) L. Ruzicka, J. B. Buijs and M. Stoll, *Helv. Chim. Acta*, **15**, 1220 (1932).

(14) A. Luttringhaus, *Ann.*, **528**, 185 (1937).

(15) K. Ziegler and A. Luttringhaus, *ibid.*, **511**, 1 (1934).

(16) R. Kelly, D. M. MacDonald and K. Weisner, *Nature*, **166**, 225 (1950).

(17) The procedure is analogous to that developed by J. A. Goodson, *et al.*, *Brit. J. Pharmacol.*, **3**, 62 (1948).

(18) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

(19) See J. N. Ashley, *et al.*, *J. Chem. Soc.*, 103 (1942).

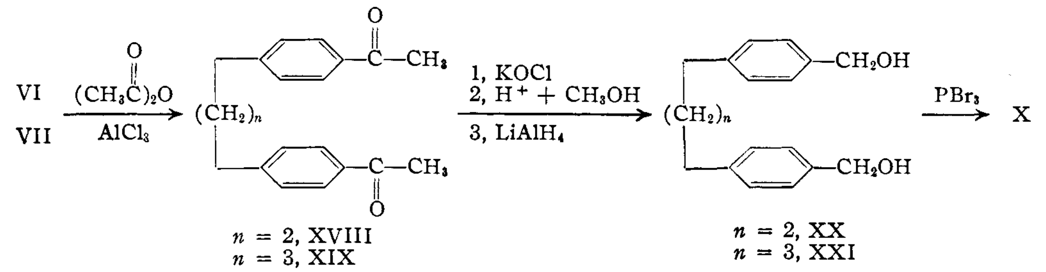
(20) M. Stoll, *Helv. Chim. Acta*, **30**, 1837 (1947).

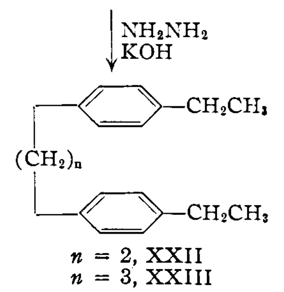
(21) E. L. Martin, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 155.

(22) V. Prelog, L. Frenkiel, M. Kobelt and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

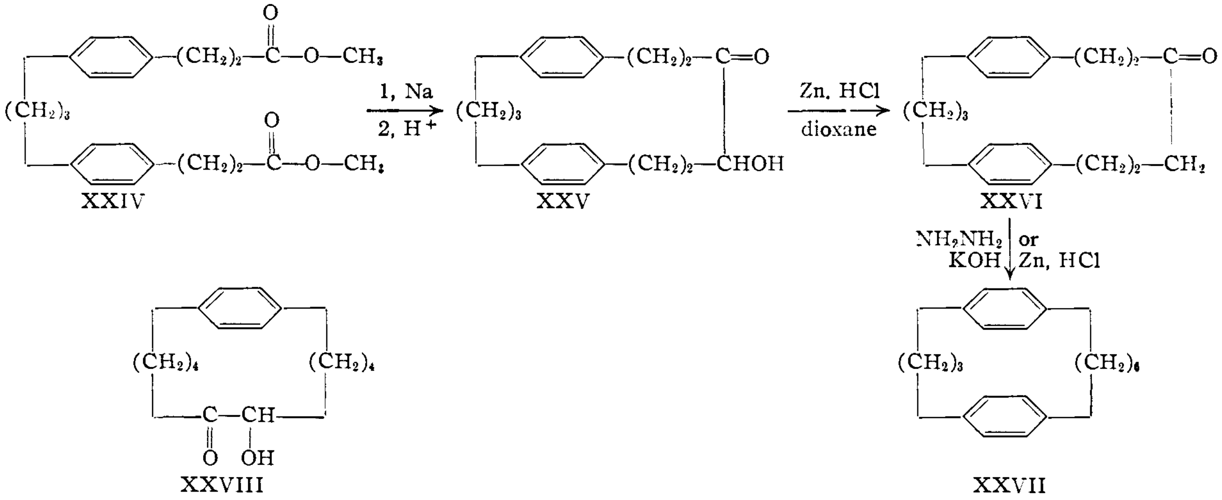
(23) M. Stoll and J. Hulstkamp, *ibid.*, **30**, 1815 (1947); M. Stoll and A. Rouve, *ibid.*, **30**, 1822 (1947).

(24) A. C. Cope and E. C. Herrick, THIS JOURNAL, **72**, 983 (1950).

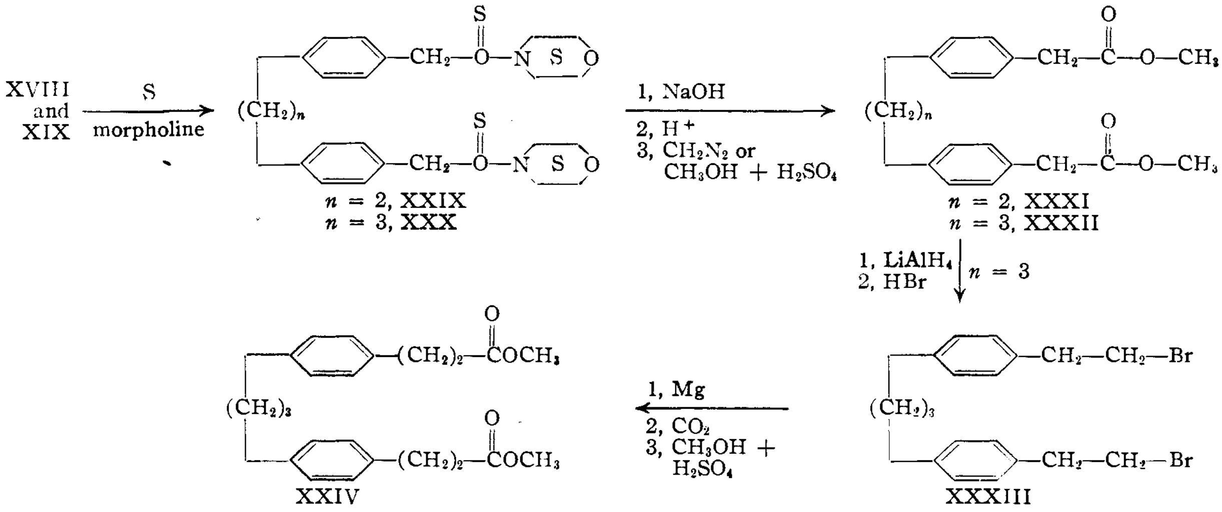




ring tied in the *p*-positions by a large methylene bridge (XXVIII).[16]



The ester XXIV was prepared by two routes from the hydrocarbon VII, one of the sequences being also partially applied to the hydrocarbon VI. Thus the ketones XVIII and XIX were submitted to the modified Willgerodt reaction[25,26] to give the thiomorpholides XXIX and XXX which upon hydrolysis and esterification with either diazomethane or methanol and sulfuric acid produced the esters XXXI and XXXII in good over-all yield. The ester XXXII was reduced with lithium aluminum hydride and the resulting carbinol was treated with hydrobromic acid to give the bromide XXXIII. Carbonation of the Grignard reagent of XXXIII and esterification of the resulting acid gave the desired ester (XXIV). The other path by which XXIV was prepared involved the propionylation of VII to give XXXIV followed by the Schwenk modification of the Willgerodt reaction[25,26] to produce the thiomorpholide XXXV, which



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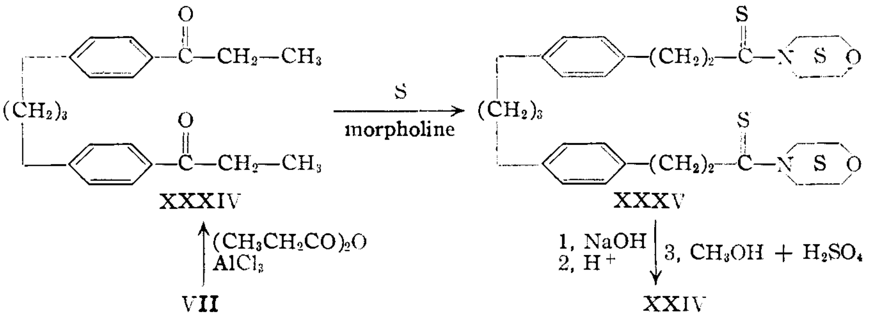
(25) E. Schwenk and E. Block, THIS JOURNAL, **64**, 3051 (1942).

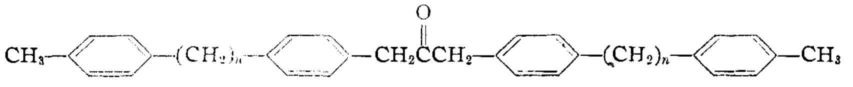
(26) E. Schwenk and D. Papa, *J. Org. Chem.*, 11, 798 (1946).



upon hydrolysis and esterification gave XXIV.

That the acetylation, propionylation, chloromethylation and bromomethylation of VII (and by analogy of VI and VIII) always took place in the para-positions of the benzene rings was shown by the series of interlocking syntheses and by the oxidation of XXXII to terephthalic acid in good yield.

When the esters XXXI and XXXII were submitted to the acyloin condensation under the same conditions found to be so successful with XXIV, complex mixtures of products were formed which gave a purple color with ferric chloride, a fact indicative of the presence of β-ketoesters formed by Claisen or Dieckmann condensations.[27] When XXXI was the starting material there was isolated the acid derived from the starting ester, 4,4′-dimethyldibenzyl (XV) and an anomalous compound, XXXVI. When XXXII was the starting material the products were the starting ester, the acid derived from the starting ester, the decarboxylated product, 1,3-bis-(p-tolyl)-propane (XVI), and two anomalous products XXXVII (mol. wt. 436) and XXXVIII (mol. wt. 254). Compounds XXVI and XXXVII might have the structures shown (the substances produced by a Claisen condensation followed by hydrolysis and decarboxylation of the three remaining ester groups).[28] The failure of the acyloin condensations of XXXI and XXXII is attributed to the activated α-hydrogens which preferentially react in Claisen-type condensation reactions.



n = 2, XXXVI
n = 3, XXXVII

Figure 1 records the ultraviolet absorption spectra of the paracyclophanes, XII, XIII and XIV as well as the open chain model XV. Figure 2 records the ultraviolet absorption spectra of the acyloin, XXV, and the paracyclophane XXVII, as well as the open chain model compound, XXIII. Figure 3 records the infrared absorption spectra of the four paracyclophanes as well as of the three open chain model compounds, 1,4-diethylbenzene, XV and XXIII. Table I contains the methods of preparation, physical properties and analyses of the starting materials as well as references to the experimental part for the procedures employed in the preparation of the substances. Table II records the physical properties and analyses of the products of the cyclization reactions.

