with stirring, over 30 min. After an additional 30 min, the mixture was diluted with 5 ml of pentane and washed twice with 20-ml portions of water, and the organic phase was separated and dried over $CaCl_2$. The product was decanted, solvent was stripped, and the residue (1.5 g,) was submitted to gc on the previously described SF-96 column (82°). Other than chloroform the only high-boiling material was the desired cyclopropane; infrared showed 3.45, 6.87, 6.99, 7.28, 8.95, 9.07, 9.37, 9.62, 9.95, 10.34 μ (CCl_4); nmr[31] gave 1.37 (singlet, methyls), 1.21 (singlet, ring); integral ratio was 3:1. Other dichlorocyclopropanes were similarly prepared.

1,1-Dichloro-*cis*-2,3-dimethylcyclopropane.—Infrared gave 3.43, 6.87, 7.22, 8.14, 8.77, 10.23, 10.50 μ (CCl_4); nmr showed a multiplet, 1.80 to 1.23 disappearing beneath a larger absorption with sharp peaks at 1.18 and 1.07.

Anal. Calcd for $C_5H_8Cl_2$: C, 43.19; H, 5.80; Cl, 51.00. Found: C, 43.34; H, 5.87; Cl, 50.82.

1,1-Dichloro-*trans*-2,3-dimethylcyclopropane.—Infrared gave 3.43, 6.91, 7.15, 8.24, 8.76, 9.23, 9.79, 10.40 μ (CCl_4); nmr showed peaks at 1.30 and 1.24 (major signal) superimposed on a multiplet extending from 1.42 to 0.87.

Anal. Calcd for $C_5H_8Cl_2$: C, 43.19; H, 5.80; Cl, 51.00. Found: C, 43.40; H, 5.76; Cl, 50.95.

1,1-Dichloro-2-ethylcyclopropane.—Infrared showed 3.40, 6.87, 7.02, 7.26, 8.17, 8.57, 8.89, 9.15, 9.64, 9.95 μ (CCl_4); nmr gave a multiplet from 1.80 to 1.28, with maximum at 1.53, running into a crude triplet centered at 1.11, and superimposed on other absorptions which tail to 0.85.

Anal. Calcd for $C_5H_8Cl_2$: C, 43.19; H, 5.80; Cl, 51.00. Found: C, 43.34; H, 5.85; Cl, 50.85.[32]

Reaction of Chloroform and Potassium *t*-Butoxide in Pentane.—In an experiment analogous to the syntheses described above, 2.0 g of potassium *t*-butoxide was treated with 3.0 g of chloroform in 20 ml of pentane, at −10°. After work-up and stripping of solvents, there remained 180 mg of yellow oil, possessing nmr absorptions identical with those of 1,1-dichloro-2,2-dimethylcyclopropane. It was not determined whether tetrachloroethene was also present in this oil. A similar experiment with tetrachlorodifluoroacetone afforded a product mixture in which the major low-boiling component was identified as III, by comparison of gc retention time and infrared spectrum with those of an authentic sample.

Competition Experiments.—All competition experiments (except for inverse addition runs) were performed under identical conditions. Apparatus was similar to that used in synthetic runs. Temperature was maintained at *ca.* −10°. An excess of carbene precursor over *t*-butoxide was used; a tenfold excess of each olefin was minimal. Reaction products were not distilled, but immediately analyzed by gc. For the CFC adducts, we used an F & M Model 500 instrument, fitted with an 8 ft × 0.25 in. DC-550 silicone oil column, with He flow of 180 ml/min, a column temperature of 65°, and an injection temperature of 140°.

Analysis of the DCC competitions was carried out on the SF-96 column, with a He flow 300 ml/min, a column temperature of 80°, and an injection temperature of 193°. An Aerograph A-90-P instrument was used. Detectors were calibrated with pure adducts in all cases.

From the product ratios determined by gc, relative rates were calculated from the standard expression $k_1/k_2 = (P_1/P_2)(O_2/O_1)$, where the P_i quotient represents the cyclopropane product ratio and the O_i quotient represents the mole ratio of starting olefins. Results appear in Tables I and II.

Registry No.—VIa, 13144-06-4; VIb, 13144-07-5; fluorochlorocarbene, 1691-88-9; dichlorocarbene, 1605-72-7; 1,1-dichloro-2,2-dimethylcyclopropane, 694-16-6; 1,1-dichloro-*cis*-2,3-dimethylcyclopropane, 1120-67-8; 1,1-dichloro-*trans*-2,3-dimethylcyclopropane, 1120-68-9; 1,1-dichloro-2-ethylcyclopropane, 13144-11-1.

Acknowledgments.—Support by the National Institutes of Health (GM-13585) and by the National Science Foundation (GP-4857) is gratefully acknowledged. We also wish to thank Mr. Ernest Anderson of The Bell Telephone Laboratories, Murray Hill, N. J., who determined the F^{19} nmr spectra.

(31) Reported in parts per million (ppm) downfield from internal tetramethylsilane (TMS).

(32) As discussed above, this prepration also yielded some 1,1-dichloro-2,2-dimethylcyclopropane.

Some Chemistry of Compounds Related to [2.2]Metacyclophane[1,2]

NORMAN L. ALLINGER, BERNER J. GORDEN, SHIH-EN HU, AND R. A. FORD

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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5,13-Dimethyl[2.2]metacyclophane has been prepared, some of its reactions have been studied, and the mechanisms of electrophilic substitution in [2.2]metacyclophanes are discussed. 4,5,9,10-Tetrahydropyrene derivatives substituted at the 1 and 2 positions have been synthesized, and the nmr spectra of various representatives of these structural types have been analyzed.

The chemistry of bridged aromatic compounds has been studied in considerable detail,[3] and has been richly rewarding. One of the first compounds of this general type to be prepared was [2.2]metacyclophane,[4] and the compound has been examined from time to time during the ensuing period.[5]

[2.2]Metacyclophane undergoes a few types of electrophilic aromatic substitution reactions, but such reactions do not lead to derivatives of the cyclophane, but rather to tetrahydropyrene derivatives (such as the formation of II as indicated in Scheme I). The formation of II from I might, *a priori*, proceed with the attack by the nitronium ion either preceding, following, or concurrent with the bridging of the two aromatic rings. Earlier[1] we presented arguments which indicated that it was most unlikely that the bridging of the aromatic rings followed the aromatic substitution, and which showed that the position of substitution and the rate of reaction were consistent with the attack by the nitronium ion on one ring, concurrent with the attack of the substituted ring on the other aromatic ring (path 2 in Scheme I).

