

ysis of phenyl esters by TRIS (0.58) is quite small when compared to that for ammonolysis (1.8)⁹ and aminolysis by imidazoles (1.7–1.9)^{4,24} but compares favorably to that for general base-catalyzed ammonolysis (0.56).⁹ However, our data do not support the aminolysis reaction with TRIS to be general base catalyzed. It would then appear as though the special molecular surroundings of the amino group of TRIS have a profound effect on its reaction at the ester carbonyl. Some plausible mechanisms are under further investigation. The rates of reaction of T⁻ and pentaerythritol anion with *p*-NPA are comparable to that reported by

(24) T. C. Bruice and G. L. Schmir, *J. Am. Chem. Soc.*, **80**, 148 (1958).

Jencks and co-workers²⁵ for the reaction of N,O-diacylserine anion with *p*-NPA. By the same criteria employed to evaluate the nucleophilicity of the anion of N,O-diacylserine we must also assume that T⁻ and pentaerythritol anion are about 10² to 10³ stronger nucleophiles toward *p*-NPA than a normal alkoxide ion.

Acknowledgments.—J. L. V. express thanks to the National Institutes of Health for a predoctoral fellowship. We should like to thank Professor F. A. Long for stimulating discussions, and the National Institutes of Health, the National Science Foundation, and the Upjohn Company for support.

(25) B. M. Anderson, E. H. Cordes and W. P. Jencks, *Federation Proc.*, **19**, 46 (1960).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Diphenylcyclobutadienoquinone. Synthesis and Structure^{1,2}

BY A. T. BLUMQUIST AND EUGENE A. LALANCETTE^{3,4}

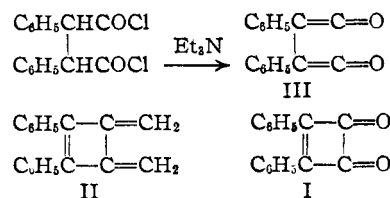
RECEIVED NOVEMBER 10, 1960

Diphenylcyclobutadienoquinone, the dioxo analog of diphenyldimethylenecyclobutene, was first sought as a product from a reaction designed to give bis-phenylketene. Failure to find the diketone amongst a complex mixture of products obtained upon dehydrochlorination of α,α' -diphenylsuccinyl chloride prompted a direct synthesis of the cyclobutenedione. This was achieved readily by acid hydrolysis of 1,2-diphenyl-3,3,4,4-tetrafluorocyclobutene. The latter compound was prepared by reaction of perfluorocyclobutene with phenyllithium. The bright yellow crystalline diketone had good thermal stability. All physical and chemical studies confirmed its structure. Permanganate oxidation of the diketone gave only benzoic acid and a Baeyer–Villiger oxidation converted it to diphenylmaleic anhydride. The infrared, ultraviolet and n.m.r. spectra supported the conclusion that the diketone was at hand. In ethanol solution, the diketone transformed to diethyl α,α' -diphenylsuccinate, presumably *via* a bis-ketene intermediate. Phenylation of perfluorocyclobutene gave an accessory product (10%) which, on the basis of extensive chemical and physical studies, is best described as 1,2,3,4-tetrafluoro-1,4-diphenyl-1,3-butadiene.

In this Laboratory the convergence of two research trails focused attention on the diketone diphenylcyclobutadienoquinone, diphenylcyclobutenedione (I). Investigations concerned generally with the chemistry of bis-ketenes⁵ led to a study of 1,2 or α -bis-ketenes, while examination of certain highly unsaturated four-membered ring hydrocarbon systems suggested that it would be pertinent to examine oxo analogs of some of these small ring compounds.

In this context the diketone I is of especial interest. It is, first of all, the dioxo counterpart of diphenyldimethylenecyclobutene (I), described earlier,⁶ and hence comparison of its stability with that of the triene II would be of theoretical interest. Secondly, the diketone I is a valence

tautomer of bis-phenylketene (III) and it might, therefore, be found as a product from a reaction designed to produce the ketene III. Finally, the



diketone I could serve as an intermediate for the realization of *bona fide* cyclobutadienes.

The likelihood that the diketone I would be isolable was supported by the knowledge that Smutny and Roberts had synthesized phenylcyclobutadienoquinone⁷ and its stability made it possible for them to carry out a most thorough study of the cyclobutenedione system.⁸

Reaction of α,α' -diphenylsuccinyl chloride with triethylamine in benzene proved to be completely disappointing. Although evidence for reaction, precipitation of the amine hydrochloride, was noted, infrared analysis of the supernatant benzene solution did not show the presence of ketenoid products, *i.e.*, no strong infrared absorption band at *ca.* 4.8 μ was observed. A complex mixture of products actually was isolated from the above reaction, but only one was obtained which appeared

(1) This is the eleventh publication concerned with the chemistry of small carbon rings. For the preceding paper in this series see A. T. Blumquist, Y. C. Meinwald, C. G. Bottomley, P. W. Martin, *Tetrahedron Letters*, No. 24, pp. 13–17 (1960).

