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

Bridged Polycyclic Compounds. V. The Addition of *p*-Thiocresol to Norbornadiene. The Question of Non-classical Free Radicals[1,2]

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Addition of thiophenol or *p*-thiocresol to norbornadiene (I) under free-radical conditions leads to mixtures of *exo*-5-norbornen-2-yl aryl thioethers *via* 1,2-addition and 3-nortricyclyl aryl thioethers *via* homoconjugative addition. Structure-proof work on the products is described. Variations of the product composition with concentration of the mercaptan in the reaction mixture demonstrate that the reaction involves addition of the thiol radical to the olefin to give an *exo*-arylthionorbornenyl radical which may (a) accept a hydrogen atom from a mercaptan molecule to give the 1,2-addition product or (b) *isomerize* to an arylthionortricyclyl radical, which transfers to give the homoconjugative addition product. Conclusive evidence is given to indicate that the two addition products do not result from a common intermediate such as the "non-classical" homoallylic radical VIII.

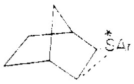
The addition of mercaptans to olefins has been shown to proceed *via* a chain mechanism involving free-radical intermediates,[3,4] *viz.*

$$RS^* + {>}C{=}C{<} \longrightarrow RS\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}{}^* \qquad (1)$$

$$RS\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}{}^* + RSH \longrightarrow RS\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H + RS^* \qquad (2)$$

We have been interested in the nature of the free-radical intermediate—in particular, in the question of whether non-classical structures analogous to those suggested for ionic reactions need be considered for radical reactions. As has already been described, no evidence for the existence of carbon-bridged structures[5] such as I or sulfur-bridged structures[1] such as II could be obtained; addition of *p*-thiocresol to norbornene gave only the unrearranged *exo*-2-norbornyl *p*-tolyl thioether,[5] and addition of thiocresol to a substituted norbornene gave entirely *cis–exo* addition of the thiol radical and the hydrogen atom.[1] Recently Berson and Jones[6] described the addition of *p*-thiocresol to *exo-cis*-1,2,3,6-tetrahydro-3,6-*endo*-methanophthalic anhydride, and to the corresponding dimethyl ester; they were unable to detect any rearrangement and therefore concluded that species analogous to I were not involved. Various examples, all involving stereochemical studies in acyclic or monocyclic systems, have recently appeared,[7-9] which support the concept that bridged radicals such as II have no significant existence as reaction intermediates.

I



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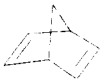

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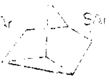
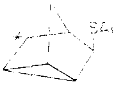


V

The present research was undertaken to investigate the addition of thiols to 2,5-norbornadiene (bicyclo[2,2,1]hepta-2,5-diene (III)) to look into the nature of the 1:1 addition products as involving 1,2-addition (IV) or 1,5-homoconjugative addition (V), and to determine whether the products are derived from the two isomeric free radicals VI and VII or from a non-classical mesomeric homoallylic radical which might be represented as VIII for which VI and VII might be considered resonance structures. The possibility of such a mesomeric radical has been discussed earlier.[10] This system is of interest in the study of radical-rearrangement processes because reactions which produce an analogous carbonium-ion intermediate are usually accompanied by homoallylic rearrangements.[11] Thus, for example, the methanolysis of cholesteryl *p*-toluenesulfonate proceeds with rearrangement to form *i*-cholesteryl methyl ether.[12,13] Winstein and co-workers demonstrated that this rearrangement proceeds *via* a mesomeric carbonium-ion intermediate.[14,15]

VI



VII

VIII

IX

Winstein, Walborsky and Schreiber[16] found that the acetolysis of *exo*-5-norbornen-2-yl *p*-toluenesulfonate proceeds through a similar intermediate to form 3-nortricyclyl acetate.

Recently, Winstein and Shatavsky[17,18] reported that the addition of bromine, and of several other

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[1] Previous paper in series: S. J. Cristol and R. P. Arganbright, THIS JOURNAL, **79**, 6039 (1957).

[2] A portion of the work described in this paper was presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, April, 1955.

[3] M. S. Kharasch, A. T. Read and F. R. Mayo, *Chemistry & Industry*, 752 (1938).

[4] S. O. Jones and E. E. Reid, THIS JOURNAL, **60**, 2452 (1938).

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

[6] J. A. Berson and W. M. Jones, *ibid.*, **78**, 6045 (1956).

[7] (a) H. L. Goering, P. I. Abell and B. F. Aycock, *ibid.*, **74**, 3588 (1952); (b) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955); (c) H. L. Goering, D. I. Relyea and D. W. Larsen, *ibid.*, **78**, 348 (1956).

[8] (a) P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955); (b) P. S. Skell, R. C. Woodworth and J. H. McNamara, *ibid.*, **79**, 1253 (1957).

[9] (a) F. G. Bordwell and W. A. Hewett, Abstracts of the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954, p. 6-O; (b) F. G. Bordwell and N. P. Neureiter, Abstracts of the 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957, p. 10-O.

[10] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3116 (1950).

[11] For a general review of such ionic rearrangements, see P. D. Bartlett in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 63–70.

[12] W. Stoll, *Z. physik. Chem.*, **207**, 147 (1932); **246**, 6 (1937).

[13] E. S. Wallis, E. Fernholz and F. T. Gephart, THIS JOURNAL, **59**, 137 (1937).