Although tetrahydropyrene underwent substitution to give the same product (II) as that obtained from metacyclophane, the possibility that the reaction occurred by path 1 (in which the aromatic rings bridged to form tetrahydropyrene as a distinct intermediate) was not seriously entertained earlier, because the yield

(1) For the previous paper in this series, see N. L. Allinger, M. A. DaRooge, and R. B. Hermann, *J. Am. Chem. Soc.*, **83**, 1974 (1961).

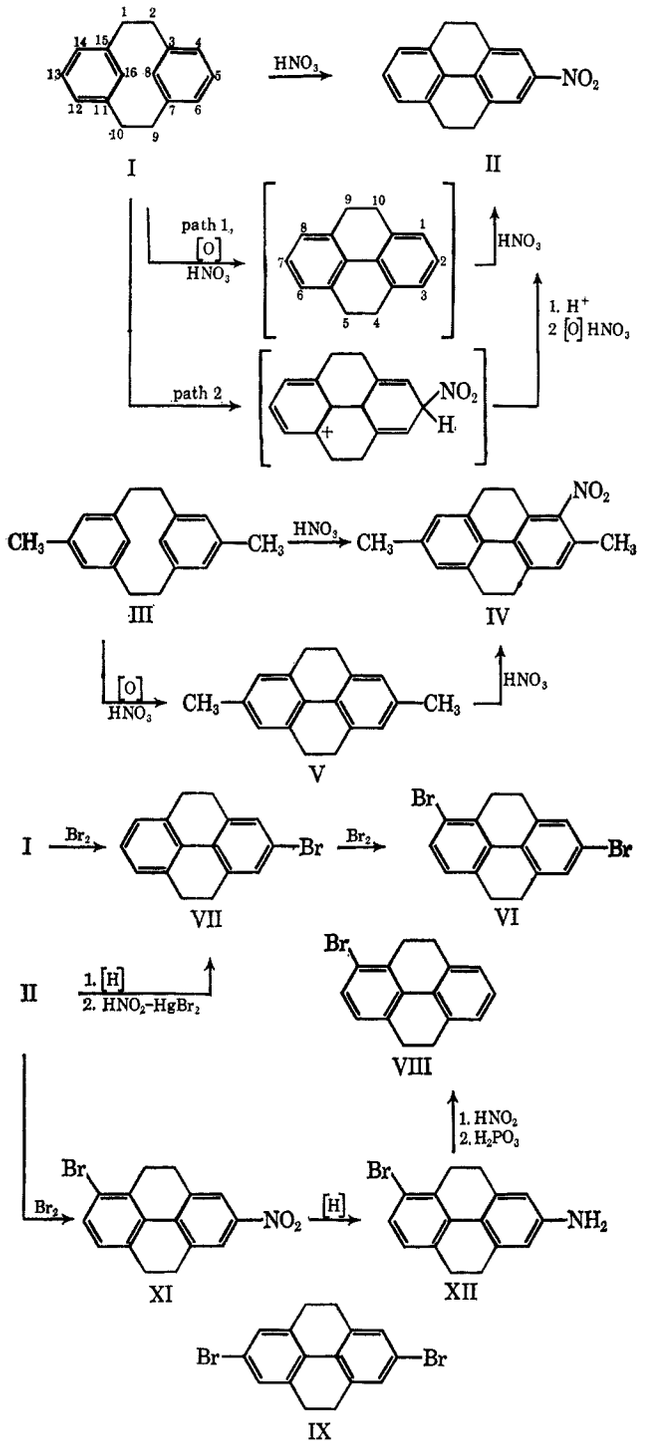
(2) This research was supported by research grant GP-4290 from the National Science Foundation.

(3) B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964.

(4) M. Pellegrin, *Rec. Trav. Chim.*, **18**, 457 (1899).

(5) Most of the pertinent literature is summarized in ref 1 and 3. Additional papers of interest include that by P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J. Chem. Soc.*, 6893 (1965), and others referred to below.

SCHEME I



of II from tetrahydropyrene was only 25–35% while from metacyclophane the yield ranged from 85 to 90%. We have considered this matter further, however, and report herein the results of this latter work.

No tetrahydropyrene could ever be detected as an intermediate in the nitration. If it is fact an intermediate, its rate of substitution under these conditions is very much faster than the rate of oxidation of [2.2]metacyclophane to yield tetrahydropyrene, and the concentration of the latter must be quite small at all times. On the other hand, if one carries out the nitration of tetrahydropyrene under the reaction conditions, the initial concentration of starting material is appreciable, and it is mostly converted to resinous product under these circumstances. This result does not preclude the possibility that low concentrations of tetrahydropyrene do not yield such products, but rather the simple nitration product. The experimental conditions of the reaction make it quite difficult to rule out this possibility.

Since tetrahydropyrene is not detectable as an intermediate in the reaction, one concludes that either it is not formed at all, or that it is reacting as rapidly as it forms; so the concentration does not build up sufficiently to permit its isolation. If the rate of reaction of tetrahydropyrene is as fast as that of the metacyclophane, since its concentration is much smaller throughout the initial stages of the reaction, the *rate constant* for the substitution of tetrahydropyrene must be appreciably larger than that for the oxidation of metacyclophane to tetrahydropyrene. Hence the following question was asked. If the methylated cyclophane III were allowed to nitrate under the same reaction conditions as were used for the nitration of I, what would one predict regarding the rates of the nitration and oxidation reactions for this compound? The one-step substitution reaction (path 2) is not possible in this case. If metacyclophane preferentially reacted by that path, then the methyl groups in III would prevent reaction by the easiest available path, and an alternative reaction (which would have to be relatively slow in metacyclophane) would take place (either oxidation or substitution). The electron-donating properties of the methyl groups would be expected to accelerate both of these reactions, but the over-all reaction would still be expected to proceed at a slower rate than in the metacyclophane.[6] On the other hand, if the reaction of metacyclophane is a two-step process (path 1), the presence of the methyl groups in III should accelerate the first (rate-determining) reaction.

