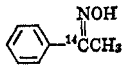
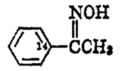
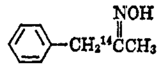
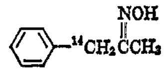
TABLE I

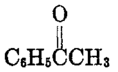
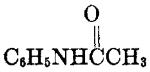
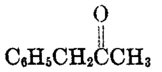
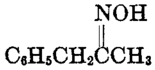
PERCENT REACTION AND RATIO OF MOLAR RADIOACTIVITIES OF RESIDUAL OXIME

Ketoxime	Temp, °C	Time, min	% reaction[a]	Ratio of molar radioactivities[b]
	26 ± 1	40	28	1.000
		100	48	1.030
		325	84	1.050
		420	91	1.067
	62 ± 1	60	36	1.034
		170	64	1.032
		255	76	1.050
		385	88	1.067
	50 ± 1	2	7	0.9959
		31	32	0.9937
		61	47	0.9967
		91	56	0.9995
	50 ± 1	2	7	1.000
		26	29	1.006
		56	44	1.001
		86	54	1.002
		163	72	1.004

[a] Determined by isotope dilution of combined ketone and unreacted oxime. [b] Obtained by dividing the molar radioactivity of the residual ketoxime–ketone mixture by the molar radioactivity of the ketoxime before reaction.

TABLE II

CHEMICAL SHIFTS OF REACTANTS AND PRODUCTS[a]

Compd	Protons	Chemical shift[b,c] ppm
 $C_6H_5\overset{O}{\overset{\|}{C}}CH_3$	C_6H_5 CH_3	7.60 2.60
 $C_6H_5\overset{NOH}{\overset{\|}{C}}CH_3$	C_6H_5 CH_3	7.51 2.28
 $C_6H_5NH\overset{O}{\overset{\|}{C}}CH_3$	C_6H_5 CH_3	7.30 2.10
 $C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_3$	C_6H_5 CH_3 CH_2	7.25 3.58 2.01
 $C_6H_5CH_2\overset{NOH}{\overset{\|}{C}}CH_3$	C_6H_5 CH_2 CH_3	7.20 3.50 1.80
 $C_6H_5CH_2\overset{NOH}{\overset{\|}{C}}CH_3$	C_6H_5 CH_2 CH_3	7.20 3.75 1.76
 $C_6H_5CH_2NH\overset{O}{\overset{\|}{C}}CH_3$	C_6H_5 CH_2 CH_3	7.13 4.15 (doublet) 1.76

[a] All spectra were taken in chloroform with the Varian A-60 nmr spectrophotometer. [b] Chemical shift measured from TMS internal standard. [c] All methylene and methyl resonances were singlets except for the methylene doublet indicated.

61–62°, and immediately transferred to a constant-temperature bath at 62 ± 1°.

At various time intervals a 10-ml aliquot of the reaction mixture was pipetted into 10 ml of cold ethanol (95%) in a 125-ml erlenmeyer flask, and 50 ml of 0.1 *N* 2,4-dinitrophenylhydrazine reagent solution (prepared by adding 15 ml of concentrated sulfuric acid, 15 ml of water, and 250 ml of ethanol to 5.0 g of 2,4-dinitrophenylhydrazine) was added. The mixture was heated on a steam bath for 30 min and was cooled to 0°; the precipitate was collected on a sintered-glass funnel. The 2,4-dinitrophenylhydrazone was washed with cold ethanol (95%) and was recrystallized to a constant melting point from chloroform–ethanol mixtures. Acetophenone oxime gives the derivative in quantitative yield; phenyl-2-propanone ketoxime gives the 2,4-dinitrophenylhydrazone in 96% yield. The use of 2,4-dinitrophenylhydrazones as derivatives was validated in other isotope effect studies.[1]

The 2,4-dinitrophenylhydrazones were burned in a Preg microcombustion apparatus similar to that described by Tolbert and Siri.[9] The labeled carbon dioxide was swept into an ionization chamber for measurement on an electrometer.

Reaction of Phenyl-2-propanone Oximes.—The procedure described for acetophenone oximes was followed except that the reaction was carried out at 50 ± 1° and the aliquots were pipetted into 10 ml of cold water instead of ethanol.

Determination of Percent Reaction.—Nonradioactive oximes were subjected to the reaction conditions described above, and the aliquots were pipetted into cold ethanol or water that contained a weighed amount of labeled oxime. After the determination of the radioactivity, the percent reaction was calculated by the isotope-dilution method.

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[9] B. M. Tolbert and W. E. Siri, "Technique of Organic Chemistry," Vol. I, Part IV, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 3431, 3432.

