pure (*S*)-**2** gave **5**, $[\alpha]_D$ −52° which would correspond to optically pure **5** of the *S* configuration.

The sample of **5**, $[\alpha]_D$ +19.7°, obtained from hydrolysis of (*R*)-**2** is therefore 38% optically pure with the predominance of the *R* isomer.

B. (*S*)-Ethoxymethoxymethylphenylphosphonium Hexachloroantimonate [(*S*)-3].—The hydrolysis of (*S*)-**3** (80% optically pure) was carried out by the identical procedure used for the hydrolysis of (*S*)- and (*R*)-**2**. A mixture of methyl methylphenylphosphinate (**5**) and ethyl methylphenylphosphinate (**6**) was obtained and analyzed by pmr and glpc for relative amounts. The two phosphinate esters, **5** and **6**, were separated by glpc (6 ft, SE-30, 150°) to give **5**, $[\alpha]_D$ −40° (77% optically pure), and **6**, $[\alpha]_D$ +22° (48% optically pure[17]). Thus, optically pure (*S*)-**3** would give, upon hydrolysis, a ratio of (*S*)-**5** to (*R*)-**5** of 98:2 and a ratio of (*S*)-**6** to (*R*)-**6** of 20:80.

Control Experiments.—That the phosphinate ester products are configurationally stable under the reaction conditions for hydrolysis was shown by submitting a sample of each to these exact conditions. Recovery of unreacted ester after 5 min yielded a product of unchanged stereochemistry.

The product ratios obtained from the hydrolyses of the dialkoxyphosphonium salts were corrected for the differential rate of hydrolysis of the various esters by the following procedure. A mixture of two phosphinate esters (A and B) of known mole per cent ratio was submitted to the conditions of the hydrolyses of the phosphonium salt. Aliquots were taken and quenched by extracting with dichloromethane and the recovered mixture of the two esters was analyzed by pmr. A plot of ln [A/B] against time yielded a slope ($k_A - k_B$, assuming pseudo-first-order kinetics). Table II contains the results of this study.

Registry No.—**2**, 34630-90-5; (*S*)-**3**, 34630-91-6; (*R*)-**3**, 34630-92-7; **4**, 34638-63-6; (*S*)-**5**, 34647-06-8; (*R*)-**5**, 34647-07-9; (*S*)-**6**, 33642-98-7; (*R*)-**7**, 34638-79-4; (*S*)-**7**, 34630-93-8.

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Three-Membered Rings. III.[1a] Ultraviolet Spectral Evidence of a Stereochemical Bias in Rigid *p*-Nitrophenylcyclopropanes[1b]

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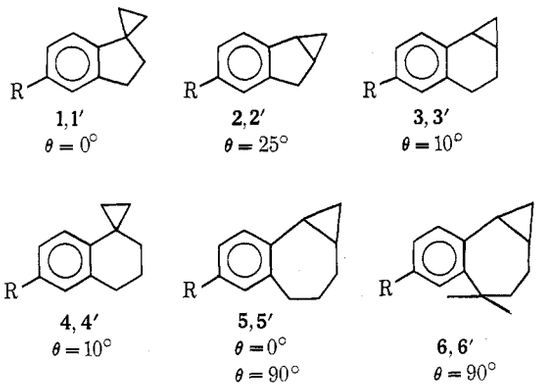
A study of the uv spectra of a series of conformatially rigid *p*-nitrophenylcyclopropanes and the parent hydrocarbons demonstrates the existence of a slight stereochemical bias for electronic interaction between the cyclopropyl group and the nitrobenzene or benzene chromophore. In the series studied, the orientation of the cyclopropane ring deviates from the bisected geometry from 0 to 90°.

