*Anal.* Calcd. for $C_{21}H_{33}NO$: C, 79.94; H, 10.54; N, 4.44. Found: C, 79.62; H, 10.64; N, 4.66.

**N-Hydroxy-17α-aza-D-homoandrost-4-en-3-one (4).**—A solution of 900 mg. of N-ethyl-17a-aza-D-homoandrost-4-en-3-one (2) in 40 ml. of methylene chloride was cooled to 0–5°. To this, a solution of 700 mg. of 85% *m*-chloroperbenzoic acid in 30 ml. of methylene chloride was added slowly within a period of 10 min. The mixture was then allowed to stand for about 15 min. at room temperature, after which it was washed successively with a cold sodium carbonate solution and water and was dried over sodium sulfate. Removal of solvent yielded 950 mg. of oily N-oxide 3, which was used without further purification.

The N-oxide 3 was dissolved in 30 ml. of xylene and heated under reflux in a nitrogen atmosphere for 20 min. The solvent was removed under reduced pressure and 850 mg. of an oily product was obtained which showed the presence of a hydroxyl band in the infrared. This oil in benzene solution was put on an alumina column. Elution of the column with benzene containing 50–75% ethyl acetate yielded identical fractions, m.p. 155–158°. These were combined to yield 600 mg. of N-hydroxy-17a-aza-D-homoandrost-4-en-3-one (4). A portion of this was recrystallized for analysis: m.p. 159–160°; $\nu_{\max}^{\text{KBr}}$ 3200 (N-OH), 1660 (3-keto), 1625 ($\Delta^4$) cm.$^{-1}$; n.m.r. 62.5 (C-18 $CH_3$), 70.5 (C-19 $CH_3$), 348.0 (C=CH of $\Delta^4$) c.p.s.; $\lambda_{\max}^{\text{methanol}}$ 237 mμ (log ε 4.08).

*Anal.* Calcd. for $C_{19}H_{29}NO_2$: C, 75.20; H, 9.63; N, 4.62. Found: C, 74.96; H, 9.70; N, 4.45.

**N-Ethyl-17a-aza-D-homoestra-1,3,5(10)-triene-3-methyl Ether (6).**—A solution of 1.8 g. of 3-methoxy-17a-aza-D-homoestra-1,3,5(10)-triene[12] (5) in 40 ml. of acetone was refluxed with 2 g. of diethyl sulfate and a solution of 2 g. of potassium hydroxide in 6 ml. of water for 4.5 hr. The solution was poured onto ice and the precipitated solids were filtered, washed, and dried to yield 1.6 g. of 6, m.p. 100–103°. A portion of this was recrystallized from ether–hexane to give pure N-ethyl-17a-aza-D-homoestra-1,3,5(10)-triene-3-methyl ether (6): m.p. 104–105°; $\nu_{\max}^{\text{KBr}}$ 1600 (C=C aromatic), 1560 (C=C aromatic), 1030 (O-$CH_3$) cm.$^{-1}$.

*Anal.* Calcd. for $C_{21}H_{31}NO$: C, 80.46; H, 9.97; N, 4.47. Found: C, 80.65; H, 9.96; N, 4.66.

**N-Hydroxy-17a-aza-D-homoestra-1,3,5(10)-triene-3-methyl Ether (8).**—A solution of 1.1 g. of the N-ethyl derivative 6 in 30 ml. of methylene chloride was cooled to 0–5° and a solution of 770 mg. of 85% *m*-chloroperbenzoic acid in 10 ml. of methylene chloride was added within a period of 10 min. The mixture was allowed to stand at room temperature for another 15 min. then was washed with cold solution of sodium carbonate and then water, and was dried over sodium sulfate. Removal of solvent yielded 1.15 g. of oily N-oxide 7. This was dissolved in 50 ml. of toluene and heated under reflux in a nitrogen atmosphere for 15 min. Toluene was removed *in vacuo*, leaving 1.08 g. of a brown oil. The oil in benzene solution was put on an alumina column. Elution of the column with benzene containing 75–80% methylene chloride provided identical fractions, m.p. 140–142°. These were combined to yield 700 mg. of N-hydroxy-17a-aza-D-homoestra-1,3,5(10)-triene-3-methyl ether (8). A portion was recrystallized from ether for analysis: m.p. 143–145°; $\nu_{\max}^{\text{KBr}}$ 3200 (N–OH), 1600 (C=C aromatic), 1560 (C=C, aromatic), 1030 (O-$CH_3$) cm.$^{-1}$.