When the nitration of III was carried out under the same conditions used for I, an insoluble, noncrystalline, amorphous powder, apparently polynitrated, was obtained. Under much milder conditions, where I scarcely reacted, III was rapidly converted to a mixture of tetrahydropyrene (V) and the nitro derivative IV. It is clear, then, that with III the two-step mechanism must obtain, and, because the rate is so much faster than in I, it would appear that only reaction by path 1 suffices to explain all the known facts.

While a two-step mechanism for the reaction of III → IV is necessarily required, it is not clear at the outset which step precedes the other. In this case, if the reaction was allowed to proceed only part way to completion, and then worked up, both the tetrahydropyrene (V) and the nitrated derivative (IV) were isolated in comparable amounts. It was shown that V was converted to IV in good yield under the reaction conditions by extending somewhat the reaction time. No trace was found of a cyclophane containing a nitro group. Hence, in this case, the oxidation step occurs first, followed by the nitration. If the methyl group affected the second step of the reaction only slightly, but accelerated the first step very much, the results are adequately explained. The earlier interpretation of the nitration of I as a concerted, transannular, aromatic substitution now appears less attractive

(6) The only other alternative would be that the rate of path 2 is slightly faster than by path 1, so that acceleration of reaction by the latter path more than compensates for the blocking of the former path.

than a preliminary oxidation to the tetrahydropyrene. Such a reaction is unusual, but not without analogy. The same compound (I) is known to undergo a catalytic dehydrogenation to yield the tetrahydropyrene.[7]

The bromination of [2.2]metacyclophane was also studied. As expected the reaction product was VII, analogous to that obtained from nitration. If the cyclophane was treated with 3 equiv of bromine, a dibromide was isolated, and this was shown to have structure VI.[8] The structure of the product of the monobromination of [2.2]metacyclophane was determined in the following way. The corresponding nitration product (II) has had its structure proven previously.[1] The nitro group was converted to an amino group as described earlier.[1] The amine underwent a Sandmeyer reaction to give a monobromide (VII), which has the same melting point as the monobromide obtained by direct bromination, and the two do not give a melting point depression. There are only two possible monobromo derivatives of tetrahydropyrene in which the bromine is on the aromatic ring. (None of the bromides obtained in this work gave a silver nitrate test, thus excluding side-chain bromides from consideration.) The other one (VIII) was synthesized separately and shown to be different from the bromination product of the cyclophane, thus establishing both of the structures.

The dibromide (VI) obtained by addition of 3 equiv of bromine to [2.2]metacyclophane has a structure which perhaps would be unexpected. In predicting where the monobromide VII would react in electrophilic substitution, one might draw analogies as follows. Biphenyl reacts with bromine to give 4-bromobiphenyl. The latter reacts with a second equivalent of bromine to give 4,4′-dibromobiphenyl. The first bromine deactivates the ring in which it is located as expected, but the bromophenyl group acts as a *para* director. 4-Nitrobiphenyl similarly substitutes in the 4′ position, and thus it appears that any deactivating group on the phenyl deactivates that ring, but the whole substituent still acts as a *para* director on the other ring. With [2.2]metacyclophane (which is presumed to brominate *via* the intermediate tetrahydropyrene) or with tetrahydropyrene, reaction with bromine occurs at the position analogous to that in biphenyl and gives bromide VII. Reasoning from the biphenyl case, one would guess that the bromophenyl ring would act as a *para* director, and that substitution would proceed to give dibromide IX. Only one dibromide was isolated from the reaction, which would have to be VI or IX, and of the methods available at the time, dipole moments appeared likely to give a definite answer as to the structure of the compound. The measured dipole moment of the dibromide was 1.03 ± 0.28 D. The dipole moment of bromobenzene is 1.56 D. If a perfectly hexagonal arrangement for the benzene rings is assumed, the moments calculated for VI and IX are 1.56 and 0 D., respectively. It seems likely that the former structure would have a buttressing effect tending to push the C–Br dipole in such a way as to lower the moment below the 1.56 D. value.[9] On the other hand, "anomalous atomic polarization" might be expected to give a small apparent moment to IX, although no evidence for such behavior is reported for closely analogous models, 4,4′-dibromobiphenyl and *p*-dibromobenzene.[10] From the dipole moment, the dibromide was assigned the structure VI.

Similarly, the nitro compound II reacted with bromine to give a bromo derivative which by analogy should be XI. That this was the correct structure was shown by the fact that reduction of the nitro group to the amine XII, following by diazotization and reduction of the diazo compound with hypophosphorus acid yielded a monobromide, which was different from VII and hence was assigned the structure VIII.

A rationalization of the observed substitution behavior can be made as follows. The bromophenyl or nitrophenyl group attached to a benzene ring is a *para* director, but presumably the benzene ring is not activated as much by the presence of the nitrophenyl as it would be by the presence of an unsubstituted phenyl. In the tetrahydropyrene, the phenyl group is a stronger *para* director than the two alkyl groups taken together are *ortho* directors, so that substitution *para* to the phenyl takes place, although the differences in rate may not be more than a factor of 10 or so. The presence of the negative group on the phenyl substituting the ring in question would lessen the activating influence of the phenyl, and while it might still be a *para* director, it is apparently no longer as influential as are the alkyl groups, and hence the observed product is formed preferentially. The reaction leading to dibromide VI is not very clean, but it is clear that this must be the principal product, since its low symmetry number would lead to a relatively high entropy of solution, hence a relatively high solubility, and a low likelihood of isolating it as the product of the reaction unless it strongly predominated over the more symmetrical isomer (IX).

An attempt to obtain side-chain bromination of [2.2]metacyclophane with N-bromosuccinimide did not succeed. The nmr spectrum of the product mixture showed that the brominated products were not cyclophanes, but rather tetrahydropyrenes.

The nmr spectra of some of the compounds prepared in the present work were examined and showed some features of interest. The parent [2.2]metacyclophane was restudied in some detail. The spectrum has been previously reported,[1,11] and analysis of the aliphatic pattern has been carried out in one case.[11c] In another case,[11b] analysis of the entire molecule has been carried out by a less rigorous method. (See Table I.) As there was slight disagreement between the earlier workers, we have repeated the analysis of the spectrum by the

(7) W. Baker, J. F. W. McOmie, and J. M. Norman, *J. Chem. Soc.*, 1114 (1951).