The ability of the para-enriched carbon–carbon orbitals of cyclopropane to conjugate with neighboring unsaturated systems has been demonstrated.[2-4] Several recent studies have dealt with the effects of the cyclopropyl substituent on the electronic spectra of π systems.[5-8] Goodman and Eastman[7] studied the uv spectra of a series of rigid phenylcyclopropanes (**1–3**) in order to ascertain the preferred geometry for expression of olefinic character. On the basis of small spectral variations, they concluded that there is no preferred geometry for conjugation of a cyclopropane ring with a phenyl nucleus. Strait, *et al.*,[9] have demonstrated the usefulness of the nitrobenzene chromophore in evaluating the electronic properties of three-membered rings. Hahn and coworkers[8] extended the study of Goodman and Eastman[7] by including **4** and **5** and in addition studied the para-nitro derivatives (**1′–5′**), and concluded that conjugation in cyclopropyl aromatic systems is a detectable function of cyclopropane geometry if the interacting chromophore is sufficiently electron attracting.



1–6, R = H
1′–6′, R = NO_2

θ = Deviation in degrees from bisected geometry

According to Bernett,[10] total overlap between the sp^5 bent bonds of the cyclopropane ring and an adjacent p orbital decrease only slightly for deviations up to 39° (Figure 1B) from the optimum geometry (Figure 1A) and thereafter decreases more rapidly to a minimum at 90° (Figure 1C).

Compound **5** and its nitration products are the most crucial in their study[8] because they represent the only compounds having a large deviation (θ = 90°) from optimum geometry. There are two conformations of **5**; the sterically preferred conformation has the least preferred geometry for orbital overlap (θ = 90°), whereas the sterically less preferred conformation has the optimum geometry for overlap (θ = 0°). It

(1) (a) Paper II: L. A. Strait, D. Jambotkar, R. Ketcham, and M. Hrenoff, *J. Org. Chem.*, **31**, 3976 (1966). (b) Taken in part from the Ph.D. Thesis of L. C. M. Presented, in part, at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 12, 1968. (c) U. S. Public Health Service Predoctoral Trainee.

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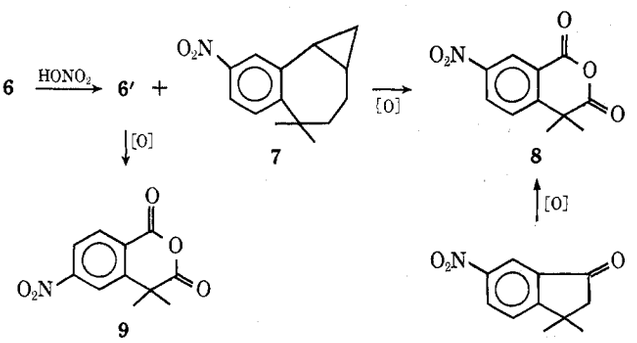
(10) W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967). (Figure 1 is taken from this reference.)

seemed possible that stabilization gained from overlap might significantly overcome the small steric effects so that one could not assume that **5** and especially **5′** would be exclusively in the conformation having $\theta = 90°$. We have chosen to eliminate this uncertainty by introduction of two methyl substituents at C-5 (**6**) which further reduces the stability of the conformation $\theta = 0°$ whereas it has an insignificant effect on the other ($\theta = 90°$), thus ensuring that **6** exists exclusively in the least favored conformation for overlap ($\theta = 90°$).

The cyclopropyl group in **1–4** is clearly a stronger ortho, para director than the other alkyl substituents $(CH_2)_n$; however, the weakness of overlap in **5** and **6** permits significant amounts of nitration meta to the cyclopropyl substituent (**7**). The weakness of this interaction also makes spectroscopic structural assignments for the two 1,2,4-trisubstituted products difficult. The two methyl substituents provide a means for an unambiguous chemical determination of structure for these two nitration products, since oxidation of **7** stops at a dimethylhomophthalic acid derivative (**8**) which can be synthesized in an unambiguous fashion.



Results and Discussion

Uv Spectra.—The nitro compounds **1′–4′** and **6′** have characteristic nitrobenzenelike uv spectra with absorption maxima ranging from 276 to 290 nm in hexane. The pattern of differences is clearly interpretable, particularly when compared with *p*-nitrophenylcyclopropane, which absorbs at 280 nm in hexane (Table I).