Discussion

The use of the Wurtz reaction to close large rings might represent the second application of the principle of high dilution occurring at a metal–organic solvent interface,[29] although the reaction might also be a two-stage process, the formation of the metal-alkyl being heterogeneous, and the formation of the cycle being a homogeneous nucleophilic displacement of halide ion by a carbanion. Unfortunately in this application of the Wurtz synthesis utilizing benzyl halides, side reactions such as reduction account for a considerable amount of starting material. The yields of paracyclophanes unexpectedly did not vary markedly with the number of methylene groups intervening between the two benzene rings in the starting material, and although XII and XIII are considerably more strained than XIV, the last substance was produced in lower yield. An investigation of the closing of rings through this reaction in which the halogen atoms are not alpha to a benzene ring is in progress.

The absorption spectra (Figs. 1 and 2) of the paracyclophanes as compared to their open chain models (there is no difference in spectra among the models) indicate that the ordinary resonance of the benzene rings in the cycles with which the absorption of light is associated has been modified. An examination of molecular models of the cycles (see Fig. 4) suggests two possible explanations for this phenomenon: the benzene rings, particularly in XII and XIII and less in XIV may be distorted from planarity; the proximity of the two rings held directly over one another in space and pressed well within their van der Waals radii (at least in the three cycles of lowest molecular weight) gives rise to an inter-benzenoid overlap of the π-orbitals that are thrust out perpendicularly from each benzene ring. That the aromatic rings are not planar in XII has been proven by an analysis of the crystal structure by the X-ray diffraction method.[30] A cross-section of the scale model of this molecule (A) reveals that the benzene rings are puckered, the carbon atoms of the rings bearing the methylene bridges being bent out of the plane of the other sets of four carbon atoms by 0.13 Å., the angle of distortion amounting to about 11°. The inter-benzenoid distance between the carbons carrying the bridges

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[27] J. M. Snell and S. M. McElvain, THIS JOURNAL, **53**, 750 (1931), demonstrated that in several linear acyloin reactions, Claisen-condensation products were produced that gave a positive ferric chloride test.

[28] For other anomalous products of acyloin condensations see N. J. Leonard and P. M. Mader, *ibid.*, **72**, 5388 (1950).

[29] Hansley, U. S. Patent 2,228,268 [*C. A.*, **35**, 2534 (1941)], reported the first example of this technique which was applied to the acyloin condensation of esters of long dicarboxylic acids.

[30] The crystal structure of this compound, its method of preparation (high temperature pyrolysis of p-xylene), its melting point and solubility characteristics were reported while the present investigation was in progress (ref. 7). The properties of the two preparations of the compound correspond well with one another.

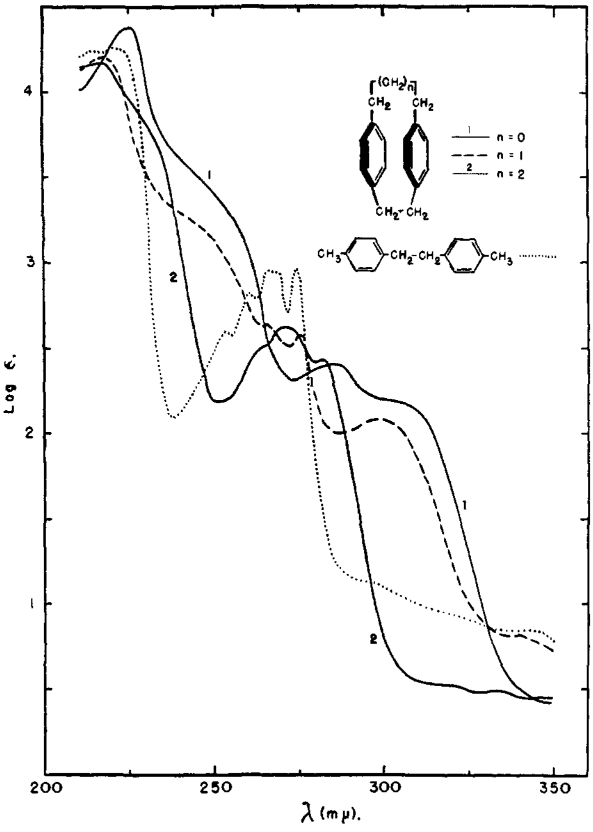


Fig. 1.—Ultraviolet absorption spectra of *p,p'*-dimethylene-1,2-diphenylethane, *p,p'*-trimethylene-1,2-diphenylethane, *p,p'*-tetramethylene-1,2-diphenylethane and 4,4'-dimethyldibenzyl taken in cyclohexane with a Beckman quartz spectrophotometer (model DU).

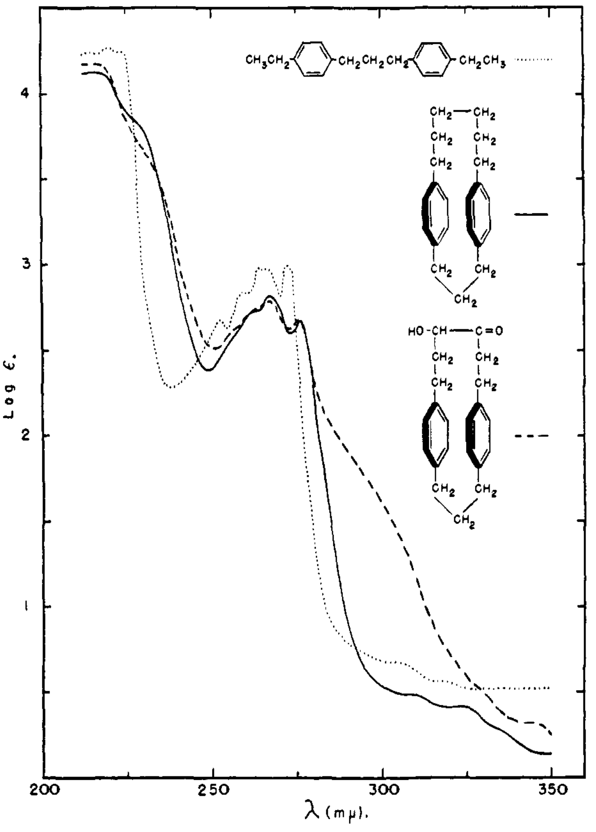
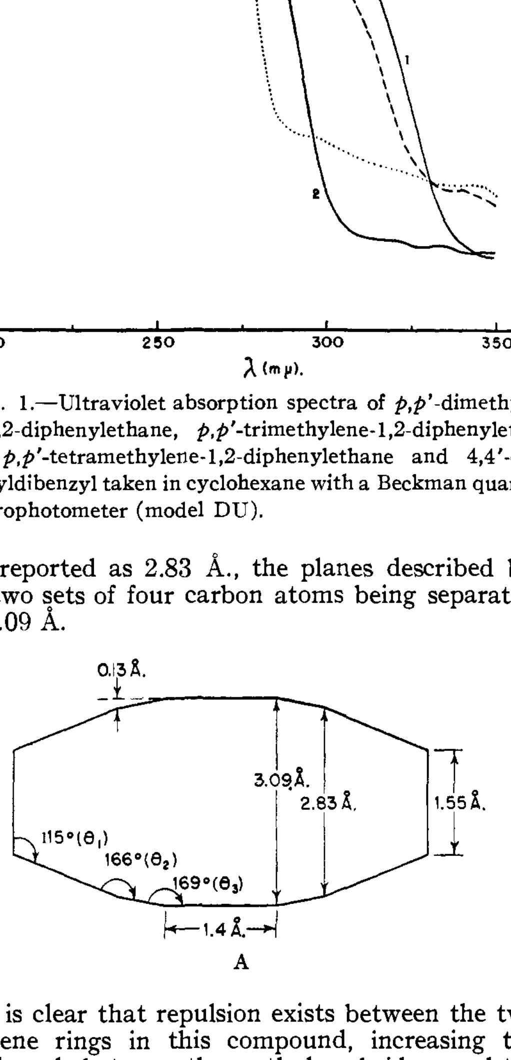


Fig. 2.—Ultraviolet absorption spectra of 1,3-bis-(4-ethylphenyl)-propane, *p,p'*-hexamethylene-1,3-diphenylpropane and 3-keto-4-hydroxy-*p,p'*-hexamethylene-1,3-diphenylpropane taken in cyclohexane with a Beckman quartz spectrophotometer (model DU).

was reported as 2.83 Å., the planes described by the two sets of four carbon atoms being separated by 3.09 Å.



A

It is clear that repulsion exists between the two benzene rings in this compound, increasing the bond angle between the methylene bridges and the benzene rings (θ_1) from what would otherwise be 90 to 115°,[31] thus leaving only 6° of strain in this angle. The remaining strain incurred by repulsion between the two rings is distributed almost equally between the other bond angles θ_2 and θ_3. These configurations illustrate the principle that the distribution of strain between several bond angles is more economical in terms of energy than concentrating the same number of degrees of strain in only one bond angle.

The molecular model of XXVII (Fig. 4) reveals the substance to be completely strain free, and the spectrum (ultraviolet) of this substance closely resembles that of the open chain model compounds except for the appearance of a shoulder in the region of 220 to 250 mμ, and a slight modification of the fine structure in the region of 270 mμ. Since the benzene rings of XXVII are probably planar, and since the only difference between XXVII and the open chain models is the proximity of the aromatic nuclei held in a semi-rigid configuration with respect to each other, the absorption band at 225 mμ, log *E* 3.90, (this band appears as a shoulder due to the overlap of this and the stronger band at 217 mμ, log *E* 4.13) is attributable to trans-spacial overlap of the π-orbitals of the two benzene rings. This shoulder is more distinct and has moved to longer wave lengths in XII, XIII and XIV (244 mμ, log *E* 3.52; 243 mμ, log *E* 3.24; and 226 mμ, log *E* 3.94, respectively), the wave length increasing with the decrease in distance between the benzene rings; hence the energy of the transition in question decreases with the increase in the amount of inter-ring bonding. The bands found at 302 mμ (log *E* 2.19) and 299 mμ (log *E* 2.09) in XII and XIII, respectively, and entirely missing in XIV and

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[31] That this angle is greater than the normal bond angle of 109° is taken as evidence that repulsive forces are thrusting the rings away from one another.

