Trimethyltin β-Chloropropionate (I, Y = Cl).—The reaction conditions were the same as the corresponding bromide. Purification of the adduct was made by sublimation of the reaction mixture under reduced pressure. Product was isolated as a white needles in 75% yield: mp 88.5–89.4°; ir ($CHCl_3$) 1662 cm^{-1} (C=O); nmr ($CHCl_3$) τ 9.45 (s, with two satellites; $J_{Sn^{117}-H}$ = 60.2 and $J_{Sn^{119}-H}$ = 62.4 Hz, 9 H, CH_3Sn), 7.36 (t, 2 H, CH_2CO) and 6.36 (t, 2 H, CH_2Cl). *Anal.* Calcd for $C_6H_{13}ClO_2Sn$: C, 26.56; H, 4.84; Cl, 43.30. Found: C, 26.75; H, 4.97, Cl; 43.34.

Kinetic Study.—Trimethylmetal(IV) compounds (1 mmol) were dissolved in 9.00-ml samples of ethylene dichloride and kept at 65 ± 0.5°. β-Propiolactone (1 mmol) was added by means of a syringe and the solution was diluted to 10.00 ml. At a suitable time, a sample was withdrawn by syringe and the remaining amounts of β-propiolactone were determined with the characteristic infrared absorption at 1835 cm^{-1}. Second-order rate constants were calculated from the slope of the plot $1/(\beta - PL)$ *vs.* time. On account of the low reactivity of trimethyltin bromide, chloride, and trimethylsilyl ethyl sulfide, the following method was performed. Metal compound (20 mmol) was dissolved in 4.0 ml of ethylene dichloride and 0.5 mmol of β-propiolactone was added by microsyringe. The total volume was diluted to 5.00 ml and the following measurements were the same as above. The second-order rate constants were estimated from $k_2 = (2.303/t) \log [b(a - x)/a(b - x)]$.

Registry No.—β-Propiolactone, 57-57-8; I (Y = SMe), 18386-59-9; I (Y = Br), 18386-60-2; I (Y = Cl), 18386-61-3; II [Y = $N(C_2H_5)_2$], 13340-30-2.

1,1,2-Triphenylbenzocyclobutene

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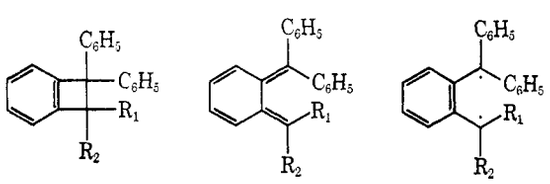
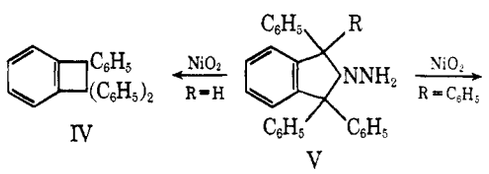
Following the demonstration[1] of the intermediacy of *o*-quinodimethanes in the reactions of benzocyclobutenes, a reexamination of the synthesis of one of the *gem*-diphenylbenzocyclobutenes was considered of interest in connection with the question, first raised many years ago by Wittig and Leo,[2] of the relationship between cyclic structure I and the corresponding *o*-quinodimethane and diradical structures II and III.

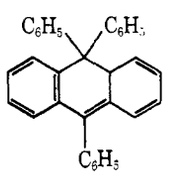


I II III

Applying a method which had proved successful in the synthesis of the *cis*- and *trans*-1,2-diphenyl derivatives, namely, oxidation of the corresponding N-aminodihydroisoindoles,[3–5] we examined the synthesis of 1,1,2-triphenyl- and 1,1,2,2-tetraphenylbenzocyclobutene. During the course of these studies, Quinkert[6] and coworkers described a method for the generation of the tetraphenyl derivative (I, $R_1 = R_2 = C_6H_5$) and, in fact, settled the question of the relationship between this labile hydrocarbon and its various isomers. It was demonstrated that I ($R_1 = R_2 = C_6H_5$) is stable at low temperatures but above 0° undergoes isomerization to VI. We also observed the formation of the same yellow hydrocarbon VI on oxidation of V (R = C_6H_5) by means of activated manganese dioxide or nickel peroxide.[7] On the other hand, the corresponding