(2) For preliminary communications of portions of this investigation see: (a) Abstracts of Papers Presented at the National Meeting of the American Chemical Society in Boston, Mass., April, 1959, p. 54-O; (b) Abstracts of Papers Presented at the Sixteenth National Organic Chemical Symposium of the American Chemical Society, Seattle, Wash., June 15–17, 1959, p. 11.

(3) Supported by funds from the Sage Fellowship, Summer, 1957; Procter and Gamble Fellow, Summer, 1958; American Cyanamid Fellow, Summer, 1959; Allied Chemical and Dye Fellow, 1959–1960.

(4) The work reported here was abstracted from part of the dissertation presented by Eugene A. LaLancette in June, 1960, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree Doctor of Philosophy.

(5) A. T. Blumquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **79**, 202 (1957).

(6) A. T. Blumquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959).

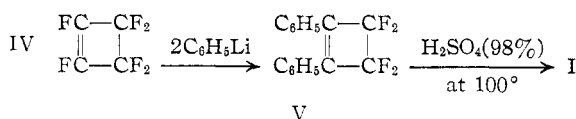
(7) E. J. Smutny and J. D. Roberts, *ibid.*, **77**, 3420 (1955).

(8) E. J. Smutny, M. C. Caserio and J. D. Roberts, *ibid.*, **82**, 1793 (1960).

to be a pure compound. The latter was a bright yellow crystalline solid of good thermal stability, m.p. 394–396°, $\lambda_{\text{max}}^{\text{KBr}}$ 5.65 μ , and mol. wt. 531.⁹

In view of the results described it seemed desirable to prepare the diketone I by a direct route and to learn something about its properties. With this knowledge it might then be possible to set about seeking the diketone I in the complex mixture of products obtained in the dehydrochlorination experiments.

The diketone I was, in fact, obtained easily from perfluorocyclobutene (IV) by the two-step sequence diagrammed.



Phenylation of the fluorocarbon IV¹⁰ with phenyllithium, as described by Dixon,¹¹ gave a crimson oil (23%) which comprised a mixture which, after a difficult separation, gave the desired 1,2-diphenyl-3,3,4,4-tetrafluorocyclobutene (V) (90%) and a previously unreported compound (10%), isomeric with V, which is probably 1,2,3,4-tetrafluoro-1,4-diphenyl-1,3-butadiene (VI).

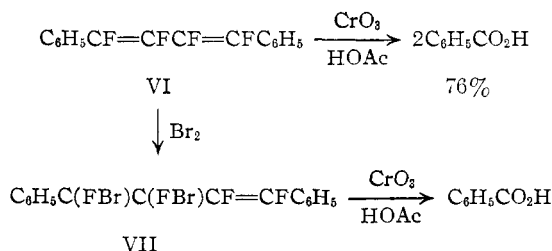
The ultraviolet spectrum of the compound V, in ethanol, shows maxima characteristic of a *cis*-stilbene chromophore in a four-membered ring: a doublet at 224 and 230 $m\mu$ (ϵ 's, 8,600 and 8,000, resp.) together with a single band at 293 $m\mu$ (ϵ 17,750).¹² The isomeric product VI has maxima in the ultraviolet at 238 $m\mu$ (ϵ 7,100) and 271 $m\mu$ (ϵ 11,400). The infrared spectrum of VI (KBr pellet) shows a band of medium intensity at 6.01 μ .

The proton n.m.r. spectrum of the product VI indicated the presence of only aromatic hydrogens (7.18 p.p.m. downfield from tetramethylsilane). That the two phenyl groups are perhaps equivalent was indicated by the observation that the half-width of the above signal was not greater than 0.08 p.p.m. At frequencies of 40 and 56.4 Mc./sec. and under conditions of the highest resolution, the F¹⁹ n.m.r. spectrum of compound VI comprised two doublets of equal intensities. The four resonances calibrated at 40 Mc./sec. were found at 39.6,

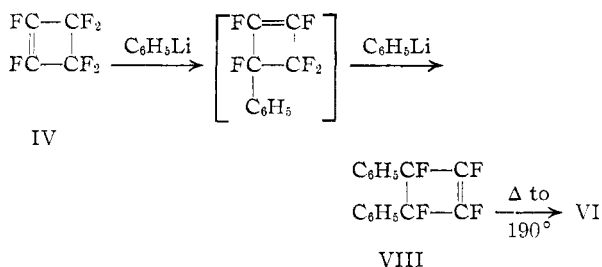
39.9, 59.6 and 59.9 p.p.m. to high field with respect to trifluoroacetic acid.

