By heating, the 1,1,2,2-tetraphenyl-1,2-dichloroethane was converted to 1,1,2,2-tetraphenylethylene, m.p. 220.5–222° (lit.[29] m.p. 220–221°).

Anal. Calcd. for $C_{26}H_{20}$: C, 93.93; H, 6.07. Found: C, 93.93; H, 6.31.

The original carbon tetrachloride filtrate was concentrated to leave a red oil, 85 g. An infrared spectrum indicated that this oil was a mixture of dichlorodiphenylmethane and triphenylchloroallene. There was no band around the acetylenic absorption region at 2230 cm.$^{-1}$. A 10.0-g. portion of the red oil was hydrolyzed in alcoholic aqueous sulfuric acid to give 3.1 g. of recovered dichlorodiphenylmethane and 5.4 g. of β,β-diphenylacrylophenone. This corresponds to at least a 56% yield of triphenylchloroallene.

Attempted Rearrangement of Methyl 1,1,3-Triphenylpropargyl Ether (VI).—The ether was prepared from Ib in methanol–sulfuric acid as reported[13] in 94% yield, m.p. 118–122°, infrared absorption at 2220 cm.$^{-1}$, lit. m.p. 124°.

To a stirred cold solution of 3.0 ml. of 100% sulfuric acid in 200 ml. of anhydrous methanol was added dropwise a solution of 5.0 g. of the ether in 15 ml. of anhydrous benzene.[30] The liquid quickly turned yellow and a white solid formed; this precipitate slowly dissolved as the mixture was stirred for 18 hr. The acid catalyst was then neutralized with anhydrous potassium carbonate and the mixture was partitioned between 500 ml. of water and 500 ml. of ether. The ether layer was separated, dried, and concentrated at reduced pressure to yield 5.5 g. of yellow solid, m.p. 62–72°; infrared indicated this to be mainly β,β-diphenylacrylophenone containing a little starting ether. Chromatography gave pure samples of both the ether and ketone. In a similar experiment carried out with concentrated sulfuric acid the neutralization with potassium carbonate was omitted. Chromatography gave 1.2 g. (24%) of recovered starting material and 3.8 g. (76%) of β,β-diphenylacrylophenone, m.p. 86–88°, lit[31] m.p. 89°.

Ethyl 1,1,3-Triphenylpropargyl Ether.—A solution of 1.0 g. (0.025 mole) of Ib in 70 ml. of anhydrous ethanol and 10 ml. of concentrated sulfuric acid was stirred for 5 min. at 0°. A mixture of 250 ml. of water and 100 ml. of ether was added and the layers were separated; the ether solution was washed with water, sodium bicarbonate solution, and water and then dried over calcium chloride. Evaporation left a yellow oil which was chromatographed in pentane on neutral activated alumina to yield 5.7 g. (73%) of a colorless oil. Standing for 5 days at 0° in a little petroleum ether (b.p. 60–70°) gave white crystals, m.p. 49–50°, infrared absorption at 2220 cm.$^{-1}$, lit. m.p. 51°.

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.34; H, 6.45. Found: C, 88.45; H, 6.37.

An ether with the same melting point (mixture showed no depression) and infrared spectrum was obtained from 0.25 g. (0.00072 mole) of IIb (X = Br) which was allowed to stand for 2 days in 25 ml. of anhydrous ethanol in which had been dissolved 0.5 g. (0.022 g.-atom) of sodium. Purification involved similar chromatography. The yield was 85%, m.p. 49–50°.

Reaction of VI with Hydrogen Chloride.—Dry hydrogen chloride was passed into a stirred solution of 3.0 g. (0.01 mole) of VI in 500 ml. of benzene containing 5 g. of calcium chloride. The solution was filtered and concentrated to give a light green liquid. Chromatography in pentane on alumina gave 1.9 g. (60%) of chloroallene IIb, m.p. 60–65°, and 0.7 g. (23%) of β,β-diphenylacrylophenone, m.p. 88–89°. Both products showed the expected spectra.

