(0.0172 mole) of silver perchlorate in 50 ml. of water. After filtration, the solution was evaporated to near dryness at aspirator pressure and last traces of water were removed by drying over phosphorus pentoxide in a vacuum desiccator to give 3.8 g. (0.0156 mole) of 4-carboxycyclohex-1-ylamine perchlorate. To a mixture of 3.8 g. of the amine perchlorate in 20 ml. of glacial acetic acid, cooled in an ice bath, was added 3.24 g. (0.047 mole) of sodium nitrite over a period of about 30 min. The ice bath was removed and the mixture stirred for an additional 6 hr. The mixture was poured into 250 ml. of water and extracted with 1.5 l. of ether. After evaporation of the ether, the residue gave a negative test with 2,4-dinitrophenylhydrazine reagent. Aqueous sodium hydroxide (10%) was added to the residue until the *p*H was 12 and the solution was extracted continuously with ether for 2 days. Evaporation of the ether gave no residue. After acidification of the basic solution with concentrated hydrochloric acid to *p*H 2 and continuous extraction for 2 days with ether, evaporation of the ether and extracted acetic acid gave 90 mg., m.p. 112–127°, of acidic material. Its infrared spectrum had bands at 3440, 2600, and 1705 cm.$^{-1}$ and was almost identical with the spectrum of a mixture of *cis-* and *trans*-4-hydroxycyclohexanecarboxylic acid.

4-Ketocyclohexanecarboxylic acid (XIV). To a stirred suspension of 3.0 g. (0.0208 mole) of 4-hydroxycyclohexanecarboxylic acid in 10 ml. of water and 3.6 g. of sulfuric acid was added 4.23 g. (0.0144 mole) of potassium dichromate in small portions over a 15-min. period, during which time the temperature rose to about 50°. After the addition was complete, the reaction mixture was stirred for 3 hr. The solution was extracted with 1 l. of ether. The ether was dried over sodium sulfate and then was evaporated to give 2.39 g. of solid material. Sublimation of 0.86 g. of this material gave 0.69 g. of 4-ketocyclohexanecarboxylic acid, m.p. 67–70°. Its infrared spectrum had a band at 1705 cm.$^{-1}$ and broad absorptions from 3500–3000 cm.$^{-1}$ and 2700–2600 cm.$^{-1}$ and was identical to the spectrum of the acid obtained from diazotization of 7,7-dihydroxybicyclo[2.2.1]hept-1-ylamine perchlorate. A mixed melting point with the acid obtained from the diazotization was 68–71°.

Acknowledgment. The authors are indebted to the Research Corp. and the Alfred P. Sloan Foundation for grants in partial support of this research, and to the Monsanto Chemical Co. for a fellowship held by J. P. K. during the year 1957–58.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Bridged Polycyclic Compounds. XIV. Free-Radical Addition of *p*-Toluenesulfonyl Chloride to Some Norbornenes[1]

STANLEY J. CRISTOL AND JAMES A. REEDER

Received October 26, 1960

Free-radical addition of *p*-toluenesulfonyl chloride to norbornene (I) and to aldrin (II) led to the formation of *trans* 1,2-addition products (III and IV, respectively) without skeletal rearrangement or *cis-exo* addition products being noted. Addition to norbornadiene (V) gave the rearranged product VII. The results are discussed in terms of classical radical intermediates.

The addition of sulfonyl halides to olefins *via* free-radical paths has been noted by several groups of investigators.[2,3,4] In the course of our work on the stereochemistry of addition and of rearrangements during additions to bridged polycyclic olefins,[1,5–10] we decided to investigate the free-radical additions of arenesulfonyl chlorides to norbornenes to see whether these followed the same general pattern as other free-radical addition reactions.

Exclusive *exo-cis* addition of *p*-thiocresol to 6-chloroaldrin (*endo-exo*-1,2,3,4,6,10,10-heptachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene) has been reported.[7] The free-radical addition of bromine to various substituted norbornenes (and 7-oxa analogs) has also been shown to give considerable *exo-cis* products,[11] and ethyl bromoacetate is reported to give *exo-cis* addition to norbornene.[12] On the other hand, we have now found that *p*-toluenesulfonyl chloride adds to norbornene (I) and to aldrin (II) to give the *trans* addition product.

When norbornene (I) was heated at 75–90° with *p*-toluenesulfonyl chloride in the presence of

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[1] Previous paper in series: S. J. Cristol and R. K. Bly, *J. Am. Chem. Soc.*, **82**, 6155 (1960).

