thereby demonstrating the absence of skeletal rearrangement. Preparative hydrolysis of VI in boiling 60% aqueous acetone for 0.5 hr gave an 84% yield of 1-bicyclo[3.3.1]nonanol, mp 180–182° (lit. mp 182.5–184°).[5] In 80% ethanol a mixture of this alcohol (60%) and, presumably, the corresponding ethyl ether (40%) was obtained.[5]

The rate constants for solvolysis of 1-bromobicyclo-[3.3.1]nonane (VI) in 80% ethanol follow: at 24.1°, $(3.04 \pm 0.04) \times 10^{-6}$ sec^{-1}; at 50.1°, $(9.26 \pm 0.08) \times 10^{-5}$ sec^{-1}; at 74.9°, $(1.31 \pm 0.01) \times 10^{-3}$ sec^{-1}. These data gave $\Delta H^{\ddagger} = 23.9$ kcal/mol, $\Delta S^{\ddagger} = -3.2$ eu, and a calculated rate constant at 25° of 3.53×10^{-6} sec^{-1}. From data on the solvolysis of 1-chlorobicyclo[3.3.1]nonyl chloride in 60% ethanol, Dauben and Poulter[5] estimated this rate constant to be 6×10^{-6} sec^{-1}, a value in good agreement with our findings.

Gleicher and Schleyer predicted the rate constant of VI in 80% ethanol at 25° to be one-eighth that of *t*-butyl bromide, or 4.30×10^{-5} sec^{-1}. This predicted value is 12.2 times larger than the value we have found experimentally by interpolation and seven times larger than Dauben and Poulter's less directly estimated value. This agreement certainly is creditable.

When a plot of the calculated strain differences *vs.* the experimental rate data (Figure 1) is examined, the situation appears even better. Included in this plot are all the data for the bridgehead systems previously examined (I–IV),[3,12] the new datum for VI, as well as a point estimated for V.[4] Four points, those for compounds I, II, IV, and VI, lie very close to the correlation line; the point for V deviated by about $10^{1.9}$ and that for 1-adamantyl bromide (III) by $10^{2.2}$.[13] The average deviation of all six points is only $10^{\pm 0.78}$. This approach to the quantitative prediction of reaction rates, despite its rather crude assumptions, seems to have promise. We plan to test it further in a number of systems.

Experimental Section

Bicyclo[3.3.1]nonane (VIII).—A solution of bicyclo[3.3.1]-nonan-2-one[6] (14 g), 85% hydrazine hydrate (55 ml), and potassium hydroxide (15 g) was heated at reflux in 350 ml of diethylene glycol.[8] The water formed and the excess hydrazine were removed by means of a Dean–Stark trap, enabling the reflux temperature to rise to about 180°. Crystals, which consisted of starting material and product, sublimed onto the condenser and were recycled until no further carbonyl absorption was detected in the infrared. Final sublimation of the product gave 7.4 g (54%) of the parent hydrocarbon: mp 143–146° (lit.[14] mp 145–146°); nmr (CCl_4), broad singlet at 1.75 ppm with a small shoulder at 1.55 ppm; $\nu_{max}^{CCl_4}$ 2975, 2900, 2845, 1450 cm^{-1}.

1-Bicyclo[3.3.1]nonyl Bromide (VI).—A solution of 1 g of bicyclo[3.3.1]nonane in 2 ml of neat bromine was stirred at room temperature for 20 hr. At the end of this period the mixture was dissolved in 20 ml of CCl_4, poured into 100 ml of H_2O, and the excess bromine destroyed with sodium thiosulfate solution. The organic layer was separated, dried over $MgSO_4$, and the solvent was evaporated. Upon standing in the refrigerator, the residual yellow oil solidified. Sublimation and recrystallization from pentane gave a white crystalline product: 52% yield, mp 52–53°; nmr ($CDCl_3$), two main absorptions centered at 1.75 and 2.35 ppm; $\nu_{max}^{CCl_4}$ 2975, 2920, 2850, 1450, 1340, 1300, 1045, 950, 650 cm^{-1}.

The elemental analysis of this compound, even after purification by gas chromatography and by other means, was not satisfactory, the bromine being consistently high.