TABLE I

RIGID ARYLCYCLOPROPANES

		Hydrocarbons		Nitro compd	
Compd	θ	λ_{max} (ϵ)[a]	$\Delta\lambda$	λ_{max} (ϵ)[b]	$\Delta\lambda$
1, 1′	0	281 (17.8)	0	290 (9.5)	0
2, 2′	25	278 (13.9)	3	286.5 (9.8)	3.5
3, 3′	10	279 (10.1)	2	287 (10.5)	3
4, 4′	10	277.5 (13.9)	3.5	288 (10.5)	2
6, 6′	90	274.5[d] (2.94)	6.5	276 (10.4)	14
0, 0′[c]		275 (3.8)	6.0	280 (10.9)[e]	10

[a] $^1L_b \leftarrow A^1$, λ_{max} (nm), $\epsilon \times 10^{-2}$, solvent hexane. The same trend was found in the $^1L_a \leftarrow {}^1A$ transition. [b] λ_{max} (nm), $\epsilon \times 10^{-3}$, solvent hexane. [c] 0 and 0′ refers to PhC_3H_5 and *p*-NO_2-PhC_3H_5. [d] The most intense band in the transition is at 262.5 nm, but the 0–0 band should be at about 12 nm longer wavelength (the difference between dimethylbenzosuberane and tetralin). [e] See ref 9.

Small deviations from the optimum geometry give rise to very small spectral changes, whereas the larger value of θ in **6** produces a proportionately larger change as predicted from the suggestion of Bernett.[10] The difference between absorption maxima ($\Delta\lambda$) of **1′** ($\theta = 0°$) and **2′** ($\theta = 25°$) is only 3.5 nm, whereas the $\Delta\lambda$ between **1′** ($\theta = 0°$) and **6′** ($\theta = 90°$) is 14 nm. Thus it is evident from the uv spectra that there is a stereochemical bias for maximum electronic interaction.

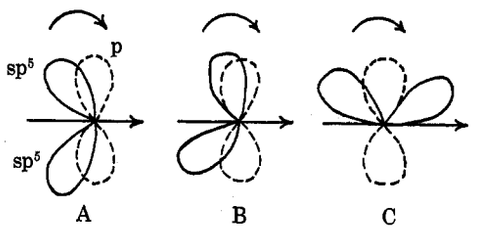


Figure 1.[10]

Review of the spectral data for the hydrocarbons[7,8] with the addition of **6** reveals that a correlation does exist between θ and the uv maxima which parallels that found in the nitro compounds. The uv spectra of **11** substituted indans[11] are very similar to that of indan [λ_{max} 273.2 nm (ϵ 1400)] in contrast to the red shift and intensity increase seen in **1** and **2**. Similar constancy is observed for a series of six substituted tetralins[12] [tetralin λ_{max} = 273.5 nm (ϵ 600)] where, again, introduction of the fused cyclopropyl ring or a spiro cyclopropyl ring produces a significant red shift.

The uv spectrum of 1,1-dimethylbenzosuberane has an absorption maximum (not the 0–0 band) at 261.5 nm (ϵ 1900); introduction of the fused cyclopropyl group (**6**) does not produce a red shift.

Nitration.—Nitration of **1–4** leads predominantly to *p*-nitrophenylcyclopropanes (**1′–4′**) as indicated by their uv and ir spectra. Glc indicated two minor nitration products which in cases where they were isolated were shown to have the nitro group ortho or meta to the cyclopropyl group. Nitration of **6** gave four products, two major products (1,2,4-trisubstituted benzenes) and two minor products (1,2,3-trisubstituted benzenes). The uv and nmr spectra of the major nitration products of **6** (**6′**, **7**) were so similar that structural assignments could not be made with certainty. Oxidation of **6′** with chromic acid gave **9** while **7** gave **8**. The structure of **8** was confirmed by independent synthesis.