[2] E. C. Ladd, U. S. Patent **2,521,068** (Sept. 5, 1950); U. S. Patent **2,573,580** (Oct. 30, 1951).

[3] M. S. Kharasch and R. A. Mosher, *J. Org. Chem.*, **17**, 453 (1952).

[4] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **77**, 4638 (1955); P. S. Skell and J. H. McNamara, *J. Am. Chem. Soc.*, **79**, 85 (1956).

[5] S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954).

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[8] S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).

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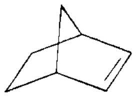
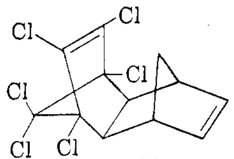
[12] J. Weinstock, Abstracts of the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 1955, p. 19-O.



I



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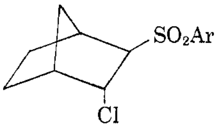
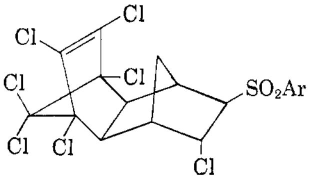


III



IV

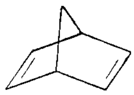
benzoyl peroxide or with ultraviolet irradiation, a substantial yield of a 1:1 addition product was obtained. The principal component of this product was shown to be *exo*-2-*p*-toluenesulfonyl-*endo*-3-chloronorbornane (III) which has been previously prepared and characterized.[6] The free-radical nature of the reaction was demonstrated by catalysis and by inhibition.

Aldrin (II) reacted with *p*-toluenesulfonyl chloride more slowly than norbornene, but addition occurred in twenty-four hours at 155° in the presence of di-*tert*-butyl peroxide to give the *trans* addition product, *endo*-3,4,5,6,7,8,9,9-heptachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo*-2-*p*-toluenesulfonyl-1,4,5,8-*exo*-*endo*-dimethanonaphthalene (IV), a product of known structure.[6] The yield in this reaction was poor, considerable hydrogen chloride evolution being noted, but no other products were isolated.

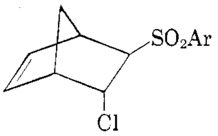
This reaction, like that with norbornene, then, is different from those previously noted in that *trans* addition is observed,[13] although similar in that no rearrangement is observed. It appears in order to rationalize the *trans* addition which occurs rather than the *cis-exo* addition previously noted. No explanation involving bridged radical intermediates appears tenable, in particular as Skell and his colleagues[4] have noted that the reactions of *p*-toluenesulfonyl iodide with *cis*- and *trans*-2-butene are not stereospecific and as we have found (*vide infra*) that *p*-toluenesulfonyl chloride adds to norbornadiene by homoconjugate addition. It seems necessary to suggest that the intermediates in these radical reactions are classical radicals,[7] and that the direction from which chain transfer occurs is controlled by steric factors.

A large steric requirement for the *p*-toluenesulfonyl group has been postulated by Bordwell and Cooper[14] to explain the inertness of chloromethyl *p*-tolyl sulfone to solvolysis, and by Weinstock, Pearson, and Bordwell[15] to explain the reduction of 2-*p*-toluenesulfonylcyclohexanone, and the corresponding cyclopentanone, with sodium borohydride to give the *cis*-substituted alcohols. A similar explanation can be advanced for the principal *trans* addition observed in the present investigation. According to this explanation, the approach of a molecule of *p*-toluenesulfonyl chloride to the 3-carbon atom of the intermediate radical is inhibited in the *exo* direction by steric interference from the large *p*-toluenesulfonyl group. Thus the occurrence of chain transfer from the *endo* direction is favored sterically.

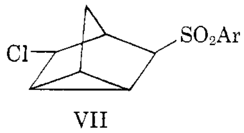
The addition of *p*-thiocresol to norbornadiene (V) has been shown to give a mixture of the products of simple 1,2- addition and 1,5-homoconjugate addition,[5] the ratio of the two modes depending upon the rate of chain transfer.[8] If *p*-toluenesulfonyl chloride added in a similar fashion to V, the products would be expected to be the *trans*-1,2-addition product VI and one or more of the isomers of the homoconjugate addition product VII. The addition of the sulfonyl chloride to V gave a product that was largely saturated,[16] and which gave upon recrystallization a 42% yield of a compound having properties anticipated for VII. This substance was inert to dilute potassium permanganate in acetone or bromine in carbon tetrachloride. The nortricyclene ring system is consistent with these data, with infrared data and with the lack of consistency of properties with the known[6] unsaturated isomer VI. The stereochemistry of the product has not yet been demonstrated. The relative completeness of the rearrangement to the nortricyclene ring system may be rationalized on the basis of the slow chain transfer of the intermediate radicals with the sulfonyl chloride allowing sufficient time for rearrangement of radical VIII to IX.[8]