[14] S. Winstein and R. Adams, *ibid.*, **70**, 838 (1948).

[15] S. Winstein and A. H. Schlesinger, *ibid.*, **70**, 3528 (1948).

[16] S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **72**, 5795 (1950).

[17] S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

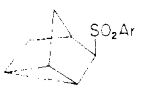
[18] S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56, (1956).

ionic reagents, to norbornadiene (III) gives products which arise as the result of two simultaneous rearrangements, one a homoallylic rearrangement resulting in 3,5-disubstituted nortricyclene derivatives (1,5-homoconjugative addition), and the other an alternative reaction of the intermediate mesomeric carbonium ion to form 5,7-disubstituted derivatives of norbornene. Winstein and his coworkers have postulated the existence of intermediates similar to IX to explain their solvolysis results[16] and the addition results.[17,18]

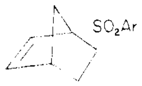
Schmerling, Luvisi and Welch[19] have also described the addition of various ionic reagents to norbornadiene to give mixtures of norbornene derivatives and nortricyclene derivatives, and Bluestone, Hyman, Lidov and Soloway[20] have noted that both 1,2- and 1,5-homoconjugative addition reactions occur in a variety of ionic and free-radical addition reactions.

In view of the demonstrated 1,3-interaction between an olefinic group and a carbonium-ion center, it was of interest to determine whether or not such an interaction might exist in the case of an olefinic group beta to a free radical center. Just such a situation would come about in a free-radical chain addition to I. One double bond would be attacked, the mercapto radical would become attached to one carbon atom, and an unshared electron would appear on the adjacent non-bridgehead carbon atom (VI). This unshared electron is beta to the olefinic double bond. Electron delocalization (*i.e.*, interaction of the odd electron with the β-double bond) should lead to the non-classical homoallylic radical VIII, which might be expected to undergo chain transfer at both unsaturated centers to give a mixture of IV and V.

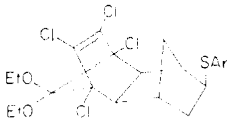
When norbornadiene was treated with an approximately equimolar amount of *p*-thiocresol, a highly exothermic reaction occurred. The resulting mixture was submittted to vacuum distillation to give yields ranging from 78–96% of a mixture of *exo*-5-norbornen-2-yl *p*-tolyl thioether (IV) and 3-nortricyclyl *p*-tolyl thioether (V). This mixture consisted of 40% of IV and 60% of V as indicated by quantitative hydrogenation. The structure of the nortricyclyl *p*-tolyl thioether component was demonstrated by oxidation of the mixture with hydrogen peroxide in acetic acid to give 3-nortricyclyl *p*-tolyl sulfone (X). Only one sulfone was isolated in this procedure. As this sulfone did not react in the cold with dilute potassium permanganate in acetone or with bromine in carbon tetrachloride, and as it did not absorb any hydrogen over a palladium-on-charcoal catalyst, an olefinic double bond was apparently not present in the molecule. The corresponding *endo*- and *exo*-norbornenyl aryl thioethers and sulfones react rapidly with all three reagents. The nortricyclene structure for the sulfone X is consistent with these properties. Infrared spectral evidence is not conclusive for V or its sulfone when Ar is *p*-tolyl, as *p*-disubstituted benzenes absorb at 11.9–12.4 μ,[21–24] a range overlapping the 12.3–12.5 μ range for nortricyclenes.[10] However, the phenyl analog had chemical properties like those of the *p*-tolyl analog and had an infrared absorption band at 12.34 μ. Hence one component of the reaction mixture is V.



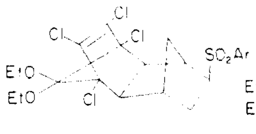
X



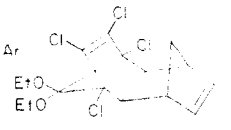
XI



XII



XIII



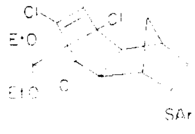
XIV

exo-5-Norbornen-2-yl *p*-tolyl thioether (IV) was identified as the other component of the reaction mixture by the formation of its Diels–Alder addition product with 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene. Thus, when the product mixture of thioethers was treated with the tetrachlorinated diene ketal, a 32% yield of the *exo*-thioether 1,2,3,4-tetrachloro-9,9-diethoxy-1,4,4a,-5,6,7,8,8a-octahydro-7-*p*-thiocresoxy-1,4,5,8-dimethanonaphthalene (XII) resulted. Oxidation of this thioether with 30% hydrogen peroxide in pyridine gave the corresponding *exo*-sulfone XIII.

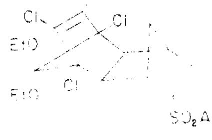
Evidence that the dehydronorbornyl thioether component of the bicycloheptadiene–mercaptan reaction mixture is *exo* stems from the formation of a Diels–Alder addition product of 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene with a known sample of *exo*-norbornenyl *p*-tolyl sulfone (XI)[5] which in turn has been related to *exo*-norbornyl *p*-tolyl sulfone by several independent methods as described in a previous paper.[5] This product was identical with the sulfone prepared from the addition reaction mixture. In addition, a sample of XII was prepared by addition of *p*-thiocresol to XIV. The two samples were identical, as were their sulfones.

