Compound **1** failed to crystallize and elemental analysis was obtained on its solid epimer **5** which was obtained by dry column chromatography of **1** on Merck acid-washed alumina (activity II[2]) and carbon tetrachloride or by isomerization of **1** under basic conditions (0.37 equiv KOH) in a 12:1 methanol-water solution. Neutralization of the basic solution with aqueous ammonium chloride solution yielded a mixture of **5** and **1** in a ratio of 7:3 (vpc on QF-1) from which **5** crystallized out in methanol. The isomerization was repeated on the residue.

Compound **2** gave colorless crystals from 2-propanol: mp 95.5-97°; ir (KBr) 1372 and 1540 (NO_2). Compound **3** gave colorless crystals from methanol: mp 91.8-92.2°; ir (KBr) 1378 and 1537 (NO_2). Compound **5** gave colorless crystals from methanol: mp 103.5-104°; ir (KBr) 1355 and 1520 (NO_2).

Anal. Calcd for $C_{16}H_{19}NO_2$: 74.68; H, 7.44; N, 5.44. Found for **2**: C, 74.42; H, 7.63; N, 5.27. Found for **3**: C, 74.29, H, 7.48; N, 5.37. Found for **5**: C, 74.47; H, 7.39; N, 5.21.

Registry No.—**1**, 28638-60-0; **2**, 28638-61-1; **3**, 28638-62-2; **5**, 28638-63-3; 1-vinylcyclopentene, 28638-58-6; *trans*-*o*-methyl-β-nitrostyrene, 28638-59-7.

Unique Formation of a Benzocyclobutene Derivative. The Diazotization of 3-Amino-4-*tert*-butyl-5-nitrobenzoic Acid[1]

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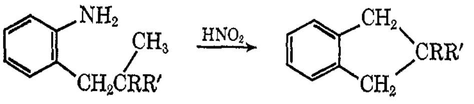
Received July 22, 1970

We have observed an unusual ring closure reaction leading to the formation of 1,1-dimethyl-4-carboxyl-6-nitrobenzocyclobutene (**4a**, the major isolated product, 41% crude yield) during the decomposition of the diazonium salt from 3-amino-4-*tert*-butyl-5-nitrobenzoic acid (**3a**). The methyl ester **3b** gave comparable results. This benzocyclobutene derivative was formed in approximately the same yield when the dilute sulfuric acid solution of the diazonium salt was heated (65°), was photolyzed (0°) with ultraviolet light, or was heated (65°) with copper bronze. However, treatment with cuprous bromide in hydrobromic acid gave the normal bromo derivative (47% yield with 44% recovered starting amine); no benzocyclobutene was observed under these conditions. The 1,1-dimethyl-4-carboxyl-6-nitrobenzoic acid was reduced to the corresponding amine which underwent normal diazotization and decomposition of the diazonium compound to give the corresponding phenol.

A recent report by Martinson[2] concerning a reaction leading to the closure of a five-membered ring to give indans (**2**) during deamination of certain *o*-alkylanilines (**1**) has prompted us to publish the following observation encountered during an attempt to synthesize 3-hydroxy-4-*tert*-butyl-5-nitrobenzoic acid.

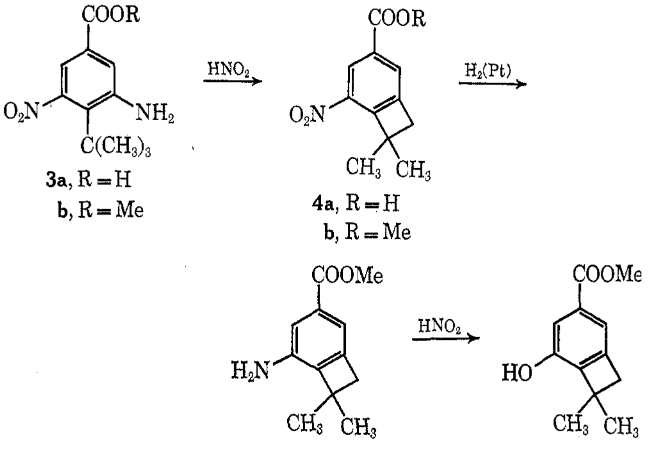
Martinson found indan (**2**, R, R′ = H; 13%), 2-methylindan (**2**, R = H; R′ = Me; 35%), and 2,2-dimethylindan (**2**, R, R′ = Me; 88%) to be formed along with the expected phenol from the diazotization of *o*-propyl-, *o*-isobutyl-, and *o*-neopentylanilines, respectively.



