

ing ester has been reformed by ion pair return—the samples were configurationally homogeneous. Oxygen-18 contents for various times are shown in the second column of Table III²⁹ and values of the isotope effect ($k_1/k_{O^{18}}$), calculated from these data (eq. 12), are given in the last column.

Determination of Optical Purity of (-)-*cis*-5-Methyl-2-cyclohexenyl Acid Phthalate.—*dl-cis*-5-Methyl-2-cyclohexenyl acid phthalate 7-C¹⁴, was prepared from pure *cis* alcohol and phthalic anhydride, 7-C¹⁴ (Tracerlab, Inc.). After purification by recrystallization, this material gave a correct carbon and hydrogen analysis, melted at 75.3–77°, and had 93,750 ± 900 d.p.m.³⁰

(30) This value is per millimole of compound and has been corrected for

A mixture of 0.8837 g. of (-)-acid phthalate, $[\alpha]^{25}_D -61.8^\circ$ (CHCl₃), lit.¹⁷ -62.2°, and 0.4444 g. of radioactive *dl*-acid phthalate was dissolved in acetone and re-resolved as the cinchonidine salt in the usual manner.^{12,17} The resulting (-)-acid phthalate, 7-C¹⁴, had $[\alpha]^{25}_D -60.00^\circ$ (CHCl₃), 20,890 ± 200 d.p.m.³⁰ From these data it can be shown that optically pure acid phthalate has $[\alpha]^{25}_D 63.4 \pm 1.5^\circ$. Thus (-)-acid phthalate, $[\alpha]^{25}_D -62.2^\circ$ (CHCl₃), as well as the corresponding (-)-IV, ether-O¹⁸, $[\alpha]^{25}_D -95.4^\circ$ (CHCl₃), are 98 ± 2% optically pure.

background and efficiency of counting. These measurements were made as described earlier (ref. 4).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

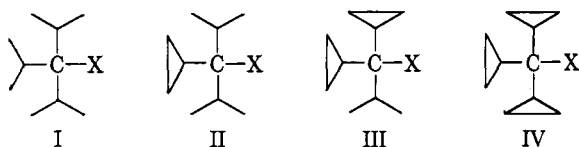
The Solvolysis of Tricyclopropylcarbinyl Benzoate¹

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Tricyclopropylcarbinyl benzoate was found to solvolyze 10⁸ times faster than dicyclopropylisopropylcarbinyl benzoate in 95% aqueous dioxane at 25°. The sole products were tricyclopropylcarbinol and benzoic acid; in methanol, the product was tricyclopropylcarbinyl methyl ether. Tricyclopropylcarbinyl derivatives solvolyze more than 10⁷ times faster than triisopropylcarbinyl compounds, and probably appreciably faster than triphenylcarbinyl compounds, indicating that all three cyclopropyl groups are remarkably effective in delocalizing the charge in the tricyclopropylcarbonium ion.

It is well known that a cyclopropyl group is uncommonly efficient at delocalizing a positive charge generated on an adjacent carbon atom, though the mechanism is still a subject of debate and experiment.² In an earlier paper³ it was shown that two cyclopropyl groups are nearly twice as effective as one at stabilizing an adjacent positive charge. The relative solvolysis rates of I, II, and III (X = *p*-nitrobenzoate, PNB) in 80%



aqueous dioxane at 60° were 1:246:23,500. Unfortunately, efforts to extend the study to include a third cyclopropyl group were thwarted then by our inability to synthesize tricyclopropylcarbinyl *p*-nitrobenzoate (IV, X = PNB).⁴

We have now synthesized tricyclopropylcarbinyl benzoate (IV, X = benzoate, B) and found that it solvolyzes with alkyl-oxygen fission.⁵ To relate it to the previous³ series, III (X = B) was also prepared and solvolyzed.

Results and Discussion

Preparation and Stability of the Esters.—Tricyclopropylcarbinyl benzoate (IX, X = B) was prepared in nearly quantitative yield by reaction of benzoyl

(1) We are grateful to the Petroleum Research Fund of the American Chemical Society and to the National Science Foundation for grants which contributed to the financial support of this research.

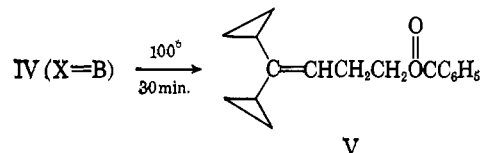
(2) For leading references, see *Annual Reports*, 208 (1962); also, R. Breslow in P. de Mayo, "Molecular Rearrangements," Interscience Publishers, Inc., New York, N. Y., 1963, pp. 259–273.