Methyl 4,4-Dimethyl-1,3-diphenyl-1,2-pentadienyl Ether (IIc, X = OCH_3).—A solution of 2.0 g. (0.087 g.-atom) of sodium in methanol was added to 1.0 g. of IIc (X = Br) and the cloudy yellow-green reaction mixture was left overnight at room temperature. Solvent was then removed at reduced pressure on a steam bath, ether was added, and the mixture was filtered. The filtrate was concentrated, diluted with pentane, and chromatographed on basic activated alumina to give IIc (X = OCH_3), 0.69 g. (80%), as a colorless oil, b.p. 140–141° (1.5 mm.), n^{25}D 1.5727, infrared absorption at 1960 cm.$^{-1}$ (very weak).

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.34; H, 8.06.

1-*t*-Butyl-1,3-diphenylpropargyl Methyl Ether (IIIc, X = OCH_3).—To a benzene solution containing 5.0 g. (0.019 mole) of Ic was added 0.75 g. (0.019 g.-atom) of potassium. Nearly all of the metal was consumed after the mixture was refluxed for 30 min. with vigorous stirring. Methyl iodide (15 g., 0.11 mole) was added and the solution was stirred for 1 hr.; a light tan precipitate formed. Water was added cautiously and the organic layer was washed with water, dried, and concentrated to leave a light yellow oil. Distillation at reduced pressure gave phenylacetylene (caught in a trap at −78°), 1.3 g. (42%) of *t*-butyl phenyl ketone, b.p. 65–66° (1.5 mm.), n^{25}D 1.5075, strong infrared band at 1675 cm.$^{-1}$, and 2.1 g. (40%) of IIIc (X = OCH_3), b.p. 145–150° (1.5 mm.). Chromatography of this last fraction gave a single material which was redistilled, b.p. 128–130° (0.9 mm.), n^{25}D 1.5628; this product could not be induced to crystallize.

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.46; H, 8.13.

The infrared spectrum showed a sharp band at 2220 cm.$^{-1}$ and was very different from the spectrum of IIc (X = OCH_3).

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[29] J. Mackenzie, *J. Chem. Soc.*, **121**, 1697 (1922).

[30] This experiment was carried out by Mr. Donald A. Babbe.

[31] H. Fiesselmann and K. Sasse, *Ber.*, **89**, 1775 (1956).

Internal Strain and Reactivity. Some Reactions of Acenaphthene*

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Received November 16, 1964

Rates of bromination of acenaphthene in 90% aqueous acetic acid and of the solvolysis of α-(5-acenaphthyl)-ethyl chloride in 90% aqueous acetone were determined at 25°. The rates are faster than can be expected on the basis of reasonable assumptions, and the increase in reactivity is ascribed to internal strain in the acenaphthene molecule.

It has recently been proposed that part of the increased reactivity of fluorene and its derivatives may be due to internal strain.[2] In this connection, we would like to report some data on the reactivity of the acenaphthene system, which is also a strained molecule. The 1,8-distance in naphthalene, to which in acenaphthene the two-carbon bridge is attached, is longer than 2 Å., and in early X-ray investigations abnormally long distances of 2.01,[3] 1.80, and 1.64 Å.[4] were reported for the aliphatic carbon–carbon bond. The results of a more recent X-ray investigation, however, indicate that the acenaphthene molecule is planar with no unusual bond lengths.[5] The carbon–carbon bond has the normal length of 1.54 ± 0.014 Å., but the strain exists in the bond angles and is shared by several

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* To Professor Louis F. Fieser.

[1] Taken from the Senior Honors Theses of D. M. Falcione, 1963, and of J. L. Riemenschneider, 1964.

[2] P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J. Chem. Soc.*, 5317 (1964).

[3] K. Bannerjee and K. L. Sinha, *Indian J. Phys.*, **11**, 21 (1937).

[4] A. I. Kitaigorodskii, *Zh. Fiz. Khim.*, **21**, 1085 (1947); **23**, 1036 (1949).

[5] H. W. W. Ehrlich, *Acta Cryst.*, **10**, 699 (1957).

angles in all three rings. This is a reasonable finding in view of the greater energy needed to stretch a bond than to bend an angle, and, even though the energy required to distort a carbon bond angle is only about 0.0175 kcal./degree^2 mole,[6] a sufficiently large number of angles are distorted to increase the internal energy of the molecule by a few kilocalories per mole.

Two sets of kinetic data are here reported, the direct bromination of acenaphthene and a solvolytic side-chain reaction. We believe that in both reactions the acenaphthene system reacts faster than expected on the basis of reasonable assumptions.

