ether, a small amount of the propenyl ether, and a trace amount of the thiol resulting from cleavage (rather than rearrangement) of the thiophenyl ethers. We have identified this substance as 2-methyl-2,3-dihydrothionaphthene[9] (III) by means of both synthetic and analytical procedures.

The identification of (III) is based on this evidence: Oxidation with 30% H_2O_2 gives a sulfone (IIIA), m.p. 116.5–117.5° (calcd. for $C_9H_{10}O_2S$: C, 59.4; H, 5.5. Found: C, 59.60; H, 5.51). The n.m.r. spectrum is in full agreement with the suggested structure showing (in deuteriochloroform) a sharp methyl proton doublet centered on $\tau = 8.54$, approximately 24 poorly resolved peaks grouped around $\tau = 6.6$ ($-\overset{\diagdown}{\underset{\diagup}{\mathrm{C}}}\mathrm{-H}$ and $\overset{\diagdown}{\underset{\diagup}{}}\mathrm{CH_2}$ protons in the sulfone ring), and a group of sharp lines in the region of $\tau = 2.5$ protons). Furthermore, the n.m.r. spectrum is very similar but not superimposable ($\tau_{CH_3} = 8.62$) on that of the isomeric (VIA) which we prepared according to path C, proceeding through (VIII) and (VI) as previously described.[10,11] The sulfones, (IIIA) and (VIA), also differ decidedly in physical properties and in the important fingerprint region of their infrared spectra.

The fact that the propenyl thiophenyl ether (V) is quantitatively recovered from reaction conditions which can effect the conversion of (I) to (III) is a good indication that (V) is not an intermediate or a precursor of (III). The absence of any Claisen thiol product (II) suggests that the ring closure reaction proceeds very rapidly under the conditions of formation of (II). The formation of 2-methylcoumaran as a minor product of rearrangement of the oxyether[1] obviously occurs much less easily. The amine medium might also be expected to greatly facilitate the prototropic shift which competitively (and, to all intents and purposes, irreversibly) removes allyl thiophenyl ether from the reaction with formation of (V). Since the amount of (V) formed is significantly reduced from what was formerly experienced[4] (under conditions which do not produce (III)), we can perceive the full magnitude of the "catalytic effect" induced by the use of these high boiling amines. This is to say that while the accelerating influence of dimethylaniline solvent on the rate of rearrangement of the oxyether is negligible[12,13] it can serve as an indispensable medium for bringing about rearrangement of (I), which under (other) normal Claisen conditions is merely tautomerized. It is not clear, as yet, whether the influence of certain amines can be correlated with empirical solvent parameters such as Kosower's[14] "*Z*" value or others which have been shown to be applicable in the Diels–Alder reaction[15] or to catalytic activity of the type recently identified for the Diels–Alder by other workers.[16,17] The close similarity of the Claisen, the Diels–Alder and a host of others now classified as four-center reactions often has been pointed out.[18] We are presently studying such relationships in terms of the rate response to changes in reaction medium and temperature, as well as photochemical catalysis.

Acknowledgment.—We are obliged to Mr. Francis Scalzi and Mr. R. W. Body for some very timely assistance and discussions.

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[9] This was once mistakenly assumed by Hurd and Greengard[5] to be the side product of the reaction conditions which have been shown[4] to lead to (V). Both in our experience and in ref. (4) (III) never has been identified previously as a product of the pyrolysis of allyl thiophenyl ether.

(10) E. G. G. Werner, *Rec. Trav. Chim.*, **68**, 509 (1949).

(11) F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **73**, 2251 (1951).

(12) J. F. Kincaid and D. S. Tarbell, *ibid.*, **61**, 3085 (1939).

(13) D. S. Tarbell and J. F. Kincaid, *ibid.*, **62**, 728 (1940).

(14) E. M. Kosower, *ibid.*, **80**, 3253, 3261, 3267 (1958).

(15) J. A. Berson, Z. Hamlet and W. A. Mueller, *ibid.*, **84**, 297 (1962).

(16) P. Yates and P. Eaton, *ibid.*, **82**, 4436 (1960).

(17) G. I. Fray and R. Robinson, *ibid.*, **83**, 249 (1961).

(18) See, for example, E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 646.

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RECEIVED FEBRUARY 28, 1962

A CONVENIENT SYNTHESIS OF 3,5-CYCLOHEPTADIENONE

Sir:

Cycloheptadienones and alkoxy- and acyloxycycloheptatrienes have proved to be valuable intermediates for the synthesis of tropone and tropolones.[1,2] Here, we wish to report the synthesis of 3,5-cycloheptadienone (IV) by a method which is not only operationally simple but which also may be useful for the synthesis of other unconjugated cycloalkadienones. 3,5-Cycloheptadienone has been prepared previously by Meinwald, *et al.*,[3] by the base degradation of tropinone methiodide.