1 **2**

We have found that deamination of the *o*-*tert*-butylaniline derivative **3a** failed to give any appreciable amount of the expected 3-hydroxy-4-*tert*-butyl-5-nitrobenzoic acid; instead, the major product was identified as 1,1-dimethyl-4-carboxy-6-nitrobenzocyclobutene **4a** (41% crude yield, 27% purified yield, isolated as its methyl ester) by its analysis and spectral properties. The deamination of the methyl ester **3b** followed a parallel course. The diazotization was carried out with sodium nitrite in sulfuric acid (nitrosoylsulfuric acid). The decomposition was either done by heating to 65°, by heating to 65° in the presence of copper bronze, or by irradiating at 0° with ultraviolet light (2537 Å, quartz vessel) with no significant change in the yield of the benzocyclobutene **4a**.

The benzocyclobutene structure of this product is derived from the following evidence. The acid **4a** no



3a, R = H
b, R = Me

4a, R = H
b, R = Me

5 **6**

longer shows an nmr signal for a *tert*-butyl group but instead has a singlet δ 1.58 (6 H) assigned to the *gem*-dimethyl protons of the cyclobutene ring. No previous examples of *gem*-dimethylbenzocyclobutenes have been published for comparison, but there is no reason to suppose that the chemical shift for such a signal would differ widely from that of a normal *tert*-butylbenzene derivative; *i.e.*, *p*-*tert*-butyltoluene, δ 1.32; *o*-*tert*-butylnitrobenzene, δ 1.40; 3-amino-4-*tert*-butyl-5-nitrobenzoic acid, δ 1.50; and *o*-*tert*-butylphenol,[3] δ 1.37. The singlet at δ 3.11 (2 H) is assigned to the methylene protons of the cyclobutene ring. This chemical shift is in accord with that reported for the methylene protons of benzocyclobutene itself (δ 3.14)[4a] and compatible with that reported for 1,1-dichloro-3,4,5,6-tetramethylbenzocyclobutene (δ 3.8).[4b] The spectrum shows two signals centered at δ 8.10 (1 H) and 8.70 (1 H) assigned

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[1] We gratefully acknowledge support by the National Institutes of Health (NIH RO1GM 16031-09).

[2] P. Martinson, *Acta Chem. Scand.*, **22**, 1357 (1968).

[3] K. C. Dewhirst and C. A. Reilly, *J. Org. Chem.*, **30**, 2870 (1965).

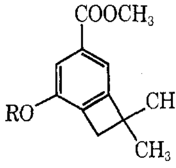
[4] (a) F. A. Bovey, "NMR Data Tables for Organic Compounds," Vol. I, Interscience, N. Y., 1967, p 203; (b) H. Hart and R. W. Fish, *J. Amer. Chem. Soc.*, **82**, 749 (1960).

to the meta aromatic protons at C-3 and C-5, respectively, and a singlet at δ 11.57 (1 H) assigned to the carboxylic acid proton.

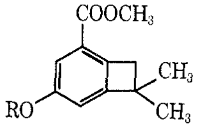
The acid **4a** is readily converted to the methyl ester **4b**, whose ir, uv, mass, and nmr spectra are completely compatible with this structure. The nmr signals for the two aromatic protons centered at δ 8.02 and 8.59 clearly show a spin–spin coupling constant of 1 Hz which is in the characteristic range for meta hydrogens.

Catalytic reduction of the nitro group of the methyl ester **4b** gave the corresponding amine **5** whose diazonium salt decomposed at 0° to yield 1,1-dimethyl-4-carbomethoxy-6-hydroxybenzocyclobutene (**6**) whose structure follows from its analysis, method of synthesis, spectral properties, and reactions characteristic of hindered phenols.

This phenol gives a negative ferric chloride test and is insoluble in sodium carbonate but does dissolve in cold 10% sodium hydroxide solution from which it can be regenerated unchanged by neutralization, as expected for a hindered phenol.[5] The evidence that this phenol has structure **6** rather than an isomeric structure such as **7a** or **7b** (R = H) rests on these "cryptophenol" properties. The relatively unhindered phenols represented by **7a** and **7b** should give a positive ferric chloride test. We therefore conclude that phenol **6** has the unrearranged structure shown and that the structure of the nitro compound is as shown in **4** and not that of an isomeric product.



