TABLE III

PROPERTIES OF ALKYLPHOSPHONYL DICHLORIDES, $RPOCl_2$

R Group	B.p. °C.	B.p. Mm.	Empirical formula	Chlorine, % Found	Chlorine, % Calcd.	$n^{20}D$	d^{20}_4
Cyclopentyl	98	6.2	$C_5H_9Cl_2OP$	38.20 38.18	37.92	1.4973	1.3171
γ-Chloropropyl	88	2	$C_3H_6Cl_3OP$	54.36 54.32	54.43	1.4928	1.4580
Methylcyclopentyl	99	5	$C_6H_{11}Cl_2OP$	37.28 37.33	35.27	....	....
Methylcyclohexyl	121.5	7	$C_7H_{13}Cl_2OP$	33.04 32.24	33.13	....	....
2,3-Dimethylbutyl	80 95	15 9	$C_6H_{13}Cl_2OP$	40.10	34.92	....	....

showed that the first acidic hydrogen could be titrated with an indicator, which changes color in the range *p*H 4.6–5.6.

Anal. Calcd. for $C_6H_{11}O_3P$: P, 20.64. Found: P, 20.48, 20.43.

Diisopropyl γ-Chloropropylphosphonate (I).—3-Chloro-1-propanol (b.p. 74–76° (28 mm.)) was prepared in a 58.2% yield by the method of Marvel and Calvery.[26] This alcohol was converted into 1-chloro-3-iodopropane (b.p. 72–74° (27 mm.)) in a 60.5% yield by the method of Case.[27] 1-Chloro-3-iodopropane (204.5 g., 1 mole) was heated to reflux under vacuum (29 mm.) and 208 g. (1 mole) of triisopropyl phosphite was added dropwise. After refluxing the mixture for 18 hours to complete the reaction and remove isopropyl iodide, the residue was distilled. There was obtained 174.7 g. (72%) of liquid, b.p. 98–105° (1.5 mm.). Redistillation produced a fraction boiling constantly at 106° (1.8 mm.), $n^{20}D$ 1.4395, d^{20}_4 1.0707.

Anal. Calcd. for $C_9H_{20}ClO_3P$: P, 12.77; *MR*D, 57.29. Found: P, 13.13, 13.14; *MR*D, 59.67.

γ-Chloropropylphosphonic Acid.—A sample of the ester I was refluxed with concentrated HCl and the solution was evaporated to dryness *in vacuo*. The white solid residue was recrystallized from benzene and chloroform, producing white plates, m.p. 106.5–107.0°; lit.[28] 95–97.5°.

Anal. Calcd. for $C_3H_8ClO_3P$: Cl, 22.37; P, 19.54. Found: Cl, 22.18, 22.24; P, 19.52, 19.50.

When the phosphonyl dichloride from cyclopropane was hydrolyzed and the acid purified in the same manner, it appeared to be identical in all respects with the above acid. The m.p. of a mixture of the two samples was 105–106°.

γ-Chloropropylphosphonyl Dichloride.—To 144.2 g. (0.593 mole) of I, was added slowly, with cooling, 248 g. (1.185 moles) of phosphorus pentachloride. The mixture was warmed slowly to 100° to cause the last of the phosphorus pentachloride to dissolve. Phosphorus oxychloride was distilled at atmospheric pressure and the high boiling residue was distilled *in vacuo*. The fraction boiling at 88–90° (2 mm.) weighed 76.3 g. (65.8%); analytical fraction, b.p. 88° (2 mm.), $n^{20}D$ 1.4960, d^{20}_4 1.4593.

Anal. Calcd. for $C_3H_6Cl_3OP$: Cl, 54.43; *MR*D, 38.24. Found: Cl, 54.36, 54.32; *MR*D, 39.12.

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(26) C. S. Marvel and H. O. Calvery, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 519.

(27) F. H. Case, THIS JOURNAL, **55**, 2929 (1933), reported a 58.3% yield of product boiling at 169–173° at atmospheric pressure.