IV V



VI

triphenylbenzocyclobutene (IV), obtained similarly from V (R = H), proved to be sufficiently stable to be isolated without difficulty. In reactions involving prior valence isomerization to II (R_1 = H; $R_2 = C_6H_5$) such as addition to tetracyanoethylene, IV proved to be more reactive than *trans*-1,2-diphenylbenzocyclobutene which, in turn, as shown earlier,[8] is more reactive than the corresponding *cis* isomer. The steric interaction which inhibits valence isomerization of the latter is also operative in the case of IV but is presumably outweighed by the additional conjugative stabilization due to the third phenyl group.

Experimental Section[9]

1,3,3-Triphenylisoindole.—Since the previous description[10] of the synthesis of this compound was unsatisfactory in our hands, the procedure was modified as described below. To a suspension of 205 g of anhydrous aluminum chloride in 380 ml of thiophene-free benzene there was added dropwise over 5 hr with stirring at room temperature a solution of 101 g of crude 1,3,3-trichloroisoindole[10] in 460 ml of benzene. The mixture was stirred for an additional 5 hr and poured into a mixture of 206 ml of concentrated hydrochloric acid and 800 g of chipped ice. The mixture, from which a viscous material had separated, was warmed on a hot plate with stirring until the benzene just began to boil. The mixture was removed from the hot plate and stirring continued at room temperature for 10–12 hr. The green-black solid was filtered and suspended in 880 ml of water and the mixture boiled for 10 min and filtered while hot. After air-drying

(1) For a review, see G. Quinkert, K. Opitz, W-W. Wiersdorf, and M. Finke, *Ann.*, **693**, 44 (1966).
(2) G. Wittig and M. Leo, *Ber.*, **64**, 2395 (1931).
(3) L. A. Carpino, *J. Amer. Chem. Soc.*, **84**, 2196 (1962).
(4) W. Baker, J. F. McOmie, and D. R. Preston, *J. Chem. Soc.*, 2971 (1961).
(5) L. A. Carpino, *Chem. Commun.*, 494 (1966).
(6) G. Quinkert, W-W. Wiersdorff, M. Finke, and K. Opitz, *Tetrahedron Lett.*, 2193 (1966).
(7) K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).
(8) R. Huisgen and H. Seidl, *Tetrahedron Lett.*, 3381 (1964).
(9) Melting and boiling points are uncorrected. Elemental analyses were by Dr. A. Bernhardt, Muhleim (Germany), and Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were taken in deuteriochloroform solution on a Varian A-60 instrument using tetramethylsilane as internal standard. Infrared and ultraviolet spectra were recorded on Perkin-Elmer 237 and 202 instruments, respectively.
(10) W. Theilacker, H. J. Bluhm, W. Heitmann, H. Kalenda, and H. J. Meyer, *Ann.*, **673**, 96 (1964).

for 1 hr the still-wet solid was divided into three portions and each portion extracted with several 300-ml portions of boiling ligroin (bp 88–98°) until only a small amount of black tarry residue (5–10 g) remained insoluble. The filtered ligroin solution (about 1.6 l.) deposited on cooling in a refrigerator a brown-black solid which was recrystallized from ethanol–nitromethane (1:4) to give 92 g (58%) of the isoindole as nearly colorless crystals, mp 146.5–148.5° (lit.[10] mp 144.5°).

1,1,3,3-Tetraphenyldihydroisoindole.—To a solution of phenyllithium freshly prepared from 30 ml of bromobenzene and 4.02 g of lithium in 390 ml of ether there was added in one portion 33 g of 1,3,3-trriphenylisoindole. Very gentle spontaneous refluxing occurred for 3–4 min after which the mixture was refluxed with stirring for 15 hr, cooled in an ice bath and treated with 150 ml of saturated ammonium chloride solution. After stirring at room temperature for 15 min 300 ml of water was added and stirring continued for 2–3 hr. Filtration gave 30 g (74%) of the crude amine, mp 183–185.5° (softening at 179°). This material was pure enough for conversion directly into the nitroso derivative. An analytical sample was obtained by recrystallization from ethanol–nitromethane (1:2) and nitromethane as white flakes: mp 184–185°; δ^{CDCl_3} 3.2 (s, broad, 1 H, NH) and 7.1 (m, 24 H, aromatic).