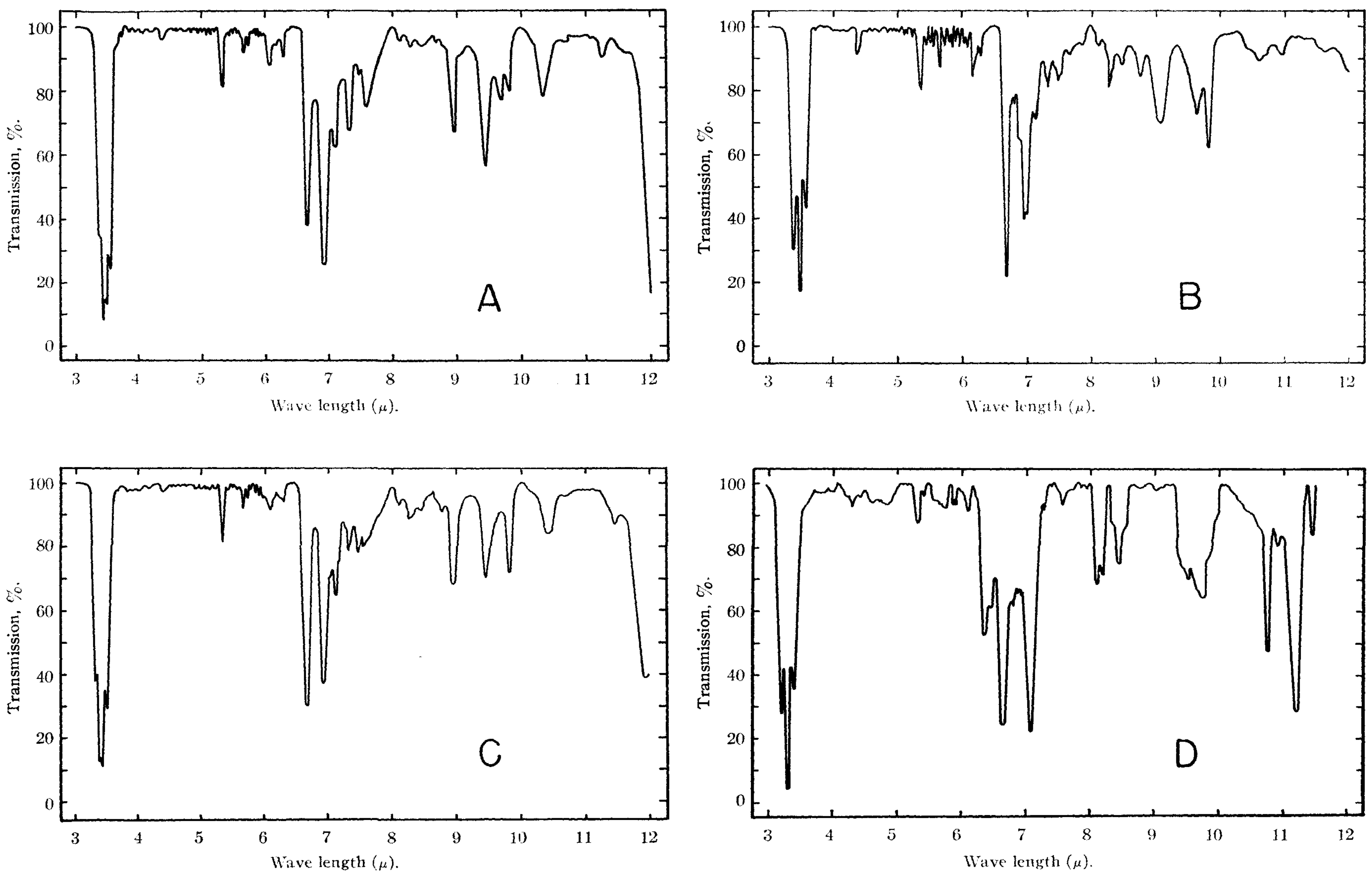
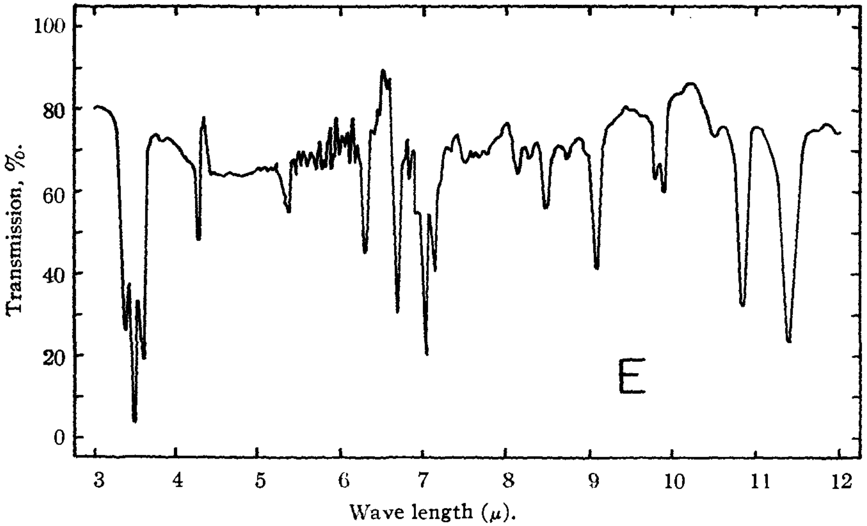
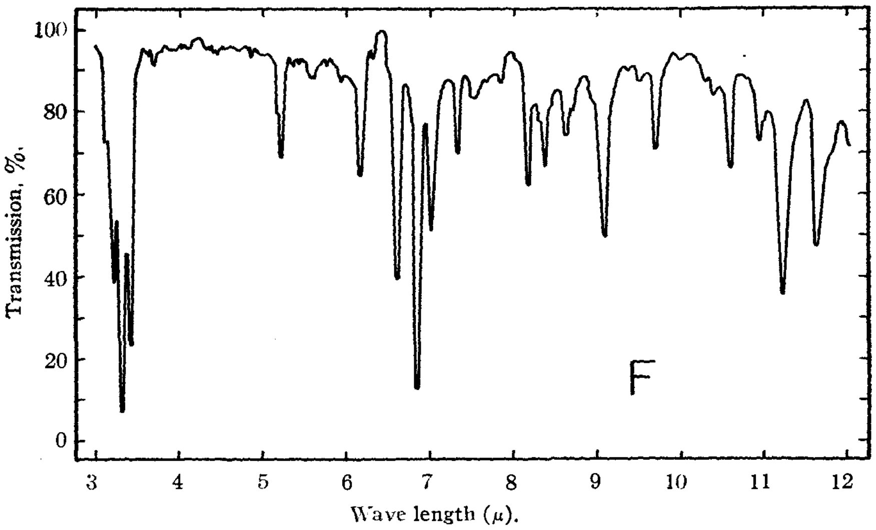

Transmission, %.
100
80
60
40
20
0
3
4
5
6
7
8
9
10
11
12
Wave length (μ).
A
B
C
D

Fig. 3.





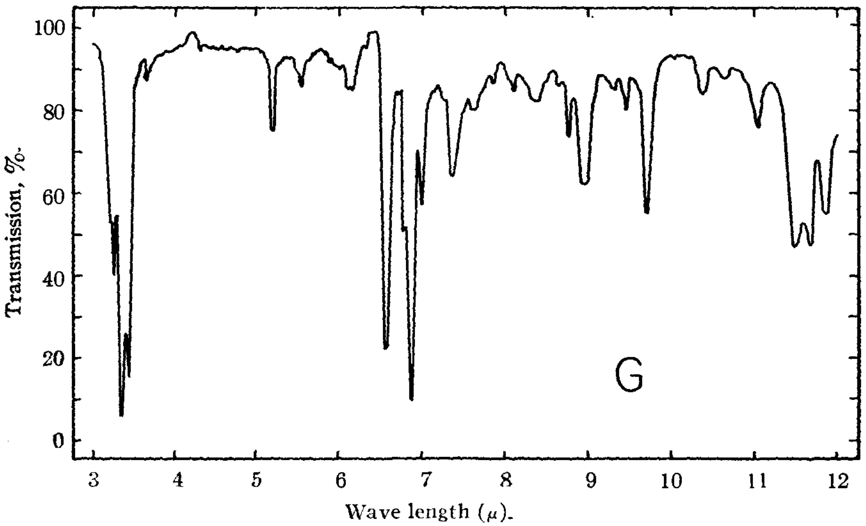


Fig. 3.—Infrared absorption spectra of 1,4-diethylbenzene (A), 4,4'-dimethyldibenzyl (B), 1,3-bis-(4-ethylphenyl)-propane (C), *p,p'*-dimethylene-1,2-diphenylethane (D), *p,p'*-trimethylene-1,2-diphenylethane (E), *p,p'*-tetramethylene-1,2-diphenylethane (F), and *p,p'*-hexamethylene-1,3-diphenylpropane (G). Spectra A, B, C and E determined with a Beckman model IR2T infrared spectrophotometer in carbon tetrachloride solution (A, 10.2 wt. %; B, 10.3 wt. %; C, 9.95 wt. %; E, 11.1 wt. %) with 0.1 mm. rock salt cells. Spectrum D determined with a Beckman model IR2 infrared spectrophotometer in chloroform solution (1.17 wt. %) with 1 mm. rock salt cell. Spectra F and G determined with a Baird Infrared Spectrophotometer in carbontetrachloride solution (F, 11.2 wt. %; G, 11.0 wt. %) with 0.1 mm. rock salt cells.

TABLE I

METHODS OF PREPARATION AND PHYSICAL PROPERTIES AND ANALYSES OF INTERMEDIATES AND DERIVATIVES OF INTERMEDIATES IN THE PREPARATION OF THE PARACYCLOPHANES

DB = dibenzyl, P = propane, Ph = phenyl, C = carbomethoxy, M = methyl, T = thioacetmorpholide

