water, and the resulting suspension was extracted with chloroform. The dark extract was washed with water, dried, filtered and the solvent was evaporated to leave a residue of 235 g. of a dark red oil. The crude thiomorpholide was hydrolyzed by refluxing it with a mixture of 118 g. (2.1 moles) of potassium hydroxide, 120 ml. of water and 440 ml. of 95% ethanol for 36 hours. The reaction mixture was diluted with water, acidified with concentrated hydrochloric acid and the light brown solid that separated was collected and partially dried under a rubber dam. This solid was further dried at 56° and 25 mm. of pressure to a constant weight, 150 g. (89%) of crude acid XI. This acid was converted without purification to its ethyl ester (procedure D).

Procedure M: 4-(β-Carbomethoxyethyl)-4′-(γ-carbomethoxypropyl)-dicyclohexylmethane (XLVII).—Diester XXVII (109 g. or 0.31 mole) prepared by a sequence involving XI → XIV → XVII → XXI → XXVII was dissolved in 150 ml. of glacial acetic acid, and 2.0 g. of platinum oxide was added to the solution. The mixture was hydrogenated catalytically under pressure at room temperature until the theoretical amount of hydrogen was absorbed, filtered and the solvent was distilled from the filtrate at reduced pressure. The yellow residue was distilled under high vacuum, and the fraction boiling at 214–215° (1 mm.) was collected to yield 100 g. (89%) of virtually colorless oil (XLVI), $n^{25}D$ 1.4817. Although this oil was undoubtedly a mixture of diastereomers, they were not separated, and the mixture was submitted directly to procedure J.

Perhydro[1.7]paracyclophane (XLIX).—Acyloin XLVIII was prepared from 61.4 g. of diester XLVII by procedure J to give a mixture of materials, which was separated into the following fractions by distillation: (1) b.p. 180–215° (~ 1 mm.), 12.14 g., $n^{25}D$ 1.4760; (2) b.p. 215–218° (~ 1 mm.), 14.52 g., $n^{25}D$ 1.4750; (3) b.p. 219–220°, 30.86 g., $n^{25}D$ 1.4723. Fractions 2 and 3 were combined and submitted to procedure K, 1.2 g. of distilled colorless oil (bath temperature 245°, 1 mm. pressure) being the product. This material was treated with 0.35 g. (0.0082 mole) of lithium aluminum hydride in anhydrous ether for two hours, and the product was isolated in the usual way as a pale yellow oil. This material was chromatographed on 100 g. of neutral alumina (activity 1)[13] with pentane as the developer. The product (XLIX) was eluted with pentane, weight 0.94 g., m.p. 78–80°. This material was recrystallized from a methanol–ethanol mixture to give 0.85 g. of white needles of XLIX, m.p. 78.4–80°.

Procedure N: [1.7]Paracyclophane (L).—The impure saturated hydrocarbon, XLIX (1.5 g. of oil) was heated in a micro Kjeldahl flask with 0.19 g. of 10% palladium-on-charcoal. Only 69% of the theoretical amount of hydrogen was evolved during 4 hours as the temperature was gradually raised from 250° to 320°. The crude product was dissolved in pentane, the solution was filtered and the solvent was evaporated in vacuum. The residual oil was distilled under high vacuum to give 1.0 g. of a colorless liquid, bath temperature 207° (1 mm.), $n^{25}D$ 1.5398. This liquid was absorbed on 500 g. of very active neutral alumina and eluted with pentane. A total of 129 50-ml. fractions of the eluate was collected and, on the basis of similarities in their ultraviolet absorption spectra, were combined in the following way to give 5 combined fractions: fraction A, flasks 1–13, contained 110 mg.; fraction B, flasks 14–35, contained 105 mg.; fraction C, flasks 36–83, contained 360 mg.; fraction D, flasks 84–121, contained 325 mg.; fraction E, flasks 122–129, contained 50 mg. The ultraviolet absorption spectrum of fraction C appeared to be the most like that expected for the desired cycle (L), and it was rechromatographed on 200 g. of very active alumina. The middle fractions of the eluate were combined, and the product was crystallized from methanol to give 0.032 g. (2%) of L, m.p. 76.5–77.2° (hard white needles).

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[13] H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

LOS ANGELES 24, CALIFORNIA

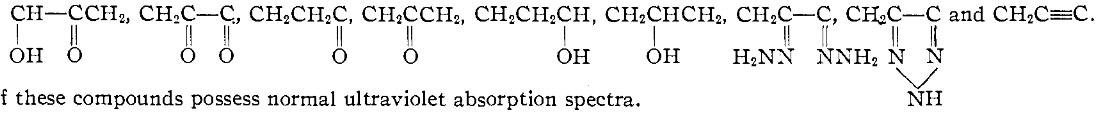
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Macro Rings. XVI. The Synthesis and Side Chain Chemistry of [9]Paracyclophane[1]

BY DONALD J. CRAM AND M. FARID ANTAR

RECEIVED JANUARY 14, 1958

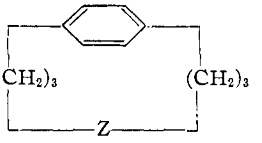
The synthesis and properties of a number of [9]paracyclophanes carrying functional groups in the methylene belt are described. These compounds possess the general structure I and Z represents the functions:



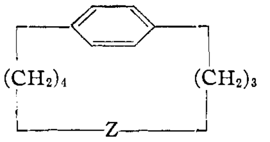
$$\underset{OH}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}CH_2,\ CH_2\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}},\ CH_2CH_2\underset{O}{\underset{\|}{C}},\ CH_2\underset{O}{\underset{\|}{C}}CH_2,\ CH_2CH_2\underset{OH}{\underset{|}{CH}},\ CH_2\underset{OH}{\underset{|}{CH}}CH_2,\ CH_2\underset{H_2NN}{\underset{\|}{C}}-\underset{NNH_2}{\underset{\|}{C}},\ CH_2\underset{N\diagdown_{NH}\diagup N}{\underset{\|\quad\|}{C-C}}\text{ and }CH_2C\equiv C.$$

All of these compounds possess normal ultraviolet absorption spectra.