(28) A. R. Stiles, F. F. Rust and W. E. Vaughan, *ibid.*, **74**, 3282 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Addition of *p*-Thiocresol to Bicyclic Olefins. Quantitative Analysis for Rearrangement Products[1]

BY JEROME A. BERSON AND WILLIAM M. JONES

RECEIVED JUNE 5, 1956

The free radical additions of *p*-thiocresol to *exo-cis*-3,6-endomethylene-Δ^4-tetrahydrophthalic anhydride and the corresponding dimethyl ester give, as major products, the unrearranged *p*-tolylthioethers. The total absence of rearrangement in the products from the reaction of *p*-thiocresol with the ester is demonstrated by isotope dilution analysis.

Although Wagner–Meerwein rearrangements are a familiar feature of the chemistry of bicyclic cations, analogous structural changes appear to be much less common in the corresponding free radicals. Thus, the bicyclic radicals generated in the decarbonylation of bicyclo[2.2.2]octane-2-carboxaldehyde[2] and in chain additions to camphene,[3] β-pinene[4] and norbornene[5] give, as major products, unrearranged materials. Nevertheless, since many of these reactions give only moderate yields of identifiable products, it is difficult to decide whether or not rearrangement is really a prohibitively unfavorable process. In the work reported here, we have scrutinized the products derived from a bicyclic radical and have demonstrated, by isotope dilution analysis, that rearranged materials are absent.

The additions of *p*-thiocresol to *exo-cis*-3,6-endomethylene-Δ^4-tetrahydrophthalic anhydride (I) and to the corresponding dimethyl ester II were investigated. Cristol and Brindell[5a] had already shown that the major product (85% yield) of the addition of *p*-thiocresol to the parent hydrocarbon, norbornene, was not rearranged. We chose to work with the anhydride and ester in the anticipation[6] that a carbonyl group properly situated might stabilize the transition state for rearrange-

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1544.

[2] W. von E. Doering, M. Farber, M. Sprecher and K. B. Wiberg, THIS JOURNAL, **74**, 3000 (1952).

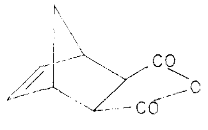
[3] G. Dupont, R. Dulou and G. Clement, *Bull. soc. chim.*, 1002 (1951).

[4] (a) G. Dupont, R. Dulou and G. Clement, *Compt. rend.*, **230**, 2027 (1950); (b) *Bull. soc. chim.*, 1115 (1950); (c) 257 (1951); (d) D. M. Olroyd, G. S. Fisher and L. A. Goldblatt, THIS JOURNAL, **72**, 2407 (1950); (e) these reactions involve ring-opening.

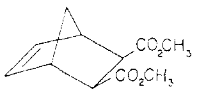
[5] (a) S. J. Cristol and G. D. Brindell, THIS JOURNAL, **76**, 5699 (1954); (b) J. Weinstock Abstracts of Papers, American Chemical Society Meeting, Minneapolis, Minn., Sept. 11–16, 1955, p. 19–O.

[6] J. A. Berson, THIS JOURNAL, **76**, 5748 (1954).

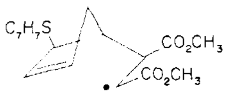
ment by resonance involving structures such as IIIa and b.



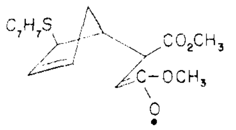
I



II

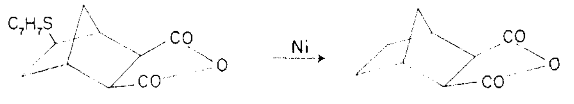


IIIa

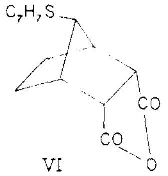


IIIb

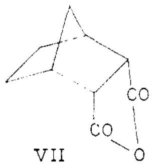
Addition of *p*-thiocresol to I gave, in 73% yield, a crystalline 1:1 adduct IV. That this material was formed by addition without rearrangement was established by its desulfurization with Raney nickel to the saturated *exo*-anhydride V. The hypothetical rearranged product VI would have been expected to give the *endo*-anhydride VII.