Starting material		Product[a]		Prd.	Yield, %	M.p., °C.	Crys. solv.	Cryst.[b] form	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Neut. equiv.[c] Calcd.	Neut. equiv. Found
DB Ketone	....	1,3-DiPhP	VII	A	90	B.p. 165–166 (0.3 mm.)[d]	....	...	....	...	...	..	..	...	...
1,3-DiPhP	VII	1,3-Bis-(4-acetylPh)-P	XIX	B	77	85–86.5	Meth.	n	$C_{19}H_{20}O_2$	81.39	81.10	7.19	7.44	...	...
1,3-Bis-(4-acetylPh)-P	XIX	1,3-Bis-(4-carboxyPh)-P	....	C	95	304–307	Gl. acet.	p	$C_{17}H_{16}O_4$	71.81	71.51	5.67	5.98	142	138
1,3-Bis-(4-carboxyPh)-P	....	1,3-Bis-(4-CPh)-P	....	D	77	92–93	Meth.	n	$C_{19}H_{20}O_4$	73.06	72.92	6.45	6.65	...	...
1,3-Bis-(4-CPh)-P	....	1,3-Bis-(4-hydroxyMPh)-P	XXII	E	94	124–125.4[e]	Benz.	n	$C_{17}H_{20}O_2$	79.65	79.47	7.86	8.08	...	...
1,3-Bis-(4-hydroxyMPh)-P	XXII	1,3-Bis-(4-bromoMPh)-P	X	F	95	131–132.5	Pet. ether	n	$C_{17}H_{18}Br_2$	53.43	53.45	4.75	4.88	...	...
DB Ketone	....	1,3-Bis-(4-bromoMPh)-P	X	G	28	130–132	Pet. ether	n	....	...	...	..	..	...	...
1,3-Bis-(4-acetylPh)-P	XIX	1,3-Bis-(4-TPh)-P	XXX	H	100	114–116	Alc.	lyr	$C_{27}H_{34}O_2N_2S_2$	67.18	67.10	7.10	7.34	...	...
1,3-Bis-(4-TPh)-P	XXX	1,3-Bis-(4-carboxyMPh)-P	....	I	74	206–208	Meth.	p	$C_{19}H_{20}O_4$	73.05	73.16	6.45	6.93	156	159
1,3-Bis-(4-carboxyMPh)-P	....	1,3-Bis-(4-CMPh)-P	XXXII	J	77	53–54	Pet. ether	pl	$C_{21}H_{24}O_4$	74.09	73.99	7.11	7.22	...	...
1,3-Bis-(4-carboxyMPh)-P	....	1,3-Bis-(4-CMPh)-P	XXXII	K	67	53–54	Pet. ether	pl	....	...	...	..	..	...	...
1,3-Bis-(4-CMPh)-P	XXXII	1,3-Bis-(4-[β-hydroxyethyl]-Ph)-P	....	E[f]	96	108.5–110	Benz.	pl	$C_{19}H_{24}O_2$	80.23	79.90	8.50	8.73	...	...
1,3-Bis-(4-[β-hydroxyethyl]-Ph)-P	....	1,3-Bis-(4-[β-bromoethyl]-Ph)-P	XXXIII	..	78	47.5–49	Pet. ether	n	$C_{19}H_{22}Br_2$	55.63	55.70	5.41	5.54	...	...
1,3-DiPhP	VII	1,3-Bis-(4-propionylPh)-P	XXXIV	B[g]	60	42.4–44	Pet. ether	pr	$C_{21}H_{24}O_2$	81.78	82.05	7.84	8.13	...	...
1,3-Bis-(4-propionylPh)-P	XXXIV	1,3-Bis-(4-thiopropionmorpholidePh)-P	XXXV	H[h]	Not isolated		....	...	....	...	...	..	..	...	...
1,3-Bis-(4-thiopropionmorpholidePh)-P	XXXV	1,3-Bis-(4-[β-carboxyethyl]-Ph)-P	....	I[i]	51[j]	185–186	Gl. acet.	pl	$C_{21}H_{24}O_4$	74.09	74.00	7.11	7.17	170	173
1,3-Bis-(4-[β-bromoethyl]-Ph)-P	XXXIII	1,3-Bis-[4-[β-carboxyethyl]-Ph)-P	....	..	74	140–162	....	...	....	...	...	..	..	...	...
1,3-Bis-(4-[β-carboxyethyl]-Ph)-P	....	1,3-Bis-(4-[β-Cethyl]-Ph)-P	XXIV	J[k]	75	123.5–125	Benz. Pet. ether	pl	$C_{23}H_{28}O_4$	74.97	74.91	7.66	7.88	...	...
1,3-Bis-(4-[β-carboxyethyl]-Ph)-P	....	1,3-Bis-(4-[β-Cethyl]-Ph)-P	XXIV	K	83	93–105	....	...	....	...	...	..	..	...	...
1,3-DiPhP	VII	1,3-Bis-(4-chloroMPh)-P	....	..	7	103–106[l]	CS_2	p	....	...	...	..	..	...	...
1,3-Bis-(4-chloroMPh)-P	....	1,3-Bis-(*p*-tolyl)-P	XVI	L	13	34–35[m]	Alc.	pl	$C_{17}H_{20}$	91.01	90.54	8.99	9.30	...	...
1,3-Bis-(4-acetylPh)-P	XIX	1,3-Bis-(4-ethylPh)-P	XXIII	A	59	33.5–34	Alc.	pl	$C_{19}H_{24}$	90.41	90.20	9.59	9.85	...	...
DB	VI	4,4'-DiacetylDB	XVIII	B	62	160–164[n]	Alc.	pl	....	...	...	..	..	...	...
4,4'-DiacetylDB	XVIII	4,4'-DicarboxyDB	....	C	92	>300[o]	Insol.	p	....	...	...	..	..	...	...
4,4'-DicarboxyDB	....	4,4'-DiCDB	....	D	54	115–119[p]	Meth.	pl	....	...	...	..	..	...	...
4,4'-DiCDB	....	4,4'-DihydroxyMDB	XX	E	51	157–159[q]	Xyl.	n	....	...	...	..	..	...	...
DB	VI	4,4'-DibromoMDB[r]	IX	G	27	129–131	Pet. ether	th.pl.	$C_{16}H_{16}Br_2$	52.20	51.99	4.38	4.56	...	...
4,4'-DihydroxyMDB	XX	4,4'-DibromoMDB	IX	F	46	126–129	Pet. ether	pl	....	...	...	..	..	...	...
4,4'-DiacetylDB	XVIII	4,4'-DiTDB	XXIX	H	100	195–196.5	Acet.	n	$C_{26}H_{32}O_2N_2S_2$	66.63	66.76	6.87	7.14	...	...
4,4'-DiTDB	XXIX	4,4'-DicarboxyMDB[s]	....	I	51	232–233	Alc.	gr	$C_{18}H_{18}O_4$	72.47	71.89	6.08	6.15	149	153
4,4'-DicarboxyMDB	....	4,4'-DiCMDB	XXXI	D	55	88–89	Meth.	n	$C_{20}H_{22}O_4$	73.59	73.56	6.79	6.84	...	...
4,4'-DicarboxyMDB	....	4,4'-DiCMBD	XXXI	K	75	88–89	Meth.	n	....	...	...	..	..	...	...
4,4'-DiacetylDB	XVIII	4,4'-DiethylDB	XXII	A[t]	34	69.5–71[u]	Alc.	pl.	$C_{18}H_{22}$	90.69	90.45	9.31	9.39	...	...
Phenylacetic acid cinnamaldehyde	....	1,4-DiPh-1,3-butadiene	...	..	32	152–153.5	Benz.-alc.	pl.	....	...	...	..	...	...	...
				..	80	51.5–53[v]	Alc.	n	....	...	...	..	..	...	...
1,4-DiPh-1,3-butadiene	....	1,4-DiPhbutane	VIII	G	26	123–125	Benz.-Pet. ether	n	$C_{18}H_{20}Br_2$	54.57	54.49	5.09	5.08	...	...
1,4-DiPhbutane	VIII	1,4-Bis-(4-bromoMPh)-butane	XI												
1,4-Bis-(4-bromoMPh)-butane	XI	1,4-Bis-(*p*-tolyl)-butane	XVII	L	16	74–75	Alc.	pl	....	...	...	..	..	...	...
Ethylbenzene	....	*p*-Ethylacetophenone	....	B[n]	27	B.p. 236–239[x]	....	...	....	...	...	..	..	...	...
p-Ethylacetophenone	....	1,4-Diethylbenzene[y]	....	A	83	B.p. 183.5–184	(n^{20}_{D} 1.4948)		....	...	...	..	..	...	...

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[a] In all cases where two different methods of preparation of the same compound are reported, admixtures of samples produced no depression of melting point. [b] n = needles, p = powder, r = rosettes, l = light, y = yellow, pl = plates, pr = prisms, th = thick, gr = granules. [c] Ref. 37, p. 116. [d] F. Straus and H. Grindel, *Ann.*, **439**, 276 (1924), reported a b.p. of 163–167° (21 mm.) for XIX. [e] Ashley, *et al.*, (ref. 19) reported a m.p. of 118–122° for XXI prepared by a different method. [f] Ether solution of product washed with water. [g] XXXIV was distilled, 245° (0.3 mm.), before it was recrystallized. [h] Reaction mixture poured into water instead of ethanol and XXXV extracted with chloroform. [i] Compound purified for analysis by hydrolysis of the methyl ester. [j] Yield based on XXXIV as the starting material. [k] Residue taken up in benzene instead of ether. [l] Ashley, *et al.*, (ref. 19)

TABLE I (*Continued*)

reported the same m.p. for this compound. [m] J. F. Sirks, *Rec. trav. chim.*, **65**, 850 (1946), reported a m.p. of 31° for XVI prepared by a different method. [n] W. C. J. Ross, *J. Chem. Soc.*, 536 (1945), reported a m.p. of 164–166° for XVIII prepared by a different method. [o] C. Fischer and R. Wolffenstein, *Ber.*, **37** 3215 (1904), reported a m.p. of >320° for this compound prepared by a different method. [p] C. Fischer and R. Wolffenstein, *ibid.*, **37**, 3215 (1904), reported a m.p. of 119° for this compound. [q] Reichstein and Oppenhauer (ref. 6) reported a m.p. of 161° (corr.) for XX prepared by a different method. [r] Goodson, *et al.*, (ref. 17) prepared IX in 34% yield by this method, used benzene as a crystallizing solvent, and reported a m.p. of 117–120°. [s] Reichstein and Oppenauer (ref. 6) prepared the compound by a different method but reported neither the m.p. nor yield. [t] Compound XXII purified by chromatography on alumina in benzene–petroleum ether (b.p. 60–70°) solution. [u] G. H. Coleman, W. H. Holst and R. D. Maxwell, THIS JOURNAL, **58**, 2310 (1936), reported a m.p. of 69.8–70.2° for XXII prepared by a different method. [v] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, 11, 137 (1928), reported a m.p. of 52° for VIII prepared by reduction of diphenylbutadiene with a platinum oxide catalyst. [w] Product isolated after hydrolysis by extraction with ether. [x] A. Klages and G. Lickroth, *Ber.*, **32**, 1558 (1899), reported a b.p. of 236° for this compound prepared by a different method. [y] J. F. Birch, *et al.*, THIS JOURNAL, **71**, 1362 (1949), reported a b.p. of 183.6° and n^{20}_{D} 1.4947 for this compound prepared by a different method (in a high degree of purity).