Experimental Section[13]

Spectroscopic Methods.—Uv spectra (Table I) were obtained in spectroquality hexane (Matheson Coleman and Bell) with a Cary Model 14 spectrophotometer. Nmr spectra were obtained in $CDCl_3$ with a Varian A-60A spectrometer using TMS as an internal standard. The ir spectra were recorded with a Perkin-Elmer 337 or 457 spectrophotometer using potassium bromide plates for liquids and potassium bromide pellets for solids.

1-Methyleneindan was synthesized using the procedure of Hahn, *et al.*,[8] with the following modifications. The Wittig reaction was carried out in dry THF under nitrogen. The re-

(11) 1-(2-piperidylmethyl)-1-indanol hydrochloride, 2-bromo-1-indanol, 1-methylindan, 2-methylindan, 1,2-dimethylindan, 1-hexyl-2-butylindan, 1,3-dimethylindan, 1,3,3-trimethyl-1-indanol, 2-decylindan, 1-hexadecylindan, and 2-hexadecylindan.

(12) 1,4-diethyltetralin, 1,1,4,4-tetramethyl-2,3-tetralindiol, 2-methyltetralin, 2-ethyltetralin, 2-butyltetralin, 2-phenyltetralin.

(13) Melting points are taken on a Thomas-Hoover melting point apparatus and are corrected. Gas chromatographic separations were carried out on an Aerograph A90C gas chromatograph. Elemental analyses were performed in the Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley.

action was warmed to reflux and allowed to proceed for 32 hr. Wet THF was added, the contents were vacuum filtered, and the filtrate was dried (anhydrous Na_2SO_4). Excess solvent was removed under vacuum. The dark yellow oil thus obtained was chromatographed twice on neutral alumina using hexane to give a colorless oil, bp 95–97° (20 mm) [lit.[7,8] bp 99.5–101.5° (29 mm), 26–28° (0.2 mm)] in 56% yield. Indene obtained from commercial sources was distilled before use.

1,2-Dihydronaphthalene was synthesized by the procedure of Hurd and Juel,[14] bp 90–91° (15 mm) [lit.[14] bp 87–89° (15 mm)].

1-Methylenetetralin was synthesized in 44% yield using the above procedure for 1-methyleneindan except that anhydrous ether was used as the solvent and the reaction was carried out for 15 hr at room temperature and then under reflux for an additional 6 hr. Wet ether was added to destroy the ylide (colorless oil), bp 94–96° (5 mm) [lit.[8,15] bp 58° (0.5 mm), 103° (14 mm)].

5,5-Dimethyl-6,7-dihydro-5*H*-benzocycloheptene.—3-Methyl-3-phenylbutyric acid was prepared from benzene and 3-methylcrotonic acid by the method of Julia, *et al.*,[16] in 86% yield, mp 45–48° (lit.[16,17] mp 57–58°).

The ethyl ester, bp 106–107° (2 mm), prepared with hydrochloric acid and absolute ethanol, was reduced with lithium aluminum hydride to give 86% of 3 methyl-3-phenyl-1-butanol, bp 112° (1 mm) [lit.[13] bp 135° (14 mm)].

3-Methyl-3-phenyl-1-butyl *p*-toluenesulfonate, bp 210° (3 mm), ir (neat) 1370 and 1175 cm^{-1}, was treated with sodiomalonic ester to give diethyl (3-methyl-3-phenylbutyl)malonate in 42% yield, bp 150–170° (3 mm) [lit.[13] bp 150–160° (2 mm)], free acid mp 162–163°.

The diethyl ester (70 g, 0.237 mol) and 60 g of potassium hydroxide in 1000 ml of methanol and 150 ml of water were refluxed for 4 hr. Dilution with ice, acidification with hydrochloric acid, and extraction with chloroform gave on distillation 42.4 g (81%) of the methyl ester, bp 161–162° (6 mm), identical in all respects with the product obtained by stepwise hydrolysis, decarboxylation, and esterification.