(8) Much of this work was carried out over the period 1958–1960 when nmr spectra were not available to us. The structure proofs may consequently seem roundabout by present standards. In cases where samples of the material remained, we have gone back and examined the nmr spectra of the compounds also.

(9) The buttressing effect should correspond to an energy of about 0.6 kcal/mole, similar to that found for *o*-xylene [H. J. Bernstein, *Trans. Faraday Soc.*, **58**, 2285 (1962)] and this would yield a bending of the C–Br bond at carbon 1 by about 4° in VI, lowering the predicted moment to 1.46 D.

(10) A. L. McClellan, "Table of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963.

(11) (a) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961); (b) D. J. Wilson, V. Boekelheide, and R. W. Griffin, Jr., *ibid.*, **82**, 6302 (1960); (c) H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, **37**, 120 (1962).

iterative method of Swalen and Reilly.[12] The X_2Y_2 system for the methylated cyclophane III has also been analyzed, and the results are compared with those of the unsubstituted compound in Table II.

TABLE I

ANALYSIS OF THE PROTON MAGNETIC RESONANCE SPECTRUM OF [2.2]METACYCLOPHANE[a]

	Ref 11a	Ref 11c	This work
A	435		429.7
B	422		416.1
M	255		252.6
J_{AB}	7.8		7.5
J_{BM}	1.2		1.6
δ_{XY}	57.6	59.1	58.6
K	11.4	−15.5	−15.5
M	8.3	9.1	9.1
N	7.8	8.0	8.1
L	14.7	16.0	15.8

[a] All values are in cycles per second (cps). Chemical shifts are measured downfield from tetramethylsilane at 60 Mc in deuteriochloroform.

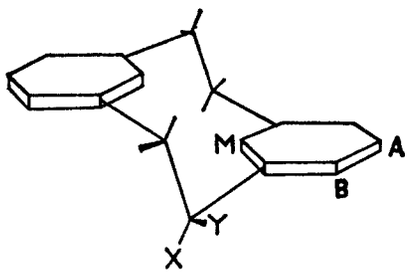
TABLE II

NUCLEAR MAGNETIC RESONANCE DATA ON COMPOUNDS I AND III

Compd	X[a]	Y[a]	$J_{X_1Y_1}$	$J_{X_1Y_2}$	$J_{X_1X_2}$	$J_{Y_1Y_2}$
I	122.3	180.9	−11.9	3.8	12.3	3.2
III	121.5	177.2	−11.8	4.4	11.7	3.1

[a] All values are in cycles per second. *A priori* assignment of the chemical shifts to the X and Y protons is tenative, and was made by examination of a Dreiding model.

The small change in the coupling constants between the aliphatic protons in III compared with I may reflect a slight flattening of the system upon addition of the methyl groups. This flattening might result in an effort to relieve the increased interaction between the Y and B protons arising from a buttressing effect due to the methyl groups. The effect is so small, however, as to make any definite conclusion impossible. The aromatic protons showed up more or less as expected with the M protons appearing as a triplet at relatively high field while the B protons were at lower field and appeared as a multiplet due to coupling with the methyls, which also gave a complex pattern in turn.



The nmr spectra of the condensed tetrahydropyrene derivatives turned out to be especially interesting. While the aromatic protons in all of the compounds studied (II, IV, VI, VII, and XI) were about as expected (see the Experimental Section) the bridge protons appeared at first glance to be quite anomalous. The bridge protons of II, IV, VII, and XI all showed some splitting, in contrast to the analogous protons in the unsubstituted tetrahydropyrene which appear as singlet due to rapid flipping of the two partially hydrogenated rings. While this splitting might be interpreted as being due to a proximity effect of the substituents, the bromo and nitro groups in VII and II seem to be too far away to have any appreciable effect. However, the best argument against the proximity effect is the fact that in VI the bridge protons show up as a singlet, even though the proximity effect of the 6-bromo should be much larger than that of the 2-bromo. Also, the nitro group in IV does not seem to have any proximity effect on the methyls, since they appear as a singlet (assignment made by integration).

An alternative interpretation of the splitting which is observed can be made, if it is assumed that the substituents have a negligible proximity effect on the bridge protons in all of these cases. The nonequivalence of the bridge protons might instead arise from a difference in the ring current of the two aromatic rings which is brought about by the electronegativity of the substituents. It may be noted that, in all cases where splitting occurs (II, IV, VII, and XI), the substituent on one ring has a different electronegativity from that on the other ring. In the case of the dibromide VI, both rings have the same substituent, and therefore the equivalence of the protons in question is maintained and no splitting occurs. It might be asked why the different ring currents in IV would have an effect on the bridge protons but not on the methyl protons. Examination of a Dreiding model reveals that the bridge protons are in quite a different region with respect to the rings than the methyl hydrogens and this could easily be enough to account for the difference, since the splitting is quite small in every case. All in all, it seems that the differential ring current effect is the best interpretation of the observed spectra, and further investigation of this phenomenon is underway.

Experimental Section

All nmr spectra were recorded on a Varian A-60A spectrometer using tetramethylsilane as an internal standard and deuteriochloroform as solvent, except as noted. All temperature readings are uncorrected. All ultraviolet spectra were recorded on a Cary Model 14 recording spectrophotometer.

[2.2]Metacyclophane (I).—In a 5-l. round-bottomed flask equipped with a mechanical stirrer and an addition funnel while under a nitrogen atmosphere, phenyllithium was prepared by adding 150 g (0.95 mole) of bromobenzene in 200 ml of reagent benzene over 5 hr to 14 g (2 g-atoms) of lithium wire or rod (Lithium Corporation of America) in 500 ml of reagent ether. External heating was applied to initiate the reaction, but was discontinued after the reaction began to reflux itself. Finally, after diluting to about 1 l. with additional ether, heating was begun to effect a gentle reflux for 12 hr. To the blackish solution was then added 175 g (0.33 mole) of α,α'-dibromo-*m*-xylene in 1 l. of reagent benzene over 10 hr. During the addition one could note a dull orange color when the addition was stopped occasionally and which disappeared again as the addition was resumed (this color is attributed to an excess of phenyllithium in the media). Refluxing and stirring were maintained for 4 days, and 2 g of fresh lithium wire was then added. Refluxing and stirring were resumed and at the end of 8 days, work-up and crystallization of an aliquot showed the starring dibromide to be spent. After cooling the reaction mixture, water was added slowly with

(12) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962). The original program was translated from IBM 7090/7094 FORTRAN IV to IBM 7070/7074 FORTRAN II. Considerable modification was necessary owing to the difference in size of the core storage. This was accomplished by dividing the program into five parts and using the IBM package link program. The parts consisted of (1) calculation of constants, (2) reiteration, (3) calculation of error, (4) calculation of transitions, and (5) plotting of spectrum.

increased stirring. The organic phase was separated, washed with additional water, and concentrated with the use of an aspirator, during which time crude cyclophane began to appear. Filtration of the crude product followed by several recrystallizations from ethanol (Norit), gave 17 g (25%) of product, mp 132.5–134° (lit.[1] 133–134°).