Cycloaddition of 6,6-Dimethylfulvene with Benzynes[1]

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Received November 24, 1965

Because of interest in the homobenzylic behavior observed at the 7-position of benzonorbornene derivatives,[2] a good synthetic method for these derivatives has been required by us. This report describes the cycloaddition of benzynes to 6,6-dimethylfulvenes (1) (Scheme I) by a modified Wittig's procedure[3,4] and some interesting properties of the derived cycloadducts, which have a new conjugated system.

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[1] Part XIII of a series on Bicyclic Systems. Part XII: H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **88**, 864 (1966).

[2] (a) H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964); (b) H. Tanida, H. Miyazaki, and H. Ishitobi, *Can. J. Chem.*, **44**, 98 (1966).

[3] G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

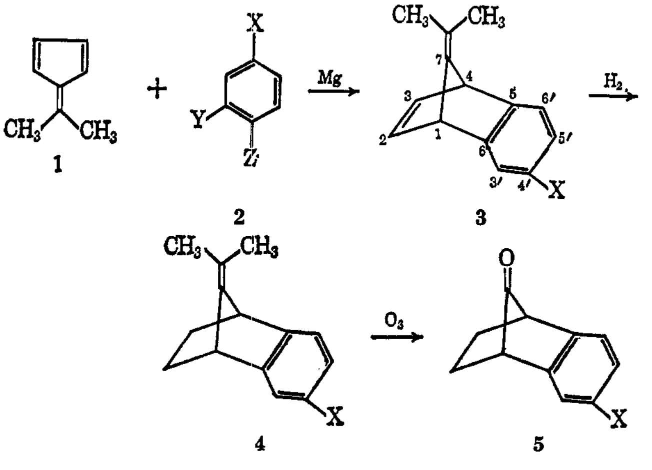
[4] H. Tanida, R. Muneyuki, and T. Tsuji, *Bull. Chem. Soc. Japan*, **37**, 40 (1964).

TABLE I

ULTRAVIOLET SPECTRA OF 4′-SUBSTITUTED 7-ISOPROPYLIDENEBENZONORBORNADIENES (3), 7-ISOPROPYLIDENEBENZONORBORNENES (4), AND RELATED COMPOUNDS IN *n*-HEPTANE

Compd	4′-Substituent	λ_{max}, mμ	$\epsilon \times 10^{-3}$
3a	H	280.5	2.62
		273.3	2.48
		267.0	1.69
		221.1 (sh)	23.9
		215.8	29.2
		209.3	26.0
		197.1	30.1
		181.5	32.8
3b	CH_3	285.7	3.04
		278.7	2.70
		277.0 (sh)	2.65
		271.5	2.00
		222.0 (sh)	27.1
		217.0	31.6
		210.6	28.2
		200.5	29.4
		185.7	28.8
3c	Cl	288.3	2.97
		280.0	2.89
		273.7	2.10
		265.7	1.70
		260.4	1.64
		251.1	1.72
		219.4	26.5
		201.2	32.9
		185.7	28.1
3d	F	284.9	3.36
		278.1	3.48
		247.5	0.95
		215.5 (sh)	20.2
		209.5	22.8
		198.0	30.3
		180.0	28.5
3e	OCH_3	293.7	3.28
		287.1	3.55
		262.9	2.34
		255.6	2.32
		210.5	28.4
		188.5	27.6
4a	H	274.1	2.36
		267.5	2.10
		261.5	1.37
		194.5	54.5
4b	CH_3	279.5	3.04
		274.0	2.58
		270.7	2.33
		265.6	1.69
		198.1	54.4
4c	Cl	281.3	2.67
		274.2	2.48
		268.7	1.75
		198.9	58.8
4d	F	278.2	3.34
		272.8	3.50
		269.3	3.06
		264.7 (sh)	2.39
		192.4	58.9
Benzobicyclo[2,2,2]-octadiene		270.3	0.430
		263.3	0.423
		256.7	0.301
		198.7	30.6
		185.0	42.2
Benzonorbornadiene		276.1	0.523
		268.7	0.603
		261.8	0.523
		231.7	1.18
		203.1	28.6
		185.8	34.2
Benzobicyclo[2,2,2]-octatriene (6)		276.6	0.769
		269.3	0.688
		262.7	0.498
		230.8 (sh)	1.20
		209.8 (sh)	26.2
		205.7	28.1
		190.8	19.9
		187.7	19.7

SCHEME I

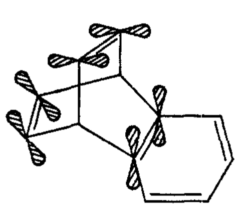


2a, X = H; Y = Br; Z = F
b, X = CH_3; Y = Br; Z = F
c, X = Cl; Y = Br; Z = F
d, X = F; Y = Br; Z = F
e, X = CH_3O; Y = I; Z = Br
3a, X = H
b, X = CH_3
c, X = Cl
d, X = F
e, X = CH_3O