7a

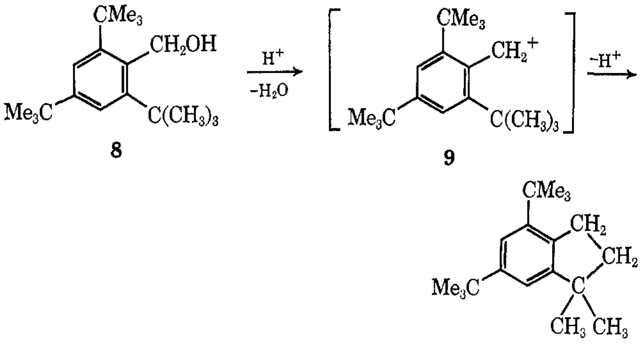


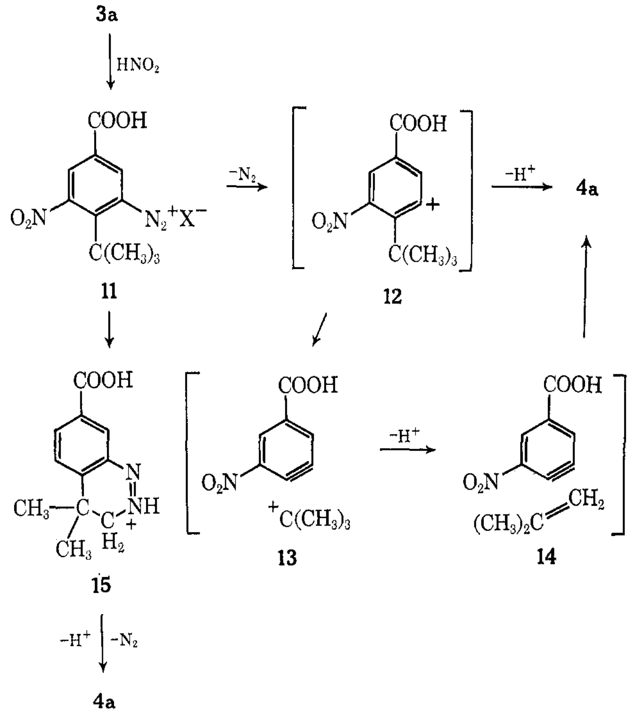
7b

The phenol **6** was converted to the methyl ether by treatment with sodium hydride and dimethyl sulfate. A degassed vacuum-sealed nmr sample showed no enhancement of the methyl ether signal when the *gem*-dimethyl signal was irradiated (negative nuclear Overhauser effect); however irradiation of the aromatic proton signal caused the methylene signals (which were a close triplet, δ 2.78, 2 H, J = 0.8 Hz) to collapse to a singlet.[6] The only reasonable explanation for this decoupling result is that the methylene protons are situated as shown in **6** and experience a long-range coupling to the neighboring aromatic proton. This also rules out the isomeric structures **7a** and **7b**.

We have not made a mechanistic study of this unusual ring closure reaction but a few comments concerning the course of the reaction seem warranted. The diazotization of **3a** in hydrobromic acid followed by warming with cuprous bromide is reported to give the corresponding bromide in the expected manner;[7] we have confirmed this. Therefore the unique benzocyclobutene formation must be associated with the conditions used in the attempted phenol formation. Furthermore, the normal conversion of methyl 3-amino-4-*tert*-butylbenzoate to its phenol has been reported.[8] Thus our results must be associated in some way with the buttressing effect of the 5-nitro group of **3**.

Our results may be accommodated by postulating an intramolecular electrophilic substitution by the carbon of an aromatic cation on the C–H of the side chain (either "front lobe" or "back lobe" attack of the sp^3 orbital) analogous to that discussed by Martinson[2] in the indan cases **1** → **2** or by Barclay and McDonald[9] in the example **8** → **9** → **10** involving a benzylic cation instead of an aromatic cation. This is repeated in the benzocyclobutene case by **12** → **4a**. Alternatively, a benzyne intermediate can be postulated[10] for the present example as shown in sequence **11** → **12** → **13** → **14** in which the benzyne reacts within the solvent cage with isobutylene to give the product **4a**. The 2 + 2 addition of benzynes is well established.[4a,9] Such a process specifically has been proposed for the decomposition of *o*-*tert*-butyl-*N*-nitrosoacetanilide[11,11a] in the pres-





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(5) G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Amer. Chem. Soc.*, **67**, 303 (1945). *o*-*tert*-Butylphenol gives a negative ferric chloride test but *o*-isopropylphenol gives a positive test.