Generally the crude product did not separate so easily, especially in smaller runs, and it often contained considerable polymer and biphenyl. Concentration of the reaction mixture in these cases often resulted in a gummy, polymeric residue. This material was then extracted with several portions of boiling ethanol, thereby leaving behind the bulk of the polymer. The extracts were either crystallized further or chromatographed on alumina or both, to remove the remaining polymer. The resulting, white material was placed in 2-g portions in 10–15 ml of diethylene glycol and gradually warmed with stirring to 70° on a steam bath, and immediately filtered by suction, thereby removing the biphenyl as melt. Two such treatments were sufficient. The insoluble solid was recrystallized from ethanol to give the pure product. Alternatively the biphenyl could be distilled quickly from the mixture at reduced pressure by rapid heating. Recrystallization of the residual solid also gave the pure product. The infrared spectrum showed the strongest absorptions at 3030, 2940, and 2860 cm^{-1} (CCl_4), and the ultraviolet spectrum showed $\lambda_{max}^{absolute\ EtOH}$ 209.5 mμ (shoulder), 213 (ε 29,130), and 272 (435). The nmr spectrum showed the AB_2 part of an AB_2M pattern centered about 420 cps and the M part at 252.2, while the X_2Y_2 pattern was centered about 151.5 (area ratio 3:2:8). The analysis of this spectrum is given in Table I.

2-Nitro-4,5,9,10-Tetrahydropyrene (II). A. Nitration of [2.2]-Metacyclophane (I).—To 2 g of [2.2]metacyclophane (I) in 150 ml of glacial acetic acid was added over 2 min 9 ml of concentrated nitric acid while stirring with a magnetic stirrer. After stirring for 5 min more, excess ice and water were added to the solution. The yellow precipitate was collected and washed by suction; recrystallization from ethanol gave 2 g (83%) of the product, mp 108–110° (lit.[1] 110–111°).

The infrared spectrum ($CHCl_3$) showed strong absorption at 3030, 2940, 2900, and 2860 cm^{-1} (CH) and 1538 and 1333 cm^{-1} (NO_2). The nmr spectrum showed a peak at 174, an AB_2 pattern at about 428, and a peak with slight shoulders at 425 cps (area ratio 2:3:8).

B. Nitration of 4,5,9,10-Tetrahydropyrene.—One gram (0.0053 mole) of commercial (Columbia-Southern) tetrahydropyrene (mp 133–136°) was placed in 75 ml of glacial acetic acid, and 4.5 ml of concentrated nitric acid was added over 3 min while stirring with a magnetic stirrer. After stirring for 3 min more, excess ice and water were added, and the yellow-red precipitate was filtered and washed by suction. Two crystallizations from ethanol gave a product, mp 94–105°, and two more crystallizations (Norit) gave 0.4 g (32%) of product, mp 102–107°. A mixture melting point with the cyclophane nitration product was not depressed, and the infrared spectra were identical.

2-Bromo-4,5,9,10-tetrahydropyrene (VII). A. Bromination of [2.2]Metacyclophane (I).—To 0.5 g of I in 20 ml of glacial acetic acid was added dropwise over 20 min at room temperature 0.39 g of bromine while stirring with a magnetic stirrer.[13] Stirring was continued for 2 hr more, during which time a yellow precipitate was formed. To this mixture was added excess ice–water, and the material was removed and washed by suction filtration. Fractional crystallization from absolute ethanol gave fine, white needles of polybrominated material, mp 180–190°. Concentration gave 0.1 g (15%) of the product, mp 96.5–98°. The nmr spectrum showed a peak at 430, an AB_2 pattern at 421, and three peaks (separation 3 and 1 cps) centered at 168 cps (area ratio 2:3:8).

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.38; N, 4.59; Br, 28.02. Found: C, 67.60; H, 4.63; Br, 28.28.

B. Bromination of Tetrahydropyrene.—To 0.5 g of tetrahydropyrene in 30 ml of glacial acetic acid was added 0.5 g of bromine in 2 ml of glacial acetic acid over 45 min from a syringe while stirring with a magnetic stirrer at room temperature. Stirring was continued for 1 hr more, during which time a fine precipitate became noticeable. Ice water was added and the yellow precipitate was collected and washed by suction filtration. Recrystallization was not successful at this point and the material was chromatographed on 36 g of neutral, activity 1 Woelm alumina collecting 100-ml fractions using the following solvent combinations: 5% benzene–hexane, benzene, 3% methanol–benzene. In the first two fractions a white compound was obtained which when recrystallized from ethanol showed mp 137–139°, and corresponded to unreacted tetrahydropyrene. In the next fractions 0.15 g (22%) of product was obtained; recrystallization from ethanol gave mp 97.5–100°. A mixture melting point with the product from the bromination of [2.2]metacyclophane was not depressed.