Anal. Calcd for $C_{32}H_{25}N$: C, 90.74; H, 5.95; N, 3.31. Found: C, 90.35; H, 6.02; N, 3.50.

2-Nitroso-1,1,3,3-tetraphenyldihydroisoindole.—Prepared in 98% yield by a method similar to that used for the triphenyl derivative, the nitroso compound had mp 236–238°; nmr δ^{CDCl_3} 7.3 (m, aromatic).

Anal. Calcd for $C_{32}H_{24}N_2O$: C, 84.93; H, 5.35; N, 6.19. Found: C, 84.70: H, 5.36; N, 6.32.

2-Amino-1,1,3,3-tetraphenyldihydroisoindole.—Several attempts to use ordinary aluminum amalgam prepared by the method of Vogel[11] failed to give satisfactory results, therefore a more active amalgam was prepared by modification of the method of Hahn and Thieler.[12] A mixture of 20 g of 8-mesh aluminum (Baker and Adamson) and 100 ml of 1.5% sodium hydroxide solution was heated until vigorous gas evolution set in. Reaction was allowed to proceed away from the source of heat until it became sluggish (2–3 min) and the cleaned aluminum washed several times with water by decantation. A second 100 ml of 1.5% sodium hydroxide solution was added followed by immediate addition of 50 ml of a 0.5% solution of mercuric chloride in warm water. The mixture, from which a yellow-orange solid separated, was swirled for 30 sec and then 0.2 g of solid potassium cyanide was added followed by swirling for 1–1.5 min. The orange-brown color disappeared on addition of the cyanide. The amalgam was washed by decantation successively with four to five portions of water, ethanol and ether, and then used at once in the normal manner.[11] Passage of hydrogen chloride gas through the dried ether solution following the usual work-up gave a tacky substance which solidified on continued passage of the gas. Filtration after 1 hr gave 9.5 g of the crude hydrochloride which was washed with ether and suspended in a separatory funnel in a mixture of 300 ml of saturated sodium bicarbonate solution and 150 ml of ether. The solid slowly dissolved on continued shaking. Spontaneous evaporation of the ether layer left a white solid which was recrystallized from nitromethane–ethanol (2:1) to give 6 g (41.3%) of well-formed bulky yellowish needles, mp 150–182°. An analytical sample was obtained by sublimation at 180° (3 mm) followed by recrystallization from nitromethane–ethanol (2:1) to give white flakes: mp 140–170° (forms yellow liquid);[13] δ^{CHCl_3} 2.92 (s, broad, 2 H, NH_2) and 7.1 (s, broad, 24 H, aromatic); uv $\lambda_{max}^{CH_2Cl_2}$ 252 mμ (log ε 3.58), 259 (3.54), 265.5 (3.49) and 271.5 (3.35).

Anal. Calcd for $C_{32}H_{26}N_2$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.49; H, 6.00; N, 6.66.

The acetyl derivative (from acetic anhydride at room temperature) had mp 280–288° (nitromethane).

Anal. Calcd for $C_{34}H_{28}N_2O$: C, 84.97; H, 5.87; N, 5.83. Found: C, 84.67; H, 5.83; N, 6.13.

2-Nitroso-1,1,3-triphenyldihydroisoindole.—1,1,3-Triphenyldihydroisoindole obtained by $LiAlH_4$ reduction of 1,3,3-triphenylisoindole was treated with $NaNO_2$ in HOAc. Recrystallization (CH_3NO_2) gave 85% of the nitroso compound as yellow crystals: mp 187–188.5°; nmr δ^{CDCl_3} 6.15 (s, 1 H, CH), 7.1 (m, 19 H, aromatic).

Anal. Calcd for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.35; N, 7.44. Found: C, 82.87; H, 5.37; N, 7.40.