Methyl 5-methyl-5-phenylhexanoate (42.2 g, 0.20 mol) in 2.32 kg of polyphosphoric acid was heated on a boiling water bath for 2 hr. The hot reaction mixture was poured onto 4 l. of ice, allowed to stand for 2 hr, and then extracted with ether. The extract was washed with sodium bicarbonate, dried, and concentrated. Vacuum distillation of the residue gave 25.2 g (67%) of 5,5-dimethyl-1-benzosuberone: bp 92° (1 mm) [lit.[18] bp 94–96° (0.3 mm)]; ir 1690 cm^{-1} (C=O); nmr δ 1.30 (s, 6 H, CH_3), 1.80 (m, 4 H, CH_2), 2.68 (m, 2 H, CH_2C=O), and 7.33 (m, 4 H, C_6H_4).

A stirred solution of the ketone (25 g, 0.134 mol) in methanol was added, in portions, to 2.55 g (0.268 mol) of sodium borohydride in 25 ml of methanol. After stirring for 4 hr water was added and the product was extracted with ether. The ether solution was washed with water, dried, and concentrated. The crude product had an ir band at 3350 cm^{-1} (alcohol).

Acetylation was accomplished by refluxing in acetic anhydride for 4 hr, followed by dilution with water, extraction with ether, and concentration. The residue and 2 g of potassium acid sulfate in a distillation flask were heated at 120° (20 mm) until acetic acid was no longer evolved, then distilled under reduced pressure to give 14.4 g (63%) of 5,5-dimethyl-6,7-dihydro-5*H*-benzocycloheptene: bp 82–83° (1 mm); nmr δ 1.9, 2.25, and 2.7 (m, 2 H each, CH_2), two triplets at 5.8 (J_{CH} = 12, J_{CH_2} = 4 Hz, 1 H, vinyl), and two triplets at 6.3 (J_{CH_2} allylic = 2 Hz, 1 H) and 7 (m, 4 H, C_6H_4).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 91.05; H, 9.15.

Spiro[cyclopropane-1,1′-indan] (1), **benzo[*a*]cyclopropa[*c*]cyclopentene(cycloprop[*a*]indene)** (2) **and benzo[*a*]cyclopropa[*c*]cyclohexene(1a,2,3,7b-tetrahydro-1*H*-cycloprop[*a*]naphthalene)** (3) were synthesized according to the procedures of Goodman and Eastman.[7]

Spiro[cyclopropane-1,1′-tetralin] (4).—A suspension of zinc–copper couple[18] (2.7 g), methylene iodide (1.0 g), and a crystal of iodine in 25 ml of ether was stirred under reflux for 30 min. A solution of 4 g of methylene iodide and 4.13 g (0.029 mol) of 1-methylenetetralin was added dropwise over 1 hr. After refluxing for 8 hr, 2.7 g of couple and 5 g of methylene iodide were added and reflux was continued for 40 hr. The solids were removed by filtration through Filteraid and the filtrate was washed three times each with saturated ammonium chloride, 5% ammonium hydroxide, and water. After removal of solvent, the yellow oil (4.34 g) was shown by glc to contain about 50% of desired product. Removal of unreacted starting material by oxidation with $KMnO_4$, followed by chromatography on neutral alumina with petroleum ether (bp 30–60°), yielded pure product having the same nmr spectrum as reported by Hahn, *et al.*[8]