C. From 2-Amino-4,5,9,10-tetrahydropyrene.—Into a cold mixture of 3.75 ml of water and 7.5 ml of concentrated sulfuric acid, 0.75 g of sodium nitrite was added with stirring. The mixture was then heated with stirring on a steam bath until a clear solution was obtained. The solution was cooled to 0° and stirred mechanically as a solution of 1.1 g of 2-amino-4,5,9,10-tetrahydropyrene in 5 ml of pyridine was added drop by drop in the course of 1 hr. After the addition was complete, the mixture was stirred for 1 hr longer, and was then diluted to a volume of 100 ml by addition of ice and water, and treated with a solution of 1 g of urea in 12.5 ml of water in order to destroy the excess nitrous acid. The solution was stirred at 0° for 1 hr, and then to it was added a solution of 14.7 g of mercuric bromide and 17.17 g of potassium bromide in 25 ml of water. The mixture was allowed to stand in the cold for 1 hr in order to coagulate the deeply colored precipitate of the double salt. The precipitate was then filtered, washed with water, and air dried for 12–20 hr. The dried double salt (8.4 g) was intimately mixed with 18 g of potassium bromide, and the mixture was heated cautiously in a 50-ml distilling flask until the temperature reached 110°. When no more nitrogen was evolved the bromo compound was sublimed from the mixture under reduced pressure. The crude product was recrystallized from absolute alcohol as pale yellow crystals, mp 102–103°, yield 45%.

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.38; H, 4.59; Br, 28.02. Found: C, 67.48; H, 4.67; Br, 27.75.

Conversion of Bromide VII to 4,5,9,10-Tetrahydropyrene.—A small sample of VII was converted to 4,5,9,10-tetrahydropyrene by hydrogenolysis as described for dibromide VI, and the product was similarly identified.

1-Bromo-7-nitro-4,5,9,10-tetrahydropyrene (XI).—To 0.5 g of 2-nitro-4,5,9,10-tetrahydropyrene II in 15 ml of glacial acetic acid was added 0.75 g of bromine over 25 min while stirring with a magnetic stirrer at room temperatue. After 4 hr, excess ice was added and the yellow precipitate was collected and washed by suction filtration. Recrystallization from ethanol gave 0.55 g (85%) of the product, mp 133.5–136°.

The infrared spectrum of XI in $CHCl_3$ showed strong absorptions at 3030, 2940, 2900, and 2860 cm^{-1} (C–H) and 1538 and 1333 cm^{-1} (NO_2). The nmr spectrum showed a peak at 475 and what appeared to be an AB pattern centered about 438 cps. (Two small extraneous peaks were considered to be impurity as integration indicated about 0.5 extra proton.) The aliphatic protons appeared as two peaks with slight shoulders and unequal intensities at 179 and 173 cps.

Anal. Calcd for $C_{16}H_{12}BrNO_2$: C, 58.20; H, 3.66; Br, 24.20. Found: C, 58.05; H, 3.81; Br, 24.60.

1-Bromo-7-amino-4,5,9,10-tetrahydropyrene (XII).—In a 100-ml, three-necked, round-bottomed flask equipped with a mechanical stirrer and reflux condenser was placed 0.5 g of XI in 50 ml of reagent benzene. The solution was brought to a gentle reflux and stirring was begun. There was added in one portion 25 g of iron filings (40 mesh) previously activated by mixing with 2.5 ml of concentrated hydrochloric acid[14] (stirring in a beaker). After the reaction mixture had stirred for 1 hr, 1 additional ml of hydrochloric acid was gradually added. The addition of 25 ml of water was begun by periodically adding 3–4-ml portions over the next 5–6 hr. At the end of this period, the mixture was allowed to reflux for 15 hr, and then while still hot, it was filtered by suction to remove iron residues. These residues were washed with additional hot benzene and the combined benzenes filtrates were washed with water. Complete removal of the benzene gave an oil, which when recrystallized from hexane (Norit) several times gave 0.4 g (89%) of the amine, mp 125.5–128.5°.

The infrared spectrum of XII in $CHCl_3$ showed NH_2 absorption at 3390 and 3330 cm^{-1}, along with the characteristic C–H quartet at 3145, 3115, and 3086, and 3050 cm^{-1}.

(13) If the theoretical amount of bromine is added (2 equiv), much more polybrominated material is obtained, and the purification of the monobromide is more difficult.

(14) S. E. Hazlet and C. A. Dornfeld, *J. Am. Chem. Soc.*, **66**, 1781 (1944).

Anal. Calcd for $C_{16}H_{14}BrN$: C, 64.01; H, 4.70; N, 4.67. Found: C, 63.99; H, 4.73; N, 4.61.

1-Bromo-7-acetamino-4,5,9,10-tetrahydropyrene.—The derivative was prepared from XII in the usual manner with acetic anhydride and pyridine, and was recrystallized from ethanol–water, mp 194.5–196°.

Anal. Calcd for $C_{18}H_{16}NBrO$: C, 63.17; H, 4.71. Found: C, 62.37; H, 4.99.

1-Bromo-4,5-9,10-tetrahydropyrene (VIII).—To 0.7 g of XII in a 50-ml beaker was added 5 ml of concentrated hydrochloric acid and 1 ml of water. The mixture was stirred and warmed on a steam bath for 20 min and then for 20 min more while gradually cooling to 5° with an ice bath. At this temperature was added with continued stirring a solution of 0.1 g of sodium nitrite in 2 ml of water over the next 15 min. To the orange solution still containing undissolved material was added in small portions enough additional solid sodium nitrite so that the solution became clear and dark red. This solution was stirred for 30 min more at 5° and then it was added in one portion to 25 ml of hypophosphorous acid. The resulting solution was kept at room temperature overnight. No usual visual evidence for similar reductions as with a model compound (4-bromo-4′-nitrobiphenyl) was noted, and only a gummy red material formed in the flask. This mixture was taken up in ether, washed with water, and dried, and the ether was removed. The yellow material obtained did not crystallize well and showed mp 37–43°. Chromatography of the material of 9 g of neutral activity 1 Woelm alumina using benzene gave in the first fractions 90 mg (14%) of a white solid which was recrystallized several times from ethanol–water, and finally sublimed to give crystals, mp 51–52°.

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.38; H, 4.59; Br, 28.02. Found: C, 67.48; H, 4.67; Br, 27.75.

1,7-Dibromo-4,5,9,10-tetrahydropyrene (VI).—To 1.5 g of VII in 65 ml of carbon tetrachloride was added during 5 min 1.5 g of bromine in 10 ml of carbon tetrachloride. After 10 min the solution was washed with aqueous sodium bisulfite, water, and aqueous sodium bicarbonate, and was dried. The solvent was evaporated, and the residue was crystallized from hexane to yield 1.0 g of product, mp 220–222°.