(6) We are most grateful to Dr. Lois Durham and Dr. M. Bramwell for conducting the NOE study and the decoupling experiments.

(7) F. Bell, *J. Chem. Soc.*, 120 (1958).

(8) M. S. Leslie and U. J. H. Mayer, *ibid.*, 611 (1961).

(9) L. R. C. Barclay and M. C. MacDonald, *Tetrahedron Lett.*, 881 (1968).

(10) R. W. Hoffmann, "Dehydrobenzenes and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 200.

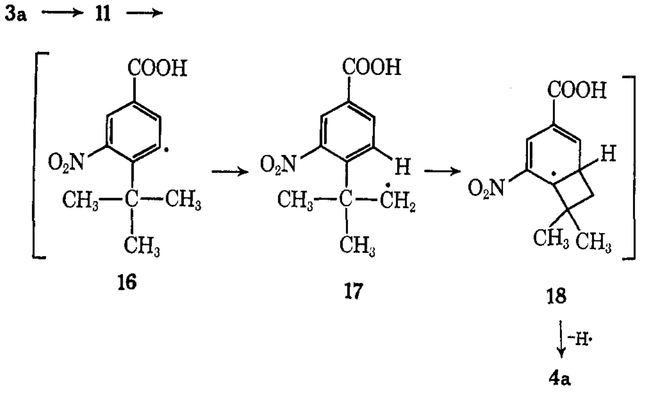
(11) R. W. Franck and K. Yanagi, *J. Amer. Chem. Soc.*, **90**, 5814 (1968).

(11a) NOTE ADDED IN PROOF.—J. Cadogan, *et al.* [*Chem. Commun.*, 1 (1971)], have found that *in situ* diazotization under anhydrous conditions favors benzyne formation.

ence of furan to give a Diels–Alder type adduct. If such a benzyne were involved, however, it seems very likely that we would have seen some of the isomeric product **7a** resulting from what would appear to be the energetically more favorable mode of addition.

An insertion of the terminal electron-deficient nitrogen of the diazonium salt **11** into a C–H bond of the methyl group, in a manner analogous to a case reported by Lansburg, *et al.*,[12] could be postulated to give an intermediate **15** which might then decompose by losing a proton and extruding nitrogen to give the observed benzocyclobutene **4a**.

Free-radical formation and subsequent intramolecular hydrogen transfer in a manner not unrelated to the Gomberg biaryl synthesis or the Pschorr ring closure is still another possibility. In this scheme the radical **16** abstracts a hydrogen internally because of the proximity of the *tert*-butyl group to give **17** which ring closes to give **18**, which in turn transfers a hydrogen atom to the solvent to give the observed product **4a**. The fact that the yield of **4a** from **3a** was not enhanced appreciably either by heating the diazonium salt in the presence of copper bronze or by irradiating with uv light, conditions which favor radical decomposition,[13] could be interpreted as evidence against a radical process. We also failed to observe benzocyclobutene formation when the reaction was conducted under the basic conditions of the Gomberg biaryl synthesis. Without more evidence it is futile to speculate further concerning these and other interesting alternatives.



3a → **11** →

16 **17** **18**

4a

Experimental Section

The infrared spectra were recorded on a Perkin-Elmer 421 spectrometer and the ultraviolet spectra on a Cary Model 14 spectrophotometer. The nuclear magnetic resonance spectra were taken in $CDCl_3$ on either a Varian A-60 instrument or HR-100 for decoupling experiments; chemical shifts were reported in δ, parts per million (ppm), downfield from tetramethylsilane as an internal standard. Melting points were in capillary, uncorrected.

3,5-Dinitro-5-*tert*-butylbenzoic Acid.—This was made by nitration of *p*-*tert*-butylbenzoic acid,[14] 53% yield.

3-Amino-4-*tert*-butyl-5-nitrobenzoic Acid (3a).—This compound was prepared in 60% yield from 4-*tert*-butyl-3,5-dinitrobenzoic acid according to the procedure of Bell,[7] mp 227–228° (lit. mp 230°).