Anal. Calcd for $C_9H_{15}Br$: C, 53.20; H, 7.39; Br, 39.41. Found: C, 52.57; H, 7.25; Br, 40.17.

Hydrogenolysis of VI.—A solution of 500 mg of 1-bicyclo-[3.3.1]nonyl bromide in 10 ml of methanol containing 0.2 g of NaOH and 1 g of Raney nickel catalyst was hydrogenated at 50 psi for 2 hr. The catalyst was then filtered and the reaction mixture was diluted with 50 ml of H_2O. The solid product was extracted with ether, dried, and the solvent was removed under vacuum, leaving 180 mg (62.2%) of a white solid whose physical and spectroscopic properties were identical in every respect with bicyclo[3.3.1]nonane.

1-Bicyclo[3.3.1]nonanol.—A solution of 105 mg of 1-bicyclo-[3.3.1]nonyl bromide in 50 ml of a 60:40 acetone–water mixture was refluxed (85°) for 0.5 hr. After cooling, the reaction mixture was extracted with petroleum ether (bp 30–60°), the extracts were dried, and the solvent was removed under vacuum leaving 60 mg (84%) of white needle-shaped crystals. Two recrystallizations from petroleum ether (bp 30–60°) gave a mp of 180–182° (lit.[5] mp 182.5–184°); $\nu_{max}^{CCl_4}$ 3600, 3350, 2985, 2905, 2850, 1485, 1470, 1450, 1090, 1000, 930, 870 cm^{-1}; nmr (δ, ppm) 1.6 and 2.1 multiplets in a ratio of 15:1 with the hydroxyl proton presumably coming beneath the main absorption.

Kinetic and Product Studies.—The kinetics were measured in the usual manner[15] in 80% aqueous ethanol.

The ethanolic solution of solvolyzed alkyl bromide was refluxed for 1 hr with 1 g of Na_2CO_3. An equivalent amount of water was added and this solution was extracted with petroleum ether (bp 30–60°) and dried over $MgSO_4$. The solvent was evaporated and the residue sublimed. Gas chromatographic analysis showed three peaks: a minor component of about 3% (not identified); a second component of about 40% (presumably the ethoxide); and the major product (60%) positively identified as the 1-bicyclo[3.3.1]nonanol by comparison of its vpc retention time and nmr with that of an authentic sample.

Registry No.—VI, 15292-76-9; VIII, 280-65-9; 1-bicyclo[3.3.1]nonanol, 15158-56-2.

Acknowledgments.—This research was supported by the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, administered by the American Chemical Society.

---

[12] On a variety of grounds, discussed in the original paper,[3] the point for *t*-butyl has been omitted from Figure 1.

[13] Our continuing efforts to improve these calculations have yielded favorable results and an average deviation of $10^{\pm 0.37}$ has been achieved with the point deviating most (III) off the correlation line by $10^{1.1}$ (J. Williams and R. Bingham, unpublished observations).

[14] A. C. Cope and M. E. Synerhold, *J. Amer. Chem. Soc.*, **72**, 5228 (1950).

[15] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **77**, 3619 (1955).

A Photochemical Cycloaddition of Thiobenzophenone to Conjugated Dienes

KAZUTOSHI YAMADA, MICHIKAZU YOSHIOKA,
AND NOBORU SUGIYAMA

*Department of Chemistry, Tokyo Kyoiku University,
Otsuka, Tokyo, Japan*

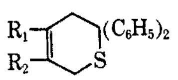
Received June 28, 1967

Although the photochemical cycloaddition to form a four-membered ring system[1] and the photochemical Diels–Alder addition of olefins to 1,2-dicarbonyl

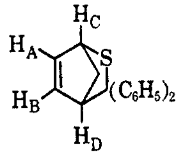
---

[1] H. Kataoka, K. Yamada, and N. Sugiyama, *Bull. Chem. Soc. Japan*, **38**, 2027 (1965); N. Sugiyama, K. Yamada, Y. Watari, and T. Koyama, *Nippon Kagaku Zasshi*, **87**, 737 (1965).