*Anal.* Calcd. for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.58; H, 9.00; N, 4.31.

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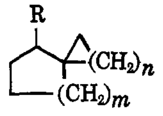
## The Decomposition of Spiranone *p*-Toluenesulfonylhydrazones. A Convenient Synthetic Route to Spirenes

A. PAUL KRAPCHO AND R. DONN[1]

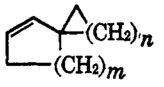
*Department of Chemistry, University of Vermont, Burlington, Vermont*

*Received July 8, 1964*

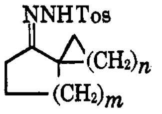
The dehydration of α-hydroxyspirans (1) to produce spirenes (2) is difficult to perform because of the tendency for carbon skeleton rearrangement to occur in these neopentyl-type systems.[2] In the dehydration of spiro[4.5]decan-6-ol (1, R = OH; $m$ = 2; $n$ = 3) over alumina about 50% of spiro[4.5]dec-6-ene (2, $m$ = 2; $n$ = 3) has been found along with the octalins resulting from ring expansion. The dehydration of this spiranol with sulfuric acid leads exclusively to octalins.[2b] The zinc chloride dehydrations of spiro[5.5]undecan-1-ol (1, R = OH; $m$ = 2; $n$ = 4) and spiro[4.5]decan-1-ol (1, R = OH; $m$ = 1; $n$ = 4) yield mainly cyclohexyl-1-cyclopentene *via* a ring contraction route[2d] and 1,2,3,4,5,6,7,8-octahydroazulene *via* a ring expansion route.[2f] The phosphoric acid dehydration of spiro[4.4]nonan-1-ol (1, R = OH; $m$ = 1; $n$ = 3) leads to 4,5,6,7-tetrahydroindane.[2d] The zinc chloride dehydration of the related system 2,2-dimethylcyclohexanol has been reported to yield olefins of rearranged carbon skeleton.[3] The products obtained from the acetolysis of α-tosyloxyspiranes (1, R = tosyl) are also predominantly rearranged olefins.[4]



1



2



3

The basic decomposition of the *p*-toluenesulfonylhydrazones (tosylhydrazones, 3) seemed to be potentially useful as a simple synthetic route to certain spirenes (2). The relative migratory aptitude of various ring sizes could also be determined and contrasted to the results of the products formed under ionic conditions.

The formation of olefins from the decomposition of tosylhydrazones was first investigated by Bamford and Stevens.[5] Friedman and Shechter have investigated the relationship between the products and the nature of the solvent in these decompositions (protonic or aprotic).[6] The decomposition of alkyl tosylhydrazones in aprotic solvents yields olefins *via* hydrogen migration and cyclopropanes *via* intramolecular insertion.[6b] The observation has been made that hydrogen migration occurs more readily than carbon skeleton rearrangement in the carbenoid decompositions. For example, the decomposition of the tosylhydrazone of pinacolone leads to *t*-butyl ethylene (52%) and 1,1,2-trimethylcyclopropane (47%). The decomposition of the tosylhydrazones of cyclopentanone and cyclohexanone yields cyclopentene and cyclohexene, respectively.[7] The tosylhydrazones of higher cycloalkanones produce intramolecular insertion products in addition to the cycloalkenes. In the decomposition of the tosylhydrazones of the $C_7$ through $C_{10}$ ketones extensive 1,3-, 1,5- and 1,6-transannular insertion

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[1] National Science Foundation Undergraduate Research Participant, 1963–1964.