The methyl ester hydrochloride was made by saturating a methanolic solution of the acid with dry hydrogen chloride, mp 171–172° dec. The free methyl ester, generated from the hydrochloride, was converted to the *N*-acetyl derivative, mp 184–185°, by allowing it to stand at room temperature with acetic anhydride for 18 hr.

Diazotization of 3-Amino-4-*tert*-butyl-5-nitrobenzoic Acid.—A cooled solution of 3-amino-4-*tert*-butyl-5-nitrobenzoic acid (2.38 g) in glacial acetic acid (5 ml) was added dropwise to a solution of sodium nitrite (0.70 g) in concentrated sulfuric acid (6 ml) at 0°. After the mixture was stirred for 15 min, it was poured onto ice, and the resulting mixture was stirred for 15 min. Unreacted starting material (0.70 g) was removed by filtration, and the filtrate was heated at 65° for 10 min, at which time nitrogen evolution had ceased. The mixture was cooled, and a brown precipitate was removed by filtration, washed with water, and dried to yield 0.65 g of crude 1,1-dimethyl-4-carboxy-6-nitrobenzocyclobutene (**4a**). This crude acid was converted to its methyl ester in methanol saturated with dry hydrogen chloride. Recrystallization of the ester from methanol–water yielded 0.36 g of **4b**: mp 138–139°; uv λ_{max} (C_2H_5OH) 227 nm (ϵ 21,200), 264 (6150), and 305 (2100); ir (KBr) 1724 (aryl ester C=O), 1611 (aryl), 1525, and 1333 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 1.58 (s, 6 H, $C(CH_3)_2$), 3.11 (s, 2 H, CH_2), 3.96 (s, 3 H, CO_2CH_3), 8.02 (d, 1 aromatic H, $J = 1$ Hz), 8.59 ppm (d, 1 aromatic H, $J = 1$ Hz); mol wt 234 (osmometer, $CHCl_3$), 235 (mass spectrometer). Chromatography of the mother liquors on silica by eluting with chloroform yielded an additional 0.10 g of **4b** (27% total yield allowing for recovered starting material).

Anal. Calcd for $C_{12}H_{13}O_4N$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.00; H, 5.22; N, 5.93.

Crude acid from another run was purified by repeated recrystallization from ethanol–water to yield 0.20 g of **4a**: mp 184–185°; uv λ_{max} (C_2H_5OH) 222 nm (ϵ 16,100), 269 (5950), and 311 (2100); ir (KBr) 3100–2500 (carboxyl OH), 1685 (aryl carboxyl C=O), 1609 (aryl), 1526, and 1334 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 1.73 (s, 6 H, $C(CH_3)_2$), 3.14 (s, $2CH_2$), 8.10 (s, 1 H, aromatic H), 8.70 (s, 1 H, aromatic H), 11.57 ppm (s, 1 H, CO_2H).

Anal. Calcd for $C_{11}H_{11}O_4N$: C, 59.72; H, 5.01; N, 6.33. Found: C, 59.53; H, 4.96; N, 6.25.

Bell[13] reported the preparation of 3-bromo-4-*tert*-butyl-5-nitrobenzoic acid by diazotization and treatment with cuprous bromide and hydrobromic acid. We have repeated this and found a 47% yield of the bromide, 44% recovery of the starting material, and no benzocyclobutene present in the crude product.

1,1-Dimethyl-4-carbomethoxy-6-hydroxybenzocyclobutene (6).—Hydrogenation of the nitro group of **4b** (100 mg) was effected at atmospheric pressure in methanol (10 ml) with platinum catalyst for 16 hr. After removing the catalyst by filtration, the solvent was evaporated to give a light yellow, crude oil of 1,1-dimethyl-4-carbomethoxy-6-aminobenzocyclobutene, which could not be induced to crystallize: ir (neat) 3400 (NH_2), 1710 cm^{-1} (aromatic ester C=O); nmr ($CTCl_3$) δ 1.46 (s, 6 H, $C(CH_3)_2$), 2.88 (s, 2 H, benzocyclobutene CH_2), 3.85 (s, 3 H, CO_2CH_3), 7.22 ppm (s, 2 H, aromatic H).