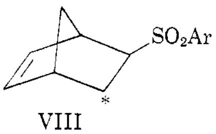
V



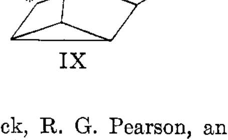
VI



VII



VIII



IX

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[14] F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5184 (1951).

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[16] The composition of the equivalent product from benzenesulfonyl chloride has been investigated in this laboratory and will be reported later (S. J. Cristol and D. I. Davies).

EXPERIMENTAL

Addition of p-toluenesulfonyl chloride to norbornene. (*a*) *Peroxide-catalyzed reaction.* A mixture of 1.67 g. (17.73 mmoles) of norbornene and 1.82 g. (9.57 mmoles) of *p*-toluenesulfonyl chloride (Matheson, redistilled, m.p. 68–69°) was prepared in a 20-ml. flask equipped with a thermometer, reflux condenser, and mechanical stirrer. To this heterogeneous mixture was added 79 mg. (0.5 mmole) of benzoyl peroxide to act as a radical-chain initiator. The stirred mixture was heated rapidly to 100°, becoming homogeneous at about 70°. No spontaneous temperature rise attributable to the heat of reaction was noted. The temperature was maintained at 85–90° for 8 hr., and then the reaction mixture was cooled slowly with stirring. It solidified to a thick white paste at 32°.

The paste was immediately dissolved in 8 ml. of ethyl acetate and chromatographed on 60 g. of alumina. Elution with a solution of 10% ethyl acetate in petroleum ether (b.p. 60–80°) yielded 1.73 g. (64% based on starting *p*-toluenesulfonyl chloride) of white solid material in three fractions, the first melting at 95–98°, the second at 109–112°, and the third at 100–104°. Two recrystallizations of this solid from methanol gave a white solid, m.p. 114–115°.

The melting point of this solid when mixed with an authentic sample[6] of *exo*-2-*p*-toluenesulfonyl-*endo*-3-chloronorbornane (III, m.p. 114–115°) was 114–115°, showing no depression.

(*b*) *Addition initiated by ultraviolet light.* A mixture of 3.00 g. (31.8 mmoles) of norbornene and 6.06 g. (31.8 mmoles) of *p*-toluenesulfonyl chloride was prepared in a 125-ml. Vycor flask equipped with a thermometer, magnetic stirrer, and reflux condenser. The flask was irradiated for 1 hr. with ultraviolet light from a Mazda AH-4 lamp placed about 2 cm. away from the flask. Heat from the lamp was sufficient to maintain the temperature inside the flask at 120–130°. The reaction mixture was cooled overnight, and the resulting viscous oil was subjected to vacuum distillation at room temperature and 0.2 mm. pressure, to recover 0.81 g. (27%) of unchanged norbornene in a trap cooled with Dry Ice–isopropyl alcohol. The flask was heated under vacuum to remove most of the starting *p*-toluenesulfonyl chloride, which solidified in the upper part of the flask. The crude solid remaining in the bottom of the flask weighed 6.12 g. and melted at 85–97°, for a crude yield of 67.5% (92.5% based on unrecovered norbornene). One recrystallization from methanol gave 4.48 g. of a white solid melting at 109–112°, for a yield of 49.5% (67.7% based on unrecovered norbornene). One more recrystallization from methanol gave pure III, m.p. 114–115°.

Proof of free-radical nature of addition reaction. A mixture of 1.00 g. (10.6 mmoles) of norbornene and 2.02 g. (10.6 mmoles) of *p*-toluenesulfonyl chloride was prepared in a 20-ml. flask equipped with a thermometer and a reflux condenser. The temperature of the flask was maintained at 75–80° for 17 hr., after which the flask was cooled to room temperature and subjected to vacuum distillation for 1 hr. at room temperature and 0.2 mm. pressure, during which time the unchanged norbornene was collected in a trap cooled in Dry Ice–isopropyl alcohol. The trap was protected from moisture by a calcium chloride drying tube. The recovery of unchanged norbornene was 0.38 g. (38%).