TABLE II

PHYSICAL PROPERTIES OF THE PRODUCTS OF THE CYCLIZATION REACTIONS

Starting material		Product		Yield. %	M.p., °C.	Crys. solv.	Crys.[a] form	Formula	Analyses, % Carbon Calcd.	Analyses, % Carbon Found	Analyses, % Hydrogen Calcd.	Analyses, % Hydrogen Found	Mol. wt. Calcd.	Mol. wt. Found
4,4'-Dibromomethyldibenzyl	IX	*p*,*p*'-Dimethylene-1,2-diphenylethane	XII	2.1	285–287	Gl. acet.	n	$C_{16}H_{16}$	92.25	92.08	7.75	7.79	208	214[b]
		4,4'-Dimethyldibenzyl	XV	17.6	79–81	....	n	.....	...	...	..	..	...	..
		Polymer	....	64.9	....	....	..	.....	...	...	..	..	...	..
1,3-Bis-(4-bromomethylphenyl)-propane	X	*p*,*p*'-Trimethylene-1,2-diphenylethanc	XII	4.6	148–149	Pet. ether	gr	$C_{17}H_{18}$	91.84	91.75	8.16	8.37	222	244[c]
		1,3-Bis-(*p*-tolyl)-propane	XXVIII	7.0	34–37	....	..	.....	...	...	..	..	...	..
		Polymer	....	11.2	....	....	..	.....	...	...	..	..	...	..
1,4-Bis-(4-bromomethylphenyl)-butane	X1	*p*,*p*'-Tetramethylene-1,2-diphenylethane	XIV	0.48	74.4–75	Alc.	pl	$C_{18}H_{20}$	91.47	91.30	8.53	8.68	236	236[c]
		1,4-Bis-(*p*-tolyl)-butane	XVII	34.5	74–75	Alc.	pl	$C_{18}H_{22}$	90.69	90.81	9.31	9.23	...	..
		....	XXVIII	4.75	49.5–51	Alc.	pl	$C_{26}H_{30}$	91.17	90.93	8.83	9.15	342	340[d]
		Polymer	....	9.17	....	....	..	.....	...	...	..	..	...	..
1,3-Bis-(4-[*β*-carbomethoxyethyl]-phenyl)-propane	XXIV	3-Keto-4-hydroxy-*p*,*p*'-hexamethylene-1,3-diphenylpropane	XXV	52.8	72–73	Pet. ether	r	$C_{21}H_{24}O_2$	81.78	81.83	7.84	7.91	308	315[c]
3-Keto-4-hydroxy-*p*,*p*'-hexamethylene-1,3-diphenylpropane	XXV	3-Keto-*p*,*p*'-hexamethylene-1,3-diphenylpropane	XXV1	70	Not isolated in pure state	....	..	.....	...	...	..	..	...	..
3-Keto-*p*,*p*'-hexamethylene-1,3-diphenylpropane	XXVI	*p*,*p*'-Hexamethylene-1,3-diphenylpropane by Method I	XXVII	91.5	B.p. 155–157 (0.3 mm.)	....	..	$C_{21}H_{26}$	90.58	90.41	9.41	9.43	278	280[c]
3-Keto-*p*,*p*'-hexamethylene-1,3-diphenylpropane	XXVI	*p*,*p*'-Hexamethylene-1,3-diphenylpropane by Method II	XXVI1	13.8	B.p. 155–165 (0.3 mm.)	....	..	$C_{21}H_{26}$	90.58	90.17	9.41	9.39	...	..
4,4'-Dicarbomethoxymethyldibenzyl	XXXI	4,4'-Dicarboxymethyl dibenzyl	....	36.4	....	....	..	.....	...	...	..	..	...	..
		4,4'-Dimethyldibenzyl	XV	10.6	80–81	Alc.	n	$C_{16}H_{18}$	91.38	91.34	8.62	9.03	...	..
		Polymer	....	11.7	....	....	..	.....	...	...	..	..	...	..
		....	XXXVI	1.1	151–152	Acet.	n	$C_{33}H_{34}O$	88.74	88.72	7.67	7.71	...	..
1,3-Bis-(4-carbomethoxymethylphenyl)-propane	XXX1I	1,3-Bis-(4-carboxymethylphenyl)-propane	....	4.16	....	....	..	.....	...	...	..	..	...	..
	Run 1	Starting material	XXX1I	15.3	....	....	..	.....	...	...	..	..	...	..
		1,3-Bis-(*p*-tolyl)-propane	XVI	4.2	....	....	..	.....	...	...	..	..	...	..
		Polymer	....	62.8	....	....	..	.....	...	...	..	..	...	..
		1,3-Bis-(4-carboxymethylphenyl)-propane	....	2.97	....	....	..	.....	...	...	..	..	...	..
	Run 2	Polymer	....	5.26	....	....	..	.....	...	...	..	..	...	..
		....	XXXV1I	0.41	117–118	Acet.	pl	$C_{35}H_{38}O$	88.56	88.26	8.07	8.22	474	463[c]
		....	XL	0.63	142–143	Acet.	n	?	?	87.66	?	7.21	?	254[c]

[a] n = needles, gr = granules, pl = plates, r = rosettes. [b] R. Signer method, *Ann.*, **478**, 246 (1930), in methylene chloride as described by E. P. Clark, "Semimicro Quantitative Organic Analysis," Academic Press, Inc., New York, N. Y., 1943, p. 78. [c] Rast method in camphor, Clark, p. 49. [d] Signer method in ether.

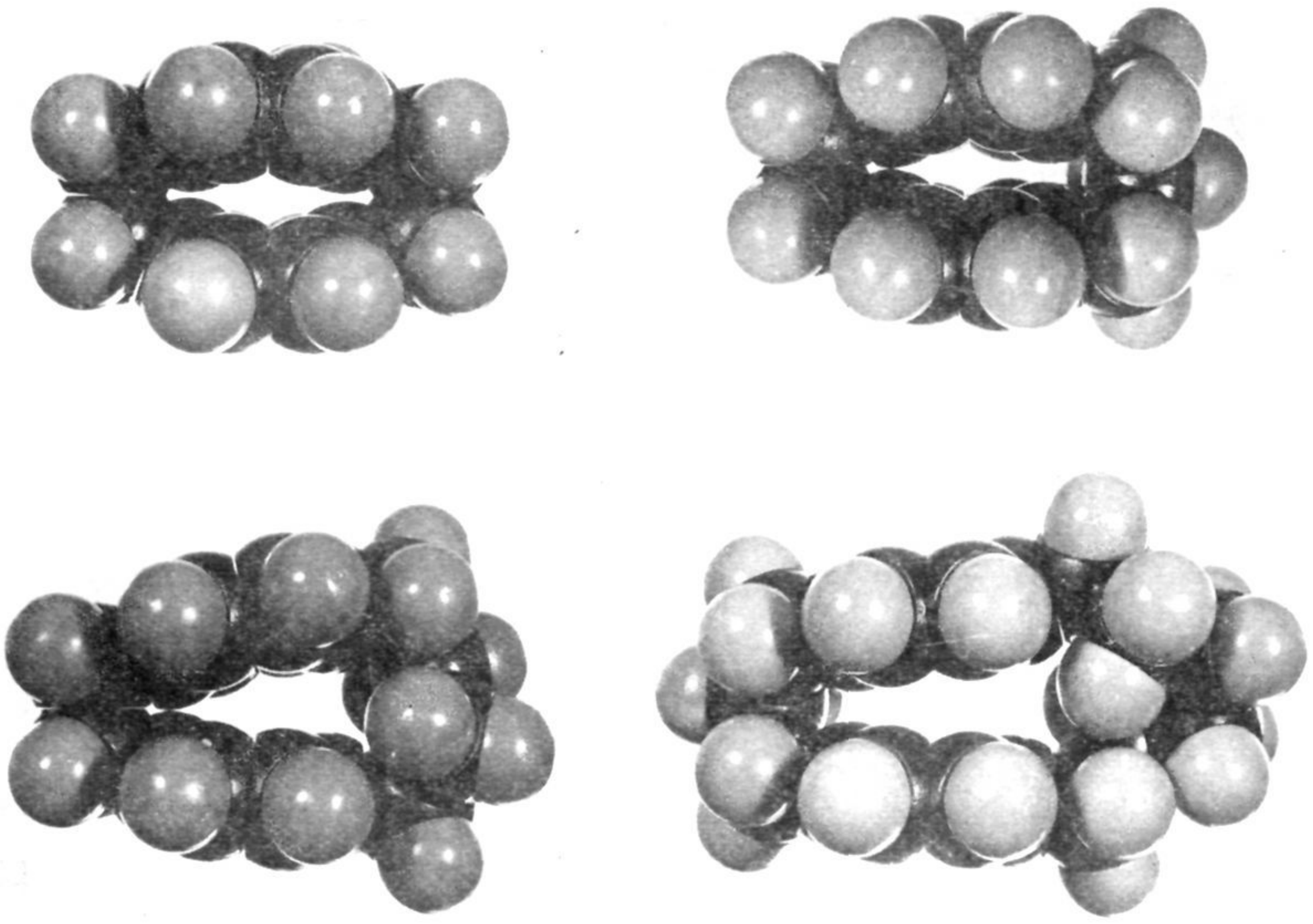
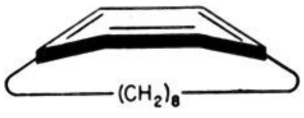


Fig. 4.—Molecular models of the four paracyclophanes.

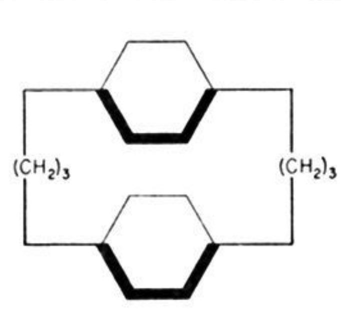
XXVII, seem to be associated with the puckering of the benzene rings.[32]

The alterations of the spectra of all four paracyclophanes in the region of 260 to 275 mμ from the spectra of the model substances is ascribed to the disturbance that both the puckering of the aromatic rings and the inter-ring overlap of π-orbitals creates in the ordinary benzenoid resonance, with which absorption in this region is associated.

In an attempt to separate the effects of the distortion of the aromatic rings from the effects of the inter-ring overlap of π-orbitals, the syntheses of compounds XXXVIII and XXXIX have been undertaken. According to molecular models, the benzene ring in XXVIII should be bent into a shallow "tub," and the absence of a second unsaturated system in the molecule should allow an assessment of the effect on the spectra of this folded configuration. On the other hand, XXXIX is an unstrained molecule in which the two benzene rings are in an ideal position to allow for maximum interlaminar bonding without any steric constraints forcing the rings together.



XXXVIII



XXXIX

Although the infrared spectra of the open chain compounds, 1,4-diethylbenzene, 4,4′-dimethyldibenzyl (XV) and 1,3-bis-(4-ethylphenyl)-propane (XXIII) do not differ markedly from one another (Fig. 3), the spectra of the paracyclophanes contain several distinguishing features that set them off as a unique group of compounds. Of the group of four cycles (as in the case of the ultraviolet absorption spectra) the infrared spectrum of XXVII is the most like the open chain model compounds, and the closer the benzene rings are pulled together, the greater the spectral differences. Thus in the double bond region an intense band appears at 6.35 and 6.30 μ for XII and XIII, respectively, but the intensity diminishes for XIV (6.16 μ) and is very weak for XXVII (6.10 μ). Since XII and XIII contain non-planar benzene rings and the same rings in XIV are possibly slightly bent but in XXVII are definitely planar, the presence and intensity of this band in the "double bond region" seems to correlate with the distortion of the geometry of the aromatic system. Possibly this absorption is associated with a vibrational transition not allowed in compounds containing planar benzene rings for symmetry reasons, the symmetry being modified when the rings become puckered.

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[32] This spectral analogy is good evidence that the aromatic nuclei of XIII are also puckered, probably more at the end of the molecule bearing the two-membered bridge than at the other, thus producing a "clam-like" configuration. The absence of the band at about 300 mμ in XIV is taken as evidence that the two rings are either planar or almost planar in this compound.

The same sort of trend is apparent for the two bands in the region of 10.70 and 11.20. Thus XII and XIII absorb strongly at 10.75 and 10.82 and at 11.20 and 11.38 mμ, respectively, whereas the intensity of the bands (10.59 and 11.24 μ) in XIV has decreased and the absorption in XXVII is so weak as to be hard to identify. Again the marked spectral changes in the cycles as compared to the model compounds seem to be associated with puckered benzene rings, and might serve as a diagnostic test for a molecule containing such a system. The bands of medium intensity from 8.36 to 8.45 μ in XII, XIII and XIV but absent in the other compounds might serve the same purpose.