The crude amine (100 mg) was dissolved in a mixture of concentrated hydrochloric acid (1 ml) and water (1 ml), and the solution was cooled in an ice–salt mixture. To this mixture was added a solution of sodium nitrite (30 mg) in water (1 ml) cooled to 0°. A yellow oily precipitate was formed immediately, and after 30 min the reaction mixture gave a negative diazonium test with alkaline β-naphthol. The mixture was extracted with ether, and the ether extracts were washed ($NaHCO_3$ solution, H_2O), dried ($MgSO_4$), and evaporated to give a light yellow solid which was crystallized from low-boiling petroleum ether (bp 30–60°), 35 mg, mp 125–127°. After several recrystallizations from petroleum ether, the melting point of **6** was raised to 135–136°: ir (Nujol) 3420 (OH), 1710 cm^{-1} (aryl ester C=O); nmr ($CDCl_3$) δ 1.50 (s, 6 H, $C(CH_3)_2$), 2.92 (s, 2 H, methylene CH_2), 3.91 (s, 3 H, CO_2CH_3), 7.36 (s, 1, aromatic H), 7.53 ppm (s, 1, aromatic H).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.99; H, 6.91.

This product gave a negative test with ethanolic ferric chloride, indicating a strongly hindered phenol.

1,1-Dimethyl-6-methoxy-4-carbomethoxybenzocyclobutene.—A solution of the phenol **6** (185 mg) in dimethoxyethane (10 ml) was treated with a dispersion of sodium hydride (50 mg) and dimethyl sulfate (0.5 ml) at room temperature for 24 hr. The reaction mixture was filtered, diluted with ether, and treated with water, and the ether layer dried to give 190 mg of a colorless oil which was purified by glc (QF-1 fluorosilicone, 0.25 in. ×

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[12] P. T. Lansburg, J. G. Colson, and N. R. Mancuss, *J. Amer. Chem. Soc.*, **86**, 5225 (1964).

[13] H. Zollinger, "Azo and Diazo Chemistry of Aliphatic and Aromatic Compounds," Interscience, New York, N. Y., 1961, pp 161, 170.

[14] M. S. Carpenter and W. M. Easter, *J. Org. Chem.*, **19**, 87 (1954).

10 ft, 185°) to give 118 mg of the methyl ether **7a** ($R = CH_3$): mp 51-53°; nmr ($CDCl_3$) δ 1.46 (s, 6 H), 2.78 (t, 2 H, J = 0.8 Hz), 3.81 (s, 3 H), 3.87 (s, 3 H), 7.38 ppm (s, broad, 2 H).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.90; H, 7.32. Found: C, 70.99; H, 7.33.

The decoupling experiments are described in the text.

Decomposition of the Diazonium Salt 11 in the Presence of Copper Bronze.—The amino acid **3a** (2.38 g) was dissolved in glacial acetic acid (15 ml), and the solution was cooled in an ice-salt bath until it solidified. The solid was added in portions to a solution of sodium nitrite (0.70 g) in concentrated sulfuric acid (6 ml) and cooled in an ice-salt bath. Lumps which formed in the mixture were crushed. After the mixture was stirred for 15 min, it was poured onto ice. After stirring for 15 min, unreacted starting material (0.56 g) was removed by filtration. The filtrate, still at 0°, was divided into two equal portions which were treated with copper bronze under different conditions.

To one portion was added copper bronze (0.3 g) and the mixture was heated at 65° on the steam bath for 10 min whereupon it showed a negative diazonium test with β-naphthol. The mixture was cooled to 0° and the solids were removed by filtration. Washing these solids with dry methanol removed the organic material, and the methanol solution was treated with dry hydrogen chloride and allowed to stand for 16 hr. Ether was added, and this solution was washed with sodium bicarbonate solution and dried. Removal of the solvent left 0.38 g of crude methyl ester which was purified by chromatography on silica using chloroform as the eluent to yield 0.18 g of benzocyclobutene **2b** (20% yield considering recovered starting material), mp 135-136°. The second half of the original diazonium compound gave an 18% yield of **4b** when the decomposition in the presence of copper bronze was done for 16 hr at 20°.

Decomposition of the Diazonium Salt 11 in the Presence of Ultraviolet Light.—A filtered solution of the diazonium salt was prepared as in the preceeding section from the amino acid **3a** (1.19 g). The filtrate was cooled to 0° in a quartz vessel and stirred while it was irradiated for 6 hr with ultraviolet light from a Nester-Faust source (2537 Å). A white precipitate was removed by filtration and treated with methanol and dry hydrogen chloride to yield 0.22 g of crude methyl ester. Chromatography of this product on silica gel gave 95 mg of the benzocyclobutene **4b** (12%). The above aqueous filtrate was heated at 65° for 10 min, and 67 mg of a precipitate was removed and converted with the crude methyl ester **4b**. Chromatography on silica gel gave an additional 45 mg of **4b** for a total yield of 18%, mp 135-136°. The infrared spectra of each of the samples of this methyl ester obtained in the four runs were identical.

