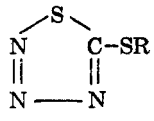
of VI, by degradative and kinetic evidence.[6,9,10] The chemical and kinetic evidence[6] further indicates a widely disparate structural alteration for the so-called *alkyl azidodithiocarbonates* over that of the so-called acyl *azidodithiocarbonates*. This evidence points to the structure, IX, for the *alkyl azidodithiocarbonates:*



IX

X · R = CH_3)

These structures easily explain the fact that the *alkyl azidodithiocarbonates* invariably formed *normal thiocyanates* while the *acyl azidodithiocarbonates* yield *isothiocyanates:*

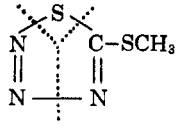
$$RSCSN_3 \longrightarrow RSCN + N_2 + S$$

$$RCOSCSN_3 \longrightarrow RNCS + N_2 + S$$

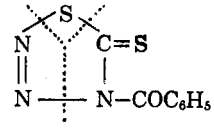
Audrieth, Johnson, and Browne[6] suggested that in the case of the acyl derivative ($R = C_6H_5$) the *normal thiocyanate* is first formed as an intermediate and immediately undergoes rearrangement to the *isothiocyanate:*

$$RCOSCN \longrightarrow RCONCS$$

Unfortunately not much is known about the above interconversion. However, the literature[11] indicates that this is not an easy process. On the other hand, by the assignment of structures X and VI, the mode of ring rupture indicated



X



VI

produces all of the degradation products without the need of postulating a rearrangement of *normal-* to an *iso-thiocyanate* in the case of the benzoyl derivative. The indicated mode of ring rupture is exactly the same as described for the 5-substituted amino-1,2,3,4-thiatriazoles,[2,3] I.

These studies are continuing and will subsequently be reported upon in detail.

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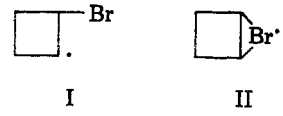
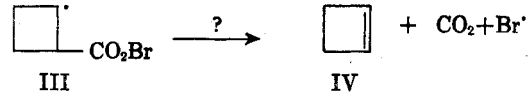
The Hunsdiecker Reaction of Optically Active Silver *trans*-Cyclobutane-1,2-dicarboxylate

Sir:

In view of recent interest in the mechanism of the brominative decarboxylation (Hunsdiecker reaction) of cyclic 1,2-dicarboxylates,[1] we wish to make a preliminary report of an experiment which further elucidates the stereochemistry of that reaction. It has been shown that brominative decarboxylations of *cis-* and *trans*-cyclobutanedicarboxylate[2] and of *cis-* and *trans*-cyclohexanedicarboxylate[1] lead to the corresponding *trans*-1,2-dibromocycloalkanes. Abell[1] had pointed out that these results may be explained in terms of the usual free-radical mechanism ($RCO_2Ag \rightarrow RCO_2Br \rightarrow R\cdot \rightarrow RBr$)[3] either by a steric effect in the addition of a bromine atom to radical I or by the intermediacy of a bridged radical, II, which would yield *trans*-dibromide if the ring opened with inversion of configuration. A third possibility is that radical III,



I II



III IV

formed in the first phase of the decomposition of the bishypobromite, might decompose to the cycloolefin, IV, which could then add bromine by an ionic mechanism.

Reaction paths involving II or IV would almost necessarily give racemic *trans*-dibromocycloalkane, whereas a stepwise, sterically controlled, stereospecific introduction of bromines by way of III and I could give optically active product from optically active *trans*-dicarboxylate.

(9) It is interesting to note that as early as 1922, Oliveri-Mandala, *Gazz. chim. ital.*, **52**, II, 139 (1922) in a general discussion on the addition of hydrazoic acid to systems containing adjacent double bonds had postulated that the addition of HN_3 to CS_2 could lead to structures III, V, and VII but rejected V and VII in favor of III on the basis of degradative evidence.

(10) The absence of the SH stretching vibration between 2600–2500 cm.$^{-1}$ coupled with the strong absorbancies for C=S; —N—C=S; and —N—C(=O)— (Table I) were decisive. Studies in this laboratory show that the very strong absorbance at 900 cm.$^{-1}$ can be taken as indicative of a heterocyclic —N—S—C— grouping.

(11) H. E. Williams, *Cyanogen Compounds*, Edward Arnold and Co., London, 2nd ed. 1948, p. 321.

(1) P. I. Abell, *J. Org. Chem.*, **22**, 769 (1957).