1,1-Dibromo-4,4-dimethylbenzo[*a*]cyclopropa[*c*]cycloheptene.—To a stirred suspension of potassium *tert*-butoxide, prepared from 5.03 g (0.129 mol) of potassium and dry, pure *tert*-butyl alcohol, in 120 ml of pentane was added first a solution of 11.0 g (0.067 mol) of olefin in 30 ml of pentane, then, dropwise, 32.5 g (0.129 mol) of bromoform over a 30-min period. After stirring for 3 hr at 0°, water was added and the phases were separated. The organic phase was dried, the pentane was removed, and the dark yellow residue was distilled, bp 140–142° (0.4 mm), to give 14.9 g (71%) of the product: nmr δ 0.7–1.15 (m, 1 H, cyclopropyl), 1.37 (s, 3 H, CH_3), and 1.48 (s, 3 H, CH_3), two broad singlets at 2.85 and 3.06 (benzylic cyclopropyl), complex multiplets around 1.6 and 2.0 (CH_2 and cyclopropyl), and signals at 7.3 (C_6H_4).

Anal. Calcd for $C_{14}H_{16}Br_2$: C, 48.84; H, 4.68; Br, 46.67. Found: C, 48.82; H, 4.63; Br, 46.38.

4,4-Dimethylbenzo[*a*]cyclopropa[*c*]cycloheptene (6).—To a stirred solution of the dibromo compound (14.9 g, 0.043 mol) in 124 ml of ether was added simultaneously a solution of 161 ml of methanol and 37 ml of water, and 14.2 g of sodium in 0.3-g pieces for a 1-hr period. After stirring over 1 hr, additional aqueous methanol (95 ml) and sodium (11.0 g) were added as above and the mixture was stirred again for 1 hr. Fourfold dilution with water, extraction with ether, and concentration of the dried extract gave a yellow oil which when distilled gave 3.4 g (43%) of the reduced cyclopropane compound, bp 124° (0.5 mm), and 7.0 g of starting dibromide, nmr δ 0.2–2.3 (m, 8 H, aliphatic), 1.38 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), and 7.1–7.5 (m, 4 H, aromatic).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.20; H, 9.78.

5′-Nitrospiro[cyclopropane-1,1′-indan] (1′).—To a stirred solution of 1.85 g (8.0 mmol) of cupric nitrate trihydrate in 20 ml of acetic anhydride at 0° was added 1.1 g (8.0 mmol) of spiro[cyclopropane-1,1′-indan] in 20 ml of acetic anhydride dropwise at a rate so that the temperature did not rise above 7° (about 0.5 hr). The reaction vessel was removed from the ice bath and allowed to stand at 25° for 2 hr. The insoluble salts were removed by filtration and the filtrate was diluted threefold with ice water to hydrolyze the acetic anhydride. The mixture was washed with 5% sodium bicarbonate and water and then dried. Removal of ether gave a yellow oil. Preparative glc on a 0.375 in. × 7 ft column of 20% SE-30 on Diatoport W with nitrogen as a carrier gas, and using traps externally cooled by liquid nitrogen under reduced pressure, gave the desired product.

There were only three components, two of which were collected. The major component had the longest retention time and solidified in the trap. This fraction was chromatographed on neutral alumina using 1:1 ether–petroleum ether. Crystallization from aqueous methanol followed by sublimation gave about 20 mg of a pale yellow solid, mp 82.5–83.5° (lit.[8] mp 81–82.5°).

4-Nitrocycloprop[*a*]indene (2′).—Treating 1 g (8.0 mmol) of 2 with 1.85 g (8.0 mmol) of cupric nitrate and 20 ml of acetic anhydride as described in 1′ gave a similar yellow oil. Preparative glc and chromatography gave 45 mg, mp 76–77° (lit.[8] mp 76–76.5°).

5-Nitro-1a,2,3-7b-tetrahydro-1*H*-cycloprop[*a*]naphthalene (3′).—Hydrocarbon 3 (0.5 g, 4.0 mmol) when nitrated with cupric nitrate trihydrate and purified in the usual way gave about 15 mg of a solid, mp 45.5–46° (lit.[8] mp 45.0–46.5°).