(3) H. Hart and J. M. Sandri, *J. Am. Chem. Soc.*, **81**, 320 (1959).

(4) This is perhaps understandable, when one considers the rates at which these esters hydrolyze. The half-life of III (X = PNB) in 80% aqueous dioxane at 25° is 8.67 min.; extrapolation of the data reported in the present paper to IV (X = PNB), if it could be prepared, predicts a half-life of 0.5 sec. under similar conditions.

(5) For a preliminary account of these results, see H. Hart and P. A. Law, *J. Am. Chem. Soc.*, **84**, 2462 (1962).

chloride with the potassium salt of tricyclopropylcarbinol in pentane.⁶ Attempts to distil or chromatograph the ester caused its decomposition or rearrangement. Elemental analysis was not possible (or indeed, in view of the facile thermal rearrangement, meaningful) but the ester gave a satisfactory saponification equivalent, and the infrared and n.m.r. spectra, as well as the solvolysis products, clearly substantiate the assigned structure. Particularly, the n.m.r. spectrum of freshly prepared ester showed no vinyl protons, but twelve cyclopropane methylene, three methine, and five aromatic protons. Ester which was kept at room temperature for a few hours, however, soon developed several new n.m.r. bands; the rearrangement to 4,4-dicyclopropylbut-3-en-1-yl benzoate (V) was complete in 30 min. at 100°. The structure of V follows from its



elemental analysis, infrared, and n.m.r. spectra (the latter included a triplet at 4.95 τ , one vinyl proton, a triplet at 5.8 τ , two ether protons, and a quartet centered at 7.47 τ , two allylic protons, all with $J = 8.0$ c.p.s., in addition to other expected bands). This rearrangement probably involves the formation of a tricyclopropylcarbonium benzoate ion pair, but the extent to which the two oxygens become equivalent during the process is not yet known. In kinetic experiments on the solvolysis of IV (X = B), either freshly prepared samples free of V were used, or the amount of V present (determined by titration) was corrected for. Independent experiments showed that V solvolyzed at a negligible

(6) This procedure and many variants thereof were entirely ineffective in attempts to prepare the *p*-nitrobenzoate. The crude product from such attempts showed no nitro absorption in the infrared, so presumably reactions of the nitro group with strong base gave side reactions which prevented synthesis of the desired ester.

rate at 15.5° even in 70% aqueous dioxane (solvolysis of IV was essentially instantaneous under these conditions).

Dicyclopropylisopropylcarbinyl benzoate (III, X = B) was prepared without difficulty by the same procedure used for IV; its structure followed unequivocally from its n.m.r. spectrum. This ester was not nearly as susceptible to thermal rearrangement as IV-benzoate, but did rearrange at 100° (30% in 5 hr.).

Solvolysis Rates and Products.—Because of its extremely rapid solvolysis rate, most kinetic experiments on tricyclopropylcarbinyl benzoate were carried out in 95% aqueous dioxane, even though most of the earlier⁸ work was done in more aqueous solvents. The sole solvolysis products in this solvent were tricyclopropylcarbinol and benzoic acid. Olefin or rearranged ester V were not formed. In order to be certain that alkyl-oxygen fission occurred, the ester was also solvolyzed in methanol; the products were benzoic acid and tricyclopropylcarbinyl methyl ether, accompanied by about 2% of ester V. Except for a slight to negligible amount of internal return, then, the products were derived from the alkyl portion of the ester, without rearrangement, in agreement with results on similar esters.³

The rates are given in Table I. Errors are rather large (as high as 13%), partly because of difficulty in determining phenolphthalein end points in solvents with such a low water content, and also because quenching may not have been complete. For this reason, it was felt that comparison of relative solvolysis rates ought to be made directly, under identical solvent and temperature conditions, rather than through extrapolations.