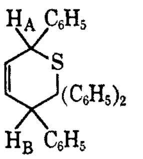
compounds[2] are well-known, few reports on the photochemical Diels–Alder addition of dienes have been found in the literature; *e.g.*, 1,4 addition of maleic anhydride to anthracene,[3] that of maleic anhydride or dimethyl maleic anhydride to conjugated dienes,[4] that of oxygen to dienes,[5] and that of benzoquinone to 2,3-dimethylbutadiene[6] have been reported. Thus, maleic anhydride, dimethyl maleic anhydride, oxygen, and benzoquinone can be added to conjugated dienes to form a six-membered ring system. We have recently found that thiobenzophenone can be added to α-phellandrene to afford 1,2 and 1,4 adducts by ultraviolet irradiation.[7] This was the first example of the photochemical cycloaddition of thiocarbonyl compounds to conjugated dienes, though the photochemical cycloaddition of thiobenzophenone to some monoenes to afford 2:1 adducts has been recently reported by Tsuchihashi and coworkers.[8] In the present paper we report the results of the application of this new reaction to isoprene, cyclopentadiene, 1,4-diphenylbutadiene, and 1,3-cyclooctadiene.



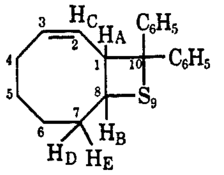
I, R$_1$ = H, R$_2$ = CH$_3$
II, R$_1$ = CH$_3$, R$_2$ = H



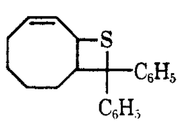
III



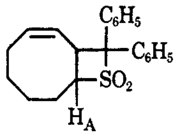
IV



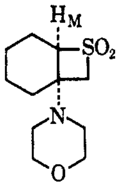
V



VI



VII



VIII

When a mixture of thiobenzophenone and an excess of conjugated diene was irradiated with Pyrex filtered ultraviolet light, gradual fading of the ultraviolet absorption maximum of thiobenzophenone at 314 mμ, accompanied by the disappearance of the blue color, was observed. At −78°, thiobenzophenone reacted with isoprene or cyclopentadiene by ultraviolet irradiation, but did not react in the dark. However, at room temperature, thiobenzophenone reacted with isoprene or cyclopentadiene, both under irradiation and in the dark. On the other hand, even at room temperature, thiobenzophenone did not react with 1,4-diphenylbutadiene or 1,3-cyclooctadiene. The photoproducts were separated by chromatography. All products were proved to be 1:1 adducts of thiobenzophenone to diene by elemental analyses. It was shown by thin layer chromatography with two solvent systems (*n*-hexane–benzene 5:1 v/v; CS$_2$) and the mixture melting point that the photoproducts (1,4 adducts) isolated from the reaction (at −78°) mixture of thiobenzophenone and isoprene or cyclopentadiene were the same as the photoproducts isolated from the reaction (at room temperature) mixture. Furthermore, by the kinetic studies of the reactions which were carried out at −78° and at room temperature, it was found that they were both first-order reactions.[9] These facts indicated that the possibility of initia 11,2 adducts rearranging 1,4 adducts was eliminated.

Photochemical Adduct of Thiobenzophenone to Isoprene (I and II).—The nmr spectrum is given in Table I. The peaks between τ 2.50 and 3.05 correspond to ten aromatic protons, and a multiplet centered at τ 4.45 corresponds to one vinyl proton. The presence of only one vinyl proton indicates that the photoproduct is not the 1,2 adduct but the 1,4 adduct. If it were the 1,2 adduct, it would show two or three vinyl protons. The two possible 1,4 adducts

TABLE I
NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA OF THE ADDUCTS

Compd	Chemical shift (τ)	Multiplicity[a]	Proton assignment		Coupling constants, cps
	2.50–3.05	m	10 H	Phenyl	
I and II	4.45	m	1 H	Vinyl	
in CCl$_4$	7.20	m	4 H	Methylene	
	8.20	s	1.2 H	Methyl	
	8.32	s	1.8 H		
	2.60–3.10	m	10 H	Phenyl	
III	3.73	dd	1 H	H$_A$ or H$_B$	
in CS$_2$	4.57	dd	1 H	H$_A$ or H$_B$	
	6.00	m	2 H	H$_C$ and H$_D$	
	8.05	m	2 H	Methylene	J_{AB} = 5.2, J_{AC} = J_{BD} = 2.5
	2.30–3.55	m	20 H	Phenyl	
IV	3.96	m	2 H	Vinyl	
in CS$_2$	5.85	m	1 H	H$_A$	
	6.25	m	1 H	H$_B$	
	2.35–3.20	m	10 H	Phenyl	
V	4.65	m	2 H	Vinyl	
in CS$_2$	5.46	dd	1 H	H$_A$	
	6.70	se	1 H	H$_B$	
	7.50–9.20	m	8 H	Methylene	J_{AB} = 3.3, J_{AC} = J_{BD} = J_{BE} = 10.0
	2.50–3.10	m	10 H	Phenyl	
VII	4.45	m	2 H	Vinyl	
in CS$_2$	5.85	m	2 H	Methyne	
	7.40–8.70	m	8 H	Methylene	