Oxidation of the product VI with chromic acid gave 76% of the two molar equivalents of benzoic acid required by the structure VI. Addition of bromine to VI gave an unsaturated dibromide (VII) which had the molecular formula C₁₆H₁₀F₄Br₂.¹⁵ The presence of unsaturation of VII was indicated by its spectral properties. In the infrared the dibromide VII had an absorption band at 6.01 μ and the ultraviolet spectrum of VII, in ethanol, showed a maximum at 260 $m\mu$ (ϵ 19,900), strong end absorption near 200 $m\mu$ together with a shoulder at 218 $m\mu$. Oxidation of the dibromide VII afforded a mixture of two acids from which 90% of one equivalent of benzoic acid was isolated.

The structure 1,2,3,4-tetrafluoro-1,4-diphenyl-1,3-butadiene for VI is in best accord with the physical and chemical properties given above.



The vigorous conditions used to separate the products V and VI did not bring about the formation of VI by isomerization of V. It was observed that the compound V when heated at 175° for 8.5 hr. was recovered unchanged. A rational path to the product VI is *via* two successive S_N2' attacks of phenyllithium¹⁶ on the fluoroolefin IV to produce 1,2,3,4-tetrafluoro-1,4-diphenylcyclobutene (VIII) followed finally by thermal isomerization of VIII to the butadiene VI.



Pyrolysis of cyclobutenes to butadienes, a reasonably well known reaction which has been briefly

(15) At 40 Mc./sec. the F¹⁹ n.m.r. spectrum of this dibromide was quite complex and exhibited four groups of signals of approximately equal intensities. The first signal, centered around 36 p.p.m. (to high field with respect to trifluoroacetic acid), consisted of a triplet split into three doublets. The second signal, centered around 45 p.p.m., was made up of two triplets. The third signal, four doublets, is found around 62 p.p.m. while the fourth signal, at 70 p.p.m., comprised two triplets.

(16) The operation of S_N2' rearrangements of several halosubstituted cyclobutenes has been demonstrated: (a) M. C. Caserio, Y. Kitahara, H. E. Simmons, E. Johnson and J. D. Roberts, Abstracts of Papers Presented at the National Meeting of the American Chemical Society in Boston, Mass., April, 1959, p. 52-O; (b) ref. 14; (c) E. F. Jenny and J. Druey, *J. Am. Chem. Soc.*, **82**, 3111 (1960). For leading references on open chain fluorocarbon systems where the departing group is fluoride ion see W. T. Miller, Jr., J. H. Fried and H. Goldwhite, *ibid.*, **82**, 3091 (1960).

(9) On the basis of the mol. wt. found (isothermal distillation from CHCl₃) the compound, in chloroform solution, had maxima in the ultraviolet at 238 $m\mu$ (ϵ 16,400) and in the visible region at 415 $m\mu$ (ϵ 45,400). No other characterization of the product was done.

(10) (a) J. Harmon, U. S. Patent 2,404,374; *C. A.*, **40**, 7234² (1946); and U. S. Patent 2,436,142; *C. A.*, **42**, 3776h (1948); (b) A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947); (c) M. W. Buxton, *et al.*, *J. Chem. Soc.*, 3834 (1952).

(11) S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

(12) A subsequent paper will present other examples of a similar bathochromic shift accompanied with increased extinction coefficient in systems which have a *cis*-stilbene chromophore as part of a four-membered ring. It should be noted, however, that the effect is weaker than in three-membered rings which contain the same chromophore.¹³ On the basis of the few examples studied to date, the ultraviolet spectrum of a compound may be useful in establishing whether a *cis*-stilbene fragment is part of a three- or a four-membered ring. A bathochromic shift is also observed when a styrene chromophore is part of a four-membered ring.¹⁴

(13) R. Breslow, R. Winter and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

(14) Y. Kitahara, M. C. Caserio, F. Scardiglia and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3106 (1960).