[2] (a) P. A. Naro and J. A. Dixon, *J. Org. Chem.*, **26**, 1021 (1961); (b) P. A. Naro and J. A. Dixon, *J. Am. Chem. Soc.*, **81**, 1681 (1959); (c) H. Christol, R. Jacquier, and M. Mousseron, *Bull. soc. chim. France*, 346 (1957); (d) *ibid.*, 1027 (1957); (e) H. Christol, M. Mousseron, and F. Plenat, *ibid.*, 543 (1959); (f) R. Mayer and W. Töpelmann, *Chem. Ber.*, **91**, 1764 (1958).

[3] H. Meerwein and J. Schafer, *J. prakt. Chem.*, **104**, 289 (1922).

[4] A. P. Krapcho and M. Benson, *J. Am. Chem. Soc.*, **84**, 1036 (1962).

[5] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

[6] (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (b) *ibid.*, **82**, 1002 (1960).

[7] L. Friedman and H. Shechter, *ibid.*, **83**, 3159 (1961).

TABLE I

TOSYLHYDRAZONE DECOMPOSITIONS

| Tosylhydrazone | Products (system 2) | Crude yield, % | V.p.c. analysis, %[a] |
|---|---|---|---|
| 2,2-Dimethylcyclohexanone | 3,3-Dimethylcyclohexene | 81 | 99 |
| Spiro[4.5]decan-6-one | Spiro[4.5]dec-6-ene ($m = 2, n = 3$) | 75 | 95 |
| Spiro[5.5]undecan-1-one | Spiro[5.5]undec-1-ene ($m = 2, n = 4$) | 82 | 99 |
| Spiro[4.5]decan-1-one | Spiro[4.5]dec-1-ene ($m = 1, n = 4$) | 90 | 99 |
| Spiro[4.4]nonan-1-one | . . . | 80 | . . . |
|  | Spiro[4.4]non-1-ene ($m = 1, n = 3$) | . . . | 53 |
|  | 4,5,6,7-Tetrahydroindane (**4**) | . . . | 12 |
|  | Spiro[bicyclo(2.1.0)pentane-4,1′-cyclopentane] (**5**) | . . . | 32 |
|  | Unidentified | . . . | 3 |

[a] On a Ucon Polar column.

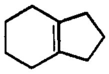
products result.[7] Powell and Whiting have investigated the decomposition of various decalone sulfonylhydrazones to ascertain the factors controlling the ultimate position of the double bond in the octalins produced.[8]

## Results

The routes to the synthesis of the spiranones and the corresponding tosylhydrazones are described in the Experimental section. The tosylhydrazones were decomposed in refluxing diglyme using commercial sodium methoxide as the base.[6,7,9] The diglyme mixture was refluxed for about 15 min. and the products were isolated from the mixture by steam distillation. The crude products were analyzed by vapor phase chromatography and were tentatively identified by infrared analysis. The olefinic carbon–hydrogen stretching region (3000 cm.$^{-1}$), the carbon–carbon double bond stretching region (1650 cm.$^{-1}$), and the olefinic carbon–hydrogen out-of-plane deformation frequencies (750 cm.$^{-1}$) were particularly revealing where only a single reaction product was obtained.[10] The structural assignments were established by nuclear magnetic resonance spectroscopy. The details of the infrared and n.m.r. analyses are listed in the Experimental section. The products from the decompositions were quantitatively hydrogenated to the corresponding spiranes (except the products from the decomposition of the tosylhydrazone of spiro[4.4]nonan-1-one which absorbed only 66% of the calculated amount of hydrogen for one double bond). The hydrogenated products were identified through the comparison of their infrared spectra and vapor phase chromatographic retention times with those of authentic spiranes prepared by the Wolff–Kishner reduction of the corresponding spiranones.

The results of this study are tabulated in Table I. The decomposition of the tosylhydrazone of 2,2-dimethylcyclohexanone is included for comparison.

From the data in Table I it can be seen in the common-size rings studied here that excellent yields of spirenes are produced, except in the decomposition of the tosylhydrazone of spiro[4.4]nonan-1-one where a competing ring expansion and an insertion product result. The contrast between these results and the products obtained under ionic conditions where skeletal rearrangement predominates should be noted. A selective hydrogen migration predominates in each case studied. In the case of the tosylhydrazone of spiro[4.4]nonan-1-one the transition state free energy for the 1,3-insertion is close to that for olefin formation and competes with hydrogen migration which leads to the introduction of a strained double bond into the five-membered ring.[11] The formation of the ring expansion product in this reaction is energetically favorable owing to the release of ring strain in the five-membered ring on expansion to a six-membered ring.[12] However, the absence of any insertion product in the decomposition of the tosylhydrazone of spiro[4.5]-decan-1-one is of interest although in this case no ring-expanded product is to be expected (ring strain increase in the six to seven transition).