2-Amino-1,1,3-triphenyldihydroisoindole Hydrochloride.—Aluminum amalgam[11] reduction of the N-nitroso compound gave the hydrazine isolated as the corresponding hydrochloride, mp 160–210° dec.

Anal. Calcd for $C_{26}H_{23}ClN_2$: C, 78.28; H, 5.81; Cl, 8.89; N, 7.02. Found: C, 78.07; H, 5.96; Cl, 8.73; N, 6.99.

The benzal derivative, obtained in the usual way, was recrystallized from nitromethane-dimethylformamide (5:1) as colorless clumps of crystals, mp 212–213.5°.

Anal. Calcd for $C_{33}H_{26}N_2$: C, 87.97; H, 5.82; N, 6.22. Found: C, 87.58; H, 5.99; N, 6.32.

1,1,2-Triphenylbenzocyclobutene.—To a suspension of 5 g of 1,1,3-triphenyl-2-aminodihydroisoindole hydrochloride in 80 ml of methylene dichloride was added 1.75 ml of triethylamine. The resulting clear solution was treated with 21 g of nickel peroxide[7] added in small portions over a period of about 15 min. The mixture was allowed to stand at room temperature for 30 min with occasional shaking, another 1-g portion of nickel peroxide added and the mixture filtered after a second 30-min period. The oxide was washed well with methylene dichloride and the solvent allowed to evaporate spontaneously from a small beaker. The residual oil on trituration with methanol (seeding, if possible) eventually solidified. Upon evaporation of the methanol the solid was crushed and washed well with water on a filter plate. After air-drying, recrystallization from methanol-nitromethane (1:1) with cooling in a refrigerator gave 3 g (72%) of cream-colored crystals, mp 105.5–108.5°. An analytical sample was obtained by recrystallization from methanol as shiny white flakes: mp 109.5–111°; nmr δ^{CDCl_3} 5.45 (s, 1 H, CH) and 6.8–7.5 (m, 19 H, aromatic); uv $\lambda_{max}^{95\%C_2H_5OH}$ 255 mμ sh (log ε 3.18), 260.5 (3.32), 266 (3.40) and 272.8 (3.33). Except for the intensity differences the ultraviolet curve matched those of *cis*- and *trans*-1,2-diphenylbenzocyclobutene.

Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06; mol wt, 332.4. Found: C, 93.99; H, 6.18; mol wt, 307 (osmometric).

α,α,α′-Triphenyl-*o*-xylene. Method A.—Hydrogenolysis of 1.5 g of 1,1,3-triphenylbenzocyclobutene in 150 ml of methanol in the presence of 0.2 g of palladium–carbon (10%) at 55 psi in a Parr apparatus for 20 hr gave 0.75 g (49.6%) of the hydrocarbon, mp 112–116°, after recrystallization from methanol–nitromethane (1:1). An analytical sample, mp 110–111.5°, was obtained by recrystallization from ethanol–nitromethane (10:1): nmr δ^{CDCl_3} 3.85 (s, 2 H, CH_2), 5.61 (s, 1 H, CH) and 7.15 (m, 19 H, aromatic); uv $\lambda_{max}^{95\%C_2H_5OH}$ 244 mμ (log ε 2.69), 250 (2.86), 257 (2.99), 260 (3.02), 262.8 (3.08), 265 sh (2.97) and 269.8 (2.95).

Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.38; H, 6.56.

Method B.—A solution of 0.5 g of *o*-benzoyltriphenylmethane,[14] 0.5 g of potassium hydroxide and 0.3 ml of 64% hydrazine in 20 ml of ethylene glycol was refluxed for 1 hr. The condenser was arranged for downward distillation and distillate was removed until the internal temperature reached 199°. After refluxing for an additional 15 hr the solution was poured into 400 ml of water. The mixture was allowed to stand at room temperature for 24 hr during which time the first-precipitated oil crystallized. Filtration gave 0.1 g (21%) of white solid which after recrystallization from ethanol was obtained as tiny white crystals, mp 109–111°. Comparison of infrared spectra demonstrated the identity of this material with the sample prepared by catalytic hydrogenation of 1,1,2-triphenylbenzocyclobutene.