Another experiment was conducted under exactly similar conditions, except that 160 mg. (1.0 mmole) of benzoyl peroxide was added to the reaction mixture before heating. In this experiment the recovery of unchanged norbornene was 0.11 g. (11%).

When a third experiment was conducted under the same conditions, but with 211 mg. (1.0 mmole) of trinitrobenzene added and no peroxide, the recovery of unchanged norbornene was 0.73 g. (73%).

The conditions under which the starting norbornene was recovered were identical in all three experiments.

Addition of p-toluenesulfonyl chloride to aldrin. A mixture of 1.82 g. (5.00 mmoles) of aldrin (II), m.p. 99–101°, 953 mg. (5.00 mmoles) of *p*-toluenesulfonyl chloride, and 61 mg. (0.5 mmole) of di-*tert*-butyl peroxide was sealed into a glass combustion tube of 10-mm. inside diameter. The tube was heated at 152–155° for a total of 24 hr. The tube was cooled to room temperature and opened, and some positive pressure inside from hydrogen chloride gas was noted. The reaction mixture inside the tube was a black glassy material. It was dissolved in glacial acetic acid and treated twice with activated charcoal (Darco G-60). Then most of the acetic acid was evaporated under a jet of dry air, and the white solid which separated was collected on a sintered glass filter funnel. After drying, the yield of this solid was 0.88 g. (32%), melting at 215–245°. Two recrystallizations from carbon tetrachloride yielded 0.36 g. (13%) of white solid, m.p. 265–268°. The infrared spectrum of this material was identical with that of a known sample[6] of IV and a mixed melting point was 265–268°, showing no depression.

In another experiment in which 1.00 g. (2.74 mmoles) of aldrin, 522 mg. (2.74 mmoles) of *p*-toluenesulfonyl chloride, and 43 mg. (0.27 mmole) of benzoyl peroxide was heated in 20 ml. of refluxing chlorobenzene for 24 hr., no product was obtained. Instead, 0.95 g. (95%) of impure aldrin was recovered which melted at 50–60°. Two recrystallizations raised the melting point to 95–98°, and a mixed melting point with pure aldrin showed no depression.

Addition of p-toluenesulfonyl chloride to norbornadiene. (*a*) *Peroxide-catalyzed addition.* A mixture of 2.00 g. (21.6 mmoles) of norbornadiene and 2.05 g. (10.8 mmoles) of *p*-toluenesulfonyl chloride was prepared in a 20-ml. flask equipped with a thermometer and reflux condenser, and 160 mg. (1.0 mmole) of benzoyl peroxide was added. The flask was heated at 75–82° for 24 hr. A white paste was obtained, which was dissolved in 10 ml. of dry chloroform and chromatographed on 60 g. of activated alumina. Elution with petroleum ether (b.p. 60–80°) yielded 988 mg. of a colorless oil with the odor of norbornadiene. This material was not investigated further. A total of 1.47 g. (47%) of white solid was eluted in thirteen 50-ml. fractions with a 10% solution of ethyl acetate in petroleum ether (b.p. 60–80°). The melting points of these fractions ranged from 100–125° to 146–152°. They were recrystallized separately to give a total of 0.95 g. of solid melting at 148–152° plus 0.33 g. of a solid melting at 152–154°. The fractions were combined to give a total yield of 1.28 g. (42%) of VII which melted at 154–155° after two more recrystallizations from methanol.

Anal. Calcd. for $C_{14}H_{15}ClO_2$: C, 59.46; H, 5.35. Found: C, 59.47; H, 5.28.

The infrared spectrum of VII showed strong absorption peaks at 11.85, 12.2, and 12.4 μ. Absorption in this region is characteristic of the nortricyclene structure.[17,18,19] Unfortunately this region overlaps that for *para* disubstituted benzenes.[20,21] A number of compounds containing a *p*-tolyl group have been examined in this laboratory, and these consistently appear to show a *single* strong absorption peak in the 12.2–12.4 μ region unless some other function is present which could be responsible for additional peaks. The infrared spectrum also showed a strong peak at 8.75 μ and a series of peaks in the 7.7 μ region, which can be attributed to the sulfone group.[21,22]

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(*b*) *Addition initiated by ultraviolet light.* A stirred solution of 1.00 g. (10.8 mmoles) of norbornadiene and 2.05 g. (10.8 mmoles) of *p*-toluenesulfonyl chloride in 50 ml. of cyclohexane was irradiated for 24 hr. in a Vycor flask, using the ultraviolet light from a Mazda AH-4 lamp. The cyclohexane was removed by evaporation and a pasty residue was obtained, which was chromatographed on 60 g. of activated alumina. Elution with 20% ethyl acetate in petroleum ether (b.p. 60–80°) gave a total of 1.62 g. (53.2%) of a white solid, m.p. 100–125°. Two recrystallizations from methanol gave X melting at 151.5–153.5°.