IV V



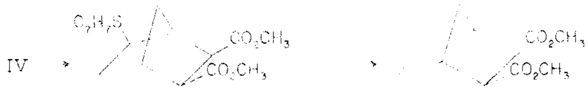
VI



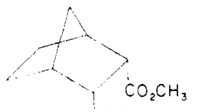
VII

The low yield in the desulfurization (38%) caused some concern. We felt it necessary to show that V was not derived by isomerization of VII (arising from rearranged product VI) under the desulfurization conditions even though we considered this an unlikely possibility. When pure V was treated with Raney nickel under the same conditions, only about 40% of the starting quantity could be recovered, despite prolonged leaching of the nickel with various solvents. Further, the yield of V in the desulfurization of IV could not be improved by shorter reaction periods. Apparently, some decomposition of V on the nickel surface occurred, and the 38% yield obtained was about the maximum that could be expected. We also showed that if VII were formed in the desulfurization, we would have isolated it, since VII was recovered (in 74% yield) after treatment with the same batch of nickel under the same conditions as were used in the desulfurization. The adduct thioether IV is therefore clearly unrearranged. We assign the *exo*-stereochemistry to the *p*-tolylthio group on the general basis of Alder's *exo*-addition rule[7] and the specific analogy to Cristol and Brindell's adduct, the stereochemistry of which was convincingly demonstrated.[5a]

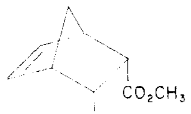
II reacted with *p*-thiocresol to give, in 78% yield, the unrearranged adduct VIII. The structure of this substance was established by desulfurization (76% yield) to the dimethyl ester IX and by synthesis from IV and acidulated methanol. That the desulfurized ester IX did not arise from its stereoisomer X during desulfurization was demonstrated by the recovery of X in 97% yield after it had been subjected to the desulfurization conditions.



VIII IX



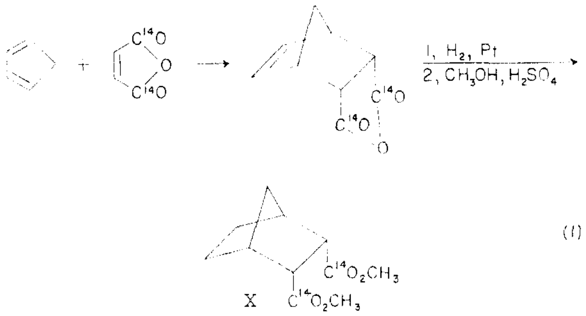
X



XI

The additions of *p*-thiocresol to I and II were rapid, even in the cold. It was therefore difficult to obtain clear-cut qualitative evidence of catalysis by peroxide initiators or by ultraviolet light. However, a small quantity of trinitrobenzene was powerfully inhibitory. From a reaction run at 0° with equimolar quantities of *p*-thiocresol and II, the adduct VIII was isolated readily in 78% yield, whereas from a parallel addition reaction mixture containing 0.1 mole of trinitrobenzene per mole of II, no product could be isolated, and 68% of the starting *p*-thiocresol was recovered (as 2,4-dinitrophenyl *p*-tolyl sulfide). This recovery of *p*-thiocresol was almost identical with that obtained when *p*-thiocresol and II were mixed and immediately worked up for *p*-thiocresol. Thus, trinitrobenzene seems to inhibit the addition almost completely. The inhibition experiments, combined with the fact that the addition does not require a mineral acid catalyst, are consistent with a free radical chain mechanism for the addition.[8]

Analysis for Rearranged Product.—The *endo*-ester X, radioactively labeled in the carbonyl carbons, was prepared by the sequence shown in (1) and re-crystallized to constant activity.



X (1)

It was necessary to show: (i) that the radioactive X was not contaminated with the *exo*-isomer IX and (ii) that the inactive *exo*-unsaturated ester II to be used in the addition experiment was not contaminated with its *endo*-isomer XI. These points were established by catalytically hydrogenating (in ethyl acetate solution) a sample of inactive II (from the same batch as was used in the analytical

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(7) K. Alder and G. Stein, *Ann.*, **515**, 185 (1935); **525**, 183 (1936).