[a] Abbreviations used are as follows: m = multiplet; s = singlet; dd = doublet of doublets; se = sextet.

---

(2) C. R. Masson, V. Bockelheide, and W. A. Noyes, Jr., in "Technique of Organic Chemistry," Vol. II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 257.

(3) J. P. Simons, *Trans. Faraday Soc.*, **56**, 391 (1960).

(4) G. O. Schenck, J. Kuhls, and C. H. Krauch, *Ann.*, **693**, 20 (1966).

(5) G. O. Schenck and K. Ziegler, *Naturwiss.*, **32**, 157 (1944).

(6) J. A. Barltrop and B. Hesp, *Proc. Chem. Soc.*, 195 (1964); *J. Chem. Soc.*, 5182 (1965).

(7) Y. Omote, M. Yoshioka, K. Yamada, and N. Sugiyama, *J. Org. Chem.*, **32**, 3676 (1967).

(8) G. Tsuchihashi, M. Yamauchi, and M. Fukuyama, *Tetrahedron Lett.*, 1971 (1967).

(9) M. Yoshioka, H. Kataoka, K. Yamada, and N. Sugiyama, VIIIth Symposium of Organic Radical Reactions, Nagoya, 1967, No. D-25.

of thiobenzophenone to isoprene are 3-methyl-6,6-diphenyl-1-thiacyclohexene-3 (I) and 4-methyl-6,6-diphenyl-1-thiacyclohexene-3 (II). Since two singlets at τ 8.20 (1.2 H) and 8.32 (1.8 H) were assigned together to the three protons of a methyl group, the photoproduct must be a mixture of I and II. Owing to similar chromatographic behavior, they could not be separated. The same product composition was obtained by the thermoreaction of the corresponding mixture at 100°.

Photochemical Adduct of Thiobenzophenone to Cyclopentadiene (III).—The nmr spectrum of III shows ten aromatic protons between τ 2.60 and 3.10, a doublet of doublets centered at 3.73 for one vinyl proton, a doublet of doublets centered at 4.57 for another vinyl proton, a multiplet centered at 6.00 for two methyne protons, and a multiplet centered at 8.05 for two methylene protons. The fact that each vinyl proton shows the same pattern indicates that the photoproduct is a 1,4 adduct, *i.e.*, 3,3-diphenyl-2-thiabicyclo[2.2.1]hept-5-ene (III). H_A gave a quartet by coupling with H_B and H_C, and H_B also gave a quartet by coupling with H_A and H_D, $J_{AB} = 5.2$ cps, $J_{AC} = J_{BD} = 2.5$ cps. The thermoreaction of the corresponding mixture at 100° afforded the same product, III.

Photochemical Adduct of Thiobenzophenone to 1,4-Diphenylbutadiene (IV).—In this case the photochemical adduct could be either the 1,2 adduct styrene derivative, or the 1,4 adduct. The latter is preferable, because the ultraviolet spectrum of the product did not show a strong absorption maximum near 250 mμ which is characteristic of styrene derivatives. Thus, the photochemical adduct was assumed to be the 1,4 adduct, 2,5,6,6-tetraphenyl-1-thiacyclohexene-3 (IV). This assumption was supported by the nmr spectral data. The nmr spectrum showed 20 aromatic protons between τ 2.35 and 3.55, a multiplet centered at 5.85 for H_A, a multiplet centered at 6.25 for H_B and a multiplet centered at 3.96 for two vinyl protons. If this compound were the 1,2 adduct, the chemical shifts of the vinyl protons should be distinctly different from each other, because one of them is adjacent to a phenyl group. The thermoreaction of the corresponding mixture at 100° gave the same product as IV.