6′-Nitrospiro[cyclopropane-1,1′-tetralin] (4′).—Fuming nitric acid (3.85 g, 0.06 mol) was added to 61 g (0.6 mol) of acetic anhydride at 20° and cooled to −50 to −55°. Hydrocarbon 4 (4.8 g, 0.03 mol) in 5 ml of acetic anhydride was added dropwise over 30 min. The temperature was allowed to rise to 0° and then stirred at 0° for 4 hr. After pouring onto ice and neutralization with solid potassium carbonate, the mixture was extracted

(14) C. D. Hurd and L. H. Juel, *J. Amer. Chem. Soc.*, **77**, 601 (1955).
(15) G. Schroeter, *Chem. Ber.*, **58**, 713 (1925).
(16) S. Julia, M. Julia, and B. Bemont, *Bull. Soc. Chim. Fr.*, 1449 (1959).
(17) J. F. J. Dippy and J. T. Young, *J. Chem. Soc.*, 3919 (1955).
(18) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

with ether and the extract was washed with water and dried. Removal of ether gave 5.7 g of a yellow oil. Preparative glc on 15% QF-1 (0.375 in. × 50 ft column) gave the desired product, which was further purified by chromatography on neutral alumina with benzene. Removal of solvent gave a solid, mp 96.5–97° (lit.[8] mp 95–96°).

6- and 7-Nitro-4,4-dimethylbenzo[*a*]cyclopropa[*c*]cycloheptene (6′ and 7).—To a solution of 24 ml of acetic anhydride and 8 ml of fuming nitric acid at −40° was added dropwise 5.75 g (0.025 mol) of **6** at a rate such that the temperature did not rise above −20°. The reaction mixture was then allowed to come to room temperature and poured into hot water, the product was extracted with ether, washed with 5% sodium bicarbonate, and dried over magnesium sulfate, and the ether was removed under vacuum. The residue was chromatographed on a silica gel column (60–200 mesh, JTB) (4 × 50 cm) and eluted with a mixture of petroleum ether and ether (80:20) to afford 4 g of pale yellow oil. It was dissolved in petroleum ether and cooled to afford 2 g of pale yellow crystals, mp 66–68°. Recrystallization from petroleum ether gave a product: mp 69.5–71° (**6′**); ir 1345 and 1520 cm^{-1} (NO_2); nmr δ 1.47 (s, 3 H, CH_3), 1.62 (s, 3 H, CH_3), 0.2–2.4 (m, 8 H, aliphatic), 7.6 (d, 1 H, aromatic) and 8.0–8.2 (m, 2 H, aromatic).

Anal. Calcd for $C_{14}H_{17}NO_2$ (**6′**) C, 72.70; H, 7.41; N, 6.06. Found: C, 72.68; H, 7.25; N, 6.32.

The mother liquor was stripped of solvent and rechromatographed on a silica gel column (4 × 50 cm) using hexane to give a pale yellow liquid: $n^{25}D$ 1.5526 (**7**); ir 1515 and 1340 cm^{-1} (NO_2); nmr δ 0.2–2.5 (m, 8 H, aliphatic), 1.41 and 1.60 (s, 3 H, CH_3), 7.9–8.2 (m, 2 H, aromatic), 7.5 (d, 1 H, aromatic).

Anal. Calcd for $C_{14}H_{17}NO_2$ (**7**): C, 72.70; H, 7.41; N, 6.06. Found: C, 72.71; H, 7.37; N, 6.02.

4-Nitro-α-α-dimethylhomophthalic Anhydride (8). A. Authentic.—Potassium nitrate (3.4 g) in 10 ml of concentrated sulfuric acid was added slowly to a solution of 4 g of 3,3-dimethylindanone in 20 ml of concentrated sulfuric acid previously cooled to 0°. The reaction mixture was maintained at 0° for 1 hr and then poured over ice and allowed to stand for 15 min and filtered to give a product, mp 132–133° (lit.[19] mp 131–133°). The nitro ketone (1 g) and 4 g of potassium dichromate were suspended in 20 ml of water and 7 ml of concentrated sulfuric acid was added. After the mixture had cooled to room temperature had been refluxed for 30 min, it was poured over ice and an off-white solid was collected. Crystallization from petroleum ether gave a product, mp 161–163°, ir 1790 and 1750 cm^{-1} (anhydride).