Experimental

Procedure A. 1,3-Diphenylpropane (VII).—Dibenzyl ketone (500 g., 2.37 moles), 450 g. of potassium hydroxide and 310 ml. of 85% hydrazine hydrate in 3 l. of triethylene glycol was treated by the general Huang-Minlon procedure[18] to give 410 g. (90% yield) of colorless product, b.p. 165–166° (25 mm.).

Procedure B. 1,3-Bis-(4-acetylphenyl)-propane (XIX).—Two moles (204 g.) of acetic anhydride was added dropwise over one hour to a vigorously stirred mixture of 196 g. (1 mole) of VII, 600 g. of anhydrous aluminum chloride, and 1 l. of carbon disulfide.[33] After refluxing the mixture for an additional hour, the condenser was set down for distillation and the carbon disulfide was removed. The still warm, dark brown, viscous reaction mixture was cautiously poured into a well-stirred mixture of chipped ice and concentrated hydrochloric acid, and the resulting yellow solid was collected. Recrystallization from methanol (with a Norite treatment) gave 116 g. (77% yield) of light yellow needles melting at 83–85°. An analytical sample was recrystallized three times from methanol, white needles, m.p. 85–86.5°.

Procedure C. 1,3-Bis-(4-carboxyphenyl)-propane.—A well-stirred mixture of 3 l. of potassium hypochlorite solution prepared from 500 g. of calcium hypochlorite[34a] and 96 g. (0.343 mole) of XIX was heated at 85° on a steam-bath to start the reaction. The mixture was then kept at 70–75° for two hours by frequent cooling, the excess hypochlorite was destroyed by the addition of 100 g. of sodium bisulfite in 400 ml. of water, and a small amount of undissolved material was removed by filtration. The filtrate was acidified with concentrated hydrochloric acid and the white precipitate was collected, slurried in 400 ml. of acetone, filtered, and the process was repeated to give 92.4 g. (95% yield) of a white powder melting at 290–295°. An analytical sample prepared by recrystallization from boiling glacial acetic acid melted at 304–307°; a second recrystallization did not change the melting point. The acid did not analyze correctly for carbon, nor could it be further purified without conversion to a derivative.

Procedure D. 1,3-Bis-(4-carbomethoxyphenyl)-propane.—1,3-Bis-(4-carboxyphenyl)-propane (50 g., 0.175 mole) was esterified in the usual manner with methanol and concentrated sulfuric acid to give, after recrystallization from methanol, 42 g. (77% yield) of white needles melting at 85–88°. A small sample recrystallized three times from methanol melted at 92–93°.

Procedure E. 1,3-Bis-(4-hydroxymethylphenyl)-propane (XXI).—1,3-Bis-(4-carbomethoxyphenyl)-propane (122 g., 0.391 mole) was treated with lithium aluminum hydride by the general procedure of Nystrom and Brown.[35] After destroying the excess reagent with methanol and acidification with dilute sulfuric acid, the ether and water layers were separated, and the water layer was filtered free of a large amount of insoluble white material which was added to the residue obtained from the ether layer by evaporation of the ether. The combined products were recrystallized from benzene to give 94 g. (94% yield) of white needles melting at 122–125°. A second recrystallization of a small sample gave long white needles, m.p. 124–125.4°.

Procedure F. 1,3-Bis-(4-bromomethylphenyl)-propane (X).—A mixture of 39 g. (1.52 moles) of XXI, 55 g. (0.204 mole) of phosphorus tribromide and 400 ml. of chloroform was refluxed for eight hours. The still warm chloroform solution was decanted from the viscous yellow oil which coated the walls of the flask and was washed with water. After drying, the chloroform was evaporated leaving a yellow oil which solidified to a white crystalline mass when cooled. Recrystallization of the material from petroleum ether (b.p. 60–70°) gave 55 g. (95% yield) of long white needles, m.p. 128–131°. Two further recrystallizations of the substance gave fine white needles, m.p. 131–132.5°.

Procedure H. 1,3-Bis-(4-thioacetmorpholidephenyl)-propane (XXX).—Compound XIX was treated with sulfur and morpholine in the modified Willgerodt procedure[25,26] to give a 100% conversion to the crude thiomorpholide. A small sample recrystallized three times from ethanol gave light yellow rosettes melting at 114–116°.

Procedure I. 1,3-Bis-(4-carboxymethylphenyl)-propane.—Compound XXX (40.4 g., 0.084 mole) was hydrolyzed with ethanolic sodium hydroxide by the procedure of Schwenk and Papa[26] to give after recrystallization from methanol (with a Norite treatment) 19.3 g. (74% yield) of a white powder melting at 200–206°. A small sample recrystallized three times from methanol melted at 206–208°.

Procedure J. 1,3-Bis-(4-carbomethoxymethylphenyl)-propane (XXXII).—The esterification was performed by the method of Clinton and Laskowski.[36] In this manner, 50 g. (0.160 mole) of 1,3-bis-(4-carboxymethylphenyl)-propane was converted into the crude ester which after recrystallization from petroleum ether (b.p. 20–40°) gave 42 g. (77% yield) of white plates, m.p. 53–54°.

Oxidation of 1-g. sample of XXXVI with potassium permanganate by the method described in Shriner and Fuson[37] gave a 61% yield of terephthalic acid.

Procedure K. 1,3-Bis-(4-carbomethoxymethylphenyl)-propane (XXXII).—A solution of 18.5 g. (0.0592 mole) of 1,3-bis-(4-carboxymethylphenyl)-propane in 500 ml. of absolute dioxane[38] was added to an ethereal solution of diazomethane prepared from 42 g. of nitrosomethylurea.[34b] The ether–dioxane solution was diluted with water and the resulting oil was extracted with ether. The ether extracts were treated as in Procedure J to give 13.4 g. (67% yield) of white plates, m.p. 53–54°.

Procedure L. 1,4-Bis-(*p*-tolyl)-butane (XVII).—Compound XI (1 g., 0.0025 mole) was reduced with zinc dust and glacial acetic acid by the method of Reichstein and Oppenauer.[6] The crude oily product was dissolved in petroleum ether (b.p. 20–40°) and poured through a column of 20 g. of alumina. Removal of the solvent from the eluate left 85 mg. (16% yield) of white plates, m.p. 73–74.5°.

1,3-Bis-(4-[β-bromoethyl]-phenyl)-propane (XXXIII).—A mixture of 30 g. (0.106 mole) of 1,3-bis-(4-[β-hydroxyethyl]-phenyl)-propane, 350 g. of 48% hydrobromic acid, and 16 g. of concentrated sulfuric acid was refluxed with vigorous stirring for 3.5 hours, cooled, poured into 1 l. of water and extracted with ether.[33] The extracts were washed with water, 10% sodium carbonate solution, and again with water. After drying and evaporating the ether, the residual oil was taken up in 300 ml. of petroleum ether (b.p. 60–70°), chromatographically adsorbed on 50 g. of alumina, and eluted with 1 l. of petroleum ether. The eluate was concentrated and again submitted to chromatography. The solvent was evaporated from the eluate and the residue was triturated with 50 ml. of cold methanol and filtered to give 33.5 g. (78% yield) of cream-colored finely crystalline material melting at 47–48.5°. Recrystallization of the substance from petroleum ether (b.p. 60–70°) gave white needles, m.p. 47.5–49°.

1,3-Bis-(4-[β-carboxyethyl]-phenyl)-propane.—Five grams of a total of 50 g. (0.122 mole) of XXXIII dissolved in 30 ml. of anhydrous ether and 6.3 g. (0.27 mole) of mag-

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[33] This procedure is modeled after the preparation of *p*-bromoacetophenone in "Organic Syntheses," Coll. Vol. I, Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 109.

[34] (a) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 429; (b) p. 165; (c) p. 229; (d) p. 129.

[35] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

[36] R. O. Clinton and S. C. Laskowski, *ibid.*, **70**, 3135 (1948).

[37] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1946, p. 164.

[38] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Second Ed., New York, N. Y., 1941, p. 369.

nesium turnings were stirred vigorously until a reaction started, and then the remainder of the XLV dissolved in 100 ml. of anhydrous ether was added dropwise. After heating the mixture an additional half-hour, it was poured with stirring onto 300 g. of Dry Ice, 500 ml. of water and 200 ml. of concentrated hydrochloric acid were added, and the lumps were dispersed. The ether was evaporated and the product was collected, dissolved in 300 ml. of 10% sodium carbonate solution, washed with ether, and acidified with concentrated hydrochloric acid. The precipitate was collected and dried in a vacuum desiccator over phosphorus pentoxide to give 34 g. (74% yield) of a white powder melting at 140–162°.

A pure sample was prepared for analysis by saponification of the methyl ester XXIV. Recrystallization of the saponified material from acetic acid gave white plates, m.p. 185–186°.

1,3-Bis-(4-chloromethylphenyl)-propane.—Ashley, *et al.*,[19] have prepared the compound using *s*-dichloromethyl ether prepared by the method of Descude[39]; however, the experimental details were not given. *s*-Dichloromethyl ether (7 g., 0.069 mole) was slowly added with stirring to a cooled mixture of 10 g. (0.05 mole) of VII and 8 g. of freshly fused zinc chloride. The mixture was kept at 30–35° for three hours in which time it solidified to a solid mass. The oily mass was suspended in benzene (in which it formed an emulsion), centrifuged, and the supernatant layer of benzene was decanted. The benzene solution was washed with water and after drying was stripped on a steam-bath leaving a red oil which solidified to an oily brown solid. Trituration of the solid in cold carbon disulfide, filtration, and recrystallization from carbon disulfide yielded 0.9 g. (7% yield) of white amorphous material melting at 103–106°.

1,4-Diphenylbutane (VIII).—A suspension of 65 g. (0.316 mole) of 1,4-diphenyl-1,3-butadiene[34c] in 600 ml. of methylcyclohexane was catalytically reduced with Raney nickel under 40 atm. of hydrogen at 45°. The catalyst was removed by filtration and the solvent was evaporated at reduced pressure leaving a colorless oil which crystallized on cooling in well defined rectangular prisms. Recrystallization of the material from ethanol gave 53 g. (80% yield) of white needles, m.p. 51.5–53°.

General Cyclization Procedure. Apparatus.—The apparatus consisted of a 3-l. three-necked, round-bottomed creased flask with standard taper side wells and an indented cone-shaped bottom which was heated by means of a Glas-Col mantle and was equipped with a high speed stirrer assembly with a stainless steel propeller[40] driven by a 14,000 r.p.m. motor. A side well was fitted with a bulb-type condenser the top of which held a 1-l. pressure-equalizing Hershberg dropping funnel.[34d] The top of the dropping funnel was connected in turn to a U-tube containing a 1-cm. head of mercury. Prepurified nitrogen (less than ten parts per million of oxygen) entered the system through a gas inlet in the stirrer bushing.