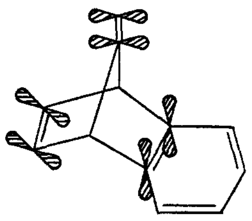
4a, X = H
b, X = CH_3
c, X = Cl
d, X = F
e, X = CH_3O
5a, X = H
b, X = CH_3
c, X = Cl
d, X = F
e, X = CH_3O

According to the same procedure described in a previous paper,[4] the reaction of *o*-bromofluorobenzene (**2a**) with **1** and magnesium in anhydrous tetrahydrofuran was carried out to give 7-isopropylidenebenzonorbornadiene (**3a**) in 31.4% yield. The nmr peaks of four aromatic protons centered at τ 3.0 (A_2B_2 multiplet), of two vinyl protons at τ 3.22 (triplet), of two bridgehead protons at τ 5.77 (triplet), and of six methyl protons at τ 8.48 (singlet) were entirely consistent with the presented structure. 4-Methylbenzyne, 4-chlorobenzyne, 4-fluorobenzyne, and 4-methoxybenzyne which were generated from 3-bromo-4-fluorotoluene (**2b**), 2-bromo-4-chlorofluorobenzene (**2c**), 2-bromo-1,4-difluorobenzene (**2d**), and 4-bromo-3-iodoanisole (**2e**), respectively, were also successfully employed for this cycloaddition, yielding 4′-substituted **3**. Catalytic hydrogenation of **3** led almost exclusively to reduction of the 2,3 double bond with uptake of 1 molar equiv of hydrogen to give 7-isopropylidenebenzonorbornenes (**4**) and then the ozonolyses of **4** gave benzonorbornene-7-ones (**5**) in satisfactory yields, which were identified with authentic samples prepared by the Oppenauer oxidation of the corresponding *anti*-7-benzonorbornenols.[2a] These transformations provide chemical confirmation for the structure of **3** and a convenient preparative method for **5**.

The chemistry of bicyclo[2.2.2]octatriene (barrelene) and its benzo analog, benzobicyclo[2.2.2]octatriene (**6**) has received considerable attentions.[5,6] The parent compound of **3**, 7-methylenebenzonorbornadiene (**7**), would be regarded as a valence-bond isomer of **6**. From this standpoint, a detailed account of the ultraviolet absorption maxima of **3** is listed in Table I, along with those of some related compounds. Of considerable interest is that red-shifted maxima and increased extinction coefficients were observed in **3** when compared with those in **6**, but a detailed research on this finding will be postponed until the parent compounds such as 7-methylenenorbornadiene and **7** are synthesized.



6



7

Experimental Section[7]

7-Isopropylidenebenzonorbornadiene (3a).—A solution of 87.5 g of *o*-bromofluorobenzene (**2a**) and 52.4 g of 6,6-dimethylfulvene (**1**) in 600 ml of anhydrous tetrahydrofuran was added dropwise onto 12.2 g of magnesium turning with vigorous stirring under nitrogen atmosphere. The dropping was adjusted at such a rate as to maintain a gentle reflux. After the addition, refluxing of the reaction mixture was further continued for about 30 min. The tetrahydrofuran was removed under reduced pressure and the residue was poured into water and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and evaporated. The residue obtained was solidified on cooling and filtered. Washing of the crystals with cold ethanol yielded 22 g of **3a**, mp 91–91.5°. Distillation of the unsolidified filtrate gave a fraction at bp 97–103° (4 mm), which on standing was solidified and recrystallized from ethanol to give 6.3 g of pure **3a**. The total yield was 31.4%. The infrared spectrum showed $\nu_{\max}^{\mathrm{CCl_4}}$ 680 (vs), 696 (m), 1011 (m), 1088 (m), 1221 (m), 1293 (m), 1298 (m), 1373 (m), 1448 (vs), 2851 (m), 2911 (s), 3007 (s), and 3071 (m) cm^{-1}.

Essentially the same procedure was applied for the preparation of **3b–3e**. Analyses and properties of **3** and **4** are summarized in Table II.

7-Isopropylidenebenzonorbornene (4a).—Catalytic reduction of **3a** was carried out over palladium on charcoal with the absorption of 1 mole of hydrogen under ice cooling. The usual work-up procedure gave crystals **4a**. The infrared spectrum showed $\nu_{\max}^{\mathrm{CCl_4}}$ 691 (vs), 837 (m), 1011 (m), 1112 (vs), 1154 (m), 1288 (m), 1373 (m), 1443 (vs), 1498 (s), 1466 (s), 2860 (s), 2920 (vs), 2980 (vs), and 3060 (m) cm^{-1}. Uptake of the second mole of hydrogen was much slower, so that the control of selective hydrogenation of the two double bonds in **3** was easy.