In papers V[2a] and XI[2b] of this series are described the preparation and reactions of compounds based on the [10]paracyclophane parent structure, of



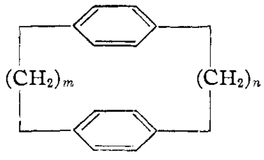
I



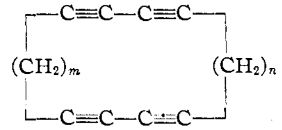
II, Z = CH═CH$_2$

III, Z = $\overset{\overset{O}{\|}}{C}\equiv CCH_2$

which II and III are representative compounds. Other investigations of paracyclophanes[3] such as IV established that if the two aromatic rings are closer than 3.4 Å. apart (normal van der Waals distance), abnormal ultraviolet spectra result. With $m = n$



IV



V

$= 4$, the spectrum is normal, but abnormal when $m = 3$, $n = 4$, since in the latter compound the benzene rings are pressed to within 2.84 Å. at their points of attachment to the smaller methylene bridge.[3] That such effects are not limited to this particular type of structure is shown by the unusual spectrum of II as compared to open chain

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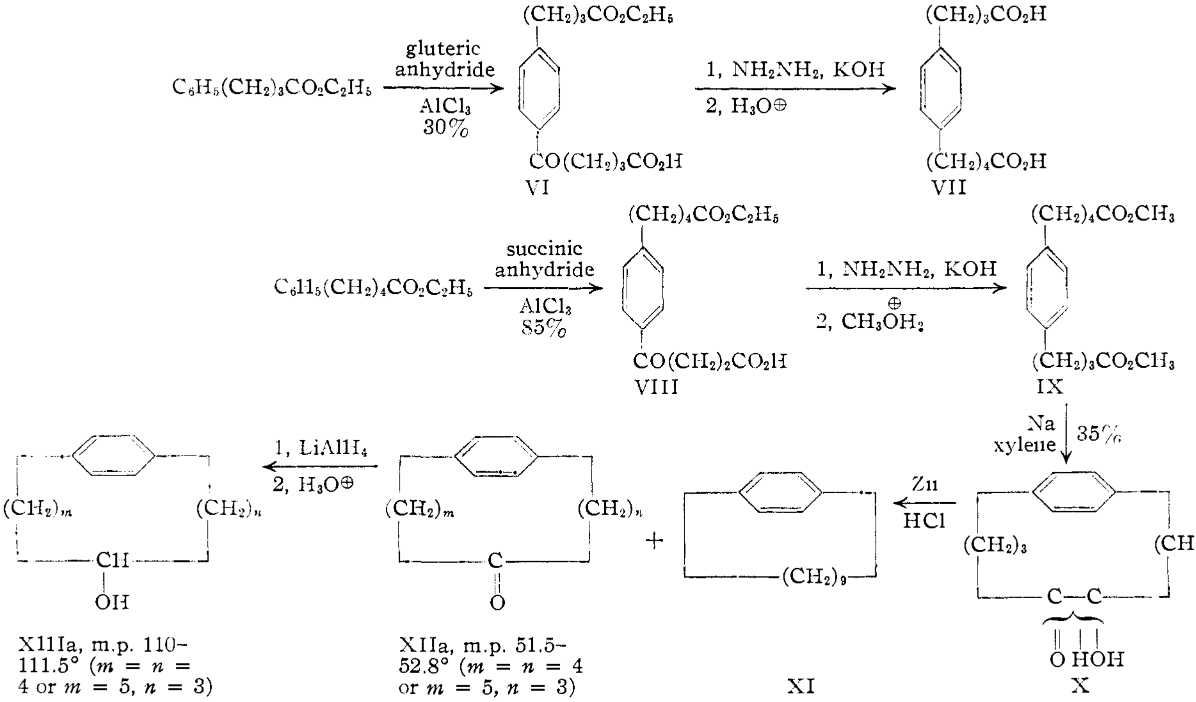
[1] This work was supported generously by a grant from the National Science Foundation.

[2] (a) D. J. Cram and H. U. Daeniker, THIS JOURNAL, **76**, 2743 (1954); (b) D. J. Cram and M. Cordon, *ibid.*, **77**, 4090 (1955).

[3] D. J. Cram, N. L. Allinger and H. Steinberg, *ibid.*, **76**, 6132 (1954).

models, and of V[4] where $m = n = 3$ as compared to either V with $n = m = 4$ or open chain models. In V with $m = n = 4$, the transannularly situated acetylenic linkages can be calculated to be 3.73 Å. apart, and with $m = n = 3$, 2.52 Å. apart, assuming that the bond lengths and bond angles are normal. Similarly, the distance between the acetylenic linkages and the benzene ring in III calculates to be 3.73 Å. and its spectral properties are normal.