TABLE I
SOLVOLYSIS RATES

| Ester | Aqueous dioxane, % | <i>t</i> , °C. | <i>k</i> ₁ × 10 ⁴ , sec. ⁻¹ |
|----------------------------|--------------------|----------------|--|
| IV (X = B) | 95 | 25.0 | 12.3 ± 1.6 |
| | | 15.5 | 4.37 ± 0.58 |
| | | 7.9 | 2.52 ± 0.07 |
| | 90 | 7.9 | 22.9 ± 1.6 |
| III (X = B) | 95 | 59.6 | 0.262 ± 0.012 ^b |
| | | 25.0 | 0.0114 ± 0.0002 ^c |
| III (X = PNB) ^a | 95 | 60 | 5.68 ± 0.13 ^d |
| | | 90 | 1.60 ± 0.01 |

^a Data from ref. 3. ^b This figure represents the sum of solvolysis and internal return to 4-cyclopropyl-5-methyl-3-hexen-1-yl benzoate; the fractions are 88.6% solvolysis, 11.4% rearrangement. ^c See footnote b; the fractions here are 83.2% solvolysis, 16.8% rearrangement. ^d See footnote b; the fraction of rearrangement here was 7.9% (ref. 3).

From data at 25° in 95% dioxane, one sees that three cyclopropyl groups are 1080 times as effective as two cyclopropyl and one isopropyl group in facilitating the solvolysis reaction.

A less direct comparison is also possible. If one uses the factor of 21.7 to correct benzoate rates to *p*-nitrobenzoates,⁷ then the rate constant for III-B at 25° in 90% aqueous dioxane becomes 0.74 × 10⁻⁵ sec.⁻¹. Using the correction of a 9.1-fold rate increase observed for IV-B on going from 95 to 90% aqueous dioxane, the rate of IV-B at 25° in 90% dioxane becomes 1.12 × 10⁻² sec.⁻¹, and the rate increase on replacement of the third isopropyl group by cyclopropyl becomes 1510.

(7) This is the experimental rate ratio for the corresponding ester of dicyclopropylisopropylcarbinol at 60° (Table I); it corresponds to a ρ of 1.72.

It is clear that the rate enhancement for the final replacement of isopropyl by cyclopropyl is about 10³, and that tricyclopropylcarbinyl esters solvolyze more than 10⁷ times faster than triisopropylcarbinyl esters. The magnitude of the effect becomes even more striking when one considers that (i) cyclopropyl groups are inductively electron withdrawing relative to isopropyl groups, (ii) cyclopropyl groups are probably less demanding sterically than isopropyl groups, and (iii) the product contains the same number of strained rings as the starting material, so that relief of ring strain is not a dominant factor. Clearly the rate enhancement must be associated with unusual stability of the tricyclopropylcarbonium ion.

Some years ago, suspecting that the tricyclopropylcarbonium ion might be particularly stable, we attempted to measure the *i*-factor⁸ of tricyclopropylcarbinol (IV, X = OH),⁹ but obtained rapidly increasing, rather than constant, values. But the n.m.r. spectrum of IV (X = OH) as a 10% solution in 96% sulfuric acid is particularly striking, consisting of a single peak (width at half-height 4.5 c.p.s.) 63 c.p.s. upfield at 60 Mc. from the methyl group of methanesulfonic acid used as an internal reference (width at half-height 1.0 c.p.s.). An identical spectrum was obtained with dicyclopropylcarbinol. Each of these carbinols gives an extremely complex proton spectrum in carbon tetrachloride solution. It may be fortuitous that all the protons (including the noncyclopropyl proton in the case of dicyclopropylcarbinol) have approximately the same chemical shift in the carbonium ions.¹¹

We conclude from our kinetic and other data that all three cyclopropyl groups are involved in delocalizing the positive charge in the tricyclopropylcarbonium ion formed during solvolysis of tricyclopropylcarbinyl benzoate. It also seems likely that this delocalization is greater than that afforded by three phenyl groups, for IV (X = B) solvolyzes faster at 8° in 95% aqueous dioxane than does triphenylmethyl benzoate at 54.5° in 50% ethanol-50% methyl ethyl ketone.¹²

Experimental

Tricyclopropylcarbinyl Benzoate (IV, X = B).—A mixture of 2.57 g. (0.066 g.-atom) of potassium and 10 g. (0.066 mole) of tricyclopropylcarbinol⁸ in 50 ml. of anhydrous pentane was stirred magnetically for 4 hr. at room temperature in a vessel protected from atmospheric moisture.¹³ At this time, all but a trace of the metal was consumed. To the clear solution, cooled in an ice bath, was added dropwise a solution of 8.4 g. (0.060 mole) of freshly distilled benzoyl chloride in 50 ml. of pentane. Addition, which was exothermic, required 1 hr., during which time potassium chloride precipitated. The mixture was filtered (N₂ atmosphere), the pentane evaporated under reduced pressure, and the residual colorless oil was stored in a desiccator at -10° under a nitrogen atmosphere. The yield was essentially quantitative. Attempts to distil or chromatograph the ester lead to decomposition and rearrangement, so the ester was used without further purification in the kinetic experiments.