**4**


**5**

This study is currently being extended to larger and smaller adjacent rings and to larger rings bearing the tosylhydrazone group to assess migratory aptitudes and intramolecular routes.

### Experimental

Elemental analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer. The vapor phase chromatographic analyses were performed on the Aerograph A-90-P. All melting points are corrected; all boiling points are uncorrected. All 60-Mc. n.m.r. spectra reported here were determined neat or in carbon tetrachloride solutions with tetramethylsilane as the internal standard and chemical shifts are reported in $\tau$-values.

**Synthesis of the Spiranones.**—Spiro[4.4]nonan-1-one was prepared in 80% yield from 2-($\omega$-bromobutyl)cyclopentanone by the procedure described by Mayer, Wenshuh, and Töpelmann.[13] Spiro[4.5]decan-6-one was prepared in a 75% yield by the procedure described by Dixon for the pinacol rearrangement of 1,1′-dihydroxy-1,1′-dicyclopentyl.[2b] Spiro[5.5]undecan-1-one was prepared in 40% yield by the reaction of 1,5-dibromopentane with cyclohexanone in the presence of potassium *t*-butoxide.[2c] Spiro[4.5]decan-1-one was prepared in 65% yield from 2-($\omega$-bromopentyl)cyclopentanone by the cyclization procedure described

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(8) J. W. Powell and M. C. Whiting, *Tetrahedron*, **12**, 168, 278 (1961).

(9) For other examples: (a) S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963); (b) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963); (c) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1680 (1963).

(10) (a) H. B. Henbest, G. D. Meakins, and G. W. Wood, *J. Chem. Soc.*, 800 (1954); (b) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p. 24.

(11) J. G. Traynham and M. F. Sehnert, *J. Am. Chem. Soc.*, **78**, 4024 (1956).

(12) K. S. Pitzer and W. E. Donath, *ibid.*, **81**, 3213 (1959).

(13) R. Mayer, G. Wenshuh, and W. Töpelmann, *Chem. Ber.*, **91**, 1616 (1958).

by Mayer.[10] The 2,2-dimethylcyclohexanone was prepared in 40% yield by the alkylation procedure described by King.[14]

**Spiro[5.5]undecan-1-one Tosylhydrazone (3, *m* = 2; *n* = 4). Typical Procedure.**—Spiro[5.5]undecan-1-one (10 g., 0.06 mole), *p*-toluenesulfonylhydrazine (11.2 g., 0.06 mole), and 35 ml. of absolute ethanol were refluxed for 2 hr. Upon brief refrigeration crystals separated which were collected and recrystallized from abolute ethanol to yield 16 g. (80%) of the pure tosylhydrazone of m.p. 112–113° dec.

*Anal.* Calcd. for $C_{18}H_{26}N_2O_2S$: C, 64.65; H, 7.84. Found: C, 64.44; H, 7.80.