The purpose of the current investigation was to prepare and examine the properties of compounds based on [9]paracyclophane as the parent structure, and in which various functional groups were introduced into the methylene bridge and thus are held over the face of the benzene ring. Since [9]-paracyclophane is the smallest cycle of its kind that has proved preparable,[3,5] a comparison of the behavior of the families of substances based on this cycle and its higher homologs might uncover interesting transannular effects. Finally, it seemed possible that the benzene ring of [9]paracyclophane might be bent into a shallow tub, and the ultraviolet absorption spectrum of the benzene ring be accordingly modified. The separation of this spectral effect from transannular electronic effects found in paracyclophanes possessing general structure IV seemed desirable.[3]



XIIIa, m.p. 110–111.5° ($m = n = 4$ or $m = 5$, $n = 3$)

XIIa, m.p. 51.5–52.8° ($m = n = 4$ or $m = 5$, $n = 3$)

XI

X

Synthesis.—The cycles needed for this investigation were all prepared through the acyloin reaction which involved ester IX as the starting material. Of the two syntheses of this ester outlined, that involving acylation of ethyl δ-phenylvalerate gave a yield much superior to that involving the lower homolog as starting material. In both cases, the competing side reaction probably was an intramolecular Friedel–Crafts acylation, which occurs less readily in the closing of a seven as compared to a six-membered ring. Thus with ethyl δ-phenylvalerate, the intermolecular acylation dominated, while with the lower homolog, the intramolecular reaction probably consumed the bulk of the starting material. The acyloin ring closure of IX went in 35% yield, as compared to yields of 75%[2a] and 70%[3] obtained for the same reaction applied to the syntheses of [10]- and [12]paracyclophanes, respectively. A mixture of hydrocarbon XI and ketone XIIa was produced when acyloin IX was submitted to the action of zinc and hydrochloric acid. The composition of this mixture was dependent on both the temperature of the reaction as well as on the quality of the zinc used. At 100° with granular zinc the hydrocarbon dominated by a factor of about two while the reverse was true when zinc foil and a temperature of 75–80° was employed. These observations are consonant with those made by others with respect to acyloin reductions.[6] That this ketone possesses structure XIIa with $m = n = 4$, or XIIa with $m = 5$, $n = 3$ is quite clear, although a unique structural assignment must await further work. The isomeric ketone XIIb ($m = 5$, $n = 3$ or $m = n = 4$), was produced utilizing the reaction[7] sequence in which acyloin acetates can be converted with trimethylenedithiol to thioketols. These ketones were subsequently reduced to their corresponding alcohols, one of which must be a racemate and the other a compound possessing a plane of symmetry.

Oxidation of acyloin X with bismuth oxide[8] gave the corresponding diketone XIV. In contrast to the next higher homolog,[2a] XV showed no tendency

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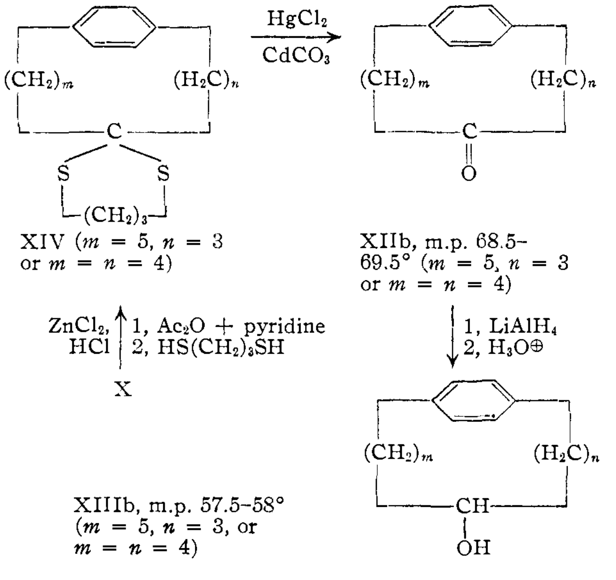
[4] Y. Amiel, F. Sondheimer and R. Wolovsky, *Proc. Roy. Soc.* (*London*), 22 (1957).

[5] M. F. Bartlett, S. K. Figdor and K. Wiesner, *Can. J. Res.*, **B28**, 561 (1950).

[6] A. C. Cope, J. W. Barthel and R. D. Smith, *Org. Syntheses*, **36**, 14 (1956).

[7] D. J. Cram and M. Cordon, THIS JOURNAL, **77**, 1810 (1955).

[8] W. Rigby, *J. Chem. Soc.*, 793 (1951).

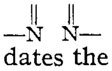


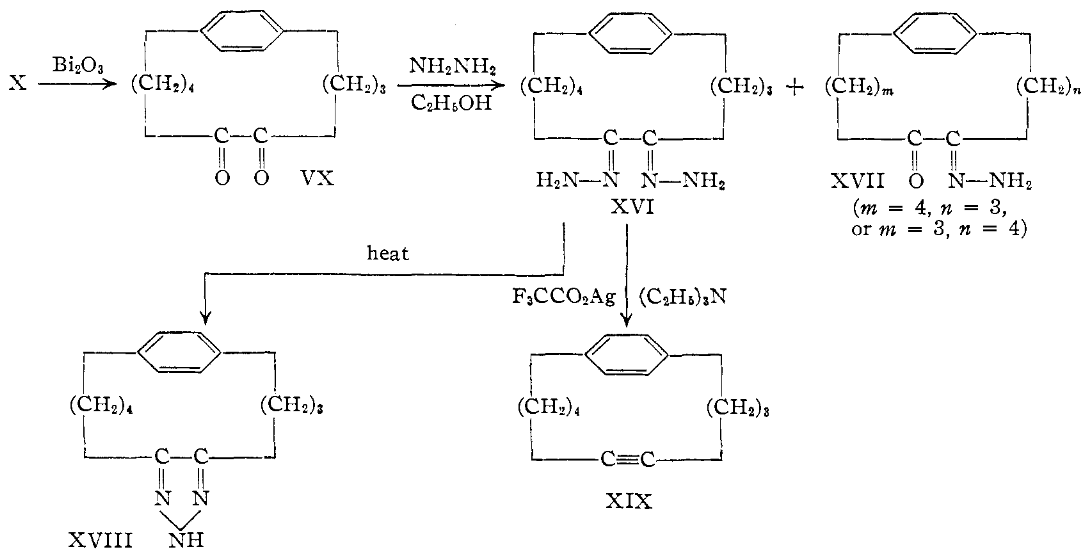
XIV (m = 5, n = 3 or m = n = 4)