On the other hand, treatment of *endo*-5-norbornen-2-yl *p*-tolyl thioether (XV)[5,25] with 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene gave the *endo*-sulfide XVI, which could be distinguished readily from the various preparations of XII. The corresponding sulfone XVII was also readily distinguished from the *exo* isomer XIII.

XV



XVI



XVII

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[19] L. Schmerling, J. P. Luvisi and R. W. Welch, THIS JOURNAL, **78**, 2819 (1956).

[20] (a) H. Bluestone, S. B. Soloway, J. Hyman and R. E. Lidov, U. S. Patent 2,730,548 (Jan. 10, 1956); (b) U. S. Patent 2,738,356 (Mar. 13, 1956); (c) U. S. Patent 2,782,238 (February 19, 1957).

[21] D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 268 (1945).

[22] H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 246 (1945).

[23] R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

[24] J. Cymerman and J. B. Willis, *J. Chem. Soc.*, 1332 (1951).

[25] K. Alder, H. F. Rickert and E. Windemuth, *Ber.*, **71**, 2451 (1938).

The free-radical chain nature of the reaction was confirmed by a study of the effect of peroxide catalysts and of peroxide inhibitors on the rate of the reaction. The addition reaction is highly exothermic, and when a mixture of 4 millimoles of *p*-thiocresol and 4 millimoles of norbornadiene was placed in a test-tube containing a thermometer, the temperature first fell, due presumably to the heat of mixing, and then rose rapidly to 125°, requiring only one minute to reach the maximum temperature (see the solid curve, Fig. 1). When about 10 mg. (0.04 mmole) of benzoyl peroxide was added in another experiment, the temperature did not fall, but rose rapidly to a maximum of 110° in 30 sec. (see the dashed curve, Fig. 1). On the other hand, when 223 mg. (1.34 mmoles) of 4-*t*-butylcatechol was added, the reaction was moderated (Fig. 1, dotted curve). The addition of 400–500 mg. of 4-*t*-butylcatechol moderated the reaction strikingly (Fig. 1, dotted curve). These results appear to be sufficient to establish the radical course of the reaction.[3]

The *p*-thiocresoxy radical appears to be much more reactive toward norbornadiene than toward either norbornene or cyclohexene. In experiments in which norbornadiene and norbornene in an equimolar ratio were made to compete for slightly more than one mole of *p*-thiocresol, pure norbornene was recovered. In a similar experiment with cyclohexene instead of norbornene, a 74% recovery of pure cyclohexene was obtained.

The mechanism for the radical-chain portion of the reaction must account for the rearranged product 3-nortricyclyl *p*-tolyl thioether (V) as well as for the unrearranged product IV. One possibility is shown by equations 3-6. This mechanism postulates that the substituted norbornenyl radical VI which is formed in reaction 3 rearranges to the substituted nortricyclyl radical VII at a finite rate, and that these may undergo chain transfer reactions 5 or 6, which trap either the unrearranged or the rearranged radicals.

$$\mathrm{ArS^* + III \longrightarrow VI} \qquad (3)$$

$$\mathrm{VI} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \mathrm{VII} \qquad (4)$$

$$\mathrm{VI + ArSH} \xrightarrow{k_5} \mathrm{IV + ArS^*} \qquad (5)$$

$$\mathrm{VII + ArSH} \xrightarrow{k_6} \mathrm{V + ArS^*} \qquad (6)$$

Another plausible mechanism is one in which the non-classical radical VIII is the intermediate, having 60% of the chain transfer reactions occurring at position 5 and 40% occurring at position 2. Such a mechanism would explain the *exo* nature of product IV, although this explanation does not appear necessary.[5] This mechanism is summarized in equations 7–9.

$$\mathrm{ArS^* + III \longrightarrow VIII} \qquad (7)$$

$$\mathrm{VIII + ArSH} \xrightarrow{k_8} \mathrm{IV + ArS^*} \qquad (8)$$

$$\mathrm{VIII + ArSH} \xrightarrow{k_9} \mathrm{V + ArS^*} \qquad (9)$$

In order to distinguish between these two mechanisms, we devised an experiment based on the method of Seubold,[26] which enabled him to decide against a mesomeric radical in the rearrangement of the neophyl free radical. If the intermediate in the reaction common to both reaction products were the non-classical radical VIII, then equations 7–9 would apply, from which the following can be deduced

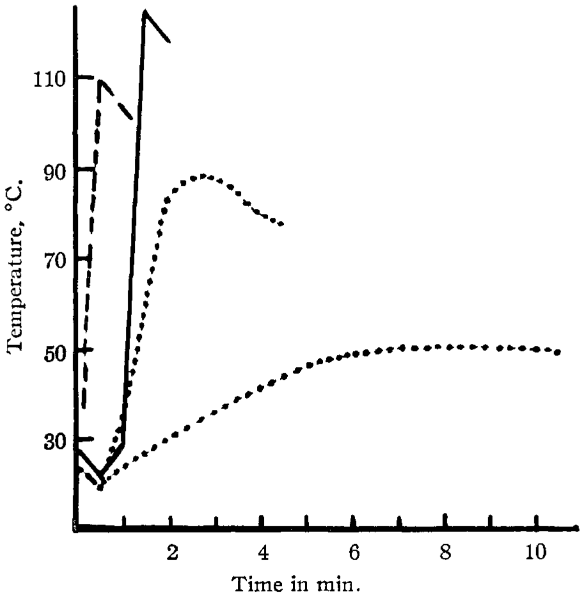

Fig. 1.—Time–temperature relationships in the reaction of *p*-thiocresol with norbornadiene: solid line, no addendum; dashed line, with benzoyl peroxide; upper dotted line, 223 mg. of 4-*t*-butylcatechol added; lower dotted line, 400–500 mg. of 4-*t*-butylcatechol added.