**Decomposition of the Tosylhydrazones. Spiro[5.5]undec-1-ene (2, *m* = 2; *n* = 4).**—Spiro[5.5]undecan-1-one tosylhydrazone (15.0 g., 0.045 mole) was added to 60 ml. of diglyme (distilled from lithium aluminum hydride). Dry reagent grade sodium methoxide (2.5 g., 0.045 mole) was added in one portion. The apparatus was connected to a mercury bubbler and the solution was heated with magnetic stirring. Upon brief warming, a solid white cake developed to which 20 ml. more of diglyme was added. On further heating the white solid redissolved and a clear red solution was obtained. A vigorous evolution of nitrogen occurred and a white solid separated out. After heating at reflux for 20 min. the gas evolution ceased and the red color disappeared. The mixture was cooled, 100 ml. of water was added, and the product was steam distilled from the mixture. The top layer in the distillate was separated and washed once with cold water to remove any diglyme. This layer was dried over anhydrous potassium carbonate and weighed 5.5 g. (82% yield). The vapor phase chromatographic analysis using a 22-ft. Ucon Polar column showed only a trace of contamination in this undistilled material (less than 0.5%). The spiro[5.5]-undec-1-ene was distilled at 205–207° (740 mm.): infrared (neat, NaCl plates) 3050 (=C—H stretch, m), 1660 (C=C stretch, vw), and 728 cm.$^{-1}$ (out-of-plane deformation of =C—H, vs); n.m.r. (neat) $\tau$ 4.50 (singlet, vinyl protons), 8.10 (multiplet, allylic protons), and 8.45 (multiplet, all other protons), relative areas 1:1:7.

*Anal.* Calcd. for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.92; H, 12.12.

**Identification of the Spirenes.**—Spiro[5.5]undec-1-ene was hydrogenated in acetic acid using platinum as a catalyst and absorbed 101 ± 2% of the calculated amount of hydrogen. The hydrogenated product was isolated by diluting the acetic acid with water. The top hydrocarbon layer was separated and washed with a 10% sodium bicarbonate solution. The layer was dried over potassium carbonate and distilled, b.p. 209–210° (740 mm.), lit.[15] b.p. 212° (723 mm.). The infrared spectrum and the retention time of this product were identical to spiro[5.5]undecane which was prepared by the Wolff–Kishner reduction of spiro[5.5]-undecan-1-one.[15]

**Spiro[4.5]dec-6-ene (2, *m* = 2; *n* = 3).**—The tosylhydrazone was obtained in a 88% yield and melted at 153–154° dec.

*Anal.* Calcd. for $C_{17}H_{24}N_2O_2S$: C, 63.73; H, 7.55. Found: C, 63.51; H, 7.61.

The decomposition of the tosylhydrazone yielded 75% of the spirene, b.p. 34° (2 mm.), micro b.p. 181° (740 mm.).

*Anal.* Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.93; H, 11.79.

The vapor phase chromatographic analysis of the undistilled material on a Ucon Polar column indicated one major component contaminated by trace amounts of two other components (less than 5%): infrared (neat, NaCl plates) 3040 (m), 1650 (vw), and 730 cm.$^{-1}$ (vs); n.m.r. (neat) $\tau$ 4.55 (singlet), 8.15 (multiplet), and 8.50 (multiplet), relative areas 1:1:6.

The sample absorbed 98 ± 2% of the calculated amount of hydrogen. The compound obtained upon hydrogenation was identical in retention time with spiro[4.5]decane (Ucon Polar column). The infrared spectrum of the reduced product was also identical with that of spiro[4.5]decane.

**Spiro[4.5]dec-1-ene (2, *m* = 1; *n* = 4).**—Spiro[4.5]decan-1-one tosylhydrazone was obtained in 85% yield and had a melting point of 152–153° dec.

*Anal.* Calcd. for $C_{17}H_{24}N_2O_2S$: C, 63.73; H, 7.55. Found: C, 63.64; H, 7.50.

The decomposition of the tosylhydrazone yielded 90% of the spirene: micro b.p. 177° (740 mm.); infrared (neat, NaCl plates) 3080 (m), 1620 (vw), and 740 cm.$^{-1}$ (vs); n.m.r. ($CCl_4$ solution) $\tau$ 4.45 (singlet), 7.75 (multiplet), 8.35 (multiplet), and 8.60 (broad singlet), relative areas 1:1:1:5.

*Anal.* Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.01; H, 11.75.

The analysis on the Ucon Polar column showed one major component with less than 1% contamination. The spirene absorbed 101 ± 2% of the calculated amount of hydrogen. The hydrogenated product was identical in retention time and infrared spectrum with spiro[4.5]decane.[15]

**3,3-Dimethylcyclohexene.**—The 3,3-dimethylcyclohexanone tosylhydrazone was obtained in 90% yield and melted at 129–130° dec.

*Anal.* Calcd. for $C_{15}H_{22}N_2O_2S$: C, 61.20; H, 7.53. Found: C, 61.00; H, 7.34.