Procedure.—The glass apparatus was dried in an oven before use and protected with calcium chloride tubes while being assembled. One liter of xylene (refluxed over and distilled from sodium, b.p. 137–140°) was siphoned into the reaction vessel under nitrogen pressure. The condenser was wrapped with glass wool, and with the passage of nitrogen through the system some xylene was distilled out the open end of the condenser to remove the last traces of moisture from the system. The reflux was stopped, and the dropping funnel containing the starting material (dissolved in one liter of xylene) was put in place. Crust-free sodium was placed in the flask, the stirrer bushing and condenser were cooled by streams of compressed air, and the xylene was brought to reflux with gentle stirring. The sodium was then highly dispersed by stirring at 5000 r.p.m. for five minutes. The stirring was then raised to some value above 6000 r.p.m. and the starting material was added dropwise. The slant of the condenser and dropping funnel were such that the drops hit the upper wall of the condenser and were further diluted with condensed xylene returning to the reaction vessel.

After the addition, the mixture was refluxed with continued stirring for one hour and then with diminished stirring was cooled to room temperature in a stream of air and finally cooled in an ice–salt-bath while the excess sodium (and sodium salts in the acyloin condensations) was destroyed by the dropwise addition of slightly more than the theoretical amount (based on the amount of starting sodium) of methanol (in the Wurtz reactions) or glacial acetic acid (in the acyloin condensations). The apparatus was dismantled and the reaction mixture was filtered in a large diameter büchner funnel. The filter cake was suspended in 500 ml. of fresh xylene in the original reaction vessel and stirred at high speed for ten minutes and refiltered. The filtrate was added to the main xylene filtrate. The filter cake was then shaken with water and filtered and the process repeated until the weight of the polymer was constant.

The xylene filtrate was concentrated under reduced pressure and the residual oil was treated as reported under the specified preparations.

***p,p'*-Dimethylene-1,2-diphenylethane** (XII).—Compound IX (41 g., 0.111 mole) was added over a period of sixty hours to 7.65 g. (0.333 mole) of sodium stirred at 7000 r.p.m. to give 15 g. of a yellow polymer and a red oil which solidified to a brown solid on cooling. The solid was triturated with 30 ml. of acetone and filtered, and the filter cake was again triturated with 50 ml. of acetone and filtered.

The acetone filtrates were heated to boiling, treated with Norite and filtered through a cake of Celite, and the yellow filtrate was evaporated to dryness on a steam-bath leaving a yellow oil which solidified to a yellow solid on cooling. The solid was sublimed at 115° (0.3 mm.) to give 4.1 g. of white needles melting at 79–81°. An admixture of this material with an authentic sample of XV (m.p. 80–81°) melted at 79–81°.

The acetone-insoluble material was sublimed at 150–200° (0.3 mm.) to give 0.67 g. of a white sublimate which was recrystallized twice from glacial acetic acid to give 0.42 g. of fuzzy needles, m.p. 285–287.2°. The filtrates when concentrated and cooled gave a solid, which when filtered and twice recrystallized gave an additional 65 mg. of white needles, m.p. 285–287°. The total yield of XII was thus 0.485 g. (2.1% yield). An analytical sample recrystallized from glacial acetic acid melted at 285–287°.

***p,p'*-Trimethylene-1,2-diphenylethane** (XIII).—Compound X (10 g., 0.0262 mole) was added over 56 hours to 2.4 g. (0.104 mole) of sodium stirred at 8000 r.p.m. to give 0.65 g. of a dark-gray polymer and a brown oil. The oil was distilled in a short path still to give 3.73 g. of a pale yellow oil at a pot temperature of 160–180° (0.3 mm.) and 1.07 g. of a yellow oil at a pot temperature of 200–250° (0.3 mm.).

The low-boiling fraction, which solidified in the receiver, was recrystallized four times from petroleum ether (b.p. 20–40°), the last time for analysis to give 46 mg. of crystalline material melting at 148–149°.

The filtrates from the recrystallizations were combined, the solvent was evaporated, and the residual oil upon standing for several days deposited a white solid which was removed by filtration and washed with a few drops of cold petroleum ether. The oily filtrate was saved and the white solid was recrystallized twice from petroleum ether to give an additional 91 mg. of XIII melting at 147.2–148.2°.

Further treatment of the filtrates yielded an additional 109 mg. of XIII melting at 146–148°.

The oily filtrate that was saved was dissolved in 5 ml. of petroleum ether, cooled and filtered. The filter cake was dissolved in 5 ml. of petroleum ether and adsorbed on a column of 50 g. of alumina, and the column eluted with petroleum ether. Eleven 30-ml. fractions were collected and evaporated to dryness. The solid residues in fractions 7 to 10 were combined and recrystallized twice from petroleum ether to give 22 mg. of XIII melting at 146–148°. The total yield of XIII was thus 268 mg. (4.6% yield).

The oils in fractions 1 to 6 were combined and upon cooling solidified to a white crystalline mass (0.41 g.), m.p. 34–37°. An admixture of this material with an authentic sample of XVI (m.p. 34–35°) melted at 34–35.5°.

***p,p'*-Tetramethylene-1,2-diphenylethane** (XIV).—Due to the limited solubility of XI in xylene the dropping funnel was electrically heated with a spiral of Nichrome wire. In this manner 40.5 g. (0.102 mole) of XI was added over 70 hours to 7.05 g. (0.306 mole) of sodium stirred at 7500 r.p.m. to give 2.21 g. of a brown polymer and a brown oil. The brown oil was distilled at 0.3 mm. in a short path still to give four fractions.

Fraction 1 was a colorless oil (12 g.) which distilled at a pot temperature of 155–170°, solidified to a soap in the re-

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(39) M. Descude, *Compt. rend.*, **138**, 1110 (1904).

(40) A. A. Morton and L. M. Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).

ceiver, and was recrystallized three times from ethanol to give 6.0 g. of white plates, m.p. 74–75.2°. An analytical sample melted at 74–75°.

An admixture of this material with an authentic sample of XVII (m.p. 73–74.5°) melted at 73–75°.

Fraction 2, a colorless oil (0.97 g.) which distilled at a pot temperature of 195–220°, solidified in the receiver to an oily mass and was combined with the filtrates of fraction 1. The mixture was evaporated to dryness and the resulting solid was recrystallized from ethanol to give an additional 1.1 g. of XVII. The ethanol was evaporated from the filtrate, and the remaining yellow oil was distilled at 0.3 mm. to give a colorless oil (3.42 g.) boiling at a pot temperature of 119–120°, and 1.14 g. of a yellow oil distilling at a pot temperature of 130–140° which solidified to a white solid on cooling. This material was recrystallized from ethanol to give 0.35 g. of flat needles (A), m.p. 44–60°. The filtrate (B) was saved.

The lower-boiling fraction was dissolved in 5 ml. of petroleum ether (b.p. 20–40°), adsorbed on 320 g. of alumina, and the column was developed with petroleum ether. Six 75-ml. fractions were taken and evaporated to dryness. Fractions 1 to 3 contained a colorless oil (C) (2.69 g.) which could not be induced to crystallize. Fraction 4 contained a viscous oil which solidified on cooling and was recrystallized three times from ethanol to give 24 mg. of flat needles, m.p. 74–75°. The filtrates were combined, concentrated, cooled in an acetone-Dry Ice-bath, filtered, and the filtered material was recrystallized twice from ethanol to give an additional 54 mg. of white plates melting at 74–75°. The solids were combined and recrystallized from ethanol to give 25 mg. of white plates, m.p., 74.4–75°.

An admixture from the ethanol recrystallizations and fractions 5 and 6 of the chromatogram were combined, concentrated to 5 ml., cooled at −80° and filtered. The filtered material was recrystallized from ethanol at −80° to give 90 mg. of white plates melting at 73–74.5°. The total yield of XIV amounted to 115 mg. (0.48% yield).

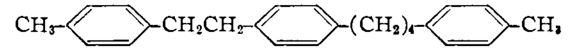
Fraction 3 consisted of 5.77 g. of a yellow oil which distilled at a pot temperature of 250–270° and which solidified to a white mass on standing. Three recrystallizations from ethanol resulted in 2 g. of an amorphous material (D) melting at 40–50°.

The filtrate from this recrystallization which was evaporated to dryness, the filtrate B which was evaporated to dryness, and C were combined and fractionally distilled at 16 mm. Fractions 1 to 3 (1.72 g.) boiled at 170–196° and were colorless oils which could not be induced to crystallize. Fractions 4 to 6 (1.04 g.) boiled at 196–236° and solidified to oily crystalline solids upon cooling. Fractions 7 and 8 (2.56 g.) boiled at 226–280° and were viscous yellow oils which solidified to oily, soapy masses on cooling.

Fractions 4 to 6 and A were combined, dissolved in 4 ml. of petroleum ether, adsorbed on 100 g. of alumina, and developed with petroleum ether containing 5% benzene. Seventeen 100-ml. fractions were collected and evaporated. Fractions 13 to 17 contained small amounts of oils which could not be crystallized. Fractions 1 to 12 were combined, solidified by cooling, and the solid was crystallized from ethanol to give 0.72 g. of XVII.

Fractions 7 and 8 from the distillation and D were combined, dissolved in 15 ml. of petroleum ether, adsorbed on 410 g. of alumina, and the column was developed with petroleum ether containing 2% benzene. Forty-nine 100-ml. fractions were collected. Fractions 50–82 were developed with 5% benzene and fractions 83–94 with 20% benzene. The fractions were evaporated to dryness and the residual oils were caused to solidify by cooling at −80°. Fractions 1 to 20 yielded 0.57 g. of XVII. Fractions 21-31 were oils which could not be caused to solidify. Fractions 32-94 were combined and recrystallized five times from ethanol to give 1.66 g. of white plates melting at 48.5–50.5°. An analytical sample melted at 49.5–51°.

This material may be the product (XL) of a reaction between the starting material and the solvent, xylene.



XL

The ultraviolet adsorption spectrum of this material is similar to the open chain compounds (II).

Fraction 4 consisted of 5.16 g. of a yellow oil that distilled at a pot temperature of 300–350° and which solidified to an oily yellow mass in the receiver. No pure material could be isolated from this fraction.

3-Keto-4-hydroxy-*p*,*p*′-hexamethylene-1,3-diphenylpropane (XXV).—Compound XXIV (27.2 g., 0.0734 mole) was added from an electrically heated dropping funnel over 60 hours to 6.8 g. (0.296 mole) of sodium stirred at 6500 r.p.m. The color of the reaction mixture progressed from light gray at the start through olive-green to bright yellow at the end. The preliminary procedure yielded 6.2 g. of a tan polymer and an orange oil which was distilled at 210–225° (0.3 mm.) to give 13.4 g. of a viscous yellow oil which solidified on standing. The solidified distillate was recrystallized from petroleum ether (b.p. 20–40°) to give 9.81 g. of white rosettes, m.p. 68–71°. Concentration of the filtrate gave an additional 2.23 g. of rosettes making the total yield 12.04 g. (52.8%).

A small sample recrystallized three times from petroleum ether for analysis melted at 72–73°.

A 3,5-dinitrobenzoate prepared by the pyridine method[41] melted at 204–205°.

Anal. Calcd. for $C_{28}H_{26}O_7N_2$: C, 66.92; H, 5.22. Found: C, 66.49; H, 5.37.