Reaction of 1-ethoxycyclohexene (I), prepared from cyclohexanone *via* the diethyl ketal,[4] with dichlorocarbene[5] gave 1-ethoxy-7,7-dichloronorcarane (II), b.p. 64–64.5° (1.0 mm.), in 87% yield (found: C, 51.86; H, 6.99). Rearrangement of this material in hot quinoline resulted in the elimination of *both* atoms of chlorine and the formation of 1-ethoxy-1,3,5-cycloheptatriene (III),[6] b.p. 52–53° (4.0 mm.) in 37% yield; $\lambda_{\text{max.}}^{\text{neat}}$ 6.18, 6.50, 7.00, 7.23, 7.42, 7.69, 7.89, 8.31, 8.59, 8.93, 9.54, 12.40, and 14.07μ; $\lambda_{\text{max}}^{C_2H_5OH}$ 290 mμ (3,840),[2] 207 mμ (17,050), (calcd: C, 79.37; H, 8.88; found: C, 79.25; H, 8.23). Hydrolysis of III with a very small quantity of hydrochloric acid in methanol–water produced 3,5-cycloheptadienone (IV), b.p. 43.5–45° (4.6 mm.), in 91% yield.

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(1) E. E. van Tamelen and G. T. Hildahl, *J. Am. Chem. Soc.*, **78**, 4405 (1956).

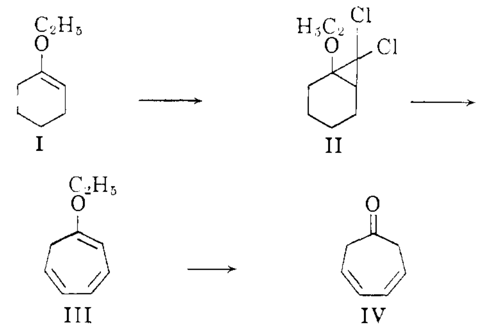
(2) O. L. Chapman and P. Fitton, *ibid.*, **83**, 1005 (1961).

(3) J. Meinwald, S. L. Emerman, N. C. Yang and G. Büchi, *ibid.*, **77**, 4401 (1955).

(4) A. Johannissian and E. Akunian, *Bull. univ. état R. S. S. Arménie*, No. **5**, 235, 245 (1930); *C. A.*, **25**, 921, 922 (1931).

(5) W. E. Parham and E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

(6) This structure, rather than one of the other two possible structures or a mixture of all three, was assigned to III because of the excellent yield of 3,5-cycloheptadienone (IV) obtained on mild acid hydrolysis. It is probable that the conditions for hydrolysis were drastic enough to hydrolyze the enol ether, but mild enough to prevent isomerization of the double bonds; *e.g.*, see F. B. Colton, L. N. Nysted, B. Riegel and A. L. Raymond, *J. Am. Chem. Soc.*, **79**, 1123 (1957). The structure of this product will be investigated in greater detail in the future.



The structure of compound IV was initially assigned on the basis of its unusual ultraviolet spectrum [$\lambda_{\max}^{\mathrm{EtOH}}$ 204 mμ (ϵ 6820), $\lambda_{\mathrm{shoulder}}^{\mathrm{EtOH}}$ 278 (ϵ 602), $\epsilon_{290\ \mathrm{m}\mu}$, 567] and the excellent correspondence of its infrared spectrum with that previously published for 3,5-cycloheptadienone.[3] The structural assignment was confirmed by the n.m.r. spectrum of the compound,[7] which showed a strong doublet at 168 and 173 cps. (weight 3.8) with very weak absorption at 134, 141, and 202 cps. (weight 0.6). The hydrogens on the double bonds formed a complex multiplet from 315 to 363 cps. (weight 3.6). Further evidence for the structure of IV was obtained by its conversion to cycloheptanone 2,4-dinitrophenylhydrazone, m.p. and m.m.p. 143–145°, to 3,5-cycloheptadienyl p-nitrobenzoate, m.p. 81–81.5° (reported 81.5–82.5°),[3] and to its Diels–Alder adduct with N-phenylmaleimide, m.p. of adduct 204–205° (reported 199–202°)[3] by the methods previously described.[3]

Application of this method to the synthesis of other cycloalkadienones and to the synthesis of the isomeric tropolones is under study.