Elemental analysis was not performed, because of extreme susceptibility of the ester to hydrolysis. It has a saponification

(8) R. J. Gillespie, *Rev. Pure Appl. Chem.*, **9**, 1 (1959).

(9) Unpublished results with Dr. Richard W. Fish; Deno, *et al.*,¹⁰ recently obtained a value of 4.1, in accord with the equation ROH + 2H₂SO₄ → R⁺ + H₃O⁺ + 2HSO₄⁻, where R = tricyclopropylmethyl.

(10) N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 2016 (1962).

(11) Deno, *et al.*,¹⁰ report similar n.m.r. results for IV (X = OH).

(12) G. S. Hammond and J. T. Rudesill, *J. Am. Chem. Soc.*, **72**, 2769 (1950).

(13) In a separate experiment, hydrolysis at this point gave over 90% recovery of tricyclopropylcarbinol (infrared, n.m.r.), showing that no C-O cleavage occurred during the reaction with potassium.

equivalent calcd. for $C_{17}H_{22}O_2$ 256.1, found 258 and 260. The ester had an intense carbonyl band at 5.86μ ; the n.m.r. spectrum in carbon tetrachloride showed complex multiplets at 9.2–9.75 (12 protons), 8.35–8.85 (3 protons), 2.05–2.30 (2 protons), and 2.50–2.80 τ (3 protons).

Rearrangement of Tricyclopropylcarbinyl Benzoate (IV, X = B).—Five grams of the ester was heated at 100° for 30 min. During this time, the n.m.r. spectrum changed progressively to a spectrum with bands at: complex multiplet at 9.1–9.85 (8 protons), multiplet at 8.2–8.7 (2 protons), quartet centered at 7.47 ($J = 7.0$ c.p.s., 2 protons), triplet at 5.8 ($J = 7.0$ c.p.s., 2 protons), triplet at 4.95 ($J = 7.0$ c.p.s., 1 proton), and complex multiplets at 1.95–2.3 and 2.5–2.95 τ (2 and 3 protons, respectively). The product, 4,4-dicyclopropylbut-3-en-1-yl benzoate, distilled from 115 – 120° at 0.04 mm.; the distillate was contaminated with benzoic anhydride, which was removed by chromatography on Florisil, with pentane as eluent. Purified product had bands at 5.86 (strong) and 6.08μ (weak).

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.44; H, 7.68.

Dicyclopropylisopropylcarbinyl Benzoate (III, X = B).—This ester was prepared by a method analogous to that described above for IV (X = B). The yield was nearly quantitative, but the ester could not be distilled without decomposition and rearrangement. The infrared spectrum had a band at 5.86μ and no bands in the 6.0 – 6.2μ region. The n.m.r. spectrum in carbon tetrachloride consisted of a complex multiplet from 9.2–9.7 (8 protons), a sharp doublet centered at 8.92 ($J = 7$ c.p.s., 6 protons) overlapped by a complex multiplet from 8.6–9.1 (2 protons), a septet at 6.76 ($J = 7$ c.p.s., 1 proton), and complex multiplets from 2.0–2.25 and 2.5–2.8 τ (2 and 3 protons, respectively). The purity of samples used in kinetic experiments was about 90%, as determined by saponification equivalent (the impurity was usually ligroin, used as a solvent when the ester was stirred with activated alumina, to remove traces of benzoyl chloride which might be present).

The ester was heated for varying periods of time, neat, at 100° , and the n.m.r. spectrum examined periodically. After 70 min., bands appeared around 4.9 and 5.8 τ and increased slowly in intensity (about 30% rearrangement in 290 min.).

Kinetic Experiments. Materials.—Dioxane, methanol, and carbon dioxide-free water were purified and prepared by standard procedures. Sodium hydroxide solution (approximately 0.01 *N*) in 70% aqueous dioxane was used as the titrant. It was standardized against primary standard benzoic acid dissolved in

aqueous dioxane having the same percentage composition as that used in the particular kinetic experiment. The indicator was phenolphthalein. If the kinetic run lasted over 3 hr., the base was restandardized. The titrant was protected by Ascarite from atmospheric carbon dioxide, and all titrations were performed in a nitrogen atmosphere. **Procedure.**—Approximately 0.001 mole of ester was accurately weighed into a dry 100-ml. volumetric flask. At zero time, 100 ml. of temperature-equilibrated solvent was pipetted into the flask, and the solution thoroughly mixed. At various times, 5-ml. aliquots were withdrawn (in temperature-equilibrated pipets), quenched by adding to 5 ml. of absolute acetone at -10° , and immediately titrated, at ice-salt bath temperature. Usually 10–15 points were taken for each run, and at least two runs were made under each set of conditions.