The decomposition of the tosylhydrazone yielded 81% of 3,3-dimethylcyclohexene: b.p. 112–113° (740 mm.), lit.[16] b.p. 115–116° (745 mm.); infrared (neat, NaCl plates) 3070 (m), 1660 (vw), and 730 cm.$^{-1}$ (vs).

The v.p.c. analysis on the Ucon Polar column showed one component with a trace of contamination. The sample absorbed 98 ± 2% of the calculated amount of hydrogen. The product isolated from the hydrogenation was identical in retention time and infrared spectrum with authentic 1,1-dimethylcyclohexane, b.p. 114–115° (740 mm.), lit.[17] b.p. 117–118°. The latter compound was prepared by the Wolff–Kishner reduction of the ketone.

**Product Identification from the Decomposition of the Tosylhydrazone of Spiro[4.4]nonan-1-one (3, *m* = 1; *n* = 3).**—Spiro[4.4]nonan-1-one tosylhydrazone was prepared in a 90% yield and melted at 146–147° dec.

*Anal.* Calcd. for $C_{16}H_{22}N_2O_2S$: C, 62.72; H, 7.24. Found: C, 62.38; H, 7.17.

The decomposition of the tosylhydrazone yielded 80% of the crude product. The analysis using the Ucon Polar column showed the presence of four components in the following percentages: 53, 32, 3, and 12, (arranged in order of increasing retention time). Upon catalytic hydrogenation the mixture absorbed 66% of the calculated amount of hydrogen for one double bond. The vapor phase chromatographic analysis of the hydrogenated product indicated three components in the percentages 56, 32, and 12, arranged in the order of increasing retention time. The component found to comprise 32% of the original mixture showed no change in retention time on hydrogenation and thus is inert to catalytic hydrogenation under the conditions utilized here (platinum and acetic acid at 23°). The component of shortest retention time (53%) in the hydrogenated product was readily identified as spiro[4,4]nonane through the comparison of the retention time and infrared spectrum to those of an authentic sample of this compound prepared by the Wolff–Kishner reduction of the spiranone. Thus the component present in the original decomposition to the extent of 53% can be identified as spiro[4.4]non-1-ene.[18] The component of longest retention time in the original decomposition mixture (12%) was identified as 4,5,6,7-tetrahydroindane, 4, by the comparison of the retention time with that of authentic sample of this compound prepared by the lithium–ethylamine reduction of indane according to the procedure of Benkeser.[19] The reduction of indane produces this compound as the major product.

The analysis of the infrared and n.m.r. data of the original decomposition products and the corresponding hydrogenated products allows one to assign a structure to the component produced in 32% yield: infrared (neat, original decomposition products) 3080 (m), 3050, 1620 (vw), 1000 (m), and 740 cm.$^{-1}$ (vs); infrared (neat, catalytic hydrogenation products) 3050 (m) and 1000 cm.$^{-1}$ (m).

Upon catalytic hydrogenation the bands at 3050 and 1000 cm.$^{-1}$ remain, clearly indicating the presence of a cyclopropane ring with a $CH_2$ grouping in the original decomposition mixture[20]; n.m.r. ($CCl_4$ solution, original decomposition products) $\tau$ 4.48 (singlet, vinyl protons), 7.70 (multiplet), 7.8 (multiplet), and 9.15 (multiplet due to cyclopropane $CH_2$); n.m.r. ($CCl_4$ solution,

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[14] F. E. King, T. J. King, and J. P. Topliss, *J. Chem. Soc.*, 919 (1957).

[15] J. A. Dixon and P. A. Naro, *J. Org. Chem.*, **25**, 2094 (1960).

[16] (a) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2550 (1961); (b) N. D. Zelinsky, K. Packendorff, and E. B. Chochlowa, *Chem. Ber.*, **68**, 98 (1935).

[17] H. L. Goering and F. H. McCarron, *J. Am. Chem. Soc.*, **78**, 2270 (1956).

[18] D. J. Cram and B. L. Van Duuren, *ibid.*, **77**, 3576 (1955).