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

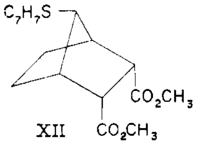
run below) in the presence of a quantity of the radioactive X of activity $\alpha = 2136 \pm 4$ c./min. Re-isolation of X by fractional crystallization gave material of undiminished activity, $\alpha = 2143 \pm 5$ c./min. This result eliminates the possibility of appreciable contamination of types (i) or (ii).

Control experiments showed that dilution of radioactive X with inactive X could be followed analytically. Apparent radioactivities on samples of X were determined by counting the material in substance as "infinitely thick" films. This technique reproduced gravimetric dilution with inactive X with satisfactory accuracy (see Experimental). Further, the method was sensitive enough to detect very small dilutions. Dilution of a sample of X, $\alpha = 2136 \pm 4$ c./min., with 2.6% of inactive X gave X with $\alpha = 2088 \pm 2$ c./min., as compared to an anticipated activity of 2080 c./min. We assume, therefore, that the counting method is capable of detecting any diminution in activity greater than the statistical counting error of about 1%.

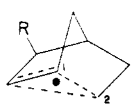
A typical reaction mixture obtained from the addition of *p*-thiocresol to inactive *exo*-ester II was treated with a weighed amount of radioactive X, $\alpha = 2136 \pm 6$ c./min. The entire material was subjected to the action of Raney nickel in boiling benzene, and the X was re-isolated. It had an activity of 2136 ± 13 c./min. Assuming the statistical counting error to be 1%, the analysis should have detected as little as 0.6% of rearrangement product (XII) with the quantities used.[9]

The present results confirm the previous conclusions[3-5] that free radical analogs of the Wagner–Meerwein change in bicyclic systems are uncommon and, further, establish the fact that compared with the barrier for chain propagation by hydrogen abstraction, the energy barrier for rearrangement is prohibitively high in the cases here described.[10] Indeed, apart from the case of di-*t*-butylcarbinyl radical, in which methyl migration has been reported,[11] there appears to be no recorded example of alkyl group or hydrogen migration in a free radical reaction.[12]

The question of whether or not "bridged" radicals[5a,13] occur in bicyclic systems (*i.e.*, intermediates such as XIII deriving stability by distribution of the odd electron over several sites) cannot yet be answered with rigor, since if XIII were formed as an intermediate, rearranged products would *necessarily* appear only if R = H, *i.e.*, when C.1 and C.2 were structurally equivalent. Nevertheless, the observed consistent failure of bicyclic free radicals to rearrange suggests that "bridging" is not a general phenomenon.[14]



XII



XIII

Experimental[15]

Reaction of *p*-Thiocresol with *exo-cis*-3,6-Endomethylene-Δ^4-tetrahydrophthalic Anhydride (I).—A mixture of 4.9 g. of I[16] and 5 cc. of warm *p*-thiocresol was heated on the steam-bath for 2 hr. with occasional stirring, treated with 15 cc. of ethyl acetate and allowed to stand overnight at room temperature. The resulting precipitate was collected to give 6.5 g. (73%) of the adduct IV, m.p., 121–124°. Recrystallization from ethyl acetate gave white staves, m.p. 124–125°.

Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.63; H, 5.60; S, 11.11. Found: C, 66.44; H, 5.88; S, 10.78.

Conversion of IV to the Methyl Ester (VIII).—A solution of 3.0 g. of the anhydride thioether IV and 2 cc. of concentrated sulfuric acid in 25 cc. of absolute methanol was heated for 2 hr. Most of the excess methanol was removed by distillation, the residue was taken up in ether, washed with water and then with sodium bicarbonate solution, dried over potassium carbonate and the solution filtered and evaporated. The residue was crystallized from methanol to give 2.2 g. of the ester VIII, m.p. 71–73.5°. A mixed m.p. with a sample prepared from II and *p*-thiocresol was not depressed.