$$\mathrm{d(IV)}/\mathrm{d}t = k_8\mathrm{(VIII)(ArSH)} \qquad (10)$$

$$\mathrm{d(V)}/\mathrm{d}t = k_9\mathrm{(VIII)(ArSH)} \qquad (11)$$

$$\frac{\mathrm{(V)}}{\mathrm{(IV)}} = \frac{k_9\mathrm{(VIII)(ArSH)}}{k_8\mathrm{(VIII)(ArSH)}} = \frac{k_9}{k_8} = \text{constant} \qquad (12)$$

Thus, the ratio of rearranged V to unrearranged product IV would be independent of the concentration of the reactants.

On the other hand, if the two classical radicals VI and VII are the actual progenitors of IV and V, then the following can be deduced from equations 3–6

$$\mathrm{d(IV)}/\mathrm{d}t = k_5\mathrm{(VI)(ArSH)} \qquad (13)$$

$$\frac{\mathrm{d(V)}}{\mathrm{d}t} = k_4\mathrm{(VI)}\frac{k_6\mathrm{(ArSH)}}{k_6\mathrm{(ArSH)} + k_{-4}} \qquad (14)$$

If k_{-4} is very large compared with k_6(ArSH), this reduces to

$$\frac{\mathrm{d(V)}}{\mathrm{d}t} = \frac{k_4k_6}{k_{-4}}\mathrm{(VI)(ArSH)} \qquad (15)$$

and the results of a rapid equilibrium between VI and VII could not be distinguished from the resonance hybrid situation VIII.

However, if k_6(ArSH) is very large compared with k_{-4}, equation 14 reduces to

$$\frac{\mathrm{d(V)}}{\mathrm{d}t} = k_4\mathrm{(VI)}\frac{k_6\mathrm{(ArSH)}}{k_6\mathrm{(ArSH)}} = k_4\mathrm{(VI)} \qquad (16)$$

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(26) F. H. Seubold, THIS JOURNAL, **75**, 2532 (1953).

and

$$\frac{(\text{V})}{(\text{IV})} = \frac{k_4(\text{VI})}{k_5(\text{VI})(\text{ArSH})} = \frac{k_4}{k_5(\text{ArSH})} \qquad (17)$$

and one notes that the ratio of rearranged product V to unrearranged product IV would be inversely proportional to the concentration of mercaptan in the reaction mixture. If k_{-4} and k_6(ArSH) are comparable in magnitude, then a variation in product composition with mercaptan concentration would be noted experimentally, although the exact relationship shown in equation 17 would, of course, not be followed.

We therefore allowed norbornadiene to react with *p*-thiocresol at various dilutions, estimating the percentage of olefin in the products by quantitative hydrogenation in 95% ethanol over 10% palladium-on-charcoal catalyst. The results are summarized in Table I. The methods of presentation of the tabulated results are as follows. The product yield was measured after two distillations, hence much of the losses was mechanical. The uncorrected ratio V/IV follows the assumption that loss of V and IV in distillation was proportional to the presence of each in the final product, *i.e.*, that there was no fractionation at this stage. One should note, however, that the olefin IV is capable of further reaction with mercaptan or with other reagents while the nortricyclene derivative V is much less reactive; hence, we have also calculated a weighted ratio, calculated by multiplying the observed yield by the observed content of V, and assuming that the remainder (isolated + loss) was IV. Experiments 1, 2 and 3 represent conditions of decreasing concentration of mercaptan; one observes that, as predicted by equation 17, the ratio of nortricyclene V to olefin IV increases markedly with decrease in concentration of mercaptan.

TABLE I

REACTION CONDITIONS, YIELDS AND PRODUCT COMPOSITIONS IN THE ADDITION OF *p*-THIOCRESOL TO NORBORNADIENE

Expt.[a]	Product yield, %[b]	Mole % hydrogen uptake[b]	Ratio V/IV Uncor.[c]	Ratio V/IV Weighted[d]
1[e]	80.2	42.9 ± 0.5[j]	1.3	0.84
2[f]	84.8	31.6 ± .3[j]	2.2	1.4
3[g]	83.2	20.3 ± .5[j]	3.9	2.0
4[h]	82.4	28.6 ± .3[k]	2.5	1.4
5[i]	85.0	45.0 ± .4[j]	1.2	0.88

[a] All experiments except 4 were cooled in an ice-bath. [b] After two distillations. [c] Ratio of rearranged to unrearranged product, assuming that isolated product represents whole product. [d] Ratio of rearranged to unrearranged product, assuming that all losses were olefin IV. [e] 1:1 molar ratio of III and ArSH, no solvent. [f] 1:1 molar ratio of III and ArSH, diluted with 10 volumes of chlorobenzene. [g] ArSH added dropwise to an equimolar quantity of III in 10 volumes of chlorobenzene. [h] Same as expt. 2, but heated to 105°. [i] Same as expt. 1, but with 10 volumes of ethylene glycol to act as heat absorber. [j] Average of 5 determinations. [k] Average of 3 determinations.