Anal. Calcd for $C_{11}H_9NO_5$: C, 56.18; H, 3.86; N, 5.96. Found: C, 56.37; H, 4.10; N, 5.91.

B. Oxidation of 7.—A solution of 100 mg of **7** and 0.6 g of chromic acid was refluxed for 1 hr, poured into 50 ml of water, and extracted with ether. Removal of solvent afforded a crystalline product, mp 161–162°. Crystallization from acetone gave an off-white crystalline product, mp 162–163°, identical with that described above.

5-Nitro-α,α-dimethylhomophthalic Anhydride (9).—A solution of 200 mg of **6′** and 1 g of chromic acid in 10 ml of acetic acid was refluxed for 1 hr, diluted with 100 ml of water, and extracted with ether. Solvent removal followed by crystallization from petroleum ether afforded off-white crystals, mp 199–200°, ir 1735 and 1750 cm^{-1} (anhydride).

Anal. Calcd: C, 56.18; H, 3.86; N, 5.96. Found: C, 56.40; H, 3.70; N, 5.83.

Registry No.—**1**, 310-53-2; **1′**, 25178-99-8; **2**, 15677-15-3; **2′**, 25178-97-6; **3**, 25033-22-1; **3′**, 25178-98-7; **4**, 25033-23-2; **4′**, 25033-28-7; **6**, 34603-14-0; **6′**, 32113-65-8; **7**, 34603-16-2; **8**, 34603-17-3; **9**, 34603-18-4; PhC_3H_5, 873-49-4; 5,5-dimethyl-6,7-dihydro-5*H*-benzocycloheptene, 34603-19-5; 1,1-dibromo-4,4-dimethylbenzo[*a*]cyclopropa[*c*]cycloheptene, 34603-20-8.

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Light-Sensitive Glycosides. I. 6-Nitroveratryl β-D-Glucopyranoside and 2-Nitrobenzyl β-D-Glucopyranoside

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Two light-sensitive glucosides, namely, 6-nitroveratryl and 2-nitrobenzyl β-D-glucopyranoside, were prepared and characterized. The two glucosides were more stable to acid hydrolysis, than benzyl β-D-glucopyranoside. They could be photolyzed, however, to give a high yield of D-glucose under conditions that leave the benzyl glucoside intact.

The utilization of light-sensitive blocking groups has great promise in synthetic carbohydrate chemistry and in synthetic chemistry in general. Ideally, such groups should be stable to a wide variety of chemical treatments, on one hand, and at the same time be sensitive to irradiation under conditions that leave other functional groups in the molecule unaffected.

Early studies utilizing photochemical cleavage of blocking groups include the work of Tănăsescu[1] and Heidt.[2] In a series of papers the former investigator used sunlight and long periods of irradiation to remove 2-nitrobenzylidene groupings. The reactions were limited by the fact that (a) not all the 2-nitrobenzylidene groups were affected and (b) di-2-nitrobenzylidene derivatives of different saccharides, namely glucose, mannose, and galactose, were claimed to yield the same galacto derivative following irradiation. The photolysis of different phenyl, benzyl, and phenylethyl glycosides upon irradiation at 254 nm was studied by Heidt.[2] The reported yields, however, were low.

We believe that many of the limitations inherent to the findings of Tănăsescu and Heidt can be overcome by the application of modern irradiation, analytical, and spectroscopic techniques. With the advent of such methods as nmr and ORD the reinvestigation of the stereochemistry of such reactions is especially worthwhile. The results of such a study should place these early contributions in their proper perspective.

Recently, the use of 2-nitrobenzyl derivatives as photosensitive blocking reagents for amino and carboxyl functions in amino acids and peptides has been described.[3–5] In these examples the blocking groups

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