Ozone Oxidation of 4a.—Oxygen containing 23 mg l.$^{-1}$ of ozone was passed into a solution of 21.5 g of **4a** in 400 ml of dichloromethane under cooling in a salt–ice bath. The gas passed through the reaction vessel was bubbled into a 1% potassium iodide solution. The flow of oxygen was adjusted at such a rate that no color was observed in the potassium iodide solution. After about 6 hr, the test solution of potassium iodide began to show a faint yellow color. The oxygen was further introduced for 40 min into the reaction mixture. To remove the excess of ozone dissolved in the solution, nitrogen was introduced. In order to destroy the ozonide, acetic acid (60 ml) was slowly added to the solution with stirring, then 20 g of zinc powder and 2.0 ml of water was added portionwise and in an alternative manner, and the solution was allowed to stand at room temperature. Survival of the ozonide was examined with 1 drop of the above solution by an iodide–starch paper. The solution was extracted with ether, and the ether solution was washed with water and aqueous sodium bicarbonate, and dried. After removal of the solvent, the residue obtained was distilled to give 13.7 g (74%) of **5a** at bp 100–103° (7 mm). Its infrared spectrum in CCl_4 showed bands at 3006 (m), 2940 (m), 1806 (s), 1792 (vs), 1470 (m), 1134 (m), 1119 (m), and 885 (m) cm^{-1}.

TABLE II

ANALYSES AND PROPERTIES OF **3** AND **4**

Compd	Mp or bp (mm), °C, and n_D (temp, °C)	Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found
3a	91-91.5	$C_{14}H_{14}$	92.26	92.57	7.74	7.92
3b	108-110 (3) 1.5650 (25)	$C_{15}H_{16}$	91.78	92.07	8.22	8.31
3c	64.5–65	$C_{14}H_{13}Cl$	77.59	77.67	6.05	6.10
3d	70-71	$C_{14}H_{13}F$	83.69	83.89	6.54	6.30
3e	74.5–75.5	$C_{15}H_{16}O$	84.87	84.89	7.60	7.72
4a	90.5–91.5	$C_{14}H_{16}$	91.21	91.33	8.75	8.79
4b	120–122 (8) 1.5530 (24)	$C_{15}H_{14}$	90.85	91.07	9.15	9.36
4c	124–125 (6) 1.5694 (24)	$C_{14}H_{15}Cl$	76.87	76.65	6.91	6.88
4d	48–49	$C_{14}H_{15}F$	83.16	83.11	7.43	7.21

Identification of 5 was carried out by comparison of physical properties including infrared spectra with authentic samples (**5a**,[2a,8] **5b**,[2b] **5c**[2b] and **5e**[2b]) prepared by the Oppenauer oxidation of the corresponding *anti*-7-benzonorbornenols.[2a]

The new ketone **5d** had bp 95–97 (3 mm), $n^{24.5}{}_{D}$ 1.5404, and $\nu_{\max}^{\mathrm{CCl_4}}$ 3017 (m), 2982 (m), 2957 (m), 2887 (m), 1802 (sh) (s), 1790 (vs), 1622 (m), 1592 (m), 1482 (s), 1462 (m), 1278 (m), 1243 (m), 1226 (m), 1115 (m), 934 (m), 880 (m), and 870 (m) cm^{-1}.

Anal. Calcd for $C_{11}H_9FO$: C, 74.98; H, 5.15. Found: C, 75.17; H, 5.04.

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(5) H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960); H. E. Zimmerman and G. L. Grunwald, *ibid.*, **86**, 1434 (1964).

(6) R. G. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963).

(7) Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Ultraviolet spectra were determined with a Beckman DK-2A spectrophotometer. Infrared spectra were recorded on a Nippon Banko IR-S spectrometer in carbon tetrachloride. Nmr spectra were determined at 60 Mc with Varian A-60 spectrometer using tetramethylsilane as internal standard.

(8) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

Bicyclic Ketones by Intramolecular Alkylations. A Reinvestigation

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Treatment of the substituted ketones I–III with base can, in theory, give rise in each case to two products of intramolecular C-alkylation and I and II (Chart I) can also give a product of intramolecular O-alkylation. This last possibility is prohibited in III because the resulting enol ether would have a double bond at the bridgehead.[2]

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[1] (1) Correspondence should be addressed to the author: Ben May Laboratory for Cancer Research, University of Chicago, Chicago, Illinois 60637.

[2] (2) J. Bredt, *Ann.*, **437**, 1 (1924); *cf.* F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).