Since the addition reaction is highly exothermic, the reaction mixture becomes hot when no diluent is used. It seemed possible that the increase in rearrangement with dilution of the reaction mixture might reflect a temperature effect rather than a concentration effect. Thus in the fourth experiment the diluted reactants were mixed at 105°, and in the fifth experiment the undiluted reactants were stirred with ethylene glycol, which did not dissolve the reactants but was present to act as a coolant. Comparison of experiments 4 and 2 shows that if there is any significant temperature effect it is small and not in the right direction to cause the dilution effect. A comparison of experiments 1 and 5 again indicates the unimportance of the temperature effect.

Thus the experimental results demonstrate quite clearly that the mesomeric radical intermediate VIII cannot be the common progenitor of IV and V, but that two separate radical species must be involved. For the present, there seems to be no experimental reason to assume that these radicals are not the classical free radicals VI and VII.[27]

It was observed that a *p*-thiocresoxy radical reacts more rapidly with norbornadiene than with norbornene and cyclohexene, and earlier it was noted[5] that norbornene was considerably more reactive than cyclohexene. As there is no evidence for the formation of resonance-stabilized radicals of type I or VIII, the enhanced reactivity of the bicyclic diolefin (and olefin) can probably be best rationalized in terms of relative destabilizations of reactants, owing to the highly strained olefinic bicyclic compounds.

Acknowledgments.—The authors are indebted to the Shell Development Co. for generous support of this work, for fellowship support (G.D.B.) and (J.A.R.), as well as for samples of norbornadiene and 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene. We are further indebted to H. Bluestone, R. E. Lidov, J. Hyman and S. B. Soloway[20] for helpful discussions and for disclosure of their results prior to publication.

Experimental

Addition of *p*-Thiocresol to Norbornadiene.—*p*-Thiocresol (37.6 g., 0.34 mole) was added in small portions with stirring to 32.2 g. (0.35 mole) of norbornadiene with cooling in an ice–salt-bath. The reaction becomes dangerously exothermic if the heat generated is not dissipated by an effective cooling medium. The reaction mixture was stirred for 20 minutes after the final addition of *p*-thiocresol, and was then subjected to vacuum distillation. A fraction boiling from 105–132° (1 mm.) was collected, which weighed 67.2 g. (91%).

The above liquid was redistilled for preparation of an analytical sample. The sample boiled at 125–131° (1 mm.) and had a refractive index $n^{20.5}$D 1.5840.

Anal. Calcd. for $C_{14}H_{16}S$: C, 77.72; H, 7.46. Found: C, 77.52; H, 7.59.

Preparation of 3-Nortricyclyl *p*-Tolyl Sulfone (X).—A slight molar excess of 30% hydrogen peroxide was added to a solution of 1.064 g. (4.93 mmoles) of the addition product in

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(27) Simonetta and Winstein[28] have calculated the stabilization due to π-electron delocalization in the case of vinyl groups β to a cationic carbon center. Their calculations indicate that the nonclassical carbonium ion IX is considerably more stable than the model electron-localized 5-norbornen-2-yl cation; this result is consistent with many experimental observations. If one utilizes the model and assumption of Simonetta and Winstein for the cation and adds a third electron to give the radical, the third electron will go into a nonbonding orbital, but the radical will have resonance energy identical with that of the cation.[29] If these calculations are proper and correct, then the two individual radicals may be best denoted by VIII and VII. Experimental evidence is not available at present to test this possibility, and we therefore will utilize the formulation of the separate radicals as VI and VII.

(28) M. Simonetta and S. Winstein, THIS JOURNAL, **76**, 18 (1954).

(29) This calculation was made by Dr. J. deHeer, to whom the authors are indebted.

4 ml. of glacial acetic acid. The mixture was heated at reflux for one hour and enough additional hydrogen peroxide was added to give a strong test with starch-iodide paper. The mixture was heated at reflux for two more hours; the solvent was then evaporated under reduced pressure. The residue was extracted with two 75-ml. portions of low-boiling petroleum ether. Concentration and cooling of the extract gave 392 mg. (32%) of white crystals, m.p. 69–76°. Two recrystallizations from ethanol–water gave crystals of X melting at 76–77° after drying.

Anal. Calcd. for $C_{14}H_{17}O_2S$: C, 67.71; H, 6.50. Found: C, 67.91; H, 6.54.

This compound did not decolorize dilute potassium permanganate in acetone or bromine in carbon tetrachloride. It absorbed no hydrogen over a 10% palladium-on-charcoal catalyst.

Preparation of 1,2,3,4-Tetrachloro-9,9-diethoxy-1,4,4a,5,6,7,8,8a-octahydro-7-*exo*-*p*-thiocresoxy-1,4,5,8-dimethanonaphthalene (XII).—A sample of the purified addition product weighing 1.022 g. (4.73 mmoles) was heated at 150° with 1.039 g. (3.56 mmoles) of 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene for 4 hours. The reaction mixture was chromatographed on a column of alumina. Elution with 1500 ml. of petroleum ether in 100-ml. fractions gave an oil which was probably diene. Elution with 200 ml. of carbon tetrachloride in two portions gave 583 mg. (32%) of a solid, m.p. 100–106°. This solid was recrystallized twice from 95% ethanol and gave crystals melting at 117–117.5°. A third ethanol recrystallization gave pure XII of 118–118.5°.

