a free radical reaction between a saturated hydrocarbon and formaldehyde. For example, if di-*tert*-butyl peroxide were to be the initiator the steps would be

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO—$$
$$(CH_3)_3CO— + RH \longrightarrow (CH_3)_3COH + R$$
$$R + HCHO \longrightarrow RCH_2O—$$
$$RCH_2O + RH \longrightarrow RCH_2OH + R.$$

This sequence of reactions does in fact take place between cyclohexane or cyclopentane and formaldehyde with formation of cycloalkyl carbinols.

The reaction was carried out in a Teflon-sealed glass polymerization bottle which was shaken for 12 hours at 135°. A two phase reaction mixture of one mole cyclohexane, 0.25 mole of formaldehyde as a 37% formalin solution, and 0.1 mole of di-*tert*-butyl peroxide gave a 38% yield (based on formaldehyde) of cyclohexyl carbinol. *Anal.* Calcd. for $C_7H_{14}O$: C, 73.6; H, 12.3. Found: C, 73.5; H, 12.3. The phenylurethan derivative melted at 82.5–83° and showed no depression when mixed with a phenylurethan derivative of authentic cyclohexyl carbinol. Comparison of the infrared spectrum of this material with that of known cyclohexyl carbinol confirmed the identity of the product.

Similarly, five moles of cyclopentane, one mole of formaldehyde and 0.05 mole of di-*tert*-butyl peroxide yielded 21.4% of cyclopentyl carbinol. Separation of the product from a small amount of unknown contaminant required gas–liquid chromatography. *Anal.* Calcd. for $C_6H_{12}O$: C, 72.0; H, 12.1. Found: C, 71.8; H, 12.0. A phenylurethan derivative of this carbinol melted at 108° (lit. value 108°)[3]; *anal.* Calcd. for $C_{13}H_{17}NO_2$: C, 71.2; H, 7.8. Found: C, 71.3; H, 7.8.

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[3] S. Nametkin and O. Morosowa, *Chem. Zentr.*, **87**, II, 250 (1916).

SHELL DEVELOPMENT COMPANY GLENN FULLER
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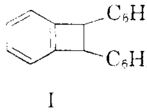
RECEIVED AUGUST 11, 1958

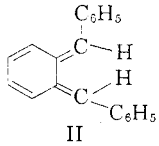
UNSATURATED FOUR-MEMBERED RING COMPOUNDS. II. 1,2-DIPHENYLBENZOCYCLOBUTENE, A COMPOUND HAVING UNUSUAL REACTIVITY

Sir:

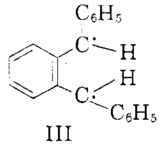
The compound 1,2-diphenylbenzocyclobutene (I) has been prepared by the reaction of sodium iodide with α,α'-dibromo-α,α'-diphenyl-*o*-xylene and by the reaction of bases with α-bromo-α,α'-diphenyl-*o*-xylene. White needles from alcohol, m.p. 94.5–95.2° (in absence of strong light), *Anal.* Calcd. for $C_{20}H_{16}$: C, 93.72; H, 6.28; M.W., 256. Found: C, 93.71; H, 6.27; M.W., 280.



I



II



III

Oxidation with chromic anhydride converts I to *o*-dibenzoylbenzene. The compound I is obtained essentially unchanged from hot alcohol and other solvents and does not decompose upon standing. The infrared spectrum has a band at 10.0 μ which is characteristic of a cycloalkane ring[1] and is common to a variety of compounds containing the benzocyclobutene ring system.[2,3] The observed values of the extinction coefficients in the ultraviolet spectrum are in agreement with the sum of the extinction coefficients of two toluene molecules and a benzocyclobutene molecule: $\lambda_{\max}^{\mathrm{MeOH}}$ 260 mμ (log ϵ = 3.24), 266 mμ (log ϵ = 3.36), 272 mμ (log ϵ = 3.32). Thus, the evidence strongly indicates that the major species present in solution is I and not II or III.

The main interest concerning I is its high degree of reactivity toward a number of reagents, a few examples of which are given here. By contrast, benzocyclobutene is inert in all of these reactions under comparable conditions.[4] With a molar amount of maleic anhydride in carbon tetrachloride at room temperature crystals appear after about two hours and after forty-eight hours a nearly quantitative yield of analytically pure 1,4-diphenyl-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride is obtained with m.p. 219.2–219.8°. *Anal.* Calcd. for $C_{24}H_{18}O_3$: C, 81.33; H, 5.12; mol. wt., 354. Found: C, 81.33; H, 5.25; mol. wt., 335. Treatment of (I) with sulfur dioxide for fifteen minutes in refluxing carbon tetrachloride or for twenty-three hours at room temperature gives a nearly quantitative yield of the analytically pure 1,3-diphenyl-1,3-dihydroisothianaphthene-2,2-dioxide. *Anal.* Calcd. for $C_{20}H_{16}SO_2$: C, 74.97; H, 5.03; S, 10.0; mol. wt., 320. Found: C, 74.81; H, 5.12; S, 9.8; mol. wt., 310. This sulfone decomposes at 232.5–234° with evolution of sulfur dioxide to yield chiefly 9-phenyl-9,10-dihydroanthracene.[5] Compound I is readily reduced by hydrogen in alcohol at room temperature with palladium on charcoal to yield *o*-dibenzylbenzene.

The simplest explanation for these observations would seem to be that II or III is formed from I in a small equilibrium amount even at room temperature. However, the low degree of reactivity of a solution of I with alcohol, water, bases and oxygen is not consistent with the high degree of reactivity expected of compounds possessing the *o*-quinoid type structure or of radicals, although structure II might be expected to possess a stability greater than that of many compounds possessing the *o*-quinoid structure. The possibility is also being considered that the reagents react directly with I. For example, the reaction with maleic anhydride could reasonably occur by a four-center type mechanism. Further work is being carried out in order to decide between these possibilities.

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RECEIVED SEPTEMBER 2, 1958

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[1] L. W. Marrison, *J. Chem. Soc.*, 1614 (1951).

[2] M. P. Cava and D. R. Napier, THIS JOURNAL, **78**, 500 (1956).

[3] Unpublished data.

[4] Benzocyclobutene reacts analogously but only at elevated temperatures.

[5] Recently it was reported that 1,3-dihydroisothianaphthene-2,2-dioxide decomposes at temperatures above 280° to form benzocyclobutene and other products. Adducts are formed when the reactions are carried out in the presence of dienophiles. M. P. Cava and A. Deana, Abstracts of the 134th Meeting of the American Chemical Society, page 7P, Chicago, Illinois, September, 1958.