Reaction of *p*-Thiocresol with the Ester II. A. Without Solvent.—A mixture of 2.0 g. of the ester II[17] and 3.0 cc. of warm *p*-thiocresol was warmed on the steam-bath for 1.5 hr., then treated with 15 cc. of absolute methanol, the mixture brought to a boil and then chilled in ice. The precipitated solid, 2.3 g. (72%) of adduct VIII, melted at 71–75°. Recrystallization from absolute methanol gave material of m.p. 74–75°.

Anal. Calcd. for $C_{18}H_{22}O_4S$: C, 64.67; H, 6.59; S, 9.58. Found: C, 64.58; H, 6.29; S, 9.26.

B. In Methanol at 0°.—A solution of 0.153 g. of *p*-thiocresol in 1.2 cc. of absolute methanol was cooled to 0° in the dark and then treated with 0.26 g. of the ester II. The reaction vessel was wrapped in aluminum foil and stored at 0° for 2 hr. It was then seeded with adduct VIII and kept at 0° an additional 18 hr. The crystalline white precipitate was filtered to give 0.322 g. (78%) of VIII, m.p. 73–75°.

C. In Methanol at 0° in the Presence of Trinitrobenzene.—A solution of 0.144 g. of *p*-thiocresol and 0.025 g. of trinitrobenzene in 1.2 cc. of absolute methanol was cooled to 0° in the dark and then treated with 0.244 g. of the ester II. The reaction vessel was wrapped in aluminum foil and stored at 0° for 4 hr. It was then seeded with adduct VIII and kept an additional 16 hr. at 0°, after which time there was no precipitate. The mixture was added to a solution of 0.047 g. of sodium hydroxide in 0.3 cc. of water and 2 cc. of ethanol and the resulting red solution immediately added to a solution of 0.237 g. of 2,4-dinitrochlorobenzene in 1 cc. of ethanol. This mixture was warmed on the steam-bath for 5 minutes and then cooled and triturated, whereupon 0.226 g. of a yellow solid, m.p. 90–101°, was obtained. Recrystallization from ethanol gave material of m.p. 102–103°, alone or mixed with an authentic sample of *p*-tolyl 2,4-dinitrophenyl sulfide; reported[18] m.p. 103°.

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(9) This assumes quantitative desulfurization of any rearranged adduct (XII) present to X and complete mixing of X formed during desulfurization with added X. We do not have direct evidence for these assumptions, since XII is not now available. However, we justify them by the observed desulfurization of VIII in good yield and the near-quantitative recovery of X from Raney nickel.

(10) We recognize that a sulfur-bridged radical could conceivably be involved in *p*-thiocresol additions,[5a] and that consequently in such additions any inherent tendency of the bicyclic radical to suffer carbon skeletal rearrangement may be obscured.

(11) M. S. Kharasch, Y. C. Liu and W. Nudenberg, *J. Org. Chem.*, **19**, 1150 (1954); **20**, 680 (1955).

(12) Phenyl migration is common: (a) S. Winstein and F. H. Seubold, THIS JOURNAL, **69**, 2916 (1947); (b) W. H. Urry and M. S. Kharasch, *ibid.*, **66**, 1438 (1944); (c) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952); (d) W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952); (e) F. H. Seubold, *ibid.*, **75**, 2532 (1953).

(13) J. A. Berson and R. Swidler, *ibid.*, **76**, 4060 (1954).

(14) Seubold's[12e] results show that there is a detectable time lag between the formation and rearrangement of the (acyclic) β-phenylisobutyl radical.

(15) Melting points are corrected. The microanalysis are by Mr. W. J. Schenck.

(16) D. Craig, THIS JOURNAL, **73**, 4889 (1951).

(17) H. Bode, *Ber.*, **70**, 1167 (1937).

(18) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 225.