XIIb, m.p. 68.5–69.5° (m = 5, n = 3 or m = n = 4)

X

XIIIb, m.p. 57.5–58° (m = 5, n = 3, or m = n = 4)

to enolize, a fact that reflects the higher strain in the compound carrying the shorter bridge. When treated with hydrazine, diketone XV gave a mixture of osazone XVI and monohydrazone XVII whose great insolubility in ethanol drove it from solution as the reaction proceeded. When the osazone was recrystallized from hot ethanol, ammonia was lost and a good yield of triazole XVIII (or a tautomer) was obtained. No such reaction was observed with the next higher homolog of XVI.[2b] This ring closure probably results from the near coplanarity and *cis* arrangement of the  $-\underset{\underset{-N}{\parallel}}{C}-\underset{\underset{N-}{\parallel}}{C}-$ linkage, which geometry best accommodates the strain associated with the nine-membered bridge. When osazone XVI was treated with mercuric oxide and base by the usual method,[9] only triazole XVIII was produced. The conversion of XVI to XIX was accomplished utilizing a solution of silver trifluoroacetate and trimethylamine as the oxidizing agent.[10]



VX

XVI

XVII (m = 4, n = 3, or m = 3, n = 4)

XVIII

XIX

Table I reports the analytical and yield data as well as the physical properties of these compounds.

Spectra.—In the ultraviolet absorption spectra of 5-keto[10]paracyclophane[2b] and of its two homologs ketones XIIa and XIIb, the small differences between the former and the two latter ketones are similar to the small differences observed between the spectra of [10]paracyclophane and [9]paracyclophane.[3] The spectra of the ketonic cycles differ in no significant way from those of the parent hydrocarbons, and no transannular spectral effects involving the carbonyl and benzene functions are visible. Unfortunately the usual λ_{max} for the carbonyl groups are not determinable because of the overlapping absorption of the benzene ring.

The ultraviolet spectra of 5,6-diketo[10]paracyclophane and 4,5-diketo[9]paracyclophane (Fig. 1) are notably different in the positions of λ_{max} at the longer wave lengths (λ_{max} 419 mμ and ϵ 15 for the former, and λ_{max} 425 mμ and ϵ 19 for the latter compound). The occurrence of λ_{max} of the smaller cycle at a longer wave length is consistent with the expectation that in the shorter bridge, a higher proportion of the molecules possesses a conformation with the two carbonyl groups eclipsing one another.[11] The smaller cycle might also be more conformationally homogeneous, as is suggested by the more compact character of the longer wave length band. Scale molecular models of the two diketones indicate that the eclipsed conformation is slightly more sterically feasible than the *trans*, particularly for the smaller cycle. Clearly no bonds attributable to charge-transfer complexing are apparent.[12]

In Fig. 2 are recorded the ultraviolet spectra of

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(9) A. T. Blomquist, R. E. Burge, Jr., L. Huang Liu, J. C. Bohrer, A. C. Sucsy and J. Klein, THIS JOURNAL, **73**, 5510 (1951).

(10) The procedure for this homogeneous reaction was developed by Dr. M. S. Newman and D. E. Reid, who kindly provided us with it prior to publication.

(11) N. J. Leonard and P. M. Mader, THIS JOURNAL, **72**, 5388 (1950).

(12) R. C. Cookson and N. Levin, *Chemistry & Industry*, 984 (1956).

TABLE I

DATA PERTAINING TO COMPOUNDS INVOLVED IN DEVELOPING [9]PARACYCLOPHANE CHEMISTRY

Compound	Yield, %	M.p., °C.	Crystn. solvent	B.p. °C.	B.p. Mm.	$n^{25}D$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
VI	30	81.5–82	Ether	.....	.	....	$C_{17}H_{22}O_5$	66.65	66.91	7.24	7.48
VII	98	121–121.6	Acetone	.....	..	....	$C_{15}H_{20}O_4$	68.16	68.10	7.63	7.62
VIII	83	81–82	Ether	.....	..	....	$C_{17}H_{22}O_5$	66.65	66.57	7.24	7.02
IX	94	....	...	165–166	0.2	1.4952	$C_{17}H_{24}O_4$	69.83	69.56	8.27	8.27
X	35	....	...	157–160	0.2	1.5502	$C_{15}H_{20}O_2$	77.55	77.33	8.68	8.52
XI	31	....	...	140–145	0.2	1.5335	$C_{15}H_{22}$	89.04	89.04	10.96	11.00
XIIa	69	51.5–52.8	Methanol	.....	..	....	$C_{15}H_{20}O$	83.28	83.57	9.32	9.35
XIIb	17	68–69.5	Methanol	.....	..	....	$C_{15}H_{20}O$	83.28	83.02	9.32	9.57
XIIIa	92	110–111.5	Hexane	.....	..	....	$C_{15}H_{22}O$	82.51	82.49	10.16	10.23
XIIIb	90	57–58	Hexane	.....	..	....	$C_{15}H_{22}O$	82.51	82.35	10.16	10.05
XV	95	57.1–58.5	Water	.....	..	....	$C_{15}H_{18}O_2$	78.23	78.05	7.88	8.04
XVI	62	147.2–149	95% Ethanol	.....	..	....	$C_{15}H_{22}N_4$	69.73	69.82	8.58	8.41
XVII	74	141.5–142.8	Ether	.....	..	....	$C_{15}H_{20}N_2O$	73.73	73.49	8.25	8.45
XIX	10	....	Methanol	.....	..	....	$C_{15}H_{18}$	90.85	90.84	9.15	8.96