Anal. Calcd. for $C_{23}H_{26}Cl_4O_2S$: C, 54.34; H, 5.16. Found: C, 54.43; H, 5.37.

Preparation of 1,2,3,4-Tetrachloro-9,9-diethoxy-1,2,3,4,4a,5,6,7,8,8a-octahydro-7-*exo*-*p*-toluenesulfonyl-1,4,5,8-dimethanonaphthalene (XIII).—A mixture of 116 mg. (0.228 mmole) of the thioether prepared in the experiment above, 5 ml. of pyridine and a small excess of 30% hydrogen peroxide was heated for 8 hr. on a steam-bath with addition of several drops of 30% hydrogen peroxide. The addition of water to the reaction mixture precipitated a fine oil which could be coagulated by adding sodium chloride. The coagulated material was crystallized from low-boiling petroleum ether to give a 64% yield of crystals, m.p. 216–222°. Recrystallization from low-boiling petroleum ether followed by recrystallization from 95% ethanol gave XIII, m.p. 225–226°.

Anal. Calcd. for $C_{23}H_{26}Cl_4O_4S$: C, 51.12; H, 4.85. Found: C, 51.31; H, 5.03.

Formation of the Diels–Alder Addition Product of *exo*-5-Norbornen-2-yl *p*-Tolyl Sulfone (XI) and 1,2,3,4-Tetrachloro-5,5-diethoxycyclopentadiene.—A sample of 51 mg. (0.205 mmole) of *exo*-norbornen-2-yl *p*-tolyl sulfone[5] was dissolved in 2 ml. of 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene and heated at 138° for 12 hours. The reaction mixture was steam distilled until the distillate showed only traces of oil. Water was decanted from the gummy residue which was then crystallized from 95% ethanol. The crystals were washed with a little ethanol. The solid weighed 81 mg. (73%), m.p. 220–221°. Another ethanol crystallization gave slightly impure XIII, m.p. 221–222°. When mixed with the sulfone XIII from the preceding experiment, it melted at 221–223.5°.

Addition of *p*-Thiocresol to 1,2,3,4-Tetrachloro-9,9-diethoxy-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene (XIV).—A sample of 3.5 g. (0.034 mole) of norbornadiene was heated for 5 hours with 6.08 g. (0.026 mole) of 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene in a sealed glass tube. A solid crystallized in the tube on standing at room temperature. Recrystallization from ethanol–water gave 2.98 g. (38%) of crystals which softened at 80° and melted completely at 105°. Recrystallization from ethanol–water gave a solid, m.p. 93–94.5°. A second crop from the first recrystallization weighing 0.32 g. melted at 92–93°. The combined yield of impure XIV was 42%. A mixture of 214 mg. (0.558 mmole) of XIV, 5 ml. of benzene, 75 mg. (0.6 mmole) of *p*-thiocresol and a trace of bicycloheptadiene (as a source of peroxides) was heated at reflux for one hour. The solvent was then removed by evaporation. The addition of a few ml. of methanol to the residue allowed a white solid to crystallize. The solid, weighing 111 mg. (40%), m.p. 108–110°, was recrystallized from a methanol–ethanol mixture to give XII, m.p. 116–118°. When mixed with the *exo*-thioether XII described above, the melting point was 117.5–118.5°.

Diels–Alder Addition Product of 1,2,3,4-Tetrachloro-5,5-diethoxycyclopentadiene and *endo*-5-Norbornen-2-yl *p*-Tolyl Thioether.—A solution of 1.26 g. (5.8 mmoles) of 5-norbornen-2-yl *p*-tolyl thioether,[5] which is known to be largely the *endo* isomer,[5] and 2.56 g. (8.8 mmoles) of 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene in 5 ml. of dry toluene was heated at reflux for 40 hours. After this time, the reaction mixture was steam distilled until the distillate showed only traces of oil. Water was decanted from the gummy residue. This residue produced 1.0 g. (34%) of XV, m.p. 125–126°. When mixed with the isomeric *exo*-thioether XIII, the m.p. was 104–108°.

Anal. Calcd. for $C_{23}H_{26}Cl_4O_2S$: C, 54.34; H, 5.16. Found: C, 54.52; H, 5.05.

Preparation of 1,2,3,4-Tetrachloro-9,9-diethoxy-1,4,4a,5,6,7,8,8a-octahydro-7-*endo*-*p*-toluenesulfonyl-1,4,5,8-dimethanonaphthalene (XVII).—A mixture of 157 mg. (0.309 mmole) of XVI, 5 ml. of pyridine and a slight excess of 30% hydrogen peroxide was heated for 8.5 hr. on a steam-bath. The solvent was evaporated, and the residue was crystallized from low-boiling petroleum ether to give 78 mg. (47%) of a solid, m.p. 198–198.5°. Two recrystallizations from petroleum ether gave XVII, m.p. 200.5–201°.

Anal. Calcd. for $C_{23}H_{26}Cl_4O_4S$: C, 51.12; H, 4.85. Found: C, 51.16; H, 4.92.