The nmr spectrum showed two peaks at 432 and 168 cps in the ratio 4:8, the low-field peak being split cleanly but by only a small amount (~1 cps).

Anal. Calcd for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32; Br, 43.90. Found: C, 52.64; H, 3.06; Br, 44.48.

The dibromide (50 mg) was dissolved in 50 ml of methanol containing 25 mg of palladium on carbon, and hydrogenation was carried out at room temperature and atmospheric pressure. The theoretical amount of hydrogen (2 equiv) was taken up, and the reaction ceased. The solution was filtered and the solvent was evaporated. The residue (100% yield) had mp 137–139° and showed no melting point depression with authentic 4,5,9,10-tetrahydropyrene.

The dipole moment of VI was determined in benzene at 25° using the apparatus and methods described earlier,[15] and gave a value of 1.03 ± 0.28 D. Other pertinent data are α = 3.127, ϵ 2.2728, d 0.8734, β = 2.236, and $P_{2\infty}$ = 101.9.

α,α'-Dibromomesitylene. A. N-Bromosuccinimide with Mesitylene (Preferred Method).—In a 1-l., three-necked, round-bottomed flask equipped with a mechanical stirrer and reflux condenser was placed 120 g of mesitylene, 356 g of N-bromosuccinimide, 3 g of benzoyl peroxide, and 350 ml of reagent carbon tetrachloride. While stirring, the reaction mixture was gradually warmed on a steam bath. When the solution was about to reflux, reaction began and external heating was discontinued. The reaction then became increasingly vigorous and occasionally had to be moderated by immersing the flask in an ice–water bath. The reaction was over in 30 min, and after cooling, the succinimide formed was collected by suction filtration and washed with additional carbon tetrachloride. The combined filtrates were concentrated to about 100 ml and chromatographed on 2 lb of Merck A-540 alumina, using carbon tetrachloride as the eluting solvent. In the early fraction there was obtained a white, solid product, which when recrystallized from ethanol (Norit) gave after drying in air 45 g (16%) of the product, mp 60.5–62.5° (lit.[16] 60–61°). A mixture melting point with the material obtained from the direct bromination of mesitylene was not depressed.

B. Direct Bromination of Mesitylene.—In a 500-ml, three-necked, round-bottomed flask equipped with a reflux condenser, mechanical stirrer, and a nonside-arm addition funnel was placed 120 g of mesitylene. The liquid was brought to reflux and 360 g of bromine was added over 3 hr with constant refluxing and while irradiated with a Sperti ultraviolet lamp. After the addition was complete, the mixture was cooled and distilled *in vacuo* to give the product, bp 155–175° (2.5 mm) [lit.[16] 180–195° (16 mm)]. Recrystallization from ethanol or petroleum ether gave 40 g (14%) of material, mp 52–56° (lit.[16] 60–61°).

The nmr spectrum (CCl_4) showed a multiplet at 482 cps and sharp peaks at 263 and 146 cps (area ratio 3:4:3).

5,13-Dimethyl[2.2]metacyclophane (III).—In a 5-l., three-necked, round-bottomed flask, equipped with a mechanical stirrer, reflux condenser, and addition funnel under a nitrogen atmosphere, phenyllithium was prepared by adding 142 g of bromobenzene in 250 ml of reagent benzene over 1 hr to 12.6 g of lithium wire in 500 ml of reagent ether. External heating was applied to initiate the reaction, but was discontinued after the reaction began. Later, heating was again applied and the solution was allowed to reflux gently overnight. A solution of 130 g of α,α'-dibromomesitylene in 500 ml of reagent ether was added over 7 hr. During the addition one could note the appearance of a dull orange color if the addition of the dibromide was halted. The resulting solution was stirred and refluxed for 7 days, after which time work-up and crystallization of an aliquot showed the starting bromide to be spent. The solution was cooled and water was added to decompose the excess phenyllithium. The organic phase was separated, washed with additional water, dried, and concentrated. The polymeric residue was extracted with several protions of hot ethanol, which were also concentrated and then treated with Norit. The crude, yellow product was chromatographed on 125 g of neutral, activity 1 Woelm alumina, eluting with ether. In the early fractions a white solid was obtained which was recrystallized from ethanol to give 6 g (11%) of the product, mp 147–149°.

On occasion the compound also contained biphenyl as in the synthesis of [2.2]metacyclophane. It was separated in the same manner. The infrared spectrum was similar to that of [2.2]-metacyclophane with an additional peak at 1370 cm^{-1} for CCH_3 absorption; $\lambda_{max}^{absolute\ EtOH}$ 277 mμ (ϵ 567) and 214.5 mμ (ϵ 38,520). The nmr spectrum showed the four low-field aromatic protons as a multiplet due to coupling with the two upfield aromatic protons (triplet at 249 cps, $J \approx 1.5$ cps) and with the methyls (multiplet at 139 cps, $J \approx 0.5$ cps). The bridge protons appeared as an A_2B_2 pattern centered about 149 cps (see Table II).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.52; H, 8.60.

2,7-Dimethyl-4,5,9,10-tetrahydropyrene.—In a 500-ml erlenmeyer flask was placed a solution of 0.75 g of III in 160 ml of glacial acetic acid. While stirring with a magnetic stirrer at room temperature there was added dropwise a solution of 5.5 ml of concentrated nitric acid in 3 ml of glacial acetic acid over 3 min. The mixture was stirred for 2 min more and excess ice water was added. The yellow precipitate was collected and washed by suction filtration. It was then taken up in hexane and chromatographed on 33 g of neutral, activity 1 Woelm alumina using the following solvent mixtures: hexane, 1, 5, 25, 50% benzene–hexane, benzene, 1, 5, 10, 25, 50% ether–benzene, ether, 1, 5, 10% methanol–ether, methanol. In the hexane fractions a white solid was obtained which was recrystallized from ethanol–water to give 142 mg (20%) of the product, mp 146.5–148°.

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.40; H, 7.79.

1-Nitro-2,7-dimethyl-4,5,9,10-tetrahydropyrene (IV).—From the previously described chromatography of 2,7-dimethyl-4,5,-9,10-tetrahydropyrene (V) a light yellow solid was obtained in the benzene–hexane fractions which was recrystallized from ethanol to give 252 mg (30%) of the product IV, mp 167–169°.