[9]paracyclophane, 4-[9]paracyclophyne and 5-[10]paracyclophyne. Evidence for transannular electronic effects involving the acetylene and benzene functions are absent in both of the two latter cycles, although of course the absorption of the acetylenic linkage itself occurs at wave lengths not observable with ordinary instruments. The spectra of 4[9]paracyclophyne and [9]paracyclophane are almost identical, a fact which suggests that the bridges in each compound buckle the benzene rings to about the same extent.

The infrared spectra of ketones XIIa and XIIb and of 5-keto[10]paracyclophane were determined (10% carbon tetrachloride solution, model 21 Perkin-Elmer spectrophotometer, sodium chloride optics). The band associated with C═O stretching occurred at essentially the same frequency (1703 to 1707 cm.$^{-1}$) for all three ketones. These frequencies are unusually high for open-chain compounds, but are comparable to those found for cyclononanone and cyclodecanone.[13] The band associated with C≡C stretching was found to occur at 2200 cm.$^{-1}$ in the spectrum of 4-[9]paracyclophyne. The homolog 5-[10]paracyclophyne possessed a band at essentially the same place[2b] so apparently in the

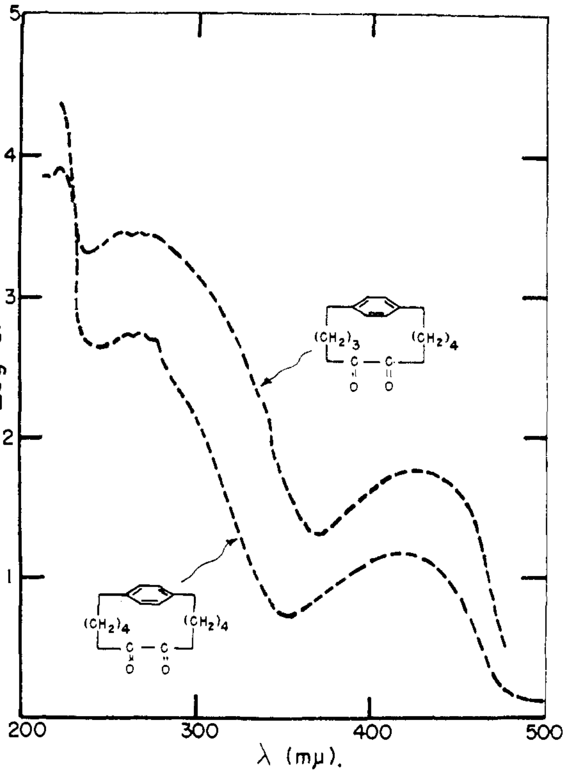

Fig. 1.—Ultraviolet absorption spectrum in 95% ethanol, Cary recording spectrophotometer model 11 MPS. The spectrum of 4,5-diketo[9]paracyclophane is displaced 0.5 log unit upward on the vertical axis.

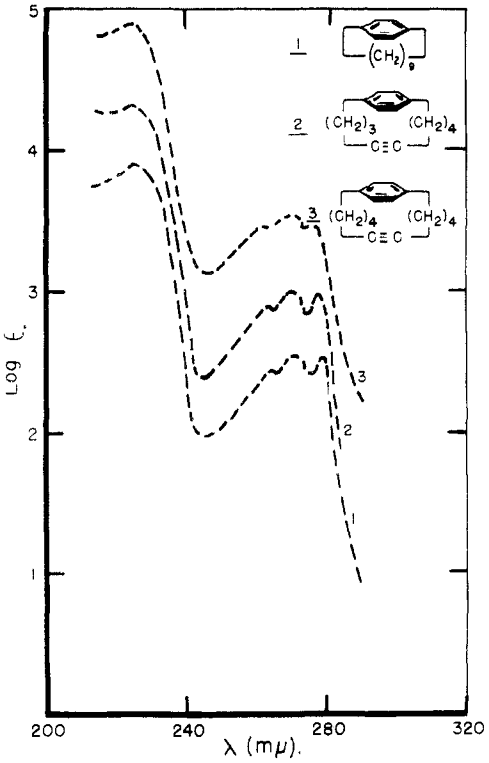

Fig. 2.—Ultraviolet absorption spectrum in 95% ethanol, Cary recording spectrophotometer, model 11 MPS. Curves 2 and 3 are displaced upward on the vertical axis by successive increments of 0.5 log unit.

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[13] A. T. Blomquist, R. B. Burge, Jr., A. C. Sucsy, L. H. Liu and J. C. Bohrer, THIS JOURNAL, 74, 3636, 3643 (1952).

smaller cycle the triple bond character is modified in no noticeable way.