Addition of Thiophenol to Norbornadiene.—In a 200-ml. three-necked flask equipped with a stirrer, thermometer and a reflux condenser, was placed 56.1 g. (0.61 mole) of norbornadiene. The diene was freshly distilled (b.p. 82–83.5° at 627 mm.) but was not kept under nitrogen. To the stirred diene was added 62.2 ml. (67 g., 0.61 mole) of thiophenol from an addition funnel through the reflux condenser. The mercaptan was added to the diene very slowly (several drops at one time) at the beginning of the reaction. It was added in larger portions as the reaction proceeded. The temperature of the reaction mixture was kept under 30° in about the first third of the reaction, under 40° in the second third and under 60° in the final third. The mercaptan was added over a 2.5-hr. period.

The colorless reaction mixture was subjected to vacuum distillation and the fraction boiling at 108–114° (0.8 mm.), $n^{21}D$ 1.5937 was collected. It consisted of 108.9 g. (88.6%) of a clear, straw-colored liquid. A hydrogenation experiment[30] indicated that this material contained about 40% olefinic material.

Anal. Calcd. for $C_{13}H_{14}S$: C, 77.18; H, 6.98. Found: C, 77.33; H, 7.13.

Preparation of Nortricyclyl Phenyl Sulfone.—A mixture of 893 mg. (4.42 mmoles) of the norbornadiene–thiophenol addition mixture, 5 ml. of dry acetic acid (containing acetic anhydride) and 1.7 ml. of 30% hydrogen peroxide was heated on a steam-bath for 30 minutes and allowed to stand at room temperature for about 36 hours. Addition of ice and water precipitated a milky oil which later crystallized. The crystals were filtered and washed with 50 ml. of cold water. When dry they weighed 0.88 g. (85%) and had a melting range of 57–77°. This material did not decolorize dilute potassium permanganate in acetone. One recrystallization from petroleum ether gave 575 mg. (55%) of white crystals, m.p. 77–79°. Two additional recrystallizations from the same solvent gave needles, m.p. 79.5–80.1°. This material did not decolorize dilute potassium permanganate in acetone on standing several hours at room temperature. The infrared spectrum of this compound showed a strong absorption peak at 12.34 μ.

Anal. Calcd. for $C_{13}H_{14}SO_2$: C, 66.64; H, 6.02. Found: C, 66.81; H, 6.09.

Hydrogenation of *endo*-5-Norbornen-2-yl *p*-Tolyl Thioether (XV).—A sample of the *endo*-norbornenyl *p*-tolyl thioether weighing 436 mg. (2.02 mmoles) was hydrogenated in 45 ml. of ethanol with reduced 10% palladium-on-charcoal catalyst. It absorbed 108 mole % of hydrogen (64.5 ml. at 26° and 630 mm.).

Competition of Norbornadiene and Norbornene for *p*-Thiocresol.—To a mixture of 921 mg. (10 mmoles) of norbornadiene and 942 mg. (10 mmoles) of norbornene cooled in an ice-bath, 1.304 g. (10.5 mmoles) of *p*-thiocresol was added

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(30) We are indebted to Dr. R. Heitz for this experiment.

and the reaction allowed to take place slowly. When the reaction was complete, the mixture was distilled at atmospheric pressure (630 mm.). Material boiling near 75° solidified in the condenser, and the plug of solid was pushed through into the receiver, which was cooled in a Dry Ice-bath. The weight of solid distillate was 0.63 g. The recovery of norbornene was 69%.

Competition of Norbornadiene and Cyclohexene for *p*-Thiocresol.—This experiment was carried out in essentially the same manner as that described above. To a mixture of 939 mg. (10.2 mmoles) of norbornadiene and 822 mg. (10.0 mmoles) of cyclohexene at Dry Ice temperature, 1.304 g. (10.5 mmoles) of *p*-thiocresol was added and the reaction allowed to take place as the reactants warmed to room temperature. The reaction mixture was distilled at 630 mm., and 591 mg. (74%) of a liquid, b.p. 69°, $n^{20}\mathrm{D}$ 1.4465, was collected. The refractive index of the starting cyclohexene, $n^{20}\mathrm{D}$, was 1.4465.

Dilution Experiments with the Addition of *p*-Thiocresol to Norbornadiene. First Experiment.—Norbornadiene, 4.49 g. (48.6 mmoles) was stirred with 6.0 g. (48.6 mmoles) of *p*-thiocresol in a flask cooled in an ice-bath. After one hour, the reaction mixture was submitted to vacuum distillation, yielding 8.97 g. (85.5%) of a light yellow oil, b.p. 110–120° (0.8 mm.). No solids or dark tarry residue were found in the distillation flask. The oil was distilled again, giving a final yield of 8.39 g. (80.2%) of colorless oil. In all distillations in this series, an electrically heated oil-bath was used to avoid overheating the products.

Second Experiment.—A solution of 6.0 g. (48.6 mmoles) of *p*-thiocresol in 50 ml. of chlorobenzene, $n^{20}\mathrm{D}$ 1.5252, was stirred with 4.49 g. (48.6 mmoles) of norbornadiene in a flask cooled with an ice-bath. After two hours, the reaction mixture was submitted to vacuum distillation. After removal of the solvent, 9.27 g. (88.3%) of a colorless oil, b.p. 88–122° (0.5 mm.), was obtained, which was redistilled to give 8.90 g. (84.8%) of colorless oil, b.p. 90–112° (0.5 mm.). No solids or dark tarry residue were found in the distillation flask in either of these distillations.