reviewed,¹⁷ has been applied very recently to the synthesis of 1,1,4,4-tetrafluorobutadiene (IX)¹⁸ and several 2-substituted derivatives of IX. The temperatures required in this latter study were probably much higher than would be necessary to effect ring opening of the proposed intermediate VIII. Vogel has shown¹⁷ that the thermal stability of cyclobutenes bearing electronegative substituents is much less if such groups occupy the 3,4-positions as opposed to attachment at the 1,2-positions. For example, dimethyl *cis*-3,4-cyclobutenedicarboxylate when heated at 120° for 10 min. is converted to dimethyl *cis-trans*-muconate; whereas long heating at 160–170° is required to effect ring opening of dimethyl-1,2-cyclobutenedicarboxylate.^{19,21}

Preparation of the diketone I from the fluorine-containing intermediate V was done easily (83%) by application of the procedure developed by Roberts, *et al.*, for the removal of *gem*-difluorine and 1,1-chlorofluoro groups.²³ The diketone I was obtained as bright yellow needles, m.p. 97–97.2°, and it could be sublimed without decomposition at 90° and 0.08 mm. pressure. The diketone readily formed mono-2,4-dinitrophenylhydrazone and mono-tosylhydrazone derivatives. Alkaline permanganate oxidation of I produced two equivalents of benzoic acid; Baeyer-Villiger oxidation gave diphenylmaleic anhydride (80%).

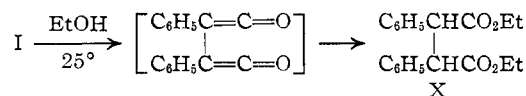
The various spectral properties of I are in support of the postulated structure. In the carbonyl region of the infrared, the spectrum of the diketone I shows absorption characteristic of a strained carbonyl group attached to a four-membered ring: $\lambda_{\text{max}}^{\text{KBr}}$ 5.60 and 5.63 μ (a doublet) together with a shoulder at 5.68 μ . Absorption characteristic of a conjugated benzene ring, 6.37 μ , is also observed.²⁴ The n.m.r. spectrum of the diketone I, in carbon tetrachloride solution, has two peaks with splitting of 0.45 p.p.m. shifted 2.85 p.p.m. to lower field than the resonance of protons in an external water

sample. The peaks of the spectrum are shaped like those characteristic of monosubstituted benzenes. Also, the n.m.r. of benzil shows similarly shaped peaks and in the same region.

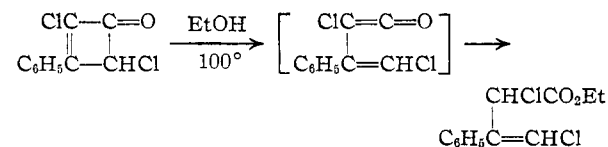
The ultraviolet spectrum of the diketone I, in acetonitrile solution, shows these various maxima in $m\mu$, ϵ 's in parentheses: 223sh (16,000), 265 (17,100) and 318 (20,600). Weaker ultraviolet absorption is observed for I in 95% ethanol: 223 (14,400), 266 (13,200), 322 (16,300) and 410 (163).

It was found too that in ethanol, at a concentration of 9.35 mg./l., the diketone I deteriorates in 12 hr. After this time the maxima characteristic of I vanish and there remains only weak absorption at 258 $m\mu$ (unconjugated benzene ring) together with a tail at 200 $m\mu$.

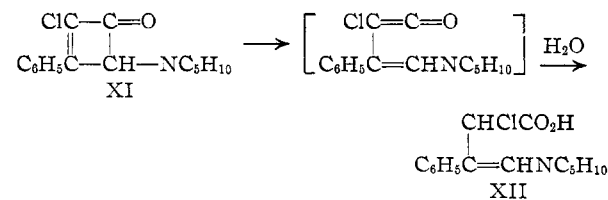
Evaporation of an ethanolic solution of the diketone I, aged at room temperature for two weeks, gave a white, crystalline solid, m.p. 97–114°, which comprised a mixture of the *meso* and *racemic* forms of diethyl α,α' -diphenylsuccinate (X). The foregoing suggests that the diketone I transforms to the diester X via *bis*-phenylketene.



Two similar transformations recently have been described. Jenny and Roberts obtained ethyl 2,4-dichloro-3-phenyl-3-butenate by heating 2,4-dichloro-3-phenylcyclobutenone with ethanol at 100°,²⁵ while Jenney and Druey observed that an



ether solution of the base XI, which had been saturated with water, deposited the unsaturated acid XII.²⁶ Both reactions presumably proceed via a vinyl-ketene intermediate.



Future publications will present other chemical studies of the diketone I, and most particularly those investigations concerned directly with an effort to obtain *bona fide* cyclobutadienes will be reported.

Experimental Part²⁷

Materials— α,α' -Diphenylsuccinyl chloride, m.p. 188.5–189.5°, was prepared from *meso*- α,α' -diphenylsuccinic

(25) E. F. Jenny and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 2005 (1956).