[19] R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *ibid.*, **77**, 3230 (1955).

[20] See S. A. Liebman and B. J. Gudzinowicz [*Anal. Chem.*, **33**, 931 (1961)] for an infrared study of cyclopropane systems.

hydrogenated products) τ 8.5 (complex broad multiplet with side peaks) and 9.15 (multiplet).

The absorption at τ 9.15 is consistent with a cyclopropyl $CH_2$ grouping in both the original and the hydrogenated reaction products.[21] Thus in the original reaction mixture to the extent of 32% can be assigned structure **5** on the basis of the infrared and n.m.r. data. No attempt was made to identify the component originally present in a 3% yield.

**Acknowledgment.**—The partial financial assistance of National Science Foundation Grant 19490 is gratefully acknowledged. The authors wish to thank Dr. Lillya of the Chemistry Department of the University of Massachusetts for running the n.m.r. spectra.

[21] (a) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (b) J. P. Chesick [*J. Am. Chem. Soc.*, **84**, 3250 (1962)] reported the cyclopropyl $CH_2$ grouping at τ 9.5 in bicyclo[2.1.0]pentane. (c) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

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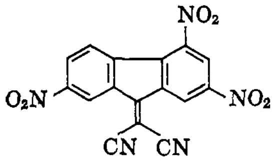
## 9-Dicyanomethylene-2,4,7-trinitrofluorene, A New Electron Acceptor

TAPAN K. MUKHERJEE[1] AND LEONARD A. LEVASSEUR

*Energetics Branch, Air Force Cambridge Research Laboratories, Bedford, Massachusetts, and Tyco Laboratories, Inc., Waltham 54, Massachusetts*

*Received July 24, 1964*

We wish to report the preparation of 9-dicyanomethylene-2,4,7-trinitrofluorene (DTF), an acceptor which has superior complexing properties to its precursor, 2,4,7-trinitrofluorenone (TNF). In addition DTF forms stable anion-radical salts of lithium and triethylammonium cations. Although the ammonium acetate–acetic acid catalyzed condensation of fluorenone and malononitrile proceeds smoothly in benzene, this procedure, when applied to TNF, led to the recovery of starting material. This failure can be attributed to the donor activity of the solvent, which evidently converts TNF completely to its benzene complex. The alternative procedure of piperidine-catalyzed condensation in methyl alcohol gave an excellent yield of DTF.



The structure of DTF has been assigned on the basis of elemental analysis and infrared spectrum. Hydrolysis in concentrated sulfuric acid led to 9-biscarboxamidomethylene-2,4,7-trinitrofluorene. Alkaline hydrolysis with sodium hydroxide in dilute tetrahydrofuran failed to regenerate 2,4,7-trinitrofluorenone.

TABLE I

CHARGE-TRANSFER COMPLEXES OF DTF

| Donor | Decompn. range, °C. | Calcd. for 1:1 complex C | H | N | Found C | H | N |
|---|---|---|---|---|---|---|---|
| Anthracene | 258–261 | 66.54 | 2.78 | 12.93 | 66.69 | 2.80 | 12.79 |
| Coronene | 400 | 72.39 | 2.58 | 7.00 | 72.73 | 2.70 | 8.72 |
| Fluorene | 212–215 | 65.78 | 2.86 | 13.22 | 65.73 | 2.93 | 13.27 |
| Perylene | 365 | 70.23 | 2.78 | 11.38 | 70.08 | 2.90 | 11.11 |
| Pyrene | 330–340 | 67.95 | 2.67 | 12.38 | 67.69 | 2.79 | 12.27 |
| Diaminodurene | 195–198 | 59.20 | 4.00 | 18.59 | 58.92 | 4.20 | 18.30 |
| N,N-Dimethyl-2-naphthylamine | 215 | 62.91 | 3.39 | 15.72 | 62.81 | 3.33 | 15.48 |
| 4-Iodoaniline | 203–204 | 45.37 | 1.90 | 14.30 | 45.53 | 2.17 | 14.45 |
| 2-Naphthylamine | 210–212 | 61.67 | 2.78 | 16.59 | 61.59 | 2.76 | 16.48 |
| Phenothiazine | 235–238 | 59.60 | 2.51 | 14.92 | 59.89 | 2.93 | 14.21 |

Solid charge-transfer complexes of DTF with aromatic hydrocarbons and amines are easily prepared by mixing chloroform or dichloromethane solutions of the components. In comparison with the TNF–hydrocarbon complexes, it was generally observed that the extent of dissociation into components on crystallization is markedly less with the corresponding DTF–hydrocarbon complexes. In Table I some of the donor–acceptor complexes of DTF are listed.