Acknowledgment. The authors are indebted to the Shell Development Co. and the Dow Chemical Co. for fellowships in support of this work. They are also indebted to Professor Philip S. Skell for drawing this reaction of sulfonyl halides to their attention. Norbornene was obtained through the generosity of the Polychemicals Department of E. I. du Pont de Nemours & Co., Inc., and norbornadiene and aldrin through that of the Shell Chemical Co.

BOULDER, COLO.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Reactions of Free Radicals with Olefins. Reactions of *t*-Butoxy and *t*-Butyl Peroxy Radicals with 4-Vinylcyclohexene[1]

J. REID SHELTON AND J. NEIL HENDERSON[2]

Received August 1, 1960

Abstraction of hydrogen (rather than addition) is demonstrated as a preliminary step in the formation of *t*-butyl vinylcyclohexenyl peroxides from 4-vinylcyclohexene with *t*-butyl hydroperoxide in the presence of cobalt ions. The olefin is shown to be peroxidated mainly in the 6-position, with minor proportions peroxidated in the 3-position and 4-position. The ratio of isomers is taken as evidence also for a strong steric effect.

Slow photolysis of di-*t*-butyl peroxide in 4-vinylcyclohexene at 40° results in the formation of four times as much dehydrodimer as any other olefin-derived product, showing that the *t*-butoxy radical prefers abstraction under these conditions. In contrast, there is as much *t*-butoxylation as dehydrodimerization of the olefin when di-*t*-butyl peroxide is decomposed at 120° in 4-vinylcyclohexene in the presence of cupric ion. These variations may be explained by differences in the nature and relative concentrations of free radicals produced.

The work described in this paper is a part of a continuing study of the reactions of free radicals with olefins. The objective of the program is to provide additional information regarding the relative reactivity of different types of free radicals with a variety of unsaturated compounds, and to determine the point of attack and the nature of the products formed. The study is particularly aimed at providing information with model compounds which relates to free-radical processes involved in polymerization, in certain cross linking reactions, and in both thermal and oxidative degradation of polymers.

In hydroperoxide decompositions induced by cobalt ions or similar metal ions, the work of the late Professor M. S. Kharasch and his colleagues[3] suggested the presence of both peralkoxy and alkoxy radicals: for example, in butadiene, *t*-butyl hydroperoxide decomposed to give $t\text{-}C_4H_9OOCH_2\text{-}CH{=}CHCH_2OOt\text{-}C_4H_9$ and isomeric peroxide along with about one-half equivalent of *t*-butyl alcohol. The roles of these radical species were originally misunderstood. It was proposed that peroxidation of olefins with a hydroperoxide (Equation 1) proceeded by addition of the peroxy radical to the

$$2\,\mathrm{ROOH} + \mathrm{R'H} \longrightarrow \mathrm{ROOR'} + \mathrm{ROH} + \mathrm{H_2O} \qquad (1)$$

double bond, followed by loss of a hydrogen atom to give, for example, 1-peralkoxyoctene-2 from octene-1. However, the untenability of this mechanism has recently been acknowledged.[4] The peroxidation of such compounds as cumene and cyclohexanone[4,5] showed that hydrogen abstraction must occur in these cases because an initial addition of $RO_2\cdot$ was not a reasonable possibility. Reexamination of the octene-1 example disclosed the presence of 3-peralkoxyoctene-1, certainly a product of hydrogen abstraction rather than of peroxy radical addition.

We had meanwhile applied the peroxidation technique to 4-vinylcyclohexene and independently concluded that the reaction must involve initial hydrogen abstraction in this case also.

The experimental work reported here involves the reaction of *t*-butoxy and *t*-butyl peroxy radicals with 4-vinylcyclohexene. This olefin provides both

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[1] Presented before the Division of Organic Chemistry, 137th Meeting, American Chemical Society, Cleveland, April 1960.

[2] Present address: Research Division, Goodyear Tire and Rubber Company, Akron, Ohio.

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