Photochemical Adduct of Thiobenzophenone to 1,3-Cyclooctadiene (V).—The nmr spectrum of V shows ten aromatic protons between τ 2.35 and 3.20, a multiplet centered at 4.65 for two vinyl protons, a doublet of doublets centered at 5.46 for one methyne proton, a sextet centered at 6.70 for another methyne proton, and a multiplet between 7.50 and 9.20 for eight methylene protons. This nmr pattern indicates that this compound is not the 1,4 but is the 1,2 adduct. The coupling patterns of two methyne protons should be the same in the two possible 1,2 adducts, V and VI. The nmr spectrum of the corresponding sulfone obtained by peracetic acid oxidation showed a multiplet centered at τ 5.85 for two methyne protons. Since H_A of VII is approximately in the same situation as H_M of VIII, H_A and H_M may appear at approximately the same field strength. In fact the chemical shift of H_M was reported as τ 5.6.[10] Thus the chemical shifts of H_A and H_M are regarded as approximately the same. Therefore, the structure of this sulfone must be VII, so that our photoproduct is 10,10-diphenyl-9-thiabicyclo[6.2.0]decene-2 (V). Furthermore, if the structure of our photoproduct were VI, the chemical shift of the proton on C-1 of the corresponding sulfone would appear at a lower field than that of VI, but, as pointed out above, such an effect was not observed. This compound was not obtained by thermoreaction at 100°.

As the two double bonds in the starting substance, 1,3-cyclooctadiene, are not in the same plane, it cannot act as a conjugated diene compound. The reason the 1,4-adduct was not formed from the mixture of thiobenzophenone and 1,3-cyclooctadiene may be attributed to this situation.

Kaiser and Wulfers[11] reported the photolytic reaction of thiobenzophenone in the presence of ethylene derivatives through a four-membered ring system by irradiation with 210–280-mμ light. They did not isolate the intermediate four-membered ring system. But, from the results of the present research, its isolation would be succeeded if light of lower energy, Pyrex filtered light, is used.

Experimental Section

All melting points are uncorrected. The infrared spectra were determined on a Hitachi EPI-2 spectrophotometer, and the ultraviolet spectra were recorded on a Hitachi EPS-033 spectrophotometer. The nmr spectra were determined on a Hitachi H-6013 spectrometer (60 Mc). Tetramethylsilane was used as an internal standard. The irradiation was carried out with a high pressure mercury lamp (Taika, Type H, 150 W) in a Pyrex tube under a nitrogen atmosphere. The per cent yields of all products are based on thiobenzophenone.

1:1 Addition of Thiobenzophenone to Isoprene. Photoreaction.—A mixture of 5 g of thiobenzophenone and 5 ml of isoprene was irradiated for 45 min at room temperature. The blue color of thiobenzophenone faded gradually with irradiation, and after 45 min, it disappeared completely. After removal of the unreacted isoprene from the irradiation mixture, the residual oil was chromatographed on 50 g of silica gel (Merck, 0.05–0.20 mm) with 5:1 *n*-hexane–benzene. A fraction which showed the same R_f value on a thin layer chromatogram was collected to yield 6.3 g (94%) of a mixture of I and II. They could not be separated from each other on account of their identical R_f value. The infrared spectrum (liquid film) showed strong bands at 2950, 2900, 1600, 1490, 1445, 750, and 700 cm^{-1}. The nmr spectrum is shown in Table I.

Anal. Calcd for $C_{18}H_{18}S$: C, 81.15; H, 6.81. Found: C, 80.93; H, 6.89.

They decomposed by heating into a blue oil, which was shown to be thiobenzophenone.

Thermoreaction.—From 5 g of thiobenzophenone and 5 ml of isoprene, 5.6 g (84%) of the addition product (the mixture of I and II) was obtained by heating at 100° for 45 min in a sealed tube under nitrogen atmosphere.