(26) E. F. Jenny and J. Druey, *ibid.*, **82**, 3111 (1960).

(27) All m.p.'s and b.p.'s are uncorrected. Infrared spectra were obtained with Perkin-Elmer spectrophotometers, model 21 and Infracord.

(28) V. A. McRae and A. S. Townshend, *Can. J. Research*, **11**, 635 (1934).

(17) (a) E. Vogel, *Angew. Chem.*, **66**, 640 (1954); (b) E. Vogel, *Ann.*, **615**, 14 (1958).

(18) (a) R. E. Putnam, J. L. Anderson and W. H. Sharkey, Abstracts of Papers Presented at The National Meeting of the American Chemical Society in New York, N. Y., Sept., 1960, p. 12-M; (b) R. E. Putnam, J. L. Anderson and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 386 (1961).

(19) Pyrolysis of cyclobutenes probably occurs via a free radical mechanism. This type mechanism already has been proposed²⁰ for the formation of cyclobutenes through cycloalkylation reactions of ethylene derivatives. Thus the pyrolysis of the intermediate VIII could conceivably take place via a resonance-stabilized diradical and therefore at a lower temperature. If such a mechanism is operative the product VI should, perhaps, have a *trans-trans* configuration. However, the stereochemistry of VI has not been ascertained.

(20) (a) E. E. Lewis and M. A. Naylor, *J. Am. Chem. Soc.*, **69**, 1968 (1947); (b) E. C. Coyner and W. S. Hillman, *ibid.*, **71**, 324 (1949).

(21) There are two arguments against the proposed butadiene structure VI. Firstly, it has been found²² that the coupling constants for two non-equivalent fluorine atoms in fluorolefins is substantially greater than that observed for the product VI (*cis*: 33 to 58 cycles sec.; *trans*: 115 to 124 cycles/sec.). Secondly, the absorption intensity in the ultraviolet region observed for VI is only about one-half of what might be expected on the basis of two isolated styrene chromophores.

(22) J. A. Pople, W. G. Schneider and H. V. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 334–337.

(23) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *J. Am. Chem. Soc.*, **75**, 4765 (1953).

(24) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 61.

acid, m.p. 215–217°,^{29,30} by slight modification of a reported procedure.³⁰ α,α' -Diphenylsuccinonitrile, m.p. 205–207°,³¹ required for this preparation of the diphenylsuccinic acid, was best prepared in quantity by the method of Davis.³²

1,2-Dichlorohexafluorocyclobutane, b.p. 59–59.5° and n_D^{20} 1.3310,¹⁰ was prepared by thermal dimerization of chlorotrifluoroethylene³³ (Genetron 1113, Allied Chemical and Dye Corp.)

Perfluorocyclobutene (IV).—To a stirred mixture of 243 g. of zinc dust (90%) in 375 ml. of absolute ethanol which had been refluxed 20–30 min.³⁴ there was added dropwise, at reflux temperature over a 6-hr. period, 375 g. of 1,2-dichlorohexafluorocyclobutene. Distillation of the mixture gave 217 g. (83%) of the perfluoroolefin IV, b.p. 1–3°.¹⁰

Reaction of IV with Phenyllithium.—This reaction was carried out as described by Dixon.¹¹ Reaction of 126 g. (0.776 mole) of IV with 1.61 moles of phenyllithium in ether at –70° gave, after the usual work up which involved a short path distillation in the last isolation step, 49.92 g. (23.3%) of a crimson oil, b.p. 114–175° (1.0 to 0.1 mm.). This oil was found subsequently to comprise 90% 1,2-diphenyl-3,3,4,4-tetrafluorocyclobutene (V) and 10% of, probably, 1,2,3,4-tetrafluoro-1,4-diphenyl-1,3-butadiene (VI). The afore-stated composition was established by quantitative infrared analysis.³⁵

Partial separation of the components V and VI present in the crimson oil was achieved by distillation through a 60-cm. Poddelniak column, which had a total take-off head. Four fractions were collected: (A) 1.24 g., b.p. 115–116° (2–1.5 mm.); (B) 0.68 g., b.p. 115–126° (1.6 mm.); (C) 16 g., b.p. 125–127° (1.8–1.2 mm.); (D) 19 g., b.p. 125° (1.8 mm.).

Crystallization of fraction B from pentane gave 0.24 g. of compound VI, m.p. 72.5–73°, and similarly fraction D gave 17.06 g. of compound V, m.p. 56–57°. Repetition of the above distillation and crystallization isolation processes afforded additional quantities of V and VI. The "crimson oil" product obtained from two consecutive preparations, on the scale described, was combined and compounds V and VI isolated by the procedures outlined. There was thus isolated 51.4 g. of the substance V (an average total of two experiments), m.p. above 55° and of satisfactory purity for the subsequent hydrolysis step, and 3.0 g. of the minor product VI, m.p. > 71°.