Experimental

Ethyl-β-(4-δ-carbethoxybutyl)-benzoylpropionic Acid (VIII).—A mixture of 90 g. (0.436 mole) of ethyl δ-phenylvalerate,[2a] 45.6 g. (0.456 mole) of succinic anhydride and 600 ml. of redistilled tetrachloroethane was cooled to −7° in an ice–salt-bath. Aluminum chloride (180 g., 1.35 moles) was added to the stirred mixture in small portions over a period of two hours, and the resulting mixture was kept below 0° for 4 hours. This material was allowed to warm to 25°, the dark yellow oil was poured over a mixture of 1 kg. of ice and 100 ml. of concentrated hydrochloric acid with vigorous stirring, and the resulting layers were separated. The aqueous solution was extracted with ether, and the extract was added to the organic layer. The combined material was washed with 2 *N* hydrochloric acid, water, dilute sodium bicarbonate solution and again with water. The solution was dried over magnesium sulfate, the ether evaporated, and the tetrachloroethane was distilled at 25 mm. pressure. After cooling, the mixture solidified as white crystals embedded in a small amount of dark red oil. The residue (167 g.) was recrystallized from ether to give 110 g. (82%) of VIII as white crystals, m.p. 79.5–81°. A small sample was recrystallized twice from ether to give white plates, m.p. 81–82°.

δ-(4-γ-Butyric acid)-phenylvaleric Acid (VII).—A mixture of 95 g. (0.31 mole) of half-ester VIII, 42 g. (0.72 mole) of hydrazine hydrate, 78 g. (1.22 moles) of 87% potassium hydroxide and 300 ml. of diethylene glycol was subjected to the conditions of the Wolff–Kishner method as described in procedure C of paper XV of this series[14] to give upon final acidification 80 g. (98%) of virtually pure material, m.p. 120–122°. A small sample was recrystallized twice from acetone to give white crystals of VIII, m.p. 121–121.6°.

Methyl δ-(4-γ-Methyl butyrate)-phenylvalerate (IX).—A mixture of 79 g. (0.3 mole) of diacid VII, 485 g. (15.2 moles) of absolute methanol and 31 ml. of concentrated sulfuric acid was held at reflux for 6 hours. The mixture was poured over ice and extracted three times with ether. The ether extract was washed with water, dilute sodium bicarbonate solution and again with water. The solution was dried over magnesium sulfate and the solvent was evaporated. The residual yellow oil was distilled under high vacuum and the fraction boiling at 165–166° (0.2 mm.) was collected to give 82 g. (94%) of IX as a colorless oil, n^{25}D 1.4952.

Acyloin X.—The acyloin condensation was carried out under high dilution conditions using the apparatus previously described.[15] Dimethyl ester IX (63 g., 0.215 mole) in 1 liter of pure xylene was added to 21.5 g. (0.94 mole) of clean molten sodium in 2 liters of xylene during 60 hours. The mixture was stirred and heated for an additional hour, cooled, and worked up as described in procedure J, paper XV of this series,[14] to give 17.5 g. (35%) of crude X. A small sample (0.5 g.) was redistilled at a bath temperature of 157–160° and 0.2 mm. pressure to yield 0.4 g. (80%) of acyloin as a yellow liquid, n^{25}D 1.5502.

[9]Paracyclophane (XI).—Acyloin X (5.8 g., 0.025 mole) was held at reflux in a mixture of 10 ml. of glacial acetic acid, 10 ml. of concentrated hydrochloric acid and 13 g. (0.2 mole) of granular, 80 mesh zinc metal.[16] Within 3 hours, four portions of 10 ml. of concentrated hydrochloric acid were added. The unreacted zinc was then collected, and the cooled filtrate was extracted three times with ether. The combined extracts were washed with water, aqueous sodium bicarbonate solution and again with water. The solution was dried over magnesium sulfate, and the solvent was evaporated through a Vigreux column to give 5.5 g. of a yellow oil which was submitted to chromatographic absorption on 350 g. of neutral alumina (activity I) and eluted with pentane. Fractions of 150 ml. were cut from the column eluate. Fractions 1–15 were taken with distilled pentane as eluate, and these when evaporated gave 1.65 g. (31% of final product). This material gave a negative carbonyl test (2,4-dinitrophenylhydrazine) and was considered as a hydrocarbon fraction which was further purified as shown below. Fractions 16–25 also were taken with distilled pentane as eluate, and these when evaporated gave no material. After up to 15% ether failed to bring any further material off the column, the eluate was changed to 20% ether. Fractions 44 to 60 gave 3.65 (69% of final product) of a white solid when the eluate was evaporated. This material gave a positive carbonyl test (2,4-dinitrophenylhydrazine) and proved to be ketone XIIa as shown below.

The hydrocarbon fraction obtained above was distilled from sodium at a bath temperature of 140–150° and a pressure of 0.1 mm. to give 1.5 g. of a colorless liquid, n^{25}D 1.5342. This material was further purified as follows: a gram of the hydrocarbon was dissolved in a mixture of 15 ml. of glacial acetic acid and 10 ml. of ethyl acetate, and shaken in an atmosphere of hydrogen with 0.1 g. of platinum oxide as catalyst. Within 5 hours 95% of the calculated amount of hydrogen (3 moles of hydrogen per mole of substrate) was absorbed and no more hydrogen was consumed in the next 15 hours. The catalyst was collected and 100 ml. of water was added to the filtrate. The resulting suspension was extracted three times with pentane, the extracts were washed with water, dilute sodium bicarbonate solution and again with water. The solution was dried and the solvent was evaporated through a Vigreux column to give 0.95 g. of slightly yellow oil. This material was distilled at a bath temperature of 110–115° and a pressure of 0.2 mm. to give a colorless oil, n^{25}D 1.4995, wt. 0.85 g. (83.5%). This saturated hydrocarbon was crystallized from absolute ethanol at −70° to give 0.62 g. of a colorless oil (at room temperature). This oil was heated to 300° with 80 mg. of 10% palladium-on-charcoal. Within 4 hours 80% of the theoretical amount of hydrogen was evolved. The mixture was cooled, dissolved in pure pentane and filtered. The solution was evaporated and the virtually colorless residue (0.48 g. or 77.5%) was absorbed on 50 g. of neutral alumina (activity I) and eluted with pure pentane. Fractions of 25 ml. were cut from the column eluate. Fractions 1–20 gave 0.45 g. of a colorless oil which was distilled at a bath temperature of 140–145° and a pressure of 0.2 mm. to yield 0.38 g. (38%) of XI as a colorless oil, n^{25}D 1.5335.