(2) E. R. Buchman, J. C. Conly, and D. R. Howton, N6onr-244/XI Tech. Rept., California Institute of Technology, 1951, p. 90; *cf.* E. Vogel, *Fortschr. chem. Forsch.*, **3**, 430 (1955).

(3) R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).

Addition of the silver salt of (−)-*trans*-cyclobutane-1,2-dicarboxylic acid[4] having $[\alpha]_D^{25}$ −83.4° (water) (about 46% racemic) to the theoretical amount of bromine in refluxing carbon tetrachloride[2] gave as 32% of the neutral product *trans*-1,2-dibromocyclobutane, distilled through a semimicro column at 20 mm. with a pot temperature of 120°. The purest fraction contained 4% (by vapor chromatographic analysis) of a higher boiling, unsaturated, unidentified contaminant, and had $[\alpha]_D^{27}$ −6.0° (carbon tetrachloride), m.p. −38 to −22°, and n_D^{25} 1.5358. *Anal.* Calcd. for $C_4H_6Br_2$: C, 22.46; H, 2.83. Found: C, 22.74; H, 2.87. (Buchman[2] had shown that the dibromide product from racemic *trans*-dicarboxylate was identical with that from addition of bromine to cyclobutene, and reported for the dibromide b.p. 72–4°/20mm., n_D^{25} 1.5343, m.p. −1° to +1°.) It was shown that the unknown contaminant was not responsible for the optical activity of the dibromide, since a higher boiling fraction of the reaction product (5 mm., pot temp. 150°) contained about 55% of the unknown and yet possessed $[\alpha]_D^{27}$ −3.3° (carbon tetrachloride).

It may be concluded that the reaction does not proceed entirely, if at all, through symmetrical intermediates such as II or IV, if we assume that neither asymmetric addition of bromine atoms to these intermediates nor asymmetric destruction of racemic dibromide in the reaction mixture occurs. These reasonable assumptions will be checked by further experiments, which should also reveal the optical yield and stereochemistry (double retention or double inversion) of the reaction.

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(4) L. J. Goldsworthy, *J. Chem. Soc.*, 125, 2012 (1924).

Ortho Alkylation of Aniline with Styrene

Sir:

Recent publications[1,2] on the *ortho* alkylation of aromatic amines in the presence of aluminum anilide type catalysts prompt us to report some unusual results which were obtained during a reinvestigation of the Hofmann-Martius[3] and Reilly-Hickinbottom[4] rearrangements. Hickinbottom[5] discovered that a mixture of aniline and its hydrochloride reacted with styrene at 200–240° (sealed tube) in 6 hr. to give a 28.4% yield of α-phenethylated anilines, 7.5% *ortho*, 17.7% *para* and 3.2% N, by isolation. Under what presumably were identical conditions, we consistently obtained an 82–85% yield of monoalkylated aniline which promptly crystallized to give a 74–77% isolated yield of *ortho-α-phenethylaniline*, m.p. and mixed m.p. 58.5–59.0°. Infrared analysis showed only 5–10% of the *para* isomer in the crude product; *N*-α-phenethylaniline was apparent (infrared) after 1 but not 6 hr. Aniline and α-phenethyl chloride gave similar, but not identical results; no alkylation of aniline by styrene was observed without the hydrochloride being present. But *N*-α-phenethylanilinium chloride, under essentially identical conditions, gave only 19–24% of mono-C-alkylate, 60–70% the *para* isomer.

We have no explanation at present for the discrepancy between our results and those of Hickinbottom. Complete details, and a rationalization of the different isomer distributions obtained by direct alkylation and by rearrangement of the anilinium salt, will be published shortly. The scope of this *ortho* alkylation is being investigated further.

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(2) G. G. Ecke, J. P. Napolitano, A. H. Filbey and A. J. Kolka, *J. Org. Chem.*, 22, 639 (1957).
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(4) J. Reilly and W. J. Hickinbottom, *J. Chem. Soc.*, 117, 103 (1920).
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Synthesis of 2-Heptafluorobutyrylthiophene

Sir:

The preparation of 2-heptafluorobutyrylthiophene has been accomplished by the Grignard method after previous failures using other synthetic techniques. Although aliphatic acids have been successfully condensed with thiophene using P_2O_5 as the condensation agent,[1,2] the use of a totally fluorinated acid such as heptafluorobutyric acid resulted only in its conversion to the acid anhydride by the condensation agent. The use of the anhydride was also unsuccessful. It has also been found that the acylation of thiophene with organic

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(2) H. Wynberg and A. Logothetis, *J. Am. Chem. Soc.*, 78, 1958 (1956).