3-Keto-*p*,*p*′-hexamethylene-1,3-diphenylpropane (XXVI).—Three grams (0.0097 mole) of XXV was treated with zinc and hydrogen chloride in dioxane solution according to the procedure of Stoll[20] to give upon distillation (175–225°, 0.3 mm.) of the crude product 2 g. (70% yield) of a viscous oil which solidified in the receiver to a white crystalline mass. The crude cyclic ketone was used directly in the Clemmensen reduction.

***p*,*p*′-Hexamethylene-1,3-diphenylpropane (XXVII). Method I.**—A mixture of 2 g. (0.0068 mole) of XXVI, 20 g. of amalgamated zinc,[42] 70 ml. of glacial acetic acid and 40 ml. of concentrated hydrochloric acid was refluxed for 22 hours. Three 15-ml. portions of concentrated hydrochloric acid were added at 5-hour intervals. The aqueous and oil layers were decanted from the unused zinc (7.7 g.) into 250 ml. of water, and the resulting mixture was extracted with ether. The extracts were washed with water, 10% sodium hydroxide solution, and again with water. After drying the solution, the ether was evaporated leaving a yellow oil which was distilled at 155–165° (0.3 mm.) to give 1.48 g. (91.5% yield) of a colorless viscous oil. This oil was purified for analysis by chromatography on alumina in petroleum ether (b.p. 20–40°) solution. The solvent was removed from the eluate and the residual oil was fractionally distilled, b.p. 155–157° (0.3 mm.), $n^{20}D$ 1.5612.

***p*,*p*′-Hexamethylene-1,3-diphenylpropane (XXVII). Method II.**—Compound XXVI (0.85 g., 0.0029 mole) in the Huang-Minlon[18] reduction (procedure A) gave 0.125 g. (15.4% yield) of a viscous colorless oil, b.p. 155–165° (0.3 mm.), $n^{20}D$ 1.5617.

The ultraviolet absorption spectrum of XXVII prepared by method II was identical with that prepared by method I.

Attempted Acyloin Condensation of 4,4′-Dicarbomethoxymethyldibenzyl (XXXI).—Compound XXXI (25 g., 0.0766 mole) was added over 32 hours to 18 g. (0.783 mole) of sodium stirred at 6500 r.p.m. to give 2.93 g. of a yellow polymer. The xylene filtrate and polymer were washed with water in this case and the washings were acidified with concentrated hydrochloric acid to give 8.3 g. of 4,4′-dicarboxymethyldibenzyl.

Removal of the xylene left an oil which solidified on cooling. The solid was partially soluble in ether. The ether soluble fraction was sublimed at 115° (0.35 mm.) to give after recrystallization from ethanol 1.7 g. of white needles (XV) melting at 80–81°. Austin and Black[43] reported a melting point of 82° for XV.

The ether-insoluble fraction was refluxed in ether for one-half hour, and the moderately soluble material obtained after filtration and removal of the ether from the filtrate was dissolved in benzene and adsorbed on 50 g. of alumina. Development of the column with benzene, removal of the solvent from the eluate and recrystallization of the residue from acetone produced 0.19 g. of fine white needles (XXXVI), m.p., 151–152°.

Attempted Acyloin Condensation of 1,3-Bis-(4-carbomethoxymethylphenyl)-propane (XXXII).—Compound

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[41] Ref. 37, p. 137.

[42] Ref. 28, p. 163.

[43] J. B. Austin and I. A. Black, THIS JOURNAL, **52**, 4552 (1930).

XXXII (34 g., 0.10 mole) was added over 43 hours to 9.2 g. (0.40 mole) of sodium stirred at 6500 r.p.m. to give 21.35 g. of polymer and an oil. The oil was dissolved in benzene and extracted with 5% sodium carbonate solution. Acidification of the extracts with concentrated hydrochloric acid gave 1.3 g. of 1,3-bis-(4-carboxymethylphenyl)-propane. The benzene was removed from the organic layer and the oil was caused to solidify at −80° and recrystallized from petroleum ether (b.p. 60–70°) to give 5.2 g. of the starting ester. The filtrate from the recrystallization was taken to dryness and the residual oil was distilled to give 0.94 g. of XVI (b.p. 170–215° at 0.3 mm.) and 0.76 g. of the starting ester (b.p. 240–270° at 0.3 mm.)

Addition of 19 g. (0.056 mole) of XXXII to 5 g. (0.217 mole) of sodium over three hours using toluene as the solvent gave 1 g. of polymer and 0.5 g. of 1,3-bis-(4-carboxymethylphenyl)-propane. Solidification of the usual residual oil and chromatography of the solid on alumina in benzene solution gave eluates, the early fractions of which yielded 0.1 g. of white plates (acetone), m.p. 117–118° (XXXVII).

Recrystallization from acetone of the residues from the later fractions gave 0.09 g. of white needles melting at 142–143° (XL).

Acknowledgment.—The authors are happy to acknowledge the value of conversations concerning the substance of this paper with Drs. K. N. Trueblood, W. G. McMillan and R. L. Scott. The analyses reported were done by Mrs. Bea Kent and Dr. A. Elek.

LOS ANGELES 24, CALIF. RECEIVED MARCH 19, 1951

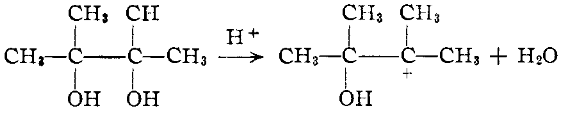
[CONTRIBUTION FROM THE SYNTHETIC FUELS RESEARCH BRANCH, BUREAU OF MINES]

Chemistry of the Oxo and Related Reactions. V. Acid Catalysis with Pinacol

BY IRVING WENDER, SOL METLIN AND MILTON ORCHIN

The reaction of pinacol with carbon monoxide and hydrogen at 185° in the presence of a cobalt catalyst gives a complex mixture of products. Four compounds more volatile than the starting material were identified; these were pinacolone, pinacolyl alcohol, 3,4-dimethylpentanol-1 and 2,2,3-trimethyltetrahydrofuran. The origin of these compounds is consistent with the formation and further reaction of a common carbonium-ion intermediate formed from pinacol under acidic conditions. The acid catalyst is probably cobalt hydrocarbonyl, $HCo(CO)_4$.

To substantiate the postulate that the homologation of alcohols with excess synthesis gas at 185° in the presence of cobalt is catalyzed by the acid $HCo(CO)_4$,[1] the reaction of pinacol with synthesis gas was examined. The pinacol–pinacolone rearrangement is a known example of an acid-catalyzed reaction. If the homologation reaction is similarly catalyzed, the transient carbonium ion (A) should be formed from pinacol



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow{H^+} CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{+}{\overset{CH_3}{C}}-CH_3 + H_2O$$

A

A study of the products of the reaction of pinacol with synthesis gas resulted in the isolation and identification of the following compounds: pinacolone (I), pinacolyl alcohol (II), 3,4-dimethylpentanol-1 (III) and 2,2,3-trimethyltetrahydrofuran (IV). All of these products may be derived from the postulated intermediate (A) according to the scheme outlined in Chart I.

Experimental

The Reaction of Pinacol with Carbon Monoxide and Hydrogen.—A solution of 74 g. (0.63 mole) of pinacol (b. p. 85.0–85.5° at 21 mm.) and 10 g. of dicobalt octacarbonyl in 80 ml. of benzene was placed in a 500-ml. stainless-steel autoclave. Synthesis gas ($2H_2$:1CO) was added until the pressure reached 3200 p. s. i. (3.3 moles of gas). The autoclave was heated, with rocking, to 185° within 160 minutes; the maximum pressure obtained was 4350 p. s. i. at 164°. The temperature of the autoclave was held at 185–189° for 4 hours, during which time the pressure dropped to 2600 p. s. i. The reaction vessel was cooled to 25°; the pressure at this temperature was 1500 p. s. i. This pressure drop corresponded to approximately 1.7 moles of gas, or 2.7 moles of gas per mole of pinacol. The gases were then discharged.

The reaction products were washed from the autoclave with benzene, and 11.5 ml. of an aqueous layer was removed from the products. The benzene solution was then distilled in a one-foot, glass, concentric tube column. Another 3.9 ml. of water distilled over as the benzene–water azeotrope; the total amount of water recovered was 15.4 ml. (0.86 mole).

Distillation of the remaining products yielded a fraction, b.p. 82–106°, which contained approximately 10.8 g. (17.2%) of pinacolone (by hydroxylamine hydrochloride titration) and 1.1 g. of pinacolyl alcohol. Addition of 2,4-dinitrophenylhydrazine to this fraction yielded the 2,4-dinitrophenylhydrazone of pinacolone, m. p. 126.2–127.6°, not depressed when mixed with an authentic sample. A 3.1-g. fraction boiling from 106–129° was mainly pinacolyl alcohol, but a small amount of another substance, probably 2,2,3-trimethyltetrahydrofuran, was present. Addition of phenyl isocyanate to this solution yielded the phenylurethan of pinacolyl alcohol, m. p. 74.8–76.7°, not depressed when mixed with the phenylurethan of pinacolyl alcohol prepared by lithium aluminum hydride reduction of pinacolone. A total of 4.2 g. (4.1%) of pinacolyl alcohol was obtained.

Distillation of the residue at atmospheric pressure in the same column yielded 19.1 g. (26.2%) of impure 3,4-dimethylpentanol-1, b. p. 164.5–166.0°, n^{25}_D 1.4290. The melting point of the dinitrobenzoate prepared from this fraction was 50.2–51.9°[2]; the dinitrobenzoate formed an addition compound with α-naphthylamine, which softened at 73.5° and melted at 76–77°.[2] A residue of 22.9 g. remained.

Attempted Thermal Rearrangement of Pinacol.—Seventy-four grams (0.63 mole) of pinacol, 80 ml. of benzene and 3 g. of $CoCO_3$ were placed in the autoclave. The bomb was filled with 3200 p. s. i. of nitrogen and heated at 185° for 4 hours. The products of the reaction were filtered and distilled in the 1-foot, glass, semi-micro column. After the benzene was removed, the boiling point rose sharply to 174°, and the first distillate at this temperature solidified in the receiver. 63.9 g. (86.4%) of the starting material was recovered unchanged. There was no other product.

Tetrahydrofurfuryl Alcohol from 1,2,5-Trihydroxypentane.—Eighteen grams (0.15 mole) of 1,2,5-trihydroxypentane,[3] 21 ml. of benzene, 100 ml. of ether and 2.7 g. of $[Co(CO)_4]_2$ were treated at 180–185° for 3 hours in an autoclave with 3,000 p. s. i. of 1:1 synthesis gas. Distillation of the reaction products from a Claisen flask yielded 3.9 g.

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[1] I. Wender, R. Levine and M. Orchin, THIS JOURNAL, 71, 4160 (1949).

[2] L. Schmerling, *ibid.*, 67, 1440 (1945).

[3] O. Grummitt, J. A. Stearns and A. A. Arters, "Organic Syntheses," Vol. 29, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 89.