Ketone XIIa.—The white crystals obtained from the chromatographic separation of the products of the acyloin reduction, m.p. 50–53°, were recrystallized three times from methanol to give 80% yield of white plates, m.p. 51.5–52.8°.

Ketone XIIb.—Acyloin X (6 g., 0.026 mole) was converted to its acetate by the usual acetic anhydride–pyridine method. The crude product (6 g.), 9.6 ml. of 1,3-propanedithiol and 9 g. of powdered, freshly fused zinc chloride were stirred in 200 ml. of dry benzene.[7] The mixture was saturated with dry hydrogen chloride until a dark red oil separated. The mixture was stirred for two hours, and the solution was decanted from the second phase. The solution was washed with dilute base and water, dried and evaporated under reduced pressure. The residual yellow oil was dissolved in 200 ml. of 95% ethanol. After most of the ethanol had been evaporated under reduced pressure, the bulk of the material precipitated as a white amorphous solid. This solid was collected and the filtrate was evaporated to dryness at a pressure of 25 mm. to give 1.45 g. of slightly yellow crystals. The amorphous solid was insoluble in most organic solvents and proved to be trimethylene disulfide dimer.[7] The yellow crystals were added to a mixture of 11.3 g. of mercuric chloride, 50 ml. of acetone, 11.5 g. of cadmium carbonate and 10 ml. of water. The resulting mixture was stirred for 24 hours during which time additional quantities of cadmium carbonate were added occasionally. The acetone solution was then filtered, and the solvent was evaporated under reduced pressure. The residual oil was extracted with pentane, the pentane solution was washed with water, potassium iodide solution and again with water. The solution was dried over magnesium sulfate, the solvent evaporated and the oil that remained crystallized upon standing to give 1.1 g. of pale yellow crystals, m.p. 65–70°. This material, which gave a positive carbonyl test (2,4-dinitrophenylhydrazine), was absorbed on 100 g. of neutral alumina (activity I) and eluted with pentane. Fractions of 100 ml. were cut from the column eluate. Fractions 1–10 were taken with distilled pentane, and these when evaporated gave 0.85 g. (17.3% based on the acyloin used), m.p. 66.5–69°. A small sample was recrystallized

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twice from methanol to give white plates of ketone XIIb, m.p. 68–69.5°.

Alcohol XIIIa.—Lithium aluminum hydride (0.68 g., 0.018 mole) was stirred with 100 ml. of anhydrous ether, and a solution of 3 g. (0.014 mole) of ketone XIIa in 50 ml. of dry ether was added dropwise. After the addition was complete, the solution was stirred for 30 minutes, and 5 ml. of ethyl acetate followed by 100 ml. of 1 *N* hydrochloric acid were added. The two layers were separated, the organic layer was washed with dilute hydrochloric acid, water, dilute sodium bicarbonate solution and again with water. The solution was dried and the solvent evaporated to give 2.76 g. (92%) of virtually white crystals, m.p. 108–112°. A small sample recrystallized twice from hexane gave hard white needles of XIIIa, m.p. 110–111.5°.

Alcohol XIIIb.—Lithium aluminum hydride (0.152 g., 0.004 mole) was stirred with 50 ml. of anhydrous ether, and a solution of 0.145 g. (0.00067 mole) of ketone XIIb in 50 ml. of dry ether was added dropwise. The product was isolated as in the preparation of alcohol XIIIa to give 0.11 g. (two recrystallizations from hexane) or 70% of XIIIb, m.p. 57.5–58°.

4,5-Diketo[9]paracyclophane (XX).—Acyloin X (9 g. or 0.039 mole) and 10 g. (0.0215 mole) of bismuth trioxide were added to 40 ml. of glacial acetic acid, and the mixture was stirred and heated at 110° for two hours. A small sample of material gave no acyloin test at the end of this time. The mixture was cooled, filtered and to the filtrate was added 60 ml. of water. This mixture was then extracted three times with benzene, and the combined benzene extracts were washed with water, dilute sodium bicarbonate solution and again with water. The solution was dried and the solvent was evaporated in vacuum under nitrogen to give 8.9 g. of a yellow oil which solidified when allowed to stand. This material was recrystallized once from ethanol to give 8.5 g. (95%) of XV as yellow needles, m.p. 55–58°. A small sample was recrystallized twice from ethanol–water to give yellow needles of α-diketone, m.p. 57.1–58.5°.

Monohydrazone of 4,5-Diketo[9]paracyclophane (XVII).—The monohydrazone of diketone XV was prepared by heating a mixture of 10 ml. of 95% hydrazine and 1 g. (0.0044 mole) of the diketone on a steam-bath for one hour. The reaction mixture was allowed to cool and the virtually white solid that precipitated was collected and washed with cold ethanol, wt. 0.90 g., m.p. 138–142°. This material was recrystallized twice from ether to give 0.75 g. (74%) of white prisms of XVII, m.p. 141.5–142.8°.