The advantage of DTF as a complexing agent is evident from spectral studies of the charge-transfer transition bands, the results of which are presented in Table II.

TABLE II

CHARGE-TRANSFER SPECTRA FOR HYDROCRBON–DTF AND HYDROCARBON–TNF COMPLEXES AND ENERGIES OF HIGHEST OCCUPIED MO'S OF THE HYDROCARBONS

| Symbol | Donor | DTF[a] | TNF[b] | $x_i$[c] |
|---|---|---|---|---|
| 1 | Acenaphthylene | 550 | 415 ± 15 | 0.637 |
| 2 | Anthracene | 662 | 541 ± 4 | 0.414 |
| 3 | 1,2-Benzanthracene | 640 | 522 ± 5 | 0.452 |
| 4 | 1,12-Benzoperylene | 675 | 570 ± 5 | 0.439 |
| 5 | 1,2-Benzopyrene | 600 | 510 ± 5 | 0.497 |
| 6 | 3,4-Benzopyrene | 726 | 590 ± 5 | 0.371 |
| 7 | 3,4-Benzoteraphene | 686 | 561 ± 5 | 0.405 |
| 8 | Chrysene | 576 | 482 ± 10 | 0.520 |
| 9 | Coronene | 650 | 512 ± 5 | 0.539 |
| 10 | 1,2,3,4-Dibenzanthracene | 610 | 505 ± 5 | 0.499 |
| 11 | 1,2,3,4-Dibenzopyrene | 647 | 548 ± 7 | 0.398 |
| 12 | 1,2,4,5-Dibenzopyrene | 689 | 562 ± 2 | 0.442 |
| 13 | Fluoranthene | 500 | 430 ± 15 | 0.618 |
| 14 | Perylene | 745 | 620 ± 5 | 0.347 |
| 15 | Phenanthrene | 500 | 435 ± 15 | 0.605 |
| 16 | Picene | 561 | 470 ± 10 | 0.501 |
| 17 | Pyrene | 650 | 520 ± 5 | 0.445 |
| 18 | Triphenylene | 508 | 425 ± 15 | 0.684 |
| 19 | Benzo[*ghi*]fluoranthene | 510 | 430 ± 15 | 0.63[b] |
| 20 | 3,4-Benzofluorene | 615 | 495 ± 5 | 0.505[b] |
| 21 | 2,3-Benzofluorene | 570 | 485 ± 5 | 0.52[b] |
| 22 | 1,2-Benzofluorene | 588 | 492 ± 5 | 0.51[b] |
| 23 | Decacyclene | 625 | 518 ± 10 | 0.47[b] |
| 24 | Fluorene | 523 | 425 ± 10 | 0.635[b] |

[a] Spectra taken in $CH_2Cl_2$ solution. [b] See ref. 2. [c] C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," 2nd Ed., Mathematical Institute, Oxford, England, and the Centre de Mecanique Ondulatoire Applique, Paris, France, 1959.

The second column lists the donors, while the third and fourth columns show charge-transfer band maxima of DTF and TNF complexes, respectively. A few of the DTF–hydrocarbon spectra were measured in KBr disks and the absorption maxima were found to be within the same range with those obtained in solution. Since no sharp peaks could be obtained in the measurement of the spectra of TNF–hydrocarbon solutions, Lepley's[2] data on the spectra of solid TNF–hydrocarbon complexes is used for comparison. The fifth column

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[1] To whom inquiries regarding this article should be sent at the Air Force Cambridge Research Laboratories, Bedford, Mass.

[2] A. R. Lepley, *J. Am. Chem. Soc.*, **84**, 3577 (1962).