Registry No.—3a, 28538-59-2; **4a,** 28538-60-5; **4b,** 28538-61-6; **5,** 28538-62-7; **6,** 28538-63-8; **7a,** 28538-64-9.

Halogenated Ketenes. XVIII. The Stereochemistry of Some Unsymmetrical Arylketene Cycloadditions[1,2]

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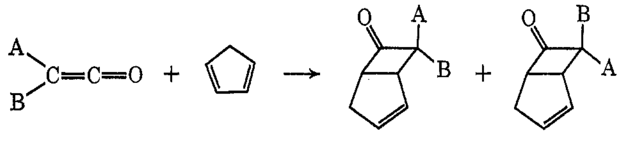
Received June 3, 1970

The (2 + 2) cycloadducts of cyclopentadiene and phenylchloro-, phenylbromo-, phenylmethyl-, phenylethyl-, phenoxymethyl-, and phenoxyketenes were prepared in good yield. The cycloadditions were stereoselective to produce only the *endo*-phenyl or *endo*-phenoxy isomer of the cycloadduct with the exception of phenoxymethylketene which yielded only the *endo*-methyl isomer of the cycloadduct. The cycloadducts of phenylmethylketene and ethyl vinyl ether, dihydropyran, cyclohexene, and cyclooctene were also prepared. Two cycloadduct isomers were formed with each of these olefins with only a small predominance of the *endo*- or *cis*-phenyl isomer. These results are interpreted to suggest that cyclopentadiene may be novel as a cycloaddition partner in ketene cycloadditions when a large difference exists between the size of the ketene substituents.

The $({}_{\pi}2_s + {}_{\pi}2_a)$ cycloaddition of ketenes and olefins is allowed to be a thermally concerted process whereby the ketene participates in an antarafacial role.[4] When the cycloaddition is effected with unequally substituted ketenes with unsymmetrical olefins, such as cyclopentadiene, the (2 + 2) cycloadduct may be a mixture of geometrical isomers. Recently, the stereochemistry of the cycloaddition of some unequally substituted ketenes with cyclopentadiene has been described and revealed a most gratifying correlation with this principle of the conservation of orbital symmetry.[5-8] The results indicate a strong preference for endo specificity for the larger ketene substituent; *i.e.*, the isomer with the larger ketene substituent in the endo position has been found to be very strongly sterically preferred. In fact, this isomer has even been formed to the exclusion of the exo isomer when a large difference in size exists between the two ketene substituents.



We now wish to describe the stereochemistry of the cycloaddition of some unsymmetrical arylketenes with cyclopentadiene and also the stereochemistry of the cycloaddition of phenylmethylketene with a variety of olefinic compounds. A preliminary report of this work has appeared.[9]

Results

Phenylchloro- and phenylbromoketenes were prepared by the dehydrochlorination of α-chloro- and α-bromophenylacetyl chlorides at room temperature. The ketenes could not be isolated but could be trapped by heating the dehydrohalogenation mixtures with cyclopentadiene to produce the (2 + 2) cycloadducts in good yield. The best yields of cycloadducts are obtained by conducting the dehydrochlorinations at room temperature and then refluxing the reaction mixtures to

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[1] Paper XVII: W. T. Brady and L. Smith, *Tetrahedron Lett.*, 2963 (1970).

[2] Abstracted in part from the Ph.D. thesis of F. H. P., North Texas State University, May 1970.

[3] NDEA, Title IV Fellow.

[4] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

[5] W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, **92**, 4618 (1970).

[6] T. DoMinh and O. P. Strausz, *ibid.*, **92**, 1766 (1970).

[7] M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chem. Acta*, **53**, 417 (1970).

[8] W. T. Brady, E. F. Hoff, R. Roe, Jr., and F. H. Parry, III, *J. Amer. Chem. Soc.*, **91**, 5679 (1969).

[9] W. T. Brady, F. H. Parry, III, R. Roe, Jr., and E. F. Hoff, *Tetrahedron Lett.*, 819 (1970).