1:1 Addition of Thiobenzophenone to Cyclopentadiene. Photoreaction.—A mixture of 2 g of thiobenzophenone and 1.34 g of cyclopentadiene was irradiated at room temperature for 10 min. At the end of this time the complete disappearance of the blue color of thiobenzophenone was observed. The reaction mixture was worked up as described above to give 1.1 g (41%) of colorless leaflets (from ethanol-water), mp 133–134° dec. The structure of this compound was proved as III by the following spectral data and elemental analysis. The infrared spectrum (KBr pellet) showed strong bands at 1590, 1480, 1440, 760, 735, and 700 cm^{-1}. The nmr spectrum is shown in Table I.

Anal. Calcd for $C_{18}H_{16}S$: C, 81.79; H, 6.10. Found: C, 81.09; H, 6.01.

Irradiation of a solution of 200 mg of thiobenzophenone and

---

[10] I. J. Borowitz, *J. Amer. Chem. Soc.*, **86**, 1146 (1964).

[11] E. T. Kaiser and T. F. Wulfers, *ibid.*, **86**, 1897 (1964).

excess cyclopentadiene in 600 ml of *n*-hexane at −78° for 52 hr gave 60 mg of colorless leaflets. This product was identified as III by the mixture melting point and spectral data.

Thermoreaction.—The mixture of 2 g of thiobenzophenone and 1.34 g of cyclopentadiene was heated at 100° for 10 min in a sealed tube. The product, 1.1 g (41%), from the reaction mixture was identified as III by the spectral data and the mixture melting point.

1:1 Addition of Thiobenzophenone to 1,4-Diphenylbutadiene. Photoreaction.—A solution of 2 g of thiobenzophenone and 1.94 g of 1,4-diphenylbutadiene in 10 ml of benzene was irradiated at room temperature for 95 hr. Although, at the end of this period, the complete disappearance of the blue color of thiobenzophenone was not yet observed, the solvent was evaporated and the residual oil was worked up as described above to afford 720 mg (18%) of colorless prisms. The structure of this compound was proved to be IV by the following spectral data and elemental analysis. The infrared spectrum (KBr pellet) showed strong bands at 1600, 1490, 1445, 840, 750, and 695 cm^{-1}. The ultraviolet absorption maxima in ethanol were at $\lambda_{\max}^{\text{ethanol}}$ 250 mμ (ε 1550), 255 (1580), 261 (1410), 267 (1080), and 275 (470). The nmr spectrum is shown in Table I.

Anal. Calcd for $C_{29}H_{24}S$: C, 86.10; H, 5.98. Found: C, 86.13; H, 6.12.

Thermoreaction.—A solution of 2 g of thiobenzophenone and 1.94 g of 1,4-diphenylbutadiene in 10 ml of benzene was heated at 100° for 95 hr. The reaction mixture was worked up as described above to yield 210 mg (5.1%) of the colorless prisms. It was identified as IV by the spectral data and mixture melting point.

1:1 Addition of Thiobenzophenone to 1,3-Cyclooctadiene. Photoreaction.—A mixture of 2 g of thiobenzophenone and 2.2 g of 1,3-cyclooctadiene was irradiated at room temperature. In this case, 82 hr were required for complete disappearance of the blue color of the mixture. The same procedure described above was followed to give 1.27 g (41%) of the colorless needles (from acetone–water), mp 110.5°. The structure of this compound was proved to be V by the following spectral data and elemental analysis. The infrared spectrum (KBr pellet) showed strong bands at 2925, 2850, 1630, 1490, 1440, 760, and 700 cm^{-1}. The nmr spectrum is shown in Table I.

Anal. Calcd for $C_{21}H_{22}S$: C, 82.45; H, 7.55. Found: C, 82.33; H, 7.25.

It was found that 1,3-cyclooctadiene did not react with thiobenzophenone by heating at 100°.

Oxidation of V with Peracetic Acid.—A mixture of 200 mg of V, 3 ml of acetic acid, and 2 ml of 30% aqueous hydrogen peroxide in 20 ml of acetone was left standing for 40 hr at room temperature. After decomposing the excess hydrogen peroxide with a small amount of manganese dioxide, the filtrate was evaporated to yield a solid substance. It was recrystallized from acetone–water to give 80 mg of colorless fine needles, mp 147–148°. The infrared spectrum (KBr pellet) showed strong bands at 2925, 2850, 1445, 1305, 1145, and 700 cm^{-1}. The nmr spectrum was shown in Table I.