A reaction mixture of *p*-thiocresol, trinitrobenzene, methanol and II, each in quantity identical to the above run, was brought to homogeneity by shaking for a few seconds at 0°. It was then immediately worked up for *p*-thiocresol with aqueous alcoholic alkali and 2,4-dinitrochlorobenzene exactly as above. The yield of crude *p*-tolyl 2,4-dinitrophenyl sulfide, m.p. 98–105°, was 0.225 g. Recrystallization from ethanol gave material melting at 101–102.5°, alone or mixed with the sample prepared above.

Desulfurization of IV.—The Raney nickel used in all the desulfurization experiments was prepared according to Mozingo.[19] Most of the water was removed by decantation and washing with absolute ethanol. Ethanol and traces of water were removed immediately prior to use by azeotropic distillation with benzene. Approximate weights of batches of nickel were determined on the basis of a preliminary weight *vs.* volume calibration. A suspension of nickel in ethanol was allowed to settle in a tared graduated cylinder until the volume occupied by the nickel was constant. The solvent was carefully removed under a current of nitrogen and the weight of the dry nickel determined. (The nickel is extremely pyrophoric at this stage and must not be exposed to air.)

Three grams of the anhydride thioether (IV) were added to a mixture of 50 cc. of dry benzene and 15 g. of Raney nickel. The mixture was heated for 2.5 hr., cooled and poured into a Soxhlet thimble. The thimble was placed in the Soxhlet extraction apparatus, the boiler was charged with 75 cc. of ethyl acetate and extraction was allowed to proceed for 24 hr. The solvents were removed on the steam-bath and the oily residue repeatedly leached with hexane. The hexane extracts, after being cooled overnight in the refrigerator, deposited 0.655 g. of crude *exo*-anhydride V, m.p. 66–75°. Recrystallization from hexane gave material melting at 75–77.5°, alone or mixed with an authentic sample[20]; reported[20] m.p. 78–79°.

Desulfurization of VIII.—To a suspension of 11.5 g. of Raney nickel in 50 cc. of dry benzene was added 1.5 g. of VIII. The mixture was heated at reflux for 3.5 hr., filtered and evaporated to dryness *in vacuo*, leaving IX as a colorless oil (0.75 g.). The infrared spectrum of this material was identical with that of an authentic sample.[17]

Recovery of *endo*-Ester X from Raney Nickel.—A mixture of 12.7 g. of Raney nickel, 1.5 g. of X and 50 cc. of benzene was heated at reflux for 4 hr., filtered, the filter cake washed with benzene and the filtrate evaporated to dryness to give 1.45 g. of crystals, m.p. 49–55°. Recrystallization from methanol gave X, m.p. 54–56°, alone or mixed with an authentic sample[17]; reported[17] m.p. 55°.

Preparation of Radioactive X.—Maleic anhydride-1-C^{14} was supplied by Nuclear Instrument and Chemical Co., Chicago, Ill., on allocation from the Atomic Energy Commission. The samples used had an activity of about 1.4 mc./millimole, and each sample had a total activity of about 0.1 mc. The radioactive sample was diluted about a thousand-fold by transferring it with benzene into a flask containing freshly recrystallized inactive maleic anhydride. The solution was warmed, filtered while hot, the filtrate treated with ligroin, allowed to cool and the crystals collected. Since maleic anhydride has an appreciable vapor pressure, it was stored in a separate desiccator to prevent radioactive contamination of other samples.

A solution of 10.0 g. of the radioactive maleic anhydride in 20.8 cc. of dry benzene was cooled in an ice-bath and treated dropwise with 6.74 g. of freshly distilled cyclopentadiene. The adduct, *endo*-*cis*-3,6-endomethylene-Δ^4-tetrahydrophthalic anhydride precipitated immediately. It was filtered off and a second crop was obtained by treating the filtrate with hexane. The yield of material melting at 161–162° was 15.2 g. (97%). This material was diluted with twice its weight of pure inactive adduct[21] and the whole recrystallized from benzene to give material melting at 164.5–165°, reported[21] m.p. 164–165°. Further recrystallization produced no change in either melting point or apparent radioactivity.