Tetracyanoethylene Adduct of 1,1,2-Triphenylbenzocyclobutene.—A solution of 0.128 g of tetracyanoethylene and 0.332 g of the benzocyclobutene in 25 ml of benzene was allowed to stand at room temperature for 5 hr and the solvent then allowed to evaporate. The resulting oil solidified on trituration with ethanol and recrystallization from ethanol–nitromethane (1:1) gave 0.32 g (69.6%) of the adduct as well-formed crystals, mp 214–216°.

(11) See L. A. Carpino, A. A. Santilli, and R. W. Murray, *J. Amer. Chem. Soc.*, **82**, 2728 (1960).

(12) F. L. Hahn and E. Thieler, *Ber.*, **57**, 671 (1924).

(13) The melting point varied with the rate of heating and always exhibited a wide range no matter how often the compound was recrystallized or sublimed.

(14) C. K. Bradsher and S. T. Webster, *J. Amer. Chem. Soc.*, **79**, 393 (1957).

Anal. Calcd for $C_{32}H_{20}N_4$: C, 83.46; H, 4.38; N, 12.17. Found: C, 82.99; H, 4.49; N, 12.44.

In order to determine the relative reactivities of *cis*-1,2-diphenyl-, *trans*-1,2-diphenyl- and 1,1,2-triphenylbenzocyclobutene toward tetracyanoethylene, 0.2 mmol of each hydrocarbon was dissolved in 1 ml of toluene contained in three separate flasks. To each solution was added 0.1 mmol of tetracyanoethylene and the time required for disappearance of the bright yellow color noted. Times required were as follows (two separate runs): 1,1,2-triphenyl derivative (4–6 min); *trans*-1,2-diphenyl derivative (60–65 min); *cis*-1,2-diphenyl derivative (5–5.5 days).

Sulfur Dioxide Adduct of 1,1,2-Triphenylbenzocyclobutene.—A solution of 0.15 g of the benzocyclobutene in 50 ml of liquid sulfur dioxide was heated in a sealed tube at 90–95° for 15 hr. Evaporation of the solvent gave 0.17 g (94.4%) of the adduct, mp 167–174°. Recrystallization from ethanol–benzene (2:1) gave the sulfone as tiny white crystals: mp 173–175° (gas evolution and yellowing), lit.[15] mp 174–174.5°; nmr δ^{CDCl_3} 5.15 (s, 1 H, CH) and 7.3 (m, 19 H, aromatic); ir λ_{max}^{Nujol} 7.61, 8.81 μ (SO_2). The ultraviolet curve matched that published by Kloosterziel and Backer[15] for 1,1,3-triphenyl-1,3-dihydroisobenzothiophene sulfone.

Registry No.—1,1,3,3-Tetraphenyldihydroisoindole, 18554-09-1; 2-nitroso-1,1,3,3-tetraphenyldihydroisoindole, 18554-10-4; 2-amino-1,1,3,3-tetraphenyldihydroisoindole, 18554-11-5; acetyl derivative of 2-amino-1,1,3,3-tetraphenyldihydroisoindole, 18554-12-6; 2-nitroso-1,1,3-triphenyldihydroisoindole, 18554-13-7; 2-amino-1,1,3-triphenyldihydroisoindole hydrochloride, 18554-14-8; benzal derivative of 2-amino-1,1,3-triphenyldihydroisoindole hydrochloride, 18554-15-9; IV, 18554-16-0; α,α,α'-triphenyl-*o*-xylene, 18554-17-1; tetracyanoethylene adduct of 1,1,2-triphenylbenzocyclobutene, 18598-44-2.

Acknowledgment.—This work was supported by a grant (NSF-GP-4283) from the National Science Foundation.

(15) H. Kloosterziel and H. J. Backer, *Rec. Trav. Chim. Pays-Bas*, **71**, 1235 (1952).