Pure V was obtained after further recrystallization from pentane; m.p. 56.5–57.5° (lit.¹¹ m.p. 58°). A sample of the pure minor product VI was obtained after several recrystallizations from pentane and a final vacuum sublimation. The compound VI then had m.p. 73–73.5°.

Anal. Calcd. for $C_{16}H_{10}F_4$: C, 69.08; H, 3.62; F, 27.32; mol. wt., 278.24. Found: C, 69.21, 69.06; H, 3.62, 3.50; F, 27.53, 27.29; mol. wt. (Rast), 280, 284.

Chromic Acid Oxidation of Compound VI.—A solution of 0.774 g. of the compound VI in 27 ml. of glacial acetic acid was stirred at 55° for 22 hr. with 1.62 g. of chromium trioxide. This mixture was then diluted with 100 ml. of water and extracted with ether continuously for 48 hr. The residue from the ether extract, obtained after acetic acid had been removed in a rotating flask evaporator, was dissolved in ether and extracted thoroughly with sodium

bicarbonate solution. Acidification of the alkaline solution gave 0.512 g. of benzoic acid. The benzoic acid isolated was 76% of two moles of benzoic acid per mole of starting compound.

Bromination of Compound VI.—A solution of 1.6 g. (0.01 mole) of bromine in 15 ml. of dry carbon tetrachloride was added in 6 min. to a solution of 2.55 g. (0.0092 mole) of compound VI in 20 ml. of carbon tetrachloride which was irradiated with a 100-watt incandescent bulb. The light source was removed, another 0.3 g. of bromine added, and the mixture stirred 1.5 hr. at room temperature. After the addition of more carbon tetrachloride the mixture was washed successively with 2% potassium bisulfite, saturated sodium bicarbonate, water, and saturated sodium chloride. The dried and filtered carbon tetrachloride solution gave a white solid residue after removal of the solvent. Crystallization of this residue gave 1.29 g. of a colorless solid dibromide VII, m.p. 87–88.5°, which after four recrystallizations from 95% ethanol had m.p. 88–89°.

Anal. Calcd. for $C_{16}H_{10}F_4Br_2$: C, 43.86; H, 2.30; F, 17.35; Br, 36.48; mol. wt., 438.07. Found: C, 43.96, 44.10; H, 2.29, 2.55; F, 17.19, 17.13; Br, 36.53, 36.56; mol. wt. (isothermal dist. from $CHCl_3$), 439.

The ether mother liquor from above gave an oil (2.65 g.) which could not be induced to crystallize. Although this was not analyzed, its infrared spectrum was identical with that of the solid dibromide VII.

Oxidation of the Dibromide VII.—Oxidation of 0.380 g. of the dibromide VII in 19 ml. of acetic acid with 0.40 g. of chromium oxide was effected by a procedure similar to that used in the oxidation of compound VI. There was isolated 164 mg. of a white crystalline acid, m.p. 83–88°. Sublimation of this solid at 0.05 mm. gave 78 mg. of benzoic acid (90% of that required by structure VII for the dibromide) together with 85 mg. of a white acidic solid, m.p. 93–94°, which failed to sublime.

Diphenylcyclobutadienoquinone (I).—The procedure used in this preparation was based on one described by Roberts and associates.²³ The tetrafluoro compound V (5 g.) was added with stirring to 20 g. of 98% sulfuric acid. The mixture was heated at 98° and stirred for 35 min. and then quenched by pouring into ice-water. The yellow solid thus produced was filtered, dried and recrystallized from chloroform–pentane to give 3.52 g. (83.5%) of the diketone I, m.p. 97–97.2°.³⁷

Anal. Calcd. for $C_{16}H_{10}O_2$: C, 82.06; H, 4.30; mol. wt., 234.24. Found: C, 82.22; H, 4.49; mol. wt. (Rast), 250.

The mono-2,4-dinitrophenylhydrazone derivative of the diketone I was prepared and recrystallized from dioxane; m.p. 253° (sharp).

Anal. Calcd. for $C_{22}H_{14}N_4O_6$: C, 63.75; H, 3.41. Found: C, 64.02; H, 3.76.

Reaction of 1.15 g. of the diketone I in methanol with 0.913 g. of *p*-toluenesulfonylhydrazine in methanol gave 1.33 g. (68%) of the monotosylhydrazone derivative of I, m.p. 188–189° from 95% ethanol.