Osazone of 4,5-Diketo[9]paracyclophane (XVI).—The bis-hydrazone of diketone XV was prepared by heating a solution of 0.1 g. (0.0004 mole) of the diketone in 10 ml. of absolute ethanol with 5 ml. of 95% hydrazine for one hour on a steam-bath. The solution was evaporated to dryness under 25 mm. of pressure, and the residual yellow oil was crystallized from 95% ethanol to give pale yellow crystals, wt. 0.07 g. (62.5%), m.p. 144–147.5°. This material was recrystallized twice from the same solvent to give pale yellow plates of osazone XVI, m.p. 147.2–149°.

Preparation of Triazine (XVIII).—A solution of 0.1 g. of diketone XV in 10 ml. of absolute ethanol and 5 ml. of 95% hydrazine was held at reflux for 2 hours. The solvent was evaporated under reduced pressure, and the residual yellow solid was recrystallized from hot 95% ethanol to give 0.08 g. (77%) of dark yellow crystals, m.p. 210–216°. This material was recrystallized three times from boiling 95% ethanol to give 0.05 g. of yellow-orange crystals, m.p. 215–218°.

Anal. Calcd. for $C_{15}H_{19}N_3$: C, 74.65; H, 7.94; N, 17.41. Found: C, 74.38; H, 8.14; N, 17.63.

4-[9]Paracyclophyne (XIX).—Silver trifluoroacetate (22.1 g., 0.1 mole) was partially dissolved in 70 ml. of acetonitrile in a 250-ml. round-bottom flask equipped with a magnetic stirring bar, an addition funnel and an exit tube which led to an audiometer. To this stirred suspension was added 5 g. (0.02 mole) of crude bis-hydrazone XVI and 8 g. (0.08 mole) of triethylamine in 80 ml. of acetonitrile. The evolution of nitrogen started after 20 minutes after which the rate of addition was adjusted so that a steady flow of nitrogen was observed. After three hours nitrogen ceased to evolve. The nitrogen evolved amounted to 250 ml. (uncorrected) which corresponds to 25% of the theoretical amount. The reaction mixture was then heated to 80° and within an hour an additional 170 ml. of nitrogen was evolved. The total amount of gas evolved was 420 ml. (uncorrected) which corresponds approximately to 46.5% of the theoretical amount which should be evolved if the reaction went to completion. The reaction mixture was stirred at 80–90° for an additional 3 hours during which no gas was evolved. The reaction mixture was allowed to cool, and the organic layer was decanted from the silver. The solution was added to 100 ml. of concentrated ammonium hydroxide. This solution was extracted three times with ether, the combined ether extracts were dried over magnesium sulfate and the solvents were evaporated under reduced pressure. The residual brown oil (4.8 g.) was absorbed on a column containing 350 g. of alumina (activity I) and eluted with pentane. Fractions of 150 ml. were cut from the column eluate. Fractions 1–7 were taken with distilled pentane as eluate, and these when evaporated gave 0.6 g. of a colorless oil. After up to 40% ether failed to bring any further material off the column, the chromatogram was developed with 50% ether. There was no break from 50 to 100% ether and 40 fractions of 250 ml. were taken before the second break and these when evaporated gave 0.55 g. of yellow oil which crystallized when allowed to stand at room temperature. This material was recrystallized from ether to give 0.45 g. of white prisms, m.p. 140–142.5°, and a mixed melting point gave no depression with the monohydrazone. The column was then eluted with methanol and fractions of 300 ml. were cut from the column eluate. These fractions were concentrated and combined, then added to 10 times their volume of water, and the resulting mixture was extracted three times with ether. The combined ether extracts were washed with water, dried, and the solvent was evaporated to give 0.4 g. of a dark brown oil which crystallized upon standing. This material was recrystallized from petroleum ether to give yellow needles, m.p. 146–149.2°, and an admixture of this material with the bis-hydrazone gave no depression in the melting point.

The pentane fraction (0.6 g.) was distilled at a bath temperature 145–150° and a pressure of 2 mm. to give 0.55 g. of a colorless oil, $n^{25}\text{D}$ 1.5502. This oil showed a weak band at 2200 cm.$^{-1}$ (4.55 μ) in the infrared region which characterizes a disubstituted acetylene.[17] The carbon and hydrogen analysis suggested that it might be contaminated with the corresponding paracyclophane. This material was absorbed on a column of very active neutral alumina (110 g.) and eluted with carefully distilled pentane. Fractions of 50 ml. were cut from the column eluate. There was no definite break in 20 fractions which when evaporated gave 0.54 g. of a colorless oil. This oil failed to crystallize when cooled and was absorbed on a column containing 150 g. of very active neutral alumina and eluted with pentane. Fractions of 10–20 ml. were cut from the column eluate. When evaporated, fractions 1–7 gave no material, while fractions 8–15 gave 58 mg. of a colorless oil which did not solidify upon cooling. Fractions 16–35 gave 0.47 g. of a colorless oil which was induced to crystallize at −5°, m.p. 33–34.4°. This material was recrystallized from methanol to give 0.4 g. of XIX as colorless needles, m.p. 33.5–35.2°. A small sample was recrystallized twice from the same solvent to give colorless needles of XIX, m.p. 34.4–35.2°.

LOS ANGELES, CALIFORNIA

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[17] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 50.