The Solvolysis of Some Substituted Cyclohexyl Methanesulfonates[1]

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In connection with other studies from these laboratories on the effect of polar substituents on the rate of solvolysis of derivatives of substituted cyclohexanols,[2,3] it was desirable to examine the reactivity of some simple cyclohexyl methanesulfonates. Though methanesulfonates have been widely used in carrying out chemical transformations in the steroid and sugar families, relatively few rate measurements have been made with them. Robertson and his coworkers, in their definitive studies of solvent isotope effects, have examined the solvolysis of simple alkyl methanesulfonates.[4] The rate for isopropyl methanesulfonate is about one-half the rate for isopropyl tosylate in water. Cyclopentyl methanesulfonate solvolyzes somewhat more slowly in methanol than does the tosylate,[5] and comparisons of the relative rates of acetolysis of cholestanyl and 4,4-dimethylcholestanyl sulfonates can be made from the reported kinetic measurements of deSousa and Moriarity[6] and of Biellman and Ourisson.[7] The tosylate and methanesulfonate show nearly identical rates.

We have prepared and measured the rate of acetolysis of *cis*- and *trans*-4-*t*-butylcyclohexyl methanesulfonates and of *cis*- and *trans*-4-methylcyclohexyl methanesulfonates. The rate measurements are summarized in Table I, with derived thermodynamic parameters in Table II.

TABLE I

RATES OF ACETOLYSIS OF 4-SUBSTITUTED CYCLOHEXYL METHANESULFONATES

Substituent	Temp, °C	$10^6 k_1$, sec^{-1}	k_{rel} (70°)	k_{OMs}/k_{OTs}[a]
Unsubstituted	50	2.42 ± 0.03		1.23[b]
	70	28.7 ± 0.6	1.16	
	70	28.8 ± 0.6		
trans-4-Methyl	50	1.49 ± 0.88		1.15[c]
	70	19.3 ± 0.3	0.78	
cis-4-Methyl	50	3.88 ± 0.32		1.18[c]
	70	48.8 ± 1.0	1.97	
	70	48.0 ± 3.0	1.94	
trans-4-*t*-Butyl	50	1.91 ± 0.02		1.20[b]
	70	24.8 ± 0.7	1.00	
cis-4-*t*-Butyl	50	7.19 ± 0.25		1.26[b]
	70	75.8 ± 2.2	3.06	

[a] Rate ratio methanesulfonate/tosylate at 75.7°, the only temperature at which data for the 4-methylcyclohexyl tosylates are available. [b] Tosylate data: S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955). [c] Tosylate data: H. Kwart and T. Takeshita, *ibid.*, **86**, 1161 (1964).

TABLE II

ACTIVATION PARAMETERS

Substituent[a]	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
trans-4-*t*-Butyl	27.6 ± 0.2	+0.5 ± 0.6
cis-4-*t*-Butyl	25.3 ± 0.4	−3.8 ± 1.1
trans-4-Methyl	27.6 ± 0.4	−0.1 ± 1.2
cis-4-Methyl	27.2 ± 0.7	+0.5 ± 2.2
Unsubstituted	26.6 ± 0.2	−2.1 ± 0.7

[a] Substituent on cyclohexyl methanesulfonate.

These rate measurements may be compared with previously determined rates for the corresponding tosylates, and the data are summarized in the last column in Table I. It is to be noted that the methanesulfonates solvolyze at rates which are very similar to those of the corresponding tosylates. In the present, unhindered cyclohexyl derivatives, the methanesulfonates, solvolyze about 20% faster than the tosylates.

Conformational Analysis.—One of the primary pur-

(1) Supported in part by grants from the National Science Foundation (GP-1572 and GP-6133X).

(2) D. S. Noyce and B. Weinstein, *J. Org. Chem.*, to be submitted.

(3) D. S. Noyce and Byron E. Johnston, *ibid.*, to be submitted.

(4) K. T. Leffek, R. E. Robertson, and S. E. Sugamori, *Can. J. Chem.*, **39**, 1989 (1961); R. E. Heppolette and R. E. Robertson, *ibid.*, **44**, 677 (1966).

(5) F. J. Chloupek and G. Zweifel, *J. Org. Chem.*, **29**, 2092 (1964).

(6) R. M. deSousa and R. M. Moriarity, *ibid.*, **30**, 1509 (1965).

(7) J. F. Biellman and G. Ourisson, *Bull. Soc. Chim. Fr.*, 341 (1962).