Anal. Calcd. for $C_{23}H_{18}N_2O_6S$: C, 68.63; H, 4.51; N, 6.96. Found: C, 68.28; H, 4.45; N, 7.11.

The mother liquors of the latter preparation gave 0.2 g. of presumably the ditosylhydrazone derivative of I, m.p. 239–240° from dioxane–ethanol.

Anal. Calcd. for $C_{30}H_{22}N_4O_8S_2$: N, 9.82. Found: N, 10.04.

Oxidation of the Diketone I. With Alkaline Permanganate.—The diketone I (150 mg.) was refluxed 30 min. with a solution of 3.7 g. of potassium permanganate and 3.3 g. of potassium hydroxide in 60 ml. of water. From this mixture there was isolated 125 mg. (80%) of impure benzoic acid, m.p. 114–116°, which gave pure benzoic acid after recrystallization from carbon tetrachloride.

With Hydrogen Peroxide.—To 250 mg. of the diketone I in 20 ml. of carbon tetrachloride three 10-ml. portions of 30–35% hydrogen peroxide were added at 2-hr. intervals with continuous shaking. The mixture was shaken for a total of 28 hr., the carbon tetrachloride layer separated and washed successively with 30 ml. of 10% ferrous sulfate solution and twice with 250 ml. of water. From the washed

(37) It was found that the rate of hydrolysis was more reproducible when experiments were done in a flask etched in previous preparations.

(29) A. Lapworth and J. A. McRae, *J. Chem. Soc.*, **121**, 1710 (1922).

(30) S. Wawzonek, *J. Am. Chem. Soc.*, **62**, 747 (1940).

(31) *Org. Syntheses*, **32**, 63 (1952).

(32) R. B. Davis, *J. Am. Chem. Soc.*, **80**, 1752 (1958).

(33) K. E. Rapp, *ibid.*, **72**, 3643 (1950).

(34) This initial refluxing of the zinc–ethanol mixture proved to be a convenient method to reduce the period of inhibition observed in the subsequent dechlorination reaction. Alternatively, the same result may be achieved by the addition of a small amount, 0.35 g., of freshly fused zinc chloride.

(35) Mixtures of compounds V and VI followed Beer's law and an application of the base line technique³⁶ with reference to the log absorptivity of the 10.57 μ band present in the infrared spectrum of compound VI made it possible to estimate compositions of V and VI mixtures. The Perkin–Elmer model 21 spectrophotometer was used to determine spectra of 1% solutions of the mixtures in carbon tetrachloride. Matched potassium bromide cells, 0.05 mm., were used.

(36) H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis," 3rd ed., D. Van Nostrand Co., Inc., Princeton, N. J., 1958, p. 140.

and dried solution there was obtained 210 mg. (79%) of a solid, m.p. 154–155°, which had m.p. 155–156° when recrystallized from 95% ethanol. This product was identical with an authentic specimen of diphenylmaleic anhydride, prepared from phenylacetonitrile.³⁸ Identity was established by comparison of infrared spectra and by m.p. of the mixture of substances.

Dehydrochlorination of α,α' -Diphenylsuccinyl Chloride.—To a deoxygenated solution of 6 g. (1.76 mmoles) of diphenylsuccinyl chloride in 130 ml. of dry benzene, there was quickly added, under a nitrogen atmosphere, 7.91 g. (7.82 mmoles) of triethylamine. The mixture rapidly colored and was brilliant crimson in 1 hour. The infrared spectra of samples of the supernatant benzene solution taken after 3 and 20 hr. were identical and showed no band at 4.8 μ but maxima at 5.72, 5.85 and 6.18 μ . The reaction mixture was filtered and the benzene solution filtrate washed suc-

cessively with three 50-ml. portions of 1.2 *N* hydrochloric acid, three 100-ml. portions of water, 10% sodium carbonate solution, water and finally dried.

Evaporation of the benzene solution left a gummy oil residue from which, after extraction with 95% ethanol, 100 mg. of a bright yellow solid was obtained, m.p. >360°. After three recrystallizations from chloroform this solid had m.p. 394–396° and $\lambda_{\text{max}}^{\text{KBr}}$ 5.65 μ .

Anal. Found for solid of m.p. 394–396°: C, 80.79; H, 4.21; mol. wt., 531 (isothermal dist. from CHCl_3).

From the ethanol extract mentioned above several fractions, ca. 1.1 g. total weight, of m.p.'s less than 100° were obtained. None was examined further. Another yellow solid product, ca. 0.5 g. and of m.p. below 100°, was isolated by aqueous washing of the precipitated triethylamine hydrochloride and in part by gradual precipitation from the acid wash of the original benzene solution.