Anal. Calcd for $C_{21}H_{22}SO_2$: C, 74.53; H, 6.55. Found: C, 74.16; H, 6.46.

Registry No.—I, 15052-31-0; II, 15052-32-1; III, 15052-33-2; IV, 15052-34-3; V, 15052-35-4; VII, 15052-36-5; thiobenzophenone, 1450-31-3.

Reaction of Bromine with Hindered Olefinic Bonds

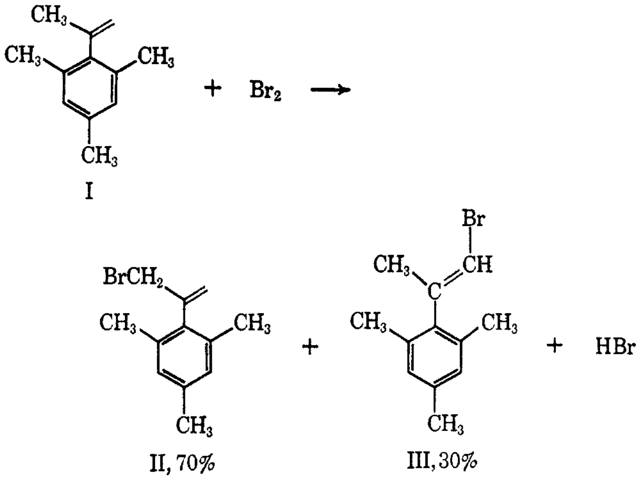
EARL S. HUYSER AND LEO KIM[1]

Department of Chemistry, University of Kansas, Lawrence, Kansas 66044

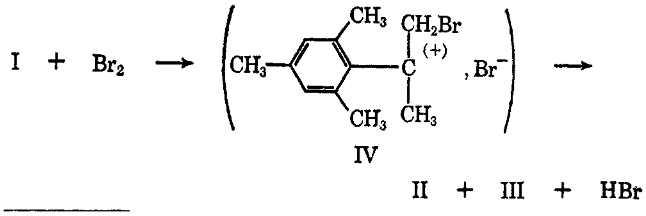
Received August 21, 1967

Bromine has been reported to react in an unexpected manner with α,*o*,*o*,*p*-tetramethylstyrene (I) yielding, rather than the expected addition product, hydrogen bromide and some unspecified substitution product.[2] We have reinvestigated this reaction to determine the structure of the substitution product and a possible mechanism for this anomalous reaction of bromine with an unsaturated linkage.

Mixing bromine with I in carbon tetrachloride at 0° results in immediate loss of the bromine color and evolution of hydrogen bromide. Gas chromatographic analysis of the reaction mixture showed that two bromination products in a ratio of about 7:3 were formed. Nmr analysis of the distilled mixture of substitution products indicated the predominant isomer to be α-bromomethyl-*o*,*o*,*p*-trimethylstyrene (II) and the other β-bromo-α,*o*,*o*,*p*-tetramethylstyrene (III). Passing a stream of nitrogen containing bromine vapor into a pentane solution of I at −78° resulted in formation of a bright yellow solid, the color of which was distinctly different from the reddish brown color of solid molecular bromine in pentane at the same temperature. No evolution of hydrogen bromide occurred, but when the mixture was warmed to room temperature, the yellow solid disappeared and hydrogen bromide, II, and III were produced. Addition of a small amount of 95% ethanol to the yellow mixture produced in the reaction of I with bromine in pentane at −78° resulted in formation of a red alcoholic solution which separated from the pentane. This red solution was neutral at −78° but on warming became acidic and the red color disappeared. Gas chromatographic analysis of the resulting colorless alcoholic solution showed the presence of II and III and a trace of I. Gas chromatographic analysis of the pentane solution from which the yellow solid had been removed by the alcohol showed only traces of II and III but considerable amounts of unreacted I.



These observations are consistent with the formation of the carbonium ion–bromide ion pair IV rather than the covalent dibromide as the reaction product



---

[1] National Institutes of Health Predoctoral Fellow, 1966–1967.

[2] M. S. Newman and N. C. Deno, *J. Amer. Chem. Soc.*, **73**, 3644 (1951); H. C. Brown and M. Grayson, *ibid.*, **75**, 20 (1953).