Third Experiment.—A solution of 4.49 g. (48.6 mmoles) of norbornadiene in 40 ml. of chlorobenzene was stirred in a flask cooled with an ice-bath, and 6.0 g. (48.6 mmoles) of *p*-thiocresol dissolved in 10 ml. of chlorobenzene was added dropwise over a period of two hours. After one additional hour the reaction mixture was submitted to vacuum distillation. After removal of the solvent, 9.22 g. (87.9%) of a colorless oil, b.p. 90–117° (0.5 mm.) was obtained, and this was redistilled to give 8.71 g. (83.2%) of colorless oil, b.p. 90–113° (0.4 mm.).

Fourth Experiment.—A solution of 6.0 g. (48.6 mmoles) of *p*-thiocresol in 50 ml. of chlorobenzene was heated in an oil-bath to 105°, and then 4.49 g. (48.6 mmoles) of norbornadiene was poured in rapidly. The temperature of 105° was maintained for two hours with stirring. The reaction mixture was immediately distilled under vacuum, yielding 9.37 g. (89.5%) of colorless oil, b.p. 110–136° (0.8 mm.) after removal of the solvent. No solid or dark tarry material was in evidence in the distillation flask. The products were distilled again, yielding 8.67 g. (82.4%) of colorless oil boiling at 100–110° (0.2 mm.).

Fifth Experiment.—A mixture of 6.0 g. (48.6 mmoles) of *p*-thiocresol and 4.49 g. (48.6 mmoles) of norbornadiene was stirred vigorously with 50 ml. of reagent-grade ethylene glycol in a flask cooled with an ice-bath. The temperature of the reaction mixture was maintained at 5–15° for 30 minutes, and then at 20–25° for two hours, after which the mixture was extracted four times with petroleum ether, b.p. 59–61°. The organic layer was dried over magnesium sulfate, and the solvent was removed. The residue was subjected to vacuum distillation, yielding 9.58 g. (91.3%) of a colorless oil, b.p. 115–134° (0.4 mm.). The residue from this distillation consisted of 0.68 g. (6.4%) of an impure solid, m.p. 58–90°, which was recrystallized six times from acetone and from petroleum ether to give an analytical sample, m.p. 116–117°. This material took up no hydrogen over a 10% palladium-on-charcoal catalyst, and analyzed for the addition product of two moles of thiocresol and one of diolefin.

Anal. Calcd. for $C_{21}H_{24}S_2$: C, 74.05; H, 7.12; S, 18.83. Found: C, 74.25; H, 6.97; S, 18.57.

In three other experiments in which water instead of ethylene glycol was used as the coolant, the crude yields of solid residue ranged from 19.2–24.8%.

The oil obtained above was redistilled, yielding 8.92 g. (85.0%) of colorless oil, b.p. 110–125 (0.4 mm.).

Estimation of Unsaturation.—In a typical experiment, 100 mg. of 10% palladium-on-charcoal catalyst was weighed into a hydrogenation flask, 15 ml. of 95% ethanol was added, and the flask was shaken on a quantitative (atmospheric pressure) hydrogenator for 10–15 minutes, during which time 2.2 ml. of hydrogen was taken up. The flask was taken off and the hydrogen atmosphere in it removed. Then 0.1140 g. (0.5253 mmole) of the oil from dilution experiment 1 was washed into the flask with 25 ml. of 95% ethanol in small portions. The flask was then shaken on the quantitative hydrogenator for 15 minutes, at which time a constant value of 6.70 ml. of hydrogen had been taken up. This volume was corrected to standard conditions by the use of the ideal gas law, and gave a value of 5.08 ml., or 43.2 mole percentage of hydrogen uptake.

BOULDER, COLORADO

[CONTRIBUTION FROM RESEARCH DEPARTMENT, HOWARDS OF ILFORD, LTD.]

Chemical Reductions of Substituted Cyclohexanones

BY K. D. HARDY AND R. J. WICKER

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Substituted cyclohexanones have been chemically reduced with four different reagents and the stereoisomeric composition of the products determined. The results obtained do not support any of the generalizations made by previous workers as to the differing effects of the reagents used.

Although a considerable number of examples of the proportions of *cis* and *trans* isomers produced by chemical reduction of substituted cyclohexanones have been reported in the literature, much of the work is of little value since the methods used in establishing the stereoisomeric compositions of the products of reduction are not reliable.[1]

Noyce and his co-workers have carried out a number of hydride reductions recently[2,3] and have developed a theory to account for their results.[3] Their analytical procedure was sound and was based on the determination of the densities of the products they obtained.

We have reduced 2-, 3- and 4-methylcyclohexanones, dihydroisophorone and 4-cyclohexylcyclohexanone with lithium aluminum hydride, potassium borohydride, sodium and alcohol, and aluminum isopropoxide, and determined the isomeric composition of the products by either density measurements or thermal analysis. The results of the present work are given in Table I, together with the results of previous workers where these are based on reliable analytical methods.

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(1) E. G. Peppiatt and R. J. Wicker, *Chemistry & Industry*, 747 (1955).

(2) D. S. Noyce and D. B. Denney, THIS JOURNAL, **72**, 5743 (1950).

(3) W. G. Dauben, G. J. Fonken and D. S. Noyce, *ibid.*, **78**, 2579 (1956).