(38) C. L. Reimer, *Ber.*, **131**, 742 (1880).

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Ionic Reactions in Bicyclic Systems. I. The Preparation and Assignment of Configuration of the Isomeric Bicyclo[3.2.1]oct-3-en-2-ols and Bicyclo[3.2.1]octan-2-ols

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RECEIVED SEPTEMBER 24, 1960

Deamination of *endo*-5-aminobicyclo[2.2.2]oct-2-ene (I) and acetolysis of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (IV) give derivatives of *exo*-(*axial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIa). *endo*-(*equatorial*)-Bicyclo[3.2.1]oct-3-en-2-ol (IIb) and the isomeric bicyclo[3.2.1]octan-2-ols (VI) have been prepared and their configurations established.

This paper describes the synthesis, properties and configurational assignments of the isomeric bicyclo[3.2.1]oct-3-en-2-ols (II) and the isomeric bicyclo[3.2.1]octan-2-ols (VI). These compounds were of interest in a study of carbonium ion (solvolytic) reactions in [2.2.2]- and [3.2.1]bicyclic systems.

Several years ago the conversion of *endo*-5-aminobicyclo[2.2.2]oct-2-ene (I) to bicyclo[3.2.1]oct-3-en-2-ol (II) by nitrous acid deamination was reported by Wildman and Saunders.² The structure of the deamination product was determined by oxidation to bicyclo[3.2.1]oct-3-en-2-one (III) and reduction to a bicyclo[3.2.1]octan-2-ol (VI).² However, the configuration of the product was not established. In the present work it was found that II produced by deamination of I has the *exo* or axial configuration (IIa). Solvolysis of the *endo*-*p*-toluenesulfonate (IV) also gives derivatives of *exo*-(*axial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIa). Because of the availability of *endo*-bicyclo[2.2.2]oct-5-en-2-ol (V) and thus of the corresponding *p*-toluenesulfonate IV the latter transformation represents a convenient stereoselective synthesis of IIa. As indicated by the structural illustrations, IIa can be converted to its epimer IIb by oxidation to the ketone III and subsequent reduction of the carbonyl group. The unsaturated [3.2.1]bicyclic alcohols II can be converted to their saturated analogs VI by reduction of the double bond.

The Synthesis of the Isomeric Bicyclo[3.2.1]oct-3-en-2-ols (II).—*endo*-5-Aminobicyclo[2.2.2]oct-2-ene (I) was prepared from *endo*-5-carboxybi-

cyclo[2.2.2]oct-2-ene hydrazide by the Curtius reaction. The latter was prepared from ethyl *endo*-bicyclo[2.2.2]oct-2-en-5-carboxylate obtained from the reaction of cyclohexadiene with ethyl acrylate.³ A similar synthesis of I has been reported recently.⁴

The *endo*-amine I was converted to *exo*-(*axial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIa) in two ways: aqueous nitrous acid deamination² and nitrous acid deamination in acetic acid followed by saponification of the resulting acetate. The products obtained by the two routes were indistinguishable. Physical properties of the deamination product IIa (including the infrared spectrum) were unchanged by chromatography (Florisil) or recrystallization of the *p*-nitrobenzoate derivative to a constant melting point. However, as will be shown later, there is evidence that this product is not completely homogeneous.

The axial [3.2.1]bicyclic alcohol IIa was also prepared from *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (IV) which in turn was prepared from the corresponding alcohol V. The latter was obtained from its acetate which was prepared from cyclohexadiene and vinyl acetate.⁵ The *endo*-*p*-toluenesulfonate IV derived from V was contaminated with about 10% of a more reactive isomer which was removed readily by recrystallization from ethanol. *endo*-Bicyclo[2.2.2]oct-5-en-2-ol (V) purified by recrystallization of its *p*-nitrobenzoate derivative apparently was homogeneous and gave pure *p*-toluenesulfonate IV (identical with material from which the reactive isomer had been removed).

The infrared spectrum of a 0.1 *M* solution of the

(1) (a) Socony-Mobil Co. Fellow, 1956–1957. (b) Wisconsin Alumni Research Foundation Fellow 1956–1958; National Science Foundation Fellow 1958–1960.

(2) W. C. Wildman and D. R. Saunders, *J. Am. Chem. Soc.*, **76**, 946 (1954).

(3) R. Seka and O. Tramposch, *Ber.*, **75**, 1379 (1942).

(4) C. A. Grob, K. Kny and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

(5) K. Alder and H. Rickert, *Ann.*, **543**, 1 (1940).