The bromination of acenaphthene by molecular bromine was conducted in 90% (by volume) aqueous acetic acid under conditions in which the over-all reaction is of the second order, and free molecular bromine is the substituting agent. The conditions and the kinetic characteristics had previously been established for bromination of a series of hydrocarbons in 50, 60, and 75% aqueous acetic acid,[7] but acenaphthene is too reactive for a study of its reaction rate in these more aqueous solvents. As before, reaction was conducted in the presence of an excess of bromide ion where the rate expression is $k_{\text{obsd}} = k_2K/(K + \text{Br}^-)$, and K is the dissociation constant of the tribromide ion.[8] Rate constants were determined at different concentrations of bromide ion at a constant ionic strength at 25°, and the rate constant for bromination by free bromine, k_2, was obtained graphically from a plot of k_{obsd} *vs.* $K/(K + \text{Br}^-)$ (Table I). The value for k_2 was found to be 450 ± 8 l./mole sec. In order to compare this value with that for benzene, another compound, 2,6-dimethylnaphthalene, was studied in 90 and 75% aqueous acetic acid; in the latter solvent the compound reacted 12.4 times faster than in the former. From the value of the rate constant for bromination of naphthalene in 75% aqueous acetic acid,[9] and data obtained previously,[7] one then finds that acenaphthene is brominated 5.53×10^{10} times faster than benzene, assuming that the relative rates of bromination are not affected by differences in solvent composition. Fieser showed more than 30 years ago that, in the Friedel–Crafts succinoylation, acenaphthene is substituted in both the 3- and the 5-positions,[10] but 5-bromoacenaphthene is the only monobromination product that has been reported on bromination.[11] With this information, the partial rate factor for bromination in the 5-position of acenaphthene is 1.66×10^{11}.[12]

TABLE I

KINETIC DATA FOR THE BROMINATION OF ACENAPHTHENE AND OF 2,6-DIMETHYLNAPHTHALENE[a]

Acenaphthene in 90% acetic acid		2,6-Dimethylnaphthalene in		
		90% acetic acid		75% acetic acid
NaBr, M	k_{obsd}, l. mole^{-1} sec.$^{-1}$	NaBr, M	$10^2 \times k_{\text{obsd}}$, l. mole^{-1} sec.$^{-1}$	$10 \times k_{\text{obsd}}$,[b] l. mole^{-1} sec.$^{-1}$
0.30	8.22	0.10	5.04	9.02
0.35	6.90	0.20	2.56	4.80
0.40	5.56	0.30	1.74	3.31
0.45	4.76	0.40	1.32	2.41
0.50	4.07	0.50	1.16	1.91

[a] At 25°, μ 0.5 ($KClO_4$). [b] k_2 is 9.12 ± 0.07 l. mole^{-1} sec.$^{-1}$.

For a meaningful evaluation of the reactivity of acenaphthene in bromination, its rate of reaction can be compared with that of the methylnaphthalenes or a series of dimethylnaphthalenes, in which, as a first approximation, the activating effects of the methyl groups may be expected to be similar to that of the side chain in acenaphthene. The 4-position in 1-methylnaphthalene has a maximum partial rate factor of 1.17×10^8, compared with a partial rate factor of 1.85×10^5 for the 1-position of naphthalene.[7,9,13] The rate constant for bromination of a representative dimethylnaphthalene, 2,6-dimethylnaphthalene, in which, as in acenaphthene, two α-positions are subject to substitution, was obtained under identical conditions and is 0.733 ± 0.009 l./mole sec. If one assumes, as is reported,[14] that the only isomer in the monobromination of this compound is the 1 isomer, the partial rate factor for bromination in the 1-position of 2,6-dimethylnaphthalene is 2.70×10^8, or 600 times smaller than that for acenaphthene. The observed rates of bromination of other dimethylnaphthalenes, such as the 2,3-, 1,5-, or 2,7-dimethylnaphthalenes are similar in magnitude to the rate of the 2,6 isomer and are thus all less than that of acenaphthene.[15] 2,7-Dimethylnaphthalene in which the position of substitution is activated directly by both methyl groups, as it is in acenaphthene, has a partial rate factor in the 1-position of 1.80×10^9, or 92 times less than acenaphthene.[16] The closest analog to acenaphthene is 1,8-dimethylnaphthalene, although this molecule may itself be strained and the methyl groups distorted and therefore react at a different rate than expected by the additivity principle. Strain in 1,8-dimethylnaphthalene, as well as in acenaphthene, has been held responsible for the chemical shifts to lower fields of the aliphatic protons, compared with that of the other dimethylnaphthalenes.[17] The partial rate factor for bromination in the 4-position of 1,8-dimethylnaphthalene is 6.45×10^8, which is 257 times smaller than

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(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 252.