Acknowledgment.—This work was supported by a grant from the National Science Foundation (NSF-G14458).

[7] The n.m.r. spectrum was run at 56.4 megacycles/sec. in carbon tetrachloride using tetramethylsilane as an internal standard. We are indebted to Drs. John E. Wertz and William Schwabacher for determining this spectrum for us.

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RECEIVED FEBRUARY 10, 1962

NOVEL SELECTIVITY IN REDUCTION OF KETONES BY LITHIUM N-DIHYDROPYRIDYLALUMINUM HYDRIDE

Sir:

We have shown previously that lithium N-dihydropyridylaluminum hydride (I) is a selective reducing agent for certain aldehydes and ketones, but is without effect on carboxylic esters and acids.[1] Upon further investigation of the relative reactivities of various ketones, we have observed that diaryl ketones are much more reactive toward I[2] than are either dialkyl or arylalkyl ketones, both in intermolecular and intramolecular competition experiments. This novel selectivity is in direct contrast with the results of Brown on the rates of sodium borohydride reduction in isopropyl alcohol,[3] where the reactivity of pertinent ketones was acetone > acetophenone > benzophenone. Indeed, as far as we are aware, the reactivity sequence reported below is without precedent in previous studies of nucleophilic addition to carbonyl groups, where aryl substitution generally enhances ground state stability by resonance and further may retard nucleophilic attack because of steric effects.[3,4]

Initial competitive experiments were carried out by allowing equimolar amounts of benzophenone and a second ketone to react with excess I in pyridine for several hours. For example, after one hour the product mixture from benzophenone and 2-octanone showed only a trace of the former (weak infrared absorption at 6.1 μ), but an 83% recovery of the latter (by vapor phase chromatography). Similarly, when benzophenone and 1-tetralone were kept with I for three hours, then worked up, infrared showed essentially complete consumption of the diaryl ketone and the tetralone was recovered in 95% yield as the 2,4-dinitrophenylhydrazone. A second series of experiments was conducted on individual ketones, using aliquots of the same sample of I. The following ketones were completely reduced (by infrared) after three hours exposure to excess I[5]: benzophenone, 4,4′-dichlorobenzophenone, 4-chlorobenzophenone, 4,4-dimethylbenzophenone and fluorenone. On the other hand, after twelve hours, these ketones were incompletely reduced, using the same ratio of reactants as above (yields of product alcohol, as determined by v.p.c.): 2-octanone (69%), acetophenone (33%), 4-methoxyacetophenone (29%), 3-methoxyacetophenone (70%), and benzyl methyl ketone (58%).

It appeared especially desirable to demonstrate the above selectivity intramolecularly in suitable diketones. For this purpose, we have prepared 4-(p-benzoyl)-phenyl-2-butanone (II), m.p. 36–37°, by benzoylation of 4-phenyl-2-butanone in carbon disulfide with aluminum chloride (*Anal.* Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.68; H, 6.46: $\lambda_{\max}^{\mathrm{EtOH}}$ 259 (log ϵ 4.3)). The orientation of the entering benzoyl group was established by oxidation of II to p-benzoylbenzoic acid. The infrared spectrum of II showed well separated carbonyl bands at 5.9 μ ($R_2C{=}O$) and 6.1 μ ($Ar_2C{=}O$), which proved useful for following the course of reduction by complex I. When II (5 mmoles) reacted with excess I (30 mmoles) in pyridine for three hours, and was worked up as

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[1] P. T. Lansbury and J. O. Peterson, *J. Am. Chem. Soc.*, **83**, 3537 (1961).

[2] Concerning the structure of I, evidence that dihydropyridyl moieties coordinated to aluminum are the source of hydride ion has been previously noted (ref. 1). By studying hydride and/or deuteride transfer to benzophenone from complexes prepared from pyridine-4-D and $LiAlH_4$ or $LiAlD_4$, it has been further established that both 1,2- and 1,4-dihydropyridyl groups are present in approximately the statistical amounts. A further complication, however, is the possibility that the complex may contain from one up to four dihydropyridyl groups per aluminum (*cf.* J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 2835 (1961)) and this is supported by elemental analyses of crystalline samples of I, which do not fit any of the expected values for a single structure.

[3] H. C. Brown, O. H. Wheeler and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957).

[4] H. C. Brown and K. Ichikawa, *J. Am. Chem. Soc.*, **84**, 373 (1962).

[5] Subsequently, it was found that benzophenone and fluorenone are completely reduced in five minutes when treated with 25 mole % excess I, as above. The other diaryl ketones would most likely react at a comparable rate.