The reactive anhydride was hydrogenated over platinum in ethyl acetate. The dihydroanhydride had m.p. 165–166°; reported[21] m.p. 167–168°. It was converted to the dihydrodimethyl ester X with boiling methanol and a little sulfuric acid to give material melting at 54–56°, after recrystallization from methanol to constant m.p. and activity; reported[17] m.p. 55°.

Counting Techniques.[22]—Apparent activities were determined with a Nuclear Instrument model D46A Q-gas flow detector and a model 162 binary scaler. To reduce statistical error, the total counts recorded on each count of a given sample were always greater than 10,000. The counts were reproducible to better than ±1% average deviation (three to five counts), provided that the rate of gas flow was carefully controlled. Samples were counted as "infinitely thick" films, mounted in aluminum disks. Each disk was machined to a diameter (30 mm.) that would provide snug fit in the sample slide of the detector and was provided with an accurately machined depression about 2 mm. deep and 1.54 cm.^{2} in area. Samples were first powdered by grinding and then mounted firmly in the depression with the aid of a stainless steel plunger machined to fit the depression snugly. The plunger was pressed onto the sample and struck several smart blows with a hammer. The technique was satisfactorily reproducible as evidenced by the fact that independent mountings of a given sample had the same apparent activity within ±0.5%. "Infinite thickness" required about 50 mg. of sample. Backgrounds were determined with a disk filled with barium carbonate or inactive X. Backgrounds determined in this way were identical with each other but were slightly lower (presumably due to less backscattering) than backgrounds determined with empty disks.

Establishment of Chemical Purity of II and of Radioactive X.—A mixture of 0.40 g. of radioactive X, $\alpha = 2136 \pm 4$ c./min., and 0.60 g. of the unsaturated ester II (from the same batch used in the isotope dilution analysis for rearrangement below) was dissolved in 20 cc. of ethyl acetate and hydrogenated in the presence of 0.05 g. of platinum oxide. The theoretical quantity of hydrogen was absorbed in about 15 minutes, whereupon the mixture was filtered, evaporated to dryness, cooled and seeded with a tiny crystal of radioactive X. The crystalline precipitate was filtered and recrystallized from hexane to give 0.128 g. of the saturated *endo*-ester X, m.p. 54–55.5°, $\alpha = 2143 \pm 5$ c./min.

Control Experiments on Isotope Dilution of X.—Weighed quantities (A and B, respectively) of radioactive and inactive X were mixed and recrystallized from hexane. The original sample of radioactive X and the diluted samples were counted during the same period of operation of the counting equipment. The theoretical % residual activity, $100A/(A + B)$, and the found values $100\ \alpha_r/\alpha_A$, where α_r = activity of diluted material and α_A = activity of the original X were 34.6/35.1; 83.6/83.5; 97.4/97.7.

Isotope Dilution Analysis for Rearrangement Product.—A solution of 0.4580 g. of *p*-thiocresol and 0.7750 g. of the unsaturated *exo*-dimethyl ester II in 3.5 cc. of absolute methanol was kept at 0° for 48 hr. The solution was then added to a mixture of 9.1 g. of Raney nickel, 0.4790 g. of radioactive saturated *endo*-dimethyl ester X and 100 cc. of dry benzene. The mixture was heated at reflux for 3 hr., filtered and the filtrate concentrated to dryness *in vacuo*. The residue was cooled, seeded with a trace (less than 0.5 mg.) of radioactive X and allowed to stand overnight at 0°. The precipitated solid was filtered off and recrystallized from a small quantity of hexane to give 0.092 g. of pure X, m.p. 55–56.5° (C). This material was counted, then recrystallized again from hexane (to give D) and D re-counted. A sample of the original X was counted for comparison during the same period of operation of the counting equipment to minimize the effect of instrument fluctuations. The observed activities were: (i) original sample of X, 2136 ± 6 c./min.; (ii) C, 2132 ± 9 c./min.; (iii) D, 2136 ± 13 c./min.

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[22] We are indebted to Professor A. W. Adamson for instruction in these techniques.