The infrared spectrum (KBr) showed bands at 1538 and 1351 for the nitro group. The nmr spectrum showed two peaks at low field (415 and 419 cps) in a ratio of 1 to 2. The aliphatic protons appeared as a doublet (168 and 170 cps) for the bridge methylenes and a singlet (139 cps) for the methyls in a ratio of 4 to 3.

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.14; N, 5.02. Found: C, 77.46; H, 6.21; N, 5.00.

(15) N. L. Allinger, M. A. DaRooge, M. A. Miller, and B. Waegell, *J. Org. Chem.*, **28**, 780 (1963).

(16) W. Ried, and F. J. Königstein, *Chem. Ber.*, **92**, 2532 (1959).

Reaction of N-Bromosuccinimide with [2.2]Metacyclophane.—In a 100 ml, round-bottomed flask was placed 1 g of I, 2.5 g of N-bromosuccinimide, 0.5 g benzoyl peroxide, and 60 ml of reagent carbon tetrachloride. The mixture was allowed to reflux for 24 hr and then allowed to cool. The mixture was then freed of succinimide by suction filtration and the solvent was concentrated to about one-half of its original volume. This solution was chromatographed on 120 g of neutral, activity 1 Woelm alumina. In the first fractions a white solid was obtained which had mp 105–125° unrecrystallized, and which was mainly recovered I. Gradual elution with ether gave yellow solids, mp 140–180°. These compounds gave a very positive green Beilstein flame test; however, the nmr spectrum revealed that they no longer possessed the metacyclophane structure as evidenced by the lack of the high-field aromatic protons.

Registry No.—I, 2319-97-3; II, 10549-22-1; III, 10549-23-2; IV, 10549-24-3; V, 10549-25-4; VI, 10549-26-5; VII, 10549-27-6; VIII, 10549-28-7; XI, 13006-46-7; XII, 10549-29-8; 1-bromo-7-acetamino-4,5,9,10-tetrahydropyrene, 10549-30-1.

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Oligomers of Allene. III.[1] Tetramers Formed in the Thermal Polymerization of Liquid Allene[2,3]

BORIS WEINSTEIN AND ALLAN H. FENSELAU

Department of Chemistry, Stanford University, Stanford, California 94305

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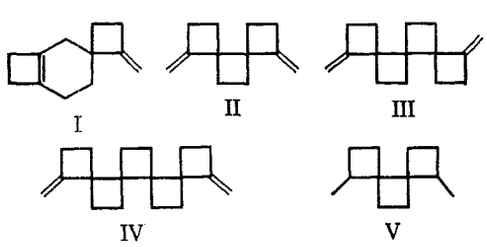
Polymerization of allene gives two tetramers, 2,6- and 2,7-dimethylenebicyclo[4.4.0]dec-9,10-ene. Hydrogenation afforded 2,6- and 2,7-dimethylbicyclo[4.4.0]dec-9,10-ene or 2,6- and 2,7-dimethylbicyclo[4.4.0]dec-9,10-ane, depending upon the exact conditions. Isomerization of the tetramer mixture by hydrogen bromide–acetic acid yielded 2,6- and 2,7-dimethyltetralin, confirmed by reduction of 2,6- and 2,7-dimethylnaphthalene. Aromatization of the tetramers by chloranil led to 2,6- and 2,7-dimethylnaphthalene. A second set of tetramers, 2-methylene-6- and -7-methylbicyclo[4.4.0]dec-9,10-ene, may have resulted either by use of propene-contaminated allene or by an internal hydrogen-transfer step.

Thermal polymerization of allene was originally reported to afford a variety of higher oligomers.[4,5] The liquid product boiling above 150° was separated by fractional distillation into four distinct components—an α-tetramer (I), a β-tetramer (II), a pentamer (III), and a hexamer (IV). The structural assignments were based on a combination of microanalytical, oxidative, and hydrogenation data. Treatment of each olefin with dilute potassium permanganate solution yielded oxalic and succinic acids, while catalytic hydrogenation in ethanol established the degree of unsaturation. For example, the β-tetramer II absorbed 2 equiv of hydrogen to give the tetrahydro-β-tetramer (V), whose saturated nature was established by a failure to react with bromine water. These

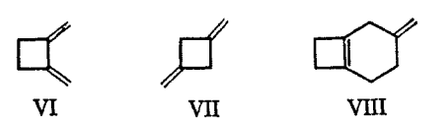


I II III

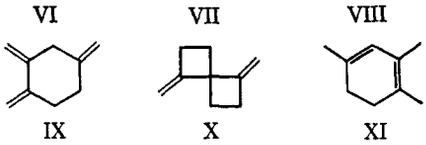
IV V

specific compounds have not been mentioned or isolated again, although the gaseous and liquid phase polymerization of allene has been extensively restudied in the last half-century.[6–14]

Recently, a new investigation on the allene oligomers provided for examination a quantity of liquid olefins. To recapitulate briefly, it can be stated that the dimer fraction is a mixture of 1,2-dimethylenecyclobutane (VI) and 1,3-dimethylenecyclobutane (VII); the trimer fraction is composed of 3-methylenebicyclo[4.2.0]-octa-1,6-ene (VIII), 1,2,3-trimethylenecyclohexane (IX), and 1,5- (or 1,6-) dimethylenespiro[3.3]heptane (X).[1] A report is now made on the exact nature of the tetrameric mixture.



VI VII VIII



IX X XI

The crude, semiviscous reaction oil was distilled under reduced pressure; the high-boiling fraction was preparatively gas chromatographed and separated into two principal products as determined by parallel analysis on a variety of substrates. The major, homogeneous component (43%) was tentatively identified as the β-tetramer II on three points: similar boiling point, similar refractive index, and similar odor ("kerosene-like"). A molecular weight determination (mass

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(2) A portion of these results was communicated earlier; see B. Weinstein and A. H. Fenselau, *Tetrahedron Letters*, 1463 (1963).

(3) Presented in part before the Division of Organic Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1964, Abstracts, p 72S.

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(12) Y. M. Slobodin and A. P. Khitrov, *ibid.*, **33**, 2822 (1963).

(13) Y. M. Slobodin and A. P. Khitrov, *ibid.*, **34**, 1727 (1964).

(14) Y. M. Slobodin and A. P. Khitrov, *Zh. Organ. Khim.*, **1**, 1531 (1965).