Solvolysis Products from Tricyclopropylcarbinyl Benzoate. Absolute Methanol.—Tricyclopropylcarbinyl benzoate (1.167 g., 4.57 mmoles) dissolved in 100 ml. of absolute methanol was kept at 25° for 48 hr. The residue, after removal of solvent *in vacuo* at room temperature, consisted of white needles (benzoic acid) and a colorless oil. The latter was taken up in pentane, washed twice with 10 ml. of 1 *N* sodium hydroxide and water, and dried over magnesium sulfate. After removal of solvent, the residue (nearly quantitative yield) had an infrared spectrum with an intense broad infrared band at 9.2μ , with no bands in the 2.75 – 3.0 or 6 – 6.2μ regions. Its n.m.r. spectrum consisted of a single sharp peak at 6.75 (3 protons) and a complex multiplet from 9.0–9.9 τ (15 protons). The infrared spectrum had a trace carbonyl peak at 5.8μ , and barely detectable in the n.m.r. spectrum were weak bands (too small for accurate integration) in the aromatic and vinyl proton regions. The product is therefore tricyclopropylcarbinyl methyl ether contaminated with about 2% of unsaturated aromatic ester, presumably 4,4-dicyclopropylbut-3-en-1-yl benzoate. Similar results were obtained in 95% dioxane–5% methanol solvent. **95% Aqueous Dioxane.**—Tricyclopropylcarbinyl benzoate (10 g., 0.066 mole) in 300 ml. of 95% dioxane–5% water was kept at 25° for 19 hr. The solvent was removed *in vacuo* mainly at room temperature, with slight warming on a steam bath at the end. After taking up the residue in pentane, washing with alkali and water, and drying with magnesium sulfate, a residue was obtained whose n.m.r. spectrum was identical in the 9.0–10.0 τ region with the very complex (approximately 24 peaks) pattern given by authentic tricyclopropylcarbinol. There were no n.m.r. bands, even in the crude hydrolysis product, in the 4.95 (vinyl), 7.47 (allyl), or 5.80 τ $-\text{CH}_2\text{OC}(=\text{O})-$ regions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

Cationic Cyclizations Involving Olefinic Bonds. II.¹ Solvolysis of 5-Hexenyl and trans-5,9-Decadienyl *p*-Nitrobenzenesulfonates

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Solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate in 98% formic acid containing sodium formate proceeds with participation of the olefinic bond at a rate which is about twice that of the formolysis of the hexyl ester. The product, after saponification, consisted of 68% cyclohexanol, 26% hexenol, 5% cyclohexene, and 1% other hydrocarbons. Formolysis of the *p*-nitrobenzenesulfonates of 4-pentenol and 6-heptenol proceeded with negligible double bond participation to give mainly the products of direct substitution. Formolysis of trans-5,9-decadienyl *p*-nitrobenzenesulfonate proceeded with rate acceleration and afforded mainly monocyclic products. Some bicyclic materials were produced and these were shown to be trans-decalin derivatives. No cis-decalin compounds were found. The exclusive formation of trans-fused bicyclic materials is of interest in connection with the biosynthesis of cycloisoprenoids.

The acid-catalyzed cyclization of dienes and polyenes generally lacks selectivity because of the indiscriminate generation of cationic sites. We are directing our attention to systems in which such sites can be generated at a specific position and under conditions which are not acidic enough to effect significant competing

protonation of the olefinic bonds. Thus our hope is to learn how to realize a considerable degree of structural as well as stereochemical control over cationic cyclizations involving olefinic bonds. These studies may be of significance in connection with the biosynthesis of cycloisoprenoids.

The first paper of this series^{1a} describes an example of the intermolecular counterpart of this principle. We have since been exploring the intramolecular re-

(1) (a) Paper I of this series: W. S. Johnson and R. A. Bell, *Tetrahedron Letters*, No. 12, 27 (1960); (b) a preliminary account of the work described in the present paper was reported at the I.U.P.A.C. Meeting in London, July 17, 1963; see W. S. Johnson, *Pure Appl. Chem.*, 7, 317 (1963).