(7) E. Berliner and M. C. Beckett, *J. Am. Chem. Soc.*, **79**, 1425 (1957); E. Berliner and J. C. Powers, *ibid.*, **83**, 905 (1961); E. Berliner and B. J. Landry, *J. Org. Chem.*, **27**, 1083 (1962); U. P. Zimmerman and E. Berliner, *J. Am. Chem. Soc.*, **84**, 3953 (1962).

(8) A value of 0.0073 mole/l. was estimated by extrapolation of the data of T. W. Nagakawa, L. J. Andrews, and R. M. Keefer, *J. Phys. Chem.*, **61**, 1007 (1957).

(9) k_2 is 0.0126 ± 0.0003 l./mole sec.; unpublished data of C. Chen, M.A. Thesis, Bryn Mawr College, 1963. Additional data for the calculation of the partial rate factors are the rate constants, k_2, for bromination of naphthalene and of benzene in 50% acetic acid, which are 0.341 and 2.74×10^{-6} l./mole sec., respectively (ref. 7). All partial rate factors are therefore referred to benzene in 50% acetic acid at 25°.

(10) L. F. Fieser, *J. Am. Chem. Soc.*, **54**, 4350 (1932).

(11) For instance, see A. Fischer, W. J. Mitchell, J. Packer, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 2892 (1963).

(12) All partial rate factors quoted in the present paper must be considered tentative maximum values until the exact isomer ratios are determined by modern techniques, but it is doubtful that they can be in error by more than 10 or 20%.

(13) An almost theoretical yield (93% of isolated product) of the 4 isomer has been reported for the bromination of 1-methylnaphthalene by R. D. Topsom and J. Vaughan [*J. Chem. Soc.*, 2842 (1957)].

(14) V. Vesely and F. Stursa, *Collection Czech. Chem. Commun.*, **4**, 21 (1932).

(15) Unpublished data of M. Link, Senior Honors Thesis, Bryn Mawr College, 1964, and of C. J. Simpson, National Science Foundation Summer Research Participant, 1964.

(16) Ng. Ph. Buu-Hoi and J. Lecocq [*J. Chem. Soc.*, 830 (1946)] reported an almost theoretical yield of the 1 isomer.

(17) C. MacLean and E. L. Mackor, *Mol. Phys.*, **3**, 223 (1960). For one estimate of the strain energy in 1,8-dimethylnaphthalene, see J. Packer, J. Vaughan, and E. Wong, *J. Am. Chem. Soc.*, **80**, 905 (1958). See also G. Suld and A. P. Stuart, *J. Org. Chem.*, **29**, 2939 (1964).

that of acenaphthene.[18] The rates of bromination of the above dimethylnaphthalenes and of acenaphthene are in the same relative order as the rates of hydrogen-deuterium exchange.[19]

The solvolytic side-chain reaction studied was the SN1 solvolysis of α-(5-acenaphthyl)ethyl chloride in 90% aqueous acetone. A series of polynuclear α-arylethyl chlorides, $ArCHClCH_3$, had previously been investigated in 80% aqueous acetone,[20] but, as in bromination, a solvent of lower water content had to be chosen because of the great reactivity of the acenaphthyl system. The first-order rate constant, averaged from four independent runs at 25°, is $8.87 \pm 0.17 \times 10^{-4}$ sec.$^{-1}$, which, with the help of a conversion factor, becomes 1.14×10^{-2} in 80% aqueous acetone. This is only slightly less than the rate constant for the solvolysis of α-(9-anthryl)ethyl chloride, and more than that of the pyrenyl and chrysenyl systems,[20] but a more direct comparison is more difficult than in bromination. Focusing on one methylene group in acenaphthene, one can analyze the data as follows. From the ratio of rates of the solvolysis of α-*p*-tolyl ($k_1 = 3.40 \times 10^{-5}$ sec.$^{-1}$)[21] to α-phenylethyl chloride, one knows that one methyl group activates the *para* position in the phenyl group by a factor of 50. The acenaphthyl compound, however, reacts 970 times faster than α-(1-naphthyl)ethyl chloride. There is reason to believe that the effect of a substituent is more compressed in the naphthalene system than in the benzene system, so that one methyl group in naphthalene may actually exert an effect of less than 50. The effect of the second methylene group in acenaphthene (a 1,5 interaction) must certainly be less than that caused by the direct 1,4 interaction, as judged, for instance, from the bromination rates. The anticipated value must therefore be considerably less than the observed rate enhancement of almost 1000, although the comparisons are less complete in the solvolytic reaction than in the substitution reaction.

The rate data here reported are meant to show that the acenaphthene system is more reactive than can reasonably be expected by comparison with other compounds, although there always remain difficulties in estimating the reactivity in the absence of strain.[22] If, however, this interpretation is valid, then the strain also manifests itself in an equilibrium reaction, because there exists an excellent linear correlation between the equilibrium constants for a series of hydrocarbons reacting with hydrogen fluoride[27] and the rate constants for bromination of the same hydrocarbons, which include acenaphthene.[28] This is not surprising, in view of the similarity of the transition state in aromatic substitution reactions and the structure of the conjugate acids of the hydrocarbons.

Experimental

Materials.—All inorganic materials were best reagent grade chemicals which were dried at 110° before use. The glacial acetic acid was purified with chromium trioxide as before.[7] The solutions of aqueous acetic acid were prepared by mixing appropriate volumes of boiled-out distilled water and acetic acid, which had been separately thermostated before mixing. Fresh solutions of aqueous acetic acid were prepared periodically, and the kinetic results were found to be reproducible. Only one solvent batch of 90% aqueous acetone was used, which was prepared from purified acetone[29] (3600 ml.) and boiled-out distilled water (400 ml.). Acenaphthene (Rütgerswerke, Frankfurt A. M., Germany), was recrystallized three times from ethanol and melted at 93.5–94.3°.[30] 2,6-Dimethylnaphthalene, from the same source, was recrystallized three times from ethanol-benzene and melted at 110.3–111.0°.

α-(5-Acenaphthyl)ethyl chloride was prepared as follows. 5-Acenaphthyl methyl ketone,[31] m.p. 68.0–68.8° (lit. m.p. 75°,[31] 68.0–68.5° [32]), was reduced with lithium aluminum hydride in absolute ether. The resulting 5-acenaphthylmethylcarbinol (65% of recrystallized product from 3.2 g. of ketone) was recrystallized from benzene–ligroin (b.p. 60–70°) and formed white needles of m.p. 108.0–108.8°.

Anal.[33] Calcd. for $C_{14}H_{14}O$: C, 84.82; H, 7.12. Found: C, 84.64; H, 7.05.

The alcohol was converted to the chloride with thionyl chloride in absolute ether in the cold. α-(5-Acenaphthyl)ethyl chloride was crystallized from ligroin and formed colorless crystals melting at 75.4–76.0°. The usual yield on runs of 0.5 g. was about 0.250 g. of crystallized product. The compound is fairly unstable, and material sufficient only for two kinetic runs was prepared at a time and stored in a refrigerator.

Anal.[33] Calcd. for $C_{14}H_{13}Cl$: C, 77.59; H, 6.04. Found: C, 77.71; H, 6.07.

Kinetic Determinations.—These were carried out as described before.[7,20] In the bromination of acenaphthene, the initial bromine concentration was determined by a blank, which was identical with the kinetic run, except that the hydrocarbon was omitted. The concentration of bromine was usually about 0.001 *M* and that of acenaphthene was 0.0013 *M*. In the bromination of 2,6-dimethylnaphthalene the concentrations of hydrocarbon were about 0.004 *M* in 90% and 0.002 *M* for reaction in 75% acetic acid. Bromination of acenaphthene was carried out to over 90% completion, that of the other compound to well over 50%. All runs were conducted at least in duplicate, and the average rate constants, listed in Table I, had an average deviation of about 3% for acenaphthene and of about 1% for 2,6-dimethylnaphthalene. Rate constants were determined graphically by the method of least squares. The bromine concentration used for the final calculation of the rate constants was obtained from the

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(18) Unpublished results obtained by C. J. Simpson. The rate constant, k_2, for bromination of 1,8-dimethylnaphthalene in 90% acetic acid at 25° is 1.75 ± 0.05 l./mole sec. Only the 4-bromo compound has been isolated in the bromination of 1,8-dimethylnaphthalene: W. J. Mitchell, R. T. Topsom, and J. Vaughan, *J. Chem. Soc.*, 2526 (1962).

(19) G. Dallinga, P. J. Smit, and E. L. Mackor, *Mol. Phys.*, **3**, 130 (1960), and ref. 17.

(20) E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957).

(21) Unpublished data of E. A. Hurd, M.A. Thesis, Bryn Mawr College, 1964.

(22) Both bromination and solvolysis reactions are known to follow a Baker–Nathan order.[23] The methyl groups in toluene or in the methylnaphthalenes should, therefore, be more activating than a single methylene group in acenaphthene, which would make the estimated reactivity of acenaphthene still smaller. In view of the X-ray data,[5] it does not seem likely that the methylene groups in acenaphthene are especially favorably disposed for hyperconjugation, as has been stated,[11] because the carbon–hydrogen bonds are in *gauche* positions relative to the aromatic plane (see ref. 24 for the strong conformational dependence of hyperconjugation, as measured by secondary isotope effects). To what extent second-order hyperconjugation[25] may be favorable in this molecule cannot be ascertained at the present state of the hyperconjugation problem, but it is generally recognized to be usually a very insignificant energy factor.[26]

(23) For instance, see summaries in E. Berliner, *Tetrahedron*, **5**, 202 (1959).

(24) V. J. Shiner and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **85**, 2416 (1963).

(25) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 150 ff; E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, **71**, 1195 (1949).

(26) A. Lofthus, *ibid.*, **79**, 24 (1957).

(27) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66, 186 (1958).

(28) E. Berliner in "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. Taft, Ed., Interscience Publishers, Inc., New York. N. Y., 1964, p. 253.

(29) J. B. Conant and W. R. Kirner, *J. Am. Chem. Soc.*, **46**, 232 (1924).

(30) All melting points are corrected.

(31) C. Graebe, *Ann.*, **327**, 77 (1903).

(32) A. G. Anderson, Jr., and R. H. Wade, *J. Am. Chem. Soc.*, **74**, 2274 (1952).

(33) Analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn.

intercept; it was always within 1% of that obtained from the blank or the initial titer. In the solvolysis reaction, the concentration of chloride was 0.008 *M*. Samples of 10 ml. were quenched by draining them into 100 ml. of ice-cold acetone, and the resulting solution was titrated with standard NaOH using a 0.5% alcoholic solution of lacmoid as indicator. Eight samples were taken within 50 min.; the ninth sample was treated with 5 ml. of water and allowed to stand for at least 24 hr. for the determination of the final titer. Runs were conducted to over 90% completion, and the final concentration of chloride was usually 95%. Rate constants were determined graphically, and the probable error in the slope was on the average 1%.

Acknowledgment.—This work was supported by National Science Foundation Grant G-19755, which is gratefully acknowledged. We also acknowledge stimulating discussions with Professor P. B. D. de la Mare.

Macro Rings. XXX. Structure of Anomalous Products of Acylation of [2.2]Paracyclophane*[1]

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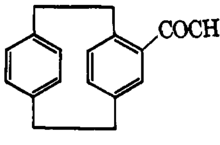
Received November 17, 1964

Acetylation of [2.2]paracyclophane with acetyl chloride–aluminum chloride in methylene chloride gave, besides 4-acetyl[2.2]paracyclophane, two isomeric methyl ketones, $C_{36}H_{36}O_2$. Oxidation of the two ketones gave two acids. The same hydrocarbon (VII) was produced from each of the two acids by decarboxylation, and the structure of VII was deduced from comparisons of its ultraviolet, infrared, and n.m.r. spectra with those of model compounds.

Although 4-acetyl[2.2]paracyclophane (I) is the main product of acetylation of [2.2]paracyclophane with acetyl chloride–aluminum chloride in methylene chloride,[2] a number of other products were detected which were not isolated or identified. The structures of these materials appeared interesting because of the possibility that either diacetylated [2.2]paracyclophanes or acetylated [2.2]parametacyclophanes (II) would be produced. The latter notion was strengthened by the observation[3] that small amounts of pyrene were produced when [2.2]paracyclophane was treated with aluminum chloride in dichloromethane.



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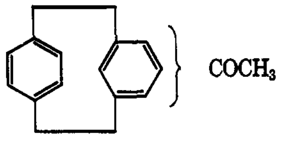


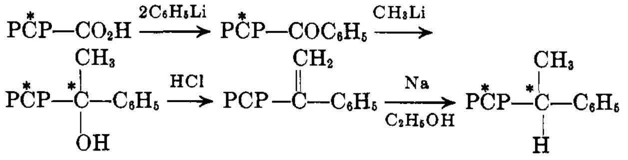
II

Structural Assignments

Careful chromatography on silica gel and fractional crystallization of the acetylated reaction mixture gave besides I (75%), 9% of compound III (m.p. 257°) and 9% of compound IV (m.p. 98–101°). Both III and IV possessed the molecular formula, $C_{36}H_{36}O_2$. Both compounds exhibited bands in their infrared spectra at 5.99 and 7.38 μ typical of acetyl groups attached to benzene rings. The two substances possessed the same ultraviolet absorption spectrum.

Compounds III and IV were oxidized with bromine and potassium hydroxide to their corresponding dicarboxylic acids (V and VI), which had nearly identical ultraviolet spectra, and which exhibited a carbonyl absorption band in their infrared spectra at 5.98 μ. Oxidation of acids V and VI with basic permanganate produced a 50% yield of terephthalic acid, identified as its dimethyl ester in a vapor phase chromatographic (v.p.c.) analysis. No benzoic, phthalic, isophthalic, or aromatic tricarboxylic acids could be detected in the products. As a model for these oxidations, 4-carboxy[2.2]paracyclophane was similarly oxidized, and the expected terephthalic and trimellitic acids were identified as their methyl esters by v.p.c. analysis. Acids V and VI were decarboxylated with copper and quinoline to give the same hydrocarbon, VII, as shown by mixture melting point determination and identical ultraviolet, infrared, and n.m.r. spectra. Thus, III and IV differed only in the placement of the acetyl groups on their aromatic nuclei.

One of the two diastereomeric hydrocarbons (IXa and IXb) was prepared as spectral model for hydrocarbon VII by the sequence formulated. Optically pure 4-benzoyl[2.2]paracyclophane was prepared from optically pure 4-carboxy[2.2]paracyclophane[2] for use in other studies. Racemic ketone was similarly prepared. Diastereomeric racemic alcohols VIIIa and VIIIb were obtained in almost equal amounts and were separated by fractional crystallization, and their relative configurations were provisionally assigned from their n.m.r. spectra. Isomer VIIIa (m.p. 123–124°) exhibited the following spectrum: protons of benzene ring, τ 2.93 (toluene, τ 2.83); center of gravity of paracyclophane aromatic protons, 3.55 (center of gravity of $PCPCH_2CH_2OCHO$, 3.6)[4]; methylene protons, 6.97; and methyl protons, 8.27. Isomer VIIIb (m.p. 145°) gave a somewhat different spectrum: protons of benzene ring, τ 2.54 (some fine structure); center of gravity of paracyclophane aromatic protons, 3.78; methylene protons, 7.08; and methyl protons, 8.22. Molecular models of the diastereomeric alcohols suggest that the conformations written for the two diastereomeric alcohols should be the most stable. Model VIIIb places the side-chain phenyl group somewhat along side of one of the benzene rings of the paracyclophane



$$\overset{*}{PCP}\text{—}CO_2H \xrightarrow{2C_6H_5Li} \overset{*}{PCP}\text{—}COC_6H_5 \xrightarrow{CH_3Li}$$

$$\overset{*}{PCP}\text{—}\overset{*}{C}(CH_3)(OH)\text{—}C_6H_5 \xrightarrow{HCl} PCP\text{—}C(=CH_2)\text{—}C_6H_5 \xrightarrow[C_2H_5OH]{Na} \overset{*}{PCP}\text{—}\overset{*}{C}H(CH_3)\text{—}C_6H_5$$

VIIIa + VIIIb IXa + IXb

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* To Professor Louis F. Fieser.

(1) The authors wish to thank the National Science Foundation for a grant used in support of this research.

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(3